

Appendix A

2019 Bathymetric Survey Results

1 Introduction

Northwest Hydro, Inc. collected bathymetry data within the Lower Duwamish Waterway (LDW) upper reach in 2019 in accordance with the *Quality Assurance Project Plan: Pre-Design Surveys of the Lower Duwamish Waterway Upper Reach* (Anchor and Windward 2019), referred to herein as the Survey QAPP. The 2019 bathymetric survey was performed to meet the following three data quality objectives (DQOs) described in Table 1 in the Survey QAPP:

- DQO 1: Inform recovery category designation modifications.
- DQO 2: Inform selection of sampling locations.
- DQO 3: Provide a base map for the remedial design.

The bathymetric survey was conducted in April and May 2019 (Figure A-1). There were no deviations from the Survey QAPP, with the exception of limited data gaps in coverage that will be surveyed during the Phase I Pre-Design Investigation (PDI) as discussed below. The bathymetric survey also met all key targets and related data requirements, as listed in Table A-1.

Table A-1
Key Targets and Related Datums

Description	Quantity or Datum
Horizontal positioning accuracy	1.6 feet minimum
Horizontal survey accuracy	3 feet at a 95% confidence interval
Horizontal datum	NAD83/91 Washington North Zone
Vertical survey accuracy	+/- 0.5 feet at a 95% confidence interval
Vertical datum	MLLW

Notes:

Source: Table 3 of the Survey QAPP (Anchor and Windward 2019)

MLLW: mean lower low weight

NAD83/91: North American Datum of 1983/1991

QAPP: quality assurance project plan

As reported to the US Environmental Protection Agency (EPA) in May 2019, there are limited gaps in the bathymetric survey coverage, as shown in Figure A-1. These missing areas will be surveyed during the Phase I PDI in order to have full bathymetric survey coverage to develop the base map for remedial design.

The results of the 2019 bathymetric survey are sufficient to meet DQO 1, and they were used to develop a sun-illumination map to inform recovery category designation modifications. The recovery category designation evaluation is described in PDI QAPP Appendix B.

The results of the 2019 bathymetric survey are sufficient to meet DQO 2, and they were used to update maps in the main body of the PDI QAPP, superseding the 2003 site-wide bathymetric survey, in order to inform selection of sampling locations and application of remedial action levels (RALs).

As noted, the 2019 bathymetric survey will require supplemental bathymetric survey coverage in data gap areas to meet DQO 3.

This appendix presents notable features of the 2019 bathymetric survey that address DQO 2, focusing on elevations that determine which RALs are applicable per the Record of Decision (ROD) (EPA 2014). In particular, this appendix discusses shoaled areas of the federal navigation channel (FNC) that are shallower than the authorized navigation depth of -15 feet mean lower low water (MLLW); areas considered intertidal (shallower than or equal to -4 feet MLLW) and subtidal (deeper than -4 feet MLLW); and areas in the elevation range denoting “potential vessel scour” between -4 and -18 feet MLLW. The updated information for these areas will inform the locations and depths of PDI samples and the application of RALs, consistent with the ROD.

The 2019 bathymetric elevations indicate an overall shallowing of the bed elevations within the upper reach, consistent with the conceptual site model of the LDW. Certain areas indicate deepening since 2003, primarily due to navigation dredging, early action area remediation, and South Park Bridge demolition and reconstruction, all of which have changed localized hydrodynamics. The survey coverage within the upper reach is more comprehensive than the 2003 bathymetric survey. The 2019 survey extended farther upstream (to river mile [RM] 5.25) than the 2003 survey (which extended to RM 4.8) and provided more coverage in the shallow subtidal and intertidal areas adjacent to banks.

2 Shoaled Areas of Federal Navigation Channel

Areas of the FNC that are shallower than the authorized navigation depth of -15 feet MLLW are shown in dark green in Figure A-2. From RM 3.0 to RM 4.26, the shoaled area within the FNC has increased since 2003 due to net sediment deposition. From RM 4.26 to RM 4.7, the shoaled area of the FNC has decreased since the 2003 survey due to navigation dredging.

3 Areas Considered Intertidal or Subtidal

In the ROD remedy, an elevation shallower than or equal to -4 feet MLLW is defined as intertidal. Such areas generally did not change from 2003 through 2019 within the upper reach, with the intertidal mudflat areas remaining stable (Figure A-3).

Two notable exceptions are two marinas within the upper reach: South Park Marina at RM 3.38 to RM 3.5 west (W), and Duwamish Yacht Club at RM 4.04 to RM 4.16 W. These two areas were historically dredged to create water depth for marina use (i.e., subtidal). These two marinas

experience higher net deposition, likely due to the waterway widening at those locations and the marinas' deeper waters (relative to adjacent upstream and downstream water depths). Since 2003, both marinas have had significant net deposition that has raised the elevations in large portions to be shallower than -4 feet MLLW. However, for the purpose of implementing the ROD remedy, these areas are not considered to be intertidal, because they will require maintenance dredging in the future to restore the permitted marina operational elevations (subtidal) consistent with each marina's site use.

4 Potential Vessel Scour Areas

Potential vessel scour areas as defined by the ROD are between -4 and -18 feet MLLW south of the 1st Avenue South Bridge. As shown in Figure A-2, most of the subtidal area in the upper reach fell within this depth range in both the 2003 and 2019 surveys. However, the area deeper than -18 feet MLLW in the FNC was smaller in the 2019 survey than in the 2003 survey due to sediment net deposition in the navigation channel.

5 Bathymetric Survey Coverage Upstream of RM 4.8

The 2003 bathymetric survey did not collect elevation information upstream of RM 4.8 due to upper reach access restrictions caused by low bridge clearance. The 2019 bathymetric survey obtained elevation information all the way to RM 5.25. No comparisons between 2003 and 2019 data were possible upstream of RM 4.8 due to a lack of 2003 elevation information.

6 References

- Anchor, Windward. 2019. Quality assurance project plan: pre-design surveys of the Lower Duwamish Waterway upper reach. Final. Anchor QEA and Windward Environmental LLC, Seattle, WA.
- EPA. 2014. Record of Decision, Lower Duwamish Waterway Superfund Site. Part 3. Responsiveness summary. US Environmental Protection Agency, Region 10, Seattle, WA.

Appendix A Figures

Appendix B
Recommended Recovery Category
Modifications Based on the 2019
Bathymetry Survey

1 Introduction

Recovery category areas are an important component of the remedial actions identified in the Lower Duwamish Waterway (LDW) Record of Decision (ROD) (EPA 2014) and are used to help identify the spatial application of remedial action levels (RALs) and selection of remedial technologies. Recovery Categories are used to assign remedial technologies to specific areas based on information about the potential for sediment contaminant concentrations to be reduced through natural recovery, or for subsurface contamination to be exposed at the surface due to erosion or scour (EPA 2014). Recovery category areas were developed in the feasibility study (FS) (AECOM 2012) based on the criteria presented in ROD Table 23. As defined in the ROD, Recovery Category 1 refers to recovery that is presumed to be limited and locations where subsurface contamination is more likely to be exposed at the surface due to erosion or scour (EPA 2014). Recovery Category 2 refers to recovery that is uncertain. Recovery Category 3 refers to greater potential for sediment contaminant concentrations to be reduced through natural recovery that is predicted to occur with some confidence (EPA 2014). The recovery category areas depicted in ROD Figure 17 were revised in the *Recovery Category Recommendations Report* (Integral et al. 2019) to serve as a starting point for this analysis (Figure B-1). Figure B-1 also shows the “analysis areas” that are referenced in this appendix to allow for area-specific recovery category discussion.¹ The use of Recovery categories allows for more aggressive remedial technologies (such as capping and dredging) to be used in areas with less potential for natural recovery and a greater likelihood of scour or other disturbance, and for less aggressive remedial technologies (such as enhanced natural recovery [ENR] and monitored natural recovery [MNR]) to be used in areas where recovery is predicted to occur more readily and disturbance is less likely (EPA 2014).

The recovery category area designations provide a general representation of the location-specific conditions within the upper reach for the purpose of applying RALs and remedial technologies at this stage of the remedial design. During remedial design, additional remediation details and assumptions (e.g., dredge prism boundaries, slopes, and depths; capping and ENR grain size specifications; etc.) may rely on location-specific hydrodynamic and bathymetry information to support design.

Recovery category areas are delineated based on the following physical and chemical criteria (EPA 2014) to estimate areas of recovery and scour potential:

1. Identification of observed vessel-induced scour areas based on a visual review of a sun-illuminated bathymetric survey map produced from a comprehensive site-wide bathymetric survey. The 2003 bathymetric survey conducted for the remedial investigation (RI)/FS was used to delineate the recovery category areas defined in the ROD.

¹ The recovery category boundaries are shown as jagged lines due to an artifact of the mapping methods used during the FS and ROD processes. Where recovery category areas have been modified, the lines are smooth.

2. Identification of berthing areas based on waterway configuration (i.e., location of docks), review of the 2002 US Army Corps of Engineers Port Series report (USACE 2002), and review of the waterway user survey with its assessment of in-water structures (Integral et al. 2018).
3. Identification of sediment transport model (STM)-predicted 100-year high-flow event scour areas (> 10 cm) and STM-predicted net-scour and net-sedimentation areas as presented in the FS.
4. Empirical contaminant trends over time.

The 2019 modifications to the ROD recovery category areas made in the *Recovery Category Recommendations Report* (Integral et al. 2019) were based on criteria 2 and 4 above; new bathymetry data were not available at the time of this report.² This appendix uses the recent 2019 bathymetric survey to develop a sun-illumination map and reassess observed vessel-induced scour areas (criterion 1). No changes have been made based on criterion 3 since the ROD. In this appendix, the 2019 bathymetric survey results are also compared with the 2003 bathymetric survey results to empirically identify net changes to waterway elevations that have developed over the past 16 years. This analysis provides supplemental lines of evidence that might identify net-scour areas that were not well captured in the sun-illumination map, and that should be considered in design.

Additional modifications to the recovery category areas within the upper reach may be identified based on Pre-Design Investigation (PDI) chemistry data (criterion 4) in the forthcoming PDI Phase I and Phase II data evaluation reports.

2 Methods

Northwest Hydro, Inc. collected multi-beam bathymetry data within the upper reach in April and May 2019, providing new data to assess observed vessel-induced scour areas. Vessel-induced scour near and in berthing areas was evaluated by examining a sun-illumination bathymetry map (Figure B-2), consistent with the analysis performed for the FS (FS Section 2.3.1.1). Multi-beam bathymetric soundings were converted into a digital terrain model of the three-dimensional mudline elevations, and the digital terrain model was then used to generate a sun-illumination map. The outlines of ROD Recovery Categories 1 and 2 are shown for reference on Figure B-2. Areas outside of Recovery Categories 1 and 2 are Recovery Category 3.

The highlights and shading on the sun-illumination map emphasize fine-scale features and vertical relief to aid in the visual identification of bedform features that may be due to scour from vessel propeller wash (propwash), vessel grounding, or anchoring or spudding from vessel operations. The features can include ridges and furrows, depressions, and other disturbance features. However, it is the actual vertical elevation difference that is important. This difference can be exaggerated in the

² Empirical contaminant trends over time (criterion 4) were evaluated but did not result in changes to the recovery category areas.

sun-illumination maps, because the angle of illumination can create shading for even very small elevation differences (e.g., inches) that imply greater bed disturbance than is actually present. Additionally, survey accuracy must be considered when evaluating bed disturbance. Changes in bathymetric elevation of +/- 4 inches are functionally considered to indicate no change in elevation, because the results are within the accuracy limits of the evaluation (vertical accuracy of individual RTK-GPS multibeam surveys in shallow water is in the range of +/- 0.3 foot [USACE 2013]). For this analysis and as a general guide, bed vertical disturbances (i.e., depressions in the bed as seen on the sun-illumination maps) of 6 inches or less were not considered sufficient to indicate scour. This applied, for example, to marina areas where areas of shadowing could be seen on the sun-illumination map but were not deep enough to indicate vessel scour sufficient to trigger a change to Recovery Category 1.

In addition to the sun-illumination maps, two supplemental lines of evidence were assessed:

- A. Analysis of changes in bed elevations between the 2003 and 2019 bathymetric surveys that could be indicative of net scour or deposition (or caused by other factors such as dredging or construction impacts) over the 16-year period
- B. Consideration of waterway use based on the configuration of docks and infrastructure using maps and satellite imagery (e.g., changed location of bridge footings)

In supplemental line of evidence A, empirical net-scour or deposition patterns were identified by changes in bathymetric elevation between the 2003 and 2019 bathymetric surveys depicted in an isopach map (Figure B-3). Changes in bathymetry may have multiple causes: ongoing natural sedimentation processes; dredging, excavation, structure removal or construction, or material placement that occurred between the two surveys; bed erosion due to surface water flows; vessel-induced scour from vessel propwash; or bed disturbance from other vessel operations (e.g., spudding, anchoring, grounding). The evidence from the isopach map can help to identify areas of positive change (referred to as deposition), negative change (referred to as scour), or no net-elevation change. While helpful, this empirical information was not used to override the predicted STM results (criterion 3) because of the longer-term duration of the STM analysis (which analyzes the impact of repetitive high-flow events, including a 100-year high-flow event). As discussed above, surveys generally have a vertical accuracy of +/- 0.3 foot; this uncertainty is compounded when comparing two surveys. Therefore, for purposes of this analysis, net elevation changes of +/-6 inches or less on the isopach map are considered non-significant changes with respect to net deposition or scour.

- Supplemental line of evidence B was used to aid in the interpretation of bedform features, including site waterway use and recent construction activities within the upper reach. This line of evidence considered the configuration of overwater structures, berthing areas, dredging and material placement areas, bridges, piles, and dolphins. For example, some docks show

evidence of high-frequency vessel traffic, while some structures block access to maneuvering vessels. In addition, several construction projects have modified the bed features of the upper reach. These actions, which were also considered in interpreting the potential for scour, included: Reconstruction (including moving foundations) of the South Park Bridge

- Dredging and material placement performed for three early action areas (EAAs) at Boeing Plant 2, Terminal 117, and Jorgensen Forge conducted between 2013 and 2015
- Navigation dredging of the outer Delta Marine Dock (2010) and the federal navigation channel (FNC) from river mile (RM) 4.26 to RM 4.7 (2018–2020).

These actions could result in short-term (dredging) or long-term (structures) modifications to the hydrodynamic system, which can take some time before a new dynamic equilibrium is reached.

For all discrete locations within the upper reach, the two supplemental lines of evidence were considered together with criterion 1 and engineering best professional judgment and knowledge of site conditions to recommend modifications to the recovery category areas identified in the ROD. Recovery Category 1 areas based on the STM predictions (criterion 3) (i.e., 100-year high-flow event scour areas and net-scour areas) were not reduced in size or shape. Thus, only areas outside of STM 100-year high-flow event scour areas and net-scour areas were considered eligible for recovery category revision.

3 Recovery Category Modifications

All areas of the upper reach were evaluated and divided into 14 analysis areas for detailed analysis. The EAAs were excluded with the exception of the Norfolk EAA.³ Table B-1 summarizes the evaluation for the analysis areas. Table B-1 identifies each analysis area by river mile and side of the LDW (east [E], FNC, and west [W]), lists the current recovery category designation (Integral et al. 2019), summarizes criterion 1 and the two supplemental lines of evidence considered in this document, and proposes any recovery category area changes. As shown in Figures B-4 to B-9, six areas were identified for recovery category area modification or refinement based on this evaluation; these six areas are discussed in the rest of this section.

3.1 Analysis Area 2, RM 3.23 to RM 3.37W: South Park Bridge

Area 2 stretches from the west bank of the LDW and is bordered by the Boeing Plant 2 EAA to the east. It includes Recovery Category 1 in the FNC (based on STM high-flow scour) and Recovery Category 3 on the west bank (Figure B-1). The South Park Bridge was reconstructed from 2011 to

³ Monitoring of the Norfolk EAA was completed during the RI phase, but because design sampling is to examine potential recontamination of surface sediments in this area, a recovery category was assigned. This will assist in identifying applicable technologies if remedial action is deemed necessary.

2014, and the sun-illumination map (criterion 1, Figure B-2) shows significant⁴ bed disturbance within the area due to construction activities during bridge replacement and the modification of river flow paths around structures. Similarly, the isopach map (supplemental line of evidence A; Figure B-3) shows areas that have deeper bed elevations in 2019 than they did in 2003, likely due to bridge replacement construction activities around the current and former alignment (supplemental line of evidence B) that modified river flow paths around structures. Downstream bank disturbances (RM 3.25 to RM 3.28) could be due to construction activities, changes in hydrodynamic current flows, or vessel-induced scour. Although it is unclear whether disturbance in the area is ongoing, it is recommended that the downstream bed disturbance areas be changed to Recovery Category 1. The recovery category for the bed disturbance area adjacent to the reconstructed bridge piers remains unchanged, because the disturbance in that area appears to be due primarily to reconstruction activities, which are complete (Figure B-4).

3.2 Analysis Area 6, RM 3.9 to RM 4.03W: McElroy Dock

McElroy Dock berthing area had been identified as Recovery Category 1 in the FS (Figure B-1). The 2019 sun-illumination map (criterion 1; Figure B-2) and isopach map (supplemental line of evidence A; Figure B-3) show evidence of continued bed disturbance; however, the delineation of the Recovery Category 1 area is recommended to be modified (Figure B-5) to capture the limits of apparent bed disturbances. To the north, the FS Recovery Category 1 boundary did not capture the extent of disturbed bed, and the Recovery Category 1 area is recommended to be expanded northward (criterion 1 and supplemental line of evidence A). To the south, the boundary is recommended to be truncated to align with the Duwamish Yacht Club Marina, which does not have evidence of vessel-induced scour (criterion 1) and shows high deposition (i.e., positive net-elevation change; supplemental line of evidence A). To the west, the boundary is recommended to be slightly adjusted to align with the dock, which represents the extent of active berthing (supplemental line of evidence B; Figure B-5).

3.3 Analysis Area 10, RM 4.03 to RM 4.26E: Slip 6

This area includes Slip 6 and the areas directly to the north and the south of the slip in the main stem of the channel (Figure B-1). This area was designated in the FS as a mixture of Recovery Categories 1, 2, and 3, depending on the location. The bathymetric evidence is consistent with these recovery categories; however, the delineation of the Recovery Category 1 area is recommended to be modified so that stable intertidal mudflats are not included in Recovery Category 1.

⁴ The term "significant" is used in this analysis to denote areas where natural recovery is presumed to be limited (consistent with the definition of Recovery Category 1) due to ongoing mixing from vessel scour or other vessel-induced bed disturbance (e.g., anchoring) deeper than the surface sediment layer.

North of Slip 6 are several mooring dolphins, the Northwest Container Services berthing area, and an intertidal mudflat. The mudflat behind the Northwest Container Services dolphins was identified as Recovery Category 1 but does not show evidence of bed disturbance (criterion 1), and the mooring structures restrict access by vessels in this area (supplemental line of evidence B). Therefore, the intertidal mudflat area and area immediately adjacent to the shoreline are recommended to be modified to Recovery Category 3 (Figure B-6). However, the southern part of the mudflat (i.e., the area just north of the mouth of Slip 6) shows signs of bed disturbance (possibly associated with dolphin structures) and is retained as Recovery Category 1. Within the Northwest Container Services area, vessel scour is minimal and deposition is high (supplemental line of evidence B), so this area remains Recovery Category 3, consistent with the delineation in the ROD.

South of the mouth of Slip 6, the Recovery Category 1 area in the intertidal mudflat along the shoreline is recommended to be changed to Recovery Category 3, because there is no evidence of vessel scour (criterion 1) and the area is too shallow for navigation (i.e., intertidal mudflat; supplemental line of evidence B; Figure B-6). However, Recovery Category 1 is maintained along the FNC, where bed disturbance is evident in the sun-illumination map and the isopach map (criterion 1 and line of evidence A).

Within Slip 6, the recovery categories are not modified from their delineation in the ROD. Recovery Category 1 is maintained adjacent to docks on the southern part of the slip where vessel scour has been evident to greater than 6 inches deep (criterion 1). To the north, Recovery Category 3 is maintained because vessel scour features are minor (generally less than 6 inches in depth; criterion 1). Within the entire slip, bathymetric elevation comparisons show that the area is highly depositional (supplemental line of evidence A).

3.4 Analysis Area 11, RM 4.17 to RM 4.26W: Delta Marine

This area includes the Delta Marine T-dock and haul-out facility, which were designated as Recovery Category 1 in the FS (Figure B-1). The lines of evidence are consistent with the FS recovery category designation in the area but with a modified boundary to capture bed disturbance noted on the sun-illumination map (criterion 1) and areas accessible to vessels (supplemental line of evidence B). The southern boundary is recommended to be modified to capture the haul-out and the area of bed disturbance at the mouth of the haul-out. The area south of the haul-out near the shoreline is changed to Recovery Category 3 (e.g., the southern boundary is reduced) because the location is not accessible to vessels due to the haul-out structure and pilings in the area (supplemental lines of evidence B). The northern boundary is recommended to be reduced to align with the extent of the berthing area and the limit of bed disturbance (criterion 1 and supplemental line of evidence B; Figure B-7).

3.5 Analysis Area 12, RM 4.4 to RM 4.5W: North Turning Basin

RM 4.4 to RM 4.5W includes strips of Recovery Category 1 due to STM modeling results plus Recovery Category 3 in the rest of the area (Figure B-1). The bedform features on the sun-illumination map (criterion 1; Figure B-2) and isopach map (supplemental line of evidence A; Figure B-3) show river flow scour immediately adjacent to the STM model-based Recovery Category 1 area. Therefore, the Recovery Category 1 area is recommended to be extended to the west and slightly south to capture the observed extent of net scour in the isopach map (supplemental line of evidence A) that is immediately adjacent to the STM model predicted net-scour area (Figure B-8). Within the FNC, bedform features (criterion 1; Figure B-2) and changes in bathymetric elevation (supplemental line of evidence A; Figure B-3) are due to navigation dredging performed between the 2003 and the 2019 surveys.

3.6 Analysis Area 14, RM 4.76 to RM 5.0: Upstream of Turning Basin

The area south of the turning basin was not designated for a recovery category in the FS, because the STM did not provide scour predictions in the area, and most of the area was not surveyed in 2003 (Figure B-1). Based on the 2019 survey, the bedform contours are consistent with relatively high-velocity river flows (criterion 1), but downstream and upstream bridges preclude vessels (other than small boats) from entering most of this area. Considered together, Recovery Category 2 is recommended for the entire area (Figure B-9). The Norfolk EAA is considered to be Recovery Category 2, consistent with the surrounding area in Analysis Area 14.

3.7 Summary and Next Steps

In summary, criterion 1 and the two supplemental lines of evidence have been reviewed and engineering judgment has been applied to recommend several modifications to the recovery category areas, as summarized in Figure B-10. Changes are recommended for six areas. Table B-2 summarizes the acreage changes to the recovery category areas.

These recovery category designations will be used in remedial design to apply the appropriate RALs and evaluate remedial technologies for areas of the site.

As noted in the introduction, additional modifications to the recovery category areas within the upper reach may be identified based on PDI chemistry data (criterion 4) in the forthcoming PDI Phase I and II data evaluation reports.

4 References

AECOM, 2012. *Final Feasibility Study, Lower Duwamish Waterway (Seattle, Washington)*. Submitted to U.S. Environmental Protection Agency (Region 10) and Washington State Department of Ecology (Northwest Regional Office). October 31, 2012.

- Anchor QEA and Woodward (Anchor QEA, LLC, and Woodward Environmental, LLC), 2019. *Remedial Design Work Plan for the Lower Duwamish Waterway Upper Reach*. Submitted to U.S. Environmental Protection Agency, Region 10.
- EPA (U.S. Environmental Protection Agency), 2014. *Record of Decision, Lower Duwamish Waterway*. Seattle, Washington. EPA ID: WA00002329803. U.S. Environmental Protection Agency Region 10, Seattle, Washington. November 2014.
- Integral, Moffatt & Nichol, and Woodward Environmental LLC, 2018. *Waterway User Survey and Assessment of In-Water Structures – Data Report*. Prepared for U.S. Environmental Protection Agency, Region 10. July 2, 2018.
- Integral, Anchor QEA, and Woodward Environmental LLC, 2019. *Recovery Category Recommendations Report – Final*. Prepared for: U.S. Environmental Protection Agency, Region 10. February 11, 2019.
- USACE (U.S. Army Corps of Engineers), 2002. Port of Seattle, Washington, Port Series No. 36, Washington Port and Harbor Conditions Publication. NDC-02-P-1. June 2002.
- USACE, 2013. *Engineering and Design: Hydrographic Surveying*. EM 1110-2-1003. Department of the Army, U.S. Army Corps of Engineers. November 2013.

**Table B-1
Upper Reach Recovery Category Evaluation Summary**

Analysis Area #	River Mile	Location	River Side	Current Recovery Category Designation	RC Criterion 1	Supplemental Lines of Evidence		Conclusion and Rationale
					Vessel-Induced Scour (Analysis of Bed Sediment Disturbance Using the Sun-Illumination Map) ¹	A) Analysis of Changes in Bathymetry from 2003 to 2019 Using the Isopach Map	B) Waterway Usage	
1	3.0 to 3.23	Duwamish Waterway Park and adjacent FNC and south to the South Park Bridge Area	W	RC3 (W shoreline)	No vessel-induced scour features.	Mixture of measurable deposition areas or no detectable changes.	No water-dependent industry or infrastructure in the location.	No changes to RCs.
			FNC	RC1 (deeper water/FNC)	No significant vessel-induced scour features.	Mixture of measurable deposition areas or no detectable changes.	FNC transiting.	No change. RC1 area (based on STM high-flow scour prediction) is not modified.
2	3.23 to 3.37	South Park Bridge and Cable Area west bank and FNC. See Figure B-4	W	RC3 (W shoreline)	Bed disturbances showing as depressions and mounds along the shallow subtidal west bank from the South Park Marina boat launch northward under the South Park Bridge and to the north approximately 500 feet from the bridge. Possibly due to bridge reconstruction activities and change in river flows around the new bridge structure.	Mixture of areas with measurable deposition and several depressions of apparent net scour downstream of the bridge. The apparent net scour may be ongoing or may represent the new stable condition of the bed. Around the South Park Bridge footprint, changes in bathymetry are observed that are likely due to bridge modifications.	Construction/demolition of bridge structure. Residential boat launch at RM 3.24W and South Park Marina boat launch at RM 3.36W support recreational vessels and are not expected to significantly disturb the bed.	Convert RC3 to RC1 in two areas to capture bed disturbance (criterion 1) and depressions of apparent net scour downstream of the South Park Bridge (supplemental line of evidence A).
			FNC	RC1 and RC3 (FNC)	No significant vessel-induced scour features.	Mixture of areas with measurable deposition and depressions of apparent net scour downstream under the bridge.	Construction/demolition of bridge structure.	Convert RC3 to RC1 in one area to capture the depression of apparent net scour immediately under the South Park Bridge (supplemental line of evidence A).
3	3.37 to 3.5	South Park Marina and adjacent FNC	W	RC3 (marina)	No significant vessel-induced scour features. Evidence of boat slips and the presence of piling in the survey.	No data (not surveyed in 2003).	Marina activities.	No change.
			FNC	RC1 and RC3 (FNC)	No significant vessel-induced scour features.	Measurable deposition areas, especially on the west side of the FNC.	FNC transiting.	No change. The sliver of RC1 in the east side of the FNC (based on STM high-flow scour prediction) is not modified.
4	3.5 to 3.7	Area between Terminal 117 EAA (W bank) and Boeing Plant 2 / Jorgensen Forge EAAs (E bank)	FNC	Primarily RC1 (FNC) with some of RC3 (western fringes)	No significant vessel-induced scour features.	West side of FNC: Measurable deposition areas. East side of FNC: Deeper bathymetry due to EAA construction.	FNC transiting.	No change. RC1 area (most of the area; based on STM high-flow scour prediction) is not modified.
5	3.7 to 3.9	Straight navigation channel with gradual intertidal slopes on both sides. Activated carbon pilot intertidal plot (RM 3.85E)	W	RC3 (W)	No significant vessel-induced scour features.	Mixture of measurable deposition areas and no change.	No water-dependent industry.	No change.
			FNC	RC1 (FNC)	No significant vessel-induced scour features.	Measurable deposition areas, especially on the west side.	FNC transiting.	No change. RC1 based on STM high-flow scour prediction is not modified.
			E	RC2 (E)	No significant vessel-induced scour features.	No change with isolated areas of net scour along the slope to the FNC. Pilot plot shows increased elevation due to material placement.	No water-dependent industry.	No change.

**Table B-1
Upper Reach Recovery Category Evaluation Summary**

Analysis Area #	River Mile	Location	River Side	Current Recovery Category Designation	RC Criterion 1	Supplemental Lines of Evidence		Conclusion and Rationale
					Vessel-Induced Scour (Analysis of Bed Sediment Disturbance Using the Sun-Illumination Map) ¹	A) Analysis of Changes in Bathymetry from 2003 to 2019 Using the Isopach Map	B) Waterway Usage	
6	3.9 to 4.03	McElroy dock (W bank). See Figure B-5	W	RC1	Bed disturbance evident.	Mixed areas of net scour and deposition.	Active berthing area.	RC1 is modified to capture bed disturbance from the sun-illumination map (criterion 1) and net-scour areas from the isopach map (supplemental line of evidence A). Northern boundary: RC1 area expanded to capture several net-scour depressions on the sun-illumination map (criterion 1) and isopach map (supplemental line of evidence A). Southern boundary: RC1 area modified to align with the Duwamish Yacht Club Marina, which is highly depositional (supplemental line of evidence A) and does not indicate significant vessel-induced scour (criterion 1). Western boundary: The boundary will be refined to align with the dock, which represents the extent of active berthing (criterion 1 and supplemental lines of evidence A and B). Eastern boundary: Boundary remains at the FNC.
7	3.9 to 4.03	FNC	FNC	RC1 and RC3	No evidence for vessel-induced scour.	Measurable deposition areas.	FNC transiting.	No change. RC1 based on STM-predicted high-flow scour is not modified.
8	3.9 to 4.03	Natural bank, activated carbon pilot intertidal plot (RM 3.9E)	E	RC2	No evidence for vessel-induced scour.	Mostly no change with some areas of deepening elevations in the intertidal. Pilot plot shows increased bed elevation.	No water-dependent industry.	No change. Bathymetric features (criterion 1) and waterway usage (supplemental line of evidence B) consistent with RC3; however, due to minimal change in the intertidal area (supplemental line of evidence A), RC2 is reasonable.
9	4.03 to 4.17	Duwamish Yacht Club and adjacent navigation channel	W	RC3	No evidence for vessel-induced scour. Generally flat marina bathymetry with piling showing on the survey with shallower bathymetry in the southern portion.	Duwamish Yacht Club: High rates of sediment deposition.	Marina activities.	No change.
			FNC	RC3	Bathymetric evidence for maintenance dredging (stair step at RM 4.4).	FNC: Mix of shallower and deeper bathymetry due to sediment deposition combined with navigation dredging.	FNC transiting. Bed disturbance from maintenance dredging.	No change.

**Table B-1
Upper Reach Recovery Category Evaluation Summary**

Analysis Area #	River Mile	Location	River Side	Current Recovery Category Designation	RC Criterion 1	Supplemental Lines of Evidence		Conclusion and Rationale
					Vessel-Induced Scour (Analysis of Bed Sediment Disturbance Using the Sun-Illumination Map) ¹	A) Analysis of Changes in Bathymetry from 2003 to 2019 Using the Isopach Map	B) Waterway Usage	
10	4.03 to 4.26	Slip 6 and Surrounding Area. See Figure B-6	E (RC3 Area north of Slip 6)	RC3 area north of Slip 6	Evidence of minor bed disturbance within the berthing area. No evidence for bed disturbance in the intertidal area.	Northwest Container Services berthing area: Measurable deposition. Intertidal mudflat: No change.	Northwest Container Services berthing area: Barge mooring. Intertidal mudflat: No vessel access.	No change.
			E (RC1 Area just north of Slip 6)	RC1 area including mouth of Slip 6 and the slope to the north)	Southern dolphin area (slope from intertidal to Slip 6): Evidence of bed disturbance. Intertidal mudflat: No evidence for bed disturbance.	Southern dolphin area (slope from intertidal to Slip 6): Deeper bathymetry due to ongoing disturbance. Intertidal mudflat: No change.	Southern dolphin area (slope from intertidal to Slip 6): Barge mooring. Intertidal mudflat: No vessel access; too shallow for vessel activity.	Reduce the RC1 area to exclude the intertidal mudflat without vessel activity. Minimal change in bathymetry elevations is observed, and vessel-induced scour is not evident (criterion 1 and both supplemental lines of evidence).
			E (Slip 6)	RC1 (within Slip 6) RC2 (northern part of the berthing area within Slip 6) RC3 (fringe areas within Slip 6)	Head of Slip 6: Evidence for minor bed disturbance. Mouth of Slip 6: Some evidence for bed disturbance although deep vessel track lines evident in 2003 survey have filled in.	Head of Slip 6: Highly depositional. Mouth of Slip 6: Variably depositional.	Active vessel maneuvering.	No change. Criterion 1 and both supplemental lines of evidence show a high rate of deposition (supplemental line of evidence A), minor bed disturbance (criterion 1), and active site waterway use (supplemental line of evidence B). RC3 fringe areas show no evidence of disturbance (criterion 1) and have high deposition (supplemental line of evidence B).
			E (South of Slip 6)	RC1 south of Slip 6 mouth	South of mouth of Slip 6: Evidence for bed disturbance along the steep slopes transitioning to the FNC.	South of mouth of Slip 6: Deeper bathymetry elevations along the steep slopes transitioning to the FNC; measurable deposition areas due to deposition in the intertidal.	Active vessel maneuvering in the adjacent FNC; no vessel activity in the intertidal mudflat.	Modify the RC1 area to exclude the intertidal mudflat, where the RC1 designation is not supported. Maintain the RC1 area along the FNC where bed disturbance is evident in the sun-illumination map and the isopach (criterion 1 and line of evidence A).

**Table B-1
Upper Reach Recovery Category Evaluation Summary**

Analysis Area #	River Mile	Location	River Side	Current Recovery Category Designation	RC Criterion 1	Supplemental Lines of Evidence		Conclusion and Rationale
					Vessel-Induced Scour (Analysis of Bed Sediment Disturbance Using the Sun-Illumination Map) ¹	A) Analysis of Changes in Bathymetry from 2003 to 2019 Using the Isopach Map	B) Waterway Usage	
11	4.17 to 4.30	Delta Marine T-dock and haul-out, FNC. See Figure B-7	W	RC1 (Delta Marine berthing area)	Outer face of the dock: Flat with vessel-induced scour track lines to the north and south of the berth. Inner T-dock north area: No data. Inner T-dock south area: Shallow with evidence of vessel maneuvering toward the FNC. Haul-out: Evidence of dredging and/or vessel maneuvering near the mouth and to the north and south of the mouth.	Deeper bathymetry elevations due to dredging in the berth area. Measurable deposition areas on the fringes of the dredging areas.	Active vessel maneuvering.	Criterion 1 and the supplemental lines of evidence are consistent with RC1 in the area. The Delta Marine RC1 area is modified to capture bed disturbance from the sun-illumination map (criterion 1) and areas that vessels can access (supplemental line of evidence B). Southern boundary: RC1 area modified to align with the southern extent of the haul-out and the area of bed disturbance at the mouth of the haul-out. The shoreline area south of the haul-out, where vessels cannot access, modified to RC3 (criterion 1 and supplemental line of evidence B). Northern boundary: RC1 area reduced to align with the extent of the berthing area and the limit of bed disturbance (criterion 1 and supplemental line of evidence B).
			FNC	RC1 and RC3 (FNC)	FNC: Evidence for bed disturbance from dredging.	Deeper bathymetry elevations due to dredging in the berth and the FNC.	FNC: Bed disturbance from maintenance dredging.	RC1 area (based on STM-predicted high-flow scour) is not modified.
12	4.30 to 4.52	Hamm Creek south to the turning basin	W	RC3 (W)	RM 4.4 to RM 4.5W indicates a high-flow scour feature at the base of the bank.	RM 4.26 to RM 4.40W: Predominantly no change. RM 4.40 to RM 4.50W: Narrow strip of deeper bathymetry elevation at the base of the bank.	No water-dependent industry.	Expand RC1 area slightly to the west to capture an adjacent sliver of net-scour area (criterion 1 and supplemental line of evidence A).
			FNC	RC1 (strips within and west of the FNC) RC3 (rest of the area)	FNC: Bed disturbance from maintenance dredging.	FNC: Deeper bathymetry elevations due to maintenance dredging.	FNC: Sediment disturbance from maintenance dredging.	No change.
			E	RC3 (E)	No evidence for vessel-induced scour.	RM 4.26 to RM 4.40E: Measurable deposition areas in the mudflat and net scour due to bed disturbance along the slope to the FNC. RM 4.40 to RM 4.50E: No net elevation change in the shallow elevations with deeper bathymetry elevation on the steep slope to the FNC that is likely the result of dredging activities.	No water-dependent industry.	No change.
13	4.52 to 4.8	Turning basin. See Figure B-8	W, FNC, E	RC1 (strips near either bank near the turning basin) RC3 (rest of the area)	Mudflats, river flow deposition, and erosional features, evidence of maintenance dredging.	Mixture of shallower and deeper bathymetry elevations due to deposition, high-flow net scour, and FNC dredging.	Turning basin.	No change. The turning basin is a dynamic net-depositional environment with frequent maintenance dredging (criterion 1 and both supplemental lines of evidence).

**Table B-1
Upper Reach Recovery Category Evaluation Summary**

Analysis Area #	River Mile	Location	River Side	Current Recovery Category Designation	RC Criterion 1	Supplemental Lines of Evidence		Conclusion and Rationale
					Vessel-Induced Scour (Analysis of Bed Sediment Disturbance Using the Sun-Illumination Map) ¹	A) Analysis of Changes in Bathymetry from 2003 to 2019 Using the Isopach Map	B) Waterway Usage	
14	4.8 to 5.0	Upstream of Oxbow Footbridge. See Figure B-9	W and E	Not assigned	Evidence of river flow features.	No data (not surveyed in 2003).	Not accessible to vessels.	RC2 based on lack of vessel access (supplemental line of evidence B) and no observable bed disturbance (criterion 1).

Notes:
 1. The term "significant" is used in this analysis to denote areas where natural recovery is presumed to be limited (consistent with the definition of Recovery Category 1) due to ongoing mixing from vessel scour.
 E: east
 FNC: federal navigation channel
 RC: recovery category
 RM: river mile
 STM: sediment transport model
 W: west

Table B-2
Recovery Category Acreage in the Upper Reach and Recommended Changes

Recovery Category Areas	Acreages from ROD Figure 17	Acreages After Recommended Modifications
1	33.2	31.2
2	4.9	20.2
3	66.4	60.8
Not designated	9.6	0
EAA ¹	17.3	19.3

Notes:

1. EAA boundaries have been modified from the ROD to account for the final as-built areas for the T-117 and Boeing Plant 2 early action areas.

EAA: Early Action Area

ROD: Record of Decision

T-117: Terminal 117

Appendix B Figures

Appendix C
Health and Safety Plan

Lower Duwamish Waterway Group

Port of Seattle / City of Seattle / King County / The Boeing Company

LOWER DUWAMISH WATERWAY PRE-DESIGN INVESTIGATION - QUALITY ASSURANCE PROJECT PLAN: APPENDIX C: HEALTH AND SAFETY PLAN

FINAL

Prepared for

Lower Duwamish Waterway Group

For submittal to

US Environmental Protection Agency

May 19, 2020

Prepared by:



200 West Mercer Street • Suite 401
Seattle, Washington • 98119

in association
with



1201 3rd Avenue • Suite 2600
Seattle, Washington • 98101

Title and Approval Page: LDW Pre-Design Investigation Health and Safety Plan

By their signature, the undersigned certify that this health and safety plan is approved and that it will be used to govern health and safety aspects of fieldwork described in the quality assurance project plan to which it is attached.



May 18, 2020

Date

Tom Wang
Anchor QEA Project Manager



May 18, 2020

Date

Kathy Godtfredsen
Windward Project Manager



May 18, 2020

Date

David Templeton
Corporate Health and Safety Manager



May 18, 2020

Date

Thai Do
Windward Field Coordinator/Health and Safety Officer



May 18, 2020

Date

Matt Woltman
Anchor QEA Field Coordinator/Health and Safety Officer

Site Emergency Procedures

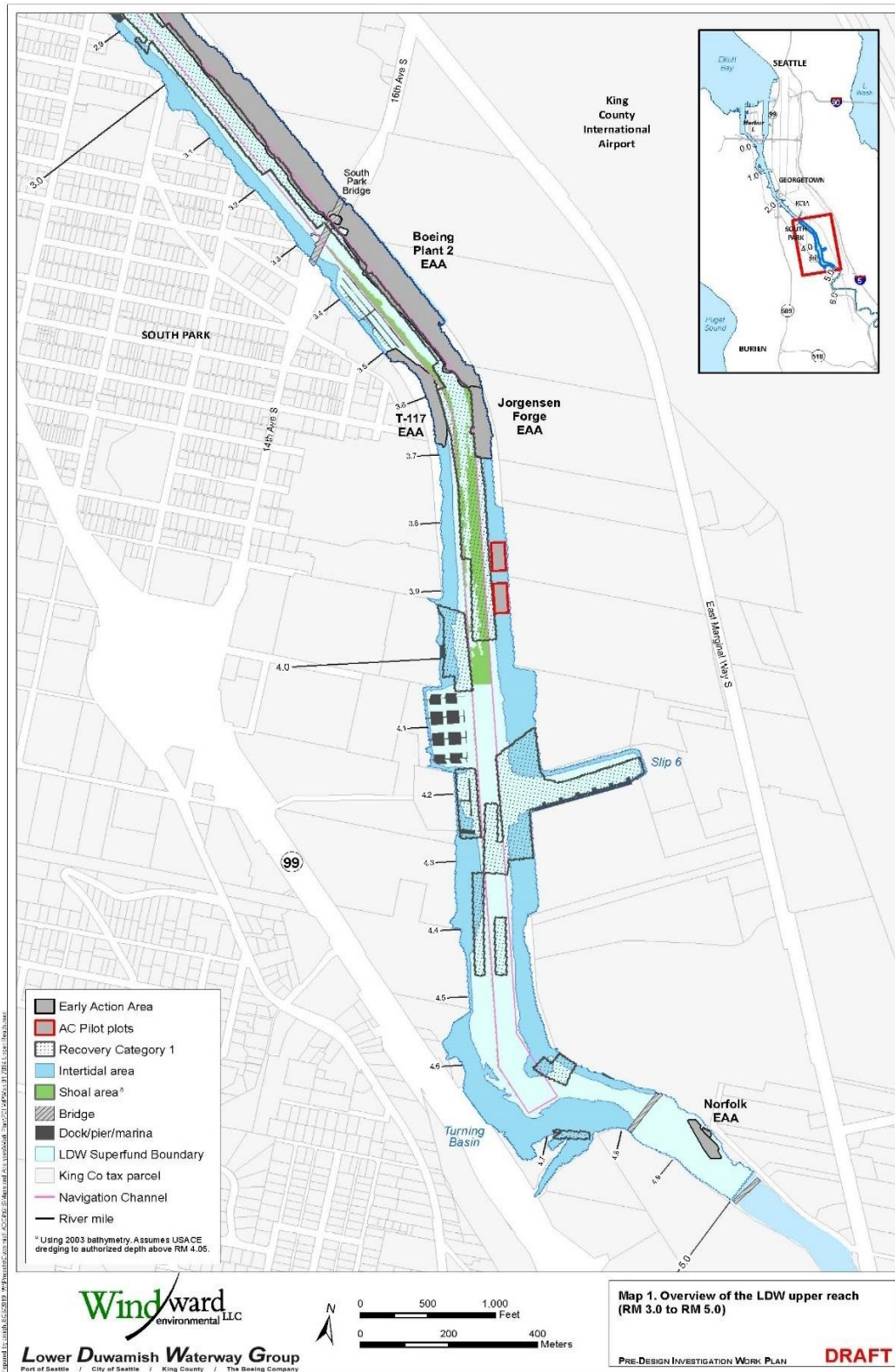


Figure C-i. General site location overview

EMERGENCY CONTACT INFORMATION

Table C-i. Site emergency form and emergency phone numbers

Category	Information	
Possible Chemicals of Concern	Metals, PCBs, PAHs, dioxin/furans, hydrogen sulfide	
Minimum Level of Protection	Modified Level D PPE	
Site(s) Location Address	Lower Duwamish Waterway, Seattle, Washington	
Emergency Phone Numbers		
Ambulance	911	
Fire	911	
Police	911	
Poison Control	(800) 222-1222	
PM	Tom Wang	Office: (206) 903-3314 Cell: (206) 465-0900
Windward FC/H&S Coordinator	Thai Do	Office: (206) 812-5407 Cell: to be provided
Anchor QEA FC/H&S Coordinator	Matt Woltman	Office: (206) 903-3327 Cell: to be provided
Anchor QEA CHSM	David Templeton	Office: (206) 287-9130 Cell: (206) 910-4279
	Gloria Palermo	Cell: (315)-622-3723
USCG	Emergency: (206) 286-5400 General Information: (206) 442-5295 VHF Channel 16	
Ecology NW Region Spill Response (24hr emergency line)	(206) 649-7000	

In the event of any emergency, contact the PM and FC.

For local resources, please visit: <http://www2.epa.gov/emergency-response/emergency-response-my-community>.

The National Response Center hotline is 1-800-424-8802.

CHSM – Corporate Health and Safety Manager

Ecology – Washington State Department of Ecology

FC – field coordinator

PCB – polychlorinated biphenyls

PAH – polycyclic aromatic hydrocarbons

PM – project manager

PPE – personal protective equipment

USCG – US Coast Guard

Table C-ii. Hospital information

Category	Information
Hospital Name	Harborview Medical Center
Address	325 9th Avenue
City, Province	Seattle, Washington 98104
Phone	(206) 323-3074
Emergency Phone	911

HOSPITAL ROUTE MAP AND DRIVING DIRECTIONS

The name, address, and telephone number of the hospital that will be used to provide medical care is as follows:

Harborview Medical Center
325 - 9th Avenue
Seattle, WA
206.323.3074

Directions from the vicinity of the LDW to Harborview Medical Center are as follows (Figure A-ii):

From the Duwamish River boat ramp (at South River Street, beneath the 1st Avenue South bridge):

- ◆ Drive east on South River Street.
- ◆ Turn left on Occidental Avenue South.
- ◆ Turn left on East Marginal Way South.
- ◆ Turn right on South Michigan Street.
- ◆ Look for entrance ramps to I-5 Northbound.
- ◆ Drive north on I-5.
- ◆ Take the James Street exit.
- ◆ Drive east on James Street to 9th Avenue.
- ◆ Turn right on 9th Avenue.
- ◆ Emergency entrance will be two blocks south on the right.

From the Harbor Island Marina (1001 Southwest Klickitat Way):

- ◆ From marina parking lot, turn sharp right onto Klickitat Way Southwest.
- ◆ Turn slight right onto Southwest Spokane Street
- ◆ Turn slight left to take the ramp toward WA-99 N/I-5/Columbian Way.
- ◆ Keep left at the fork in the ramp.
- ◆ Stay straight to go onto West Seattle Bridge.
- ◆ Merge onto I-5 North via the ramp on the left.
- ◆ Take the James Street exit.
- ◆ Head east on James Street to 9th Avenue.
- ◆ Turn right on 9th Avenue.
- ◆ Emergency entrance will be two blocks south on the right.

From South Park Marina (8604 Dallas Ave South):

- ◆ From marina parking lot, turn right onto Dallas Avenue South.
- ◆ Turn right onto 16th Avenue South.
- ◆ Turn left on East Marginal Way South.
- ◆ Look for entrance ramps to I-5 Northbound.
- ◆ Drive north on I-5.
- ◆ Take the James Street exit.
- ◆ Drive east on James Street to 9th Avenue.
- ◆ Turn right on 9th Avenue.
- ◆ Emergency entrance will be two blocks south on the right.



Figure C-ii. Hospital route map

PERSONAL INCIDENT RESPONSE PROCEDURES

In the event of an emergency, immediate action must be taken by the first person to recognize the event. Use the following steps as a guideline and refer to Figure A-iii:

- ◆ Survey the situation to verify that it is safe for you and the victim. Do not endanger your own life. Do not enter an area to rescue someone who has been overcome unless properly equipped and trained. Verify that all protocols are followed.
- ◆ Call the appropriate emergency number (911, if available) or direct someone else to do this immediately (see Table C-i). Explain the physical injury, chemical exposure, fire, or release and location of the incident.
- ◆ Have someone retrieve the nearest first aid kit (containing appropriate items for the particular work scope) and Automated External Defibrillator (AED), if available. Note: Only use an AED if you have been properly trained and are currently certified to do so.
- ◆ Decontaminate the victim without delaying life-saving procedures.
- ◆ Administer first aid and cardiopulmonary resuscitation (CPR), if properly trained, until emergency responders arrive.
- ◆ In the event that evacuation is required, the FL must perform a head count to verify that all Anchor QEA and Windward personnel are accounted for.
- ◆ Notify the Field Coordinator (FC) and Project Manager (PM); the PM will notify the client contact. The PM will also contact the Corporate Health and Safety Manager (CHSM). The CHSM will facilitate the incident investigation. All client requirements pertinent to personal incident reporting will also be adhered to.
- ◆ Complete the appropriate incident investigation reports.



Health and Safety Incident Flowchart

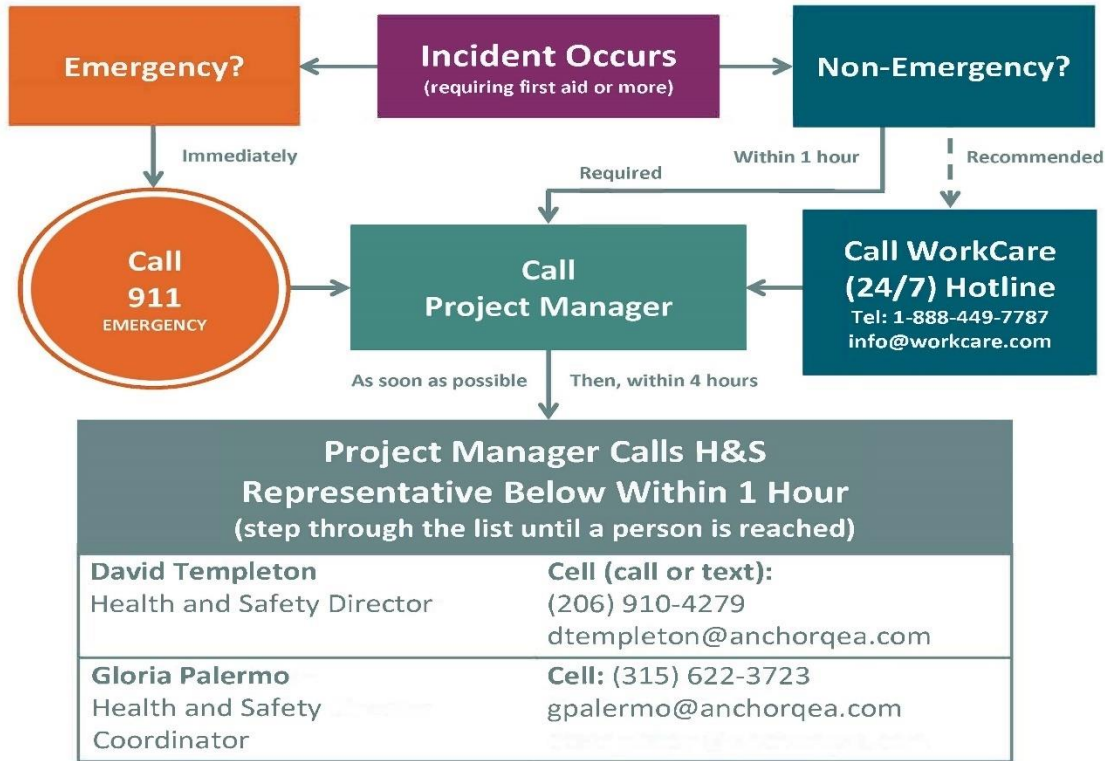


Figure C-iii. Incident flowchart

NON-PERSONAL INCIDENT RESPONSE PROCEDURES

All incidents including, but not limited to, fire, explosion, property damage, or environmental release will be responded to in accordance with the site-specific HSP. In general, this includes securing the site appropriate to the incident, turning control over to the emergency responders, or securing the site and summoning appropriate remedial personnel or equipment. Anchor QEA will immediately notify the client of any major incident, fire, equipment or property damage, or environmental incident with a preliminary report. A full report will be provided within 72 hours.

Spills and Releases of Hazardous Materials

- ◆ When required, notify the National Response Center Hotline (800-424-8802) and the US Coast Guard (USCG) (206-286-5400; VHF Channel 16). The following information should be provided: Name and telephone number
- ◆ Name and address of incident location

- ◆ Time and type of incident
- ◆ Name and quantity of materials involved, if known
- ◆ Extent of injuries
- ◆ Possible hazards to human health or the environment outside of the facility

If hazardous waste is released or produced through control of the incident, verify the following:

- ◆ Waste is collected and contained
- ◆ Containers of waste are removed or isolated from the immediate site of the emergency
- ◆ Treatment or storage of the recovered waste, contaminated soil or surface water, or any other material that results from the incident or its control is provided
- ◆ No waste that is incompatible with released material is treated or stored in the facility until cleanup procedures are completed

Verify that all emergency equipment used is decontaminated, recharged, and fit for its intended use before operations are resumed.

NEAR-MISS REPORTING

All near-miss incidents (i.e., those that could have reasonably led to an injury, environmental release, or other incident) must be reported to the FL and PM immediately, so action can be taken to verify that such conditions that led to the near-miss incident are readily corrected to prevent future occurrences.

Table of Contents

Title and Approval Page: LDW Pre-Design Investigation Health and Safety Plan	C-i
HEALTH AND SAFETY PLAN ACKNOWLEDGEMENT FORM	C-II
Site Emergency Procedures	C-iii
EMERGENCY CONTACT INFORMATION	C-IV
HOSPITAL ROUTE MAP AND DRIVING DIRECTIONS	C-V
PERSONAL INCIDENT RESPONSE PROCEDURES	C-VIII
NON-PERSONAL INCIDENT RESPONSE PROCEDURES	C-IX
Spills and Releases of Hazardous Materials	C-ix
NEAR-MISS REPORTING	C-X
Tables	C-xiii
Figures	C-xiii
Attachments	C-xiii
Acronyms	C-xiv
1 Introduction	C-1
2 Site Description and Project Scope	C-3
2.1 SITE DESCRIPTION	C-3
2.2 SCOPE OF WORK	C-3
3 Health and Safety Personnel	C-5
4 Hazard Evaluation and Control Measures	C-7
4.1 PHYSICAL HAZARDS	C-7
4.1.1 Slips, trips, and falls	C-7
4.1.2 Sampling equipment deployment	C-7
4.1.3 Falling overboard	C-8
4.1.4 Manual lifting	C-8
4.1.5 Heat stress	C-8
4.1.6 Cold stress	C-9
4.1.7 Weather	C-10
4.1.8 Small-boat Operations	C-10
4.1.9 Vessel traffic	C-11
4.1.10 Diving	C-11
4.2 BIOLOGICAL HAZARDS	C-12
4.3 CHEMICAL HAZARDS	C-14
4.3.1 Exposure routes	C-14
4.3.2 Description of chemical hazards	C-14
4.4 ACTIVITY HAZARD ANALYSIS	C-16

5	Work Zones and Shipboard Access Control	C-19
5.1	SAMPLING ZONE	C-19
5.2	DECONTAMINATION ZONE	C-19
5.3	SUPPORT ZONE	C-19
5.4	ACCESS CONTROL	C-19
6	Communications and Safe Work Practices	C-21
7	Personal Protective Equipment and Safety Equipment	C-23
7.1	LEVEL D PERSONAL PROTECTIVE EQUIPMENT	C-23
7.2	MODIFIED LEVEL D PERSONAL PROTECTIVE EQUIPMENT	C-23
7.3	SAFETY EQUIPMENT	C-24
8	Monitoring Procedures for Site Activities	C-25
9	Decontamination	C-27
9.1	MINIMIZATION OF CONTAMINATION	C-27
9.2	PERSONNEL DECONTAMINATION	C-28
9.3	SAMPLING EQUIPMENT DECONTAMINATION	C-28
10	Disposal of Contaminated Materials	C-30
10.1	PERSONAL PROTECTIVE EQUIPMENT	C-30
10.2	EXCESS SAMPLE MATERIALS	C-30
11	Training Requirements	C-31
11.1	PROJECT-SPECIFIC TRAINING	C-31
11.2	DAILY SAFETY BRIEFINGS	C-31
11.3	FIRST AID AND CPR	C-32
12	Medical Surveillance	C-33
12.1	COVID-19 PRIMARY EXPOSURE	C-34
12.2	COVID-19 SECONDARY EXPOSURE	C-34
12.3	COVID-19 TERTIARY EXPOSURE	C-34
13	Reporting and Record Keeping	C-37
14	Emergency Response Plan	C-39
14.1	PRE-EMERGENCY PREPARATION	C-39
14.2	PROJECT EMERGENCY COORDINATOR	C-39
14.3	EMERGENCY RESPONSE CONTACTS	C-40
14.4	RECOGNITION OF EMERGENCY SITUATIONS	C-41
14.5	DECONTAMINATION	C-41
14.6	FIRE	C-41
14.7	PERSONAL INJURY	C-41
14.8	OVERT PERSONAL EXPOSURE OR INJURY	C-42
	14.8.1 Skin contact	C-42
	14.8.2 Inhalation	C-42

14.8.3 Ingestion	C-42
14.8.4 Puncture wound or laceration	C-43
14.9 SPILLS AND SPILL CONTAINMENT	C-43
14.10 BOATING EMERGENCY HAZARDS	C-43
14.11 EMERGENCY ROUTES TO THE HOSPITAL	C-45

15 References **C-47**

Tables

Table C-i.	Site emergency form and emergency phone numbers	C-iv
Table C-ii.	Hospital information	C-iv
Table C-1.	Heat stress symptoms and recommended first aid	C-9
Table C-2.	Activity hazard analysis	C-16
Table C-3.	Emergency response contacts	C-40
Table C-4.	Potential boat emergency hazards and responses	C-44

Figures

Figure C-i.	General site location overview	C-iii
Figure C-ii.	Hospital route map	C-vii
Figure C-iii.	Incident flowchart	C-ix

Attachments

Attachment 1.	Modification to Health and Safety Plan Form
Attachment 2.	Daily Safety Briefing Form and Job Safety Analysis Sheets
Attachment 3.	Phase 1 Construction Restart COVID-19 Job Site Requirements

Acronyms

CDC	Centers for Disease Control and Prevention
CFR	Code of Federal Regulations
CHSM	corporate health and safety manager
COVID-19	coronavirus disease 2019
CPR	cardiopulmonary resuscitation
EPA	US Environmental Protection Agency
FC	field coordinator
HSO	health and safety officer
HSP	health and safety plan
JSA	job safety analysis
LDW	Lower Duwamish Waterway
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PFD	personal flotation device
PM	project manager
PPE	personal protective equipment
QAPP	quality assurance project plan
SVOC	Semivolatile organic compound
TCDD	tetrachlorodibenzo- <i>p</i> -dioxin
USCG	US Coast Guard
WAC	Washington Administrative Code
Windward	Windward Environmental LLC

1 Introduction

This site-specific health and safety plan (HSP) describes safe working practices for conducting field activities at potentially hazardous sites and for handling potentially hazardous materials/waste products. This HSP covers elements specified in 29 Code of Federal Regulations (CFR) 1910§120 and the Washington Administrative Code (WAC) Chapter 296-843. The procedures and guidelines contained herein are based on generally recognized health and safety practices. Any changes or revisions to this HSP will be made by a written amendment that will become a permanent part of this document. The goal of this HSP is to establish procedures for safe working practices for all field personnel and visitors.

This HSP addresses all field activities associated with the pre-design sampling in the upper reach of the Lower Duwamish Waterway (LDW). During site work, this HSP is to be implemented by the field coordinator (FC), who is also the designated site health and safety officer (HSO), in cooperation with the Anchor QEA, LLC (Anchor QEA) health and safety manager (HSM) and the Anchor QEA and Windward Environmental, LLC (Windward) project managers (PMs). All personnel involved in fieldwork on this project are required to comply with this HSP. The contents of this HSP reflect anticipation of the types of activities to be performed, knowledge of the physical characteristics of the site, and consideration of preliminary chemical data from previous investigations at the site. This HSP may be revised based on new information and/or changed conditions during site activities. Revisions will be documented in the project records.

This HSP will be modified by amendment, if necessary, to address changing field conditions or additional work tasks not already described in this document. Modifications will be proposed by the FC using the modification to HSP form included as Attachment 1. Modifications will be reviewed by the HSM or authorized representative and approved by the PM.

2 Site Description and Project Scope

2.1 SITE DESCRIPTION

The sampling area is in the upper reach of the LDW (see Figure A-i). The QAPP to which this HSP is appended provides complete details of the sampling program. This section summarizes the types of work that will be performed during field activities.

2.2 SCOPE OF WORK

Design sampling will be conducted in phases. Phase I will focus on defining the extent of sediment remedial action level (RAL) exceedances in sediment in order to identify initial remedial action areas and make initial technology assignments. Phase II will consist of the collection of data for potential additional RAL delineation, for assessment of vertical contamination in dredging/capping areas, and for obtaining area-specific information needed for design. Phase III will be conducted if data gaps remain after Phase II. Specific activities included in the QAPP are as follows:

- ◆ Collection of sediment samples from a boat using a pneumatic grab sampler
- ◆ Collection of sediment core samples from a boat using a vibracorer
- ◆ Collection of sediment samples under pier areas (if feasible) by divers¹
- ◆ Collection of sediment samples from intertidal areas using a shovel or hand corer
- ◆ Collection of soil samples from bank areas using pneumatic grab sampler, vibracorer, divers, or shovel or hand corer (dependent on bank location and elevation)
- ◆ Sample handling, processing, and shipping
- ◆ Collection of geotechnical data from a barge using a hollow-stem auger drilling rig or cone penetrometer sampling rig
- ◆ Visual inspection of banks from a vessel or from walking the shoreline in a subset of the areas
- ◆ Inspection of structures (via observations from a vessel, diver inspection or shoreline access), verification of utility locations, and assessment of thickness of sediment on top of riprap layers (via hand digging or use of jet probes)

Additional details on sampling design and methods are provided in Sections 4 and 5 of the QAPP.

¹ If divers are used, a site-specific dive HSP will be developed prior to fieldwork initiation.

3 Health and Safety Personnel

Key health and safety personnel and their responsibilities are described below. These individuals are responsible for the implementation of this HSP; they will be responsible for informing all individuals who are assigned to work on the site, or who visit the site, of the contents of this plan, and for ensuring that each person signs the Health and Safety Plan Acknowledgment Form (see front matter). By signing the Health and Safety Plan Acknowledgment Form, individuals recognize the site health and safety hazards, known or suspected, and agree to adhere to the protocols required to minimize exposure to such hazards.

Project Managers: The Anchor QEA PM will have overall responsibility for the successful outcome of the project. The PM will ensure that adequate resources and budget are provided for the health and safety staff to carry out their responsibilities during fieldwork. In consultation with the CHSM, the PM will make final decisions concerning implementation of the HSP and resolution of site health and safety issues. The PM will report directly to LDWG. The Windward PM will ensure proper implementation of the QAPP.

Field Coordinator/Health and Safety Officer: The FC/HSO will direct field sampling activities, coordinate the technical components of the field program with health and safety components, and ensure that work is performed according to the QAPP.

The FC/HSO will implement this HSP at the work location, and will be responsible for all health and safety activities and the delegation of duties to a health and safety technician in the field, if appropriate. The FC/HSO will also have stop-work authority, to be used if there is an imminent safety hazard or potentially dangerous situation. The FC/HSO or his designee will be present during sampling and operations.

Corporate Health and Safety Manager: The CHSM will have overall responsibility for preparation, approval, and revisions of this HSP. The CHSM will not necessarily be present during fieldwork, but will be readily available, if required, for consultation regarding health and safety issues during fieldwork.

Field Crew: All field crew members must be familiar and comply with the information in this HSP. They will also have the responsibility to report any potentially unsafe or hazardous conditions to the FC/HSO immediately. All field crew members will also have stop-work authority, to be used if there is an imminent safety hazard or potentially dangerous situation.

Site Visitors: Authorized visitors may come to the site to observe the sample collection/inspection activities. Visitors may be from the city, state, and federal regulatory and resource agencies that have a specific interest in the project, or visitors may be invited by the client, site contractors, or regulatory agencies. Visitors will be briefed on the hazards of the site, contents of the site-specific HSP, site safety rules, hazard control measures, and required personal protective equipment (PPE). They will

be escorted at all times by the field coordinator or a designated representative when entering work areas to observe the operations. Visitors will be expected to comply with all of the site health and safety requirements.

4 Hazard Evaluation and Control Measures

This section covers potential physical, biological (i.e., viral), and chemical hazards that may be associated with the proposed project activities, and presents control measures for addressing these hazards. An activity hazard analysis table, summarizing the potential hazards associated with each site activity and the recommended site controls for minimizing each potential hazard is presented in Section 4.4.

Confined space entry will not be necessary for this project. Therefore, hazards associated with this activity are not discussed in this HSP.

4.1 PHYSICAL HAZARDS

For this project, it is anticipated that physical and biological hazards will present a greater risk of injury than chemical hazards. Physical hazards are identified and discussed below.

4.1.1 Slips, trips, and falls

As with all field work, caution should be exercised to prevent slips on slick surfaces. In particular, sampling from a boat or other floating platform requires careful attention to minimize the risk of falling down or overboard. Extra care should be used in rainy conditions or on the shoreline where slick rocks or debris can be found. Slips can be minimized by wearing boots with good tread, made of material that does not become overly slippery when wet.

Trips are always a hazard on the uneven deck of a boat, in a cluttered work area, or in the intertidal zone where uneven substrate is common. Personnel will keep work areas as free as possible from items that interfere with walking.

Falls may be avoided by working as far from exposed edges as possible, by erecting railings, and by using fall protection when working on elevated platforms. For this project, open hatches may present a fall hazard, so hatches will remain closed when not being accessed for storage. Personnel should be aware of the area around any open hatches and use extra caution when accessing them.

4.1.2 Sampling equipment deployment

A pneumatic grab sampler deployed from a sampling vessel will be used to collect surface sediment samples and a vibracorer deployed from a sampling vessel will be used to collect subsurface sediment cores. These sampling devices and the mechanical equipment used to deploy the devices, such as motorized winches, may have rotating and reciprocating parts that if left unguarded, could pose hazards. Before sampling activities begin, there will be a training session for all field personnel to identify the potential hazards of the equipment and deployment devices onboard the sampling vessel. To control these hazards, work areas will be inspected to identify any potential pinch, grab, crush, and struck-by hazards. All field personnel will use caution and be

aware of overhead and gear hazards such as the grab sampler, vibrocorer, and A-frame. All field personnel will wear a hard hat and modified Level D PPE when working on deck. Corrective actions may involve installing guards over exposed, rotating parts; isolating or de-energizing equipment; establishing exclusion zones around high-hazard areas; and constructing guardrails around mechanical equipment to prevent inadvertent contact. Until such time as these hazards can be controlled or eliminated, project team members will avoid working in any areas where the hazard exists. For locations that cannot be accessed from a vessel, samples will be hand-collected using a stainless steel spoon, hand corer or shovel.

4.1.3 Falling overboard

Most sampling activities will be conducted from a boat. As with any work from a floating platform, there is a chance of falling overboard. USCG-approved Type II or III personal flotation devices (PFDs) will be worn while working on the deck of the boat. If a person falls overboard into the water, a life ring will be thrown to the person immediately. One onboard person (a spotter) will keep an eye on the victim and shout the distance (boat lengths) and direction (o'clock) of the victim from the vessel. All work will stop and the vessel will be used to retrieve the person in the water; the person in the water will be approached from downstream.

4.1.4 Manual lifting

Equipment and samples must be lifted and carried. Back strain can result if lifting is done improperly. During any manual handling tasks, personnel should lift with the load supported by their legs and not their backs. For heavy loads, an adequate number of people will be used, or if possible, a mechanical lifting/handling device will be used.

4.1.5 Heat stress

Heat stress could be an issue during hot days. Heat-related problems include heat rash, heat cramps, heat exhaustion, and heat stroke. The causes, symptoms, and first aid recommended by the National Institute for Occupational Health and Safety for each type of heat stress category are summarized in Table C-1. Workers should be aware of the key differences between the signs and symptoms of heat stroke and those of heat exhaustion, such as the lack of sweating, the color of the skin (red), and the rise in body temperature associated with the former. Heat stroke is a medical emergency that requires immediate medical attention.

Table C-1. Heat stress symptoms and recommended first aid

Type of Heat Stress	Cause	Symptoms	First Aid
Heat rash	Heat rash is a skin irritation caused by excessive sweating during hot, humid weather.	Formation of rash (red cluster of pimples or small blisters) usually on the neck and upper chest, in the groin, under the breasts, and/or in elbow creases.	Try to work in a cooler, less humid environment when possible.
			Keep the affected area dry. Dusting powder may be used to increase comfort.
Heat cramps	Heat cramps usually affect workers who sweat a lot during strenuous activity. This sweating depletes the body's salt and moisture levels. Low salt levels in muscles cause painful cramps. Heat cramps may also be a symptom of heat exhaustion.	Muscle pain or spasms, usually in the arms, legs, and abdomen.	Have the person stop working and move him or her to a cool, shady area.
			Have the person drink clear juice or a sports beverage. Do not let person return to work until a few hours after cramps subside.
			Seek medical attention immediately if: (1) the person has heart problems, (2) the person is on a low sodium diet, or (3) the cramps do not subside within 1 hour.
Heat exhaustion	Heat exhaustion is the body's response to an excessive loss of water and salt, usually through excessive sweating. Workers most prone to heat exhaustion are those who are elderly or have high blood pressure, and those working in a hot environment.	Heavy sweating, extreme weakness or fatigue, dizziness or confusion, nausea, clammy moist skin, pale or flushed complexion, muscle cramps, slightly elevated body temperature, and fast and shallow breathing.	Have the person stop working and move him or her to a cool, shady area.
			Give the person plenty of water, juice, or other cool nonalcoholic beverages to drink.
			Have the person take a cool shower, bath, or sponge bath.
Heat stroke	Heat stroke is the most serious heat-related disorder. It occurs when the body becomes unable to control its temperature: the body's temperature rises rapidly, the sweating mechanism fails, and the body is unable to cool down. When heat stroke occurs, the body temperature can rise to 106 degrees Fahrenheit or higher within 10 to 15 minutes. Heat stroke can cause death or permanent disability if emergency treatment is not given.	Hot dry skin (no sweating), hallucinations, chills, throbbing headache, high body temperature, confusion/dizziness, and slurred speech.	Call 911 immediately.
			Have the person stop working and move him or her to a cool, shady area.
			Cool the person using methods such as (1) soaking person's clothes with water, (2) spraying, sponging, or showering person with room temperature water, and/or (3) fanning person's body. Ice or cold packs may also be used.

Source: CDC (2018), as modified in Amec et al. (2015).

4.1.6 Cold stress

Hypothermia occurs when the body's core temperature falls below 95°F. There is a risk of hypothermia if a crew member fails to dress warmly in cold weather, gets wet from

rain or splashes, or falls into the water. To prevent hypothermia, all personnel will wear protective clothing appropriate for the weather conditions and physical activity. The FC/HSO will monitor all crew members for early symptoms of hypothermia (e.g., shivering, muscle incoordination, mild confusion). If such symptoms are observed, the FC/HSO will take immediate steps to reduce heat loss by providing extra layers of clothing, or by temporarily moving the affected crew member to a warmer environment. Other immediate steps that can be taken to reduce the symptoms of hypothermia include minimizing exposure to cold and wet conditions, limiting sitting or standing still for long periods, rehydration with warm fluids, and the removal of any wet outer layers of clothing to permit sweat evaporation during rest periods in a warm environment.

Sampling operations and conditions that might result in the occurrence of frostbite are not anticipated. The sampling will take place during the time of year when extreme weather conditions are not expected to occur.

4.1.7 Weather

In general, field team members will be equipped for the normal range of weather conditions. The FC/HSO will be aware of current weather conditions, and of the potential for those conditions to pose a hazard to the field crew. Some conditions that might force work stoppage are electrical storms, high winds, or high waves resulting from winds.

4.1.8 Small-boat Operations

Boat operations are associated with various risks, such as: 1) passengers or crew members falling overboard/drowning, 2) coming in contact with other vessels or being contacted by other vessels operating in the area, 3) losing power or steering capability and drifting into hazardous areas (i.e., shores, bridges, industrial facilities, etc.), and 4) encountering severe weather and dangerous water conditions. The risk of a boating accident can be reduced by ensuring that the boat operators are experienced, operating the vessel in compliance with USCG rules and regulations, maintaining the vessel in good mechanical order, avoiding bad weather and dangerous water conditions, and ensuring that required emergency equipment is available onboard.

Safety precautions that will be implemented as part of boat operations for this project include the following:

- ◆ The vessels must have required USCG safety equipment onboard in good conditions, including a life jacket for each project team member, a first aid kit, fire extinguishers, distress flares, a throw-able life ring, navigation charts for the work area, running lights and a horn.
- ◆ Smoking is not permitted onboard the vessels.
- ◆ All crew members must be trained so that they know the location and use of onboard safety equipment.

- ◆ For vessels less than 25 feet long, at least one fire extinguisher must be onboard. For vessels greater than 26 feet in length but less than 40 feet, at least two fire extinguishers must be onboard.
- ◆ A life jacket must be worn by project team members at all times while working on boats, piers, docks that are not equipped with guardrails, and vessels when not tied to shore.
- ◆ The VHF radio must be turned on and monitored.
- ◆ Crew members should not untie mooring lines until instructed to do so by the vessel operator.
- ◆ Crew members should never jump between the vessel and the dock or other vessels.
- ◆ Docks, piers and shoreline areas should be approached slowly. The boat should never be fended off by placing your body between the boat and any object.
- ◆ All crew members should watch for hazards such as approaching vessels or wakes. It should never be assumed that other crew members see such hazards; therefore, they should be alerted to any potential risks that are observed.
- ◆ Crew members should be aware of overhead power lines and underwater utility corridors.
- ◆ If lightening or thunder occurs before the crew is able to get safely off the water, the 30/30 rule should be used: if the time between seeing the lightening and hearing thunder is 3 seconds or less, the boat should be moved near a tall structure such as a bridge and remain there until 30 minutes after the last thunder is heard.
- ◆ If refueling is necessary, the engine should be turned off and allowed to cool before fueling is attempted.

4.1.9 Vessel traffic

Because of the high volume of vessel traffic on the LDW, precautions and safe boating practices will be implemented to ensure that the field boat does not interrupt such traffic. As practical, the field boat will stay out of the navigation channel. Vessel traffic will be monitored on VHF channel 16.

4.1.10 Diving

It is anticipated that commercial divers may be needed for select sampling and/or inspection activities conducted for this project, and that the diving work will be conducted by a specialty contractor that will provide its own site-specific diving HSP (which will be reviewed by King County prior to review by the US Environmental Protection Agency [EPA]). The diving contractor must also comply with all applicable requirements of Washington Department of Labor & Industry Standards for

Commercial Diving Operations (WAC 296-37) and provide a safe practices manual for each diving mode per WAC 296-37-530 before beginning dive operations. This manual must include the following:

- ◆ Safety procedures and checklists for diving operations
- ◆ Assignments and responsibilities of the dive team members
- ◆ Equipment procedures and checklists
- ◆ Emergency procedures for fire, equipment failure, adverse environmental conditions, and medical illness and injury

In addition, the contractor must produce a site-specific dive plan for each diving operation that specifies the means and methods that will be used to comply with all required elements of Washington State's diving standards. The dive plan document is also subject to review by King County and EPA.

4.2 BIOLOGICAL HAZARDS

In response to the global public health emergency regarding Coronavirus Disease 2019 (COVID-19), and to address the safe practices requirements mandated by the State of Washington Office of the Governor's Phase 1 Construction Restart – Proclamation 20-25, its supporting Phase 1 Construction Restart COVID-19 Job Site Requirements (Inslee 2020a, b), and the General Coronavirus Prevention Under Stay at Home-Stay Healthy guidelines (L&I 2020a), this section describes basic steps to reduce the risk of worker exposure to SARS-CoV-2, the virus that causes COVID-19, during field operations. The COVID-19 safe practices requirements provided by the state are provided in Attachment 3.

COVID-19 is a contagious respiratory disease caused by the SARS-CoV-2 virus (OSHA 2020). Infection with SARS-CoV-2 can cause mild to severe illness and can be fatal. Symptoms typically include fever (>100.4°F), coughing, and shortness of breath, but some people have reported experiencing other non-respiratory symptoms – such as chills, repeated shaking with chills, muscle pain, headache, sore throat, and a loss of taste or smell – while still others have been asymptomatic and experienced no symptoms at all. According to the US Department of Health and Human Services Centers for Disease Control and Prevention (CDC), symptoms of COVID-19 may appear in as few as 2 days or as long as 14 days after exposure (CDC 2020). The virus is primarily spread via inhalation and from person-to-person, including:

- ◆ Between people within close contact distance of one another (within approximately 6 ft)
- ◆ Through respiratory droplets, which may land in or be inhaled via the mouths or noses of people who are nearby when an infected person coughs or sneezes

The virus may also be transmitted by touching a surface or object that has SARS-CoV-2 on it and then one's own mouth, nose, or eyes, but this method is not believed to be the

primary route by which the virus spreads. It is believed that people are most contagious when they are most symptomatic (i.e., experiencing fever, cough, and/or shortness of breath), but transmission may be possible before symptoms are evident (CDC 2020).

As appropriate, site workers will implement good hygiene and infection control practices, including:

- ◆ Staying home when sick or showing symptoms²
 - ◆ If employees are showing symptoms, it is recommended that they contact their health care provider for medical advice. Further steps taken may include an examination and testing as recommended by their health care provider.
 - ◆ If employees are showing any symptoms, they will be asked to leave the site and not return for a minimum of 14 days or until released by a health care professional.
- ◆ Limiting field personnel to the minimum individuals required to safely complete the work
- ◆ Limiting time spent in groups in enclosed spaces to the extent possible
- ◆ Driving separately to and from the work site
- ◆ Monitoring workers' temperatures for signs of fever
- ◆ Following respiratory etiquette, including covering coughs and sneezes
- ◆ Washing hands frequently and thoroughly. If soap and running water are not immediately available, alcohol-based sanitizer containing at least 60% alcohol will be used.
- ◆ Wearing disposable PPE during sampling and properly disposing of PPE items as often as necessary
- ◆ Increasing physical distance among and between employees and others (i.e., use of social distancing strategies)
- ◆ Providing additional barriers to exposure, such as facemasks, face shields, and protective eyewear, when social distancing cannot be maintained at all times
- ◆ Avoiding sharing personal items and using other workers' phones, pens, work tools, and equipment, when possible
- ◆ Maintaining regular housekeeping practices, including routine cleaning and disinfecting of surfaces, equipment, and other elements of the work environment
- ◆ Considering alternative strategies to reduce exposure, such as staggering work shifts and breaks and covering common touch areas with cleanable materials

² If an employee has traveled to an affected country outside the United States or has had exposure to infected individuals within the United States, a minimum 14-day self-quarantine from the project site is required to determine if symptoms develop or if testing is positive for COVID-19.

- ◆ Following the same prevention guidelines while off-site including while traveling, at a hotel, and participating in other activities in order to address potential exposures outside the workplace

Additional compliance measures adhering to the State of Washington Office of the Governor's Phase 1 Construction Restart – Proclamation 20-25, its supporting Phase 1 Construction Restart COVID-19 Job Site Requirements (Inslee 2020a, b), and the General Coronavirus Prevention Under Stay at Home-Stay Healthy guidelines (L&I 2020a) are integrated throughout the subsequent sections of this HSP, including the hazard analysis in Section 4.4.

4.3 CHEMICAL HAZARDS

Previous investigations have shown that some chemicals are present at higher-than-background concentrations in the sampling area. For the purposes of discussing the potential exposure of individuals to chemicals in sediments, the chemicals of concern are metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), semivolatile organic compounds (SVOCs), dioxins/furans, and hydrogen sulfides.

4.3.1 Exposure routes

Potential routes of chemical exposure include inhalation, dermal contact, and ingestion. Exposure will be minimized by using safe work practices (Section 6) and by wearing the appropriate PPE. Further discussion of PPE requirements is presented in Section 7.

4.3.1.1 Inhalation

Inhalation is not expected to be an important route of exposure, because sampling will be conducted outside on a boat, in the field, or in a well-ventilated area.

4.3.1.2 Dermal exposure

Dermal exposure to hazardous substances associated with sediments, surface water, or equipment decontamination will be controlled by the use of PPE, and by adherence to detailed sampling and decontamination procedures.

4.3.1.3 Ingestion

Incidental ingestion of sediment or surface water is not considered a major route of exposure for this project. Accidental ingestion of surface water is possible. However, careful handling of equipment and containers while onboard the boat should prevent water from splashing or spilling during sample collection and handling activities.

4.3.2 Description of chemical hazards

4.3.2.1 Metals

Exposure to metals at this site may occur via ingestion or skin contact. As mentioned above, neither is a likely exposure route. Metal fumes or metal-contaminated dust will

not be encountered during field and sample handling activities. Large amounts of sediment would need to be ingested for any detrimental effects to occur. Momentary skin contact allows little, if any, opportunity for metals to pass into the body. Field procedures require immediate washing of sediments from exposed skin.

4.3.2.2 Polycyclic aromatic hydrocarbons and semivolatile organic compounds

Exposure to PAHs or SVOCs at this site may occur via ingestion or skin contact. Inhalation, the most important human health exposure pathway for this group of chemicals, is not expected to occur at this site. Large amounts of sediment would need to be ingested for any detrimental effects to occur. Some PAHs may be carcinogenic after long periods of skin contact. However, momentary skin contact allows little, if any, opportunity for compounds to pass into the body. Field procedures require immediate washing of sediments from exposed skin.

4.3.2.3 Polychlorinated biphenyls

Exposure to PCBs at this site may occur via ingestion or skin contact. Acute and chronic exposure can damage the liver and cause symptoms of edema, jaundice, anorexia, nausea, abdominal pains, and fatigue. PCBs are a suspected human carcinogen, although large amounts of sediment would need to be ingested for any detrimental effects to occur. Prolonged skin contact with PCBs may cause acne-like symptoms known as chloracne. Irritation to eyes, nose, and throat may also occur. However, momentary skin contact allows little, if any, opportunity for compounds to pass into the body. Field procedures require immediate washing of sediments from exposed skin.

4.3.2.4 Dioxins/furans

Exposure to dioxins/furans at this site may occur via ingestion or skin contact. Acute and chronic exposure can damage the liver, increase the risk of diabetes and abnormal glucose tolerance, and possibly increase the risk for reproductive and developmental effects. 2,3,7,8-TCDD is a possible human carcinogen, and a mixture of dioxins/furans with six chlorine atoms (four of the six chlorine atoms at the 2-, 3-, 7-, and 8-positions) is a probable human carcinogen. However, large amounts of sediment would need to be ingested for any detrimental effects to occur. Prolonged skin contact with dioxins/furans may cause acne-like symptoms known as chloracne. Other effects on the skin, such as red skin rashes, have been reported to occur in people following exposure to high concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Momentary skin contact allows little, if any, opportunity for the passage of any of the compounds into the body. Field procedures require the immediate washing of sediments from exposed skin.

4.3.2.5 Hydrogen sulfides

Exposure to hydrogen sulfides at this site may occur primarily via inhalation or eye and skin contact. At lower concentrations typically found in sediments, hydrogen sulfides emit a rotten egg odor. Acute and chronic exposure to this odor can irritate the

respiratory tract and eyes and cause symptoms of headaches, dizziness, nausea, and abdominal pains. Exposure to high concentrations may result in bronchitis, bronchial pneumonia, coma, unconsciousness, or respiratory arrest. However, momentary skin contact allows little, if any, opportunity for compounds to pass into the body. Field procedures require adequate ventilation and immediate washing of sediments from exposed skin.

4.4 ACTIVITY HAZARD ANALYSIS

The activity hazard analysis summarizes the hazards associated with pre-design sampling activities and along with the controls that can reduce or eliminate the risk of these hazards occurring (Table C-2). Job safety analysis (JSA) sheets are also included in Attachment 2 for description of potential hazards that may be encountered during implementation of the environmental sediment sampling (including sediment sample collection and core processing), visual shoreline inspection, geotechnical sediment sampling, and structures inspections. JSAs associated with completion of focused topographic surveys and other surveys (as necessary) will be included in the surveying HSP.

Table C-2. Activity hazard analysis

Hazard ¹	Control
Slips and trips	Use extra care when walking on uneven and unstable surfaces along the shoreline, and under wet/slippery conditions. Wear boots with good tread.
Falling overboard	Use care in boarding/departing from the vessel. Wear a PFD. Provide and make readily accessible on each boat a life ring to throw to the person in the water. Have one onboard person (a spotter) keep an eye on the victim and shout the distance (boat lengths) and direction (o'clock) of the victim from the vessel. Stop work and use the vessel to retrieve the person in the water. Approach the person from downstream.
Skin or eye contact with contaminated sediments or liquids	Wear modified Level D PPE. Immediately wash sediments from exposed skin. Use an eyewash, if necessary, for contaminated or foreign debris in the eyes.
Back strain	Use appropriate technique for lifting equipment and samples, or seek help.
Overhead hazards	Use caution and be aware of overhead and gear hazards such as the grab sampler and A-frame. Wear a hard hat and modified Level D PPE when working on deck.
Open hatches	Keep hatches closed when not being accessed. Be aware around hatch area and use caution when entering/exiting hatch.
Heat stress	Monitor crew members for signs/symptoms of heat stress. Remove person to cool area and remove extra layers of clothing. Promote evaporative cooling and rehydrate with electrolytic fluids.
Cold stress	Monitor crew members for signs/symptoms of hypothermia. Minimize prolonged exposure to wet and cold conditions. Remove person to warm area and remove wet clothing. Rehydrate with warm fluids.
Weather	Monitor weather forecast and local conditions. Stop work if conditions pose a hazard (e.g., electrical storms, high winds) and resume work when safe to do so.
Fatigue	Take regular breaks, and limit repeated excessively long work days.

Hazard ¹	Control
Pinch points and cuts	Be aware of pinch points and potential for cuts during sample collection and processing. Handle equipment and tools with care, Use safety knives if necessary, and follow instruction manuals for any power tools.
SARS-CoV-2 virus	<p>All basic program elements in the General Coronavirus Prevention Under Stay at Home-Stay Healthy guidelines (L&I 2020a) will be met, except for distancing more than 6 ft at all times (distances of less than 6 ft may occur at times on boats). Therefore, per L&I guidance referenced below, a hazard assessment was done to determine that this work site is a medium transmission risk. Based on this risk, the required PPE was identified and included in the alternative strategies in addition to basic program elements. In total, the following control actions will be taken.</p> <ul style="list-style-type: none"> • Stay at home if sick or exhibiting COVID-19 symptoms. • Avoid group meetings in enclosed spaces. • Drive separately to/from work site. Monitor workers' temperatures for signs of fever. • Maintain social distancing (i.e., minimum 6-ft distance) to extent possible from other people. • Follow proper coughing and sneezing etiquette and personal hygiene (e.g., frequent and thorough handwashing or using sanitizer with at least 60% alcohol). • Avoid sharing tools and equipment and decontaminate/disinfect all tools, equipment, and supplies frequently. • Wear modified Level D PPE, including gloves and protective face masks with safety glasses or face shields. • Limit number of personnel to minimum needed to complete the work and modify work spaces to allow greater distancing.

Notes:

1. Responses to boat emergencies are addressed in Table C-4.
2. A medium transmission risk work site condition includes a condition where large crews are outside and at least a 6-ft distance is mostly maintained, but some job tasks require several minutes of less than 6-ft distance several times a day. Under these conditions, the following masks are acceptable: dust mask, foreign system non-NIOSH approved filtering face piece respirator (such as KN95), or medical procedure masks (L&I 2020b).

COVID-19 – coronavirus disease 2019

PFD – personal flotation device

PPE – personal protective equipment

5 Work Zones and Shipboard Access Control

During sampling and sample handling activities, work zones will be established to identify where sample collection and processing are actively occurring. The intent of the zones is to limit the migration of sample material out of its zone, and to restrict unauthorized access to active work areas by defining work zone boundaries. The work zones are described below.

5.1 SAMPLING ZONE

A sampling work zone will encompass the exclusion area where sample collection and handling activities are being performed. The FC/HSO will delineate the work zone as a particular area onboard the collection vessel or at each intertidal shoreline sampling location. Only persons with appropriate training, PPE, and authorization from the FC/HSO will be allowed to enter this zone while work is in progress.

5.2 DECONTAMINATION ZONE

A decontamination zone where personnel will clean soiled boots and/or PPE prior to leaving the work zone will be set up. The zone will have the buckets, brushes, soapy water, rinse water, or wipes necessary to clean boots, PPE, or other equipment leaving the work zone. Plastic bags will be provided for expendable and disposable materials. If the sampling location does not allow for the establishment of a decontamination zone, the FC/HSO will provide alternatives to prevent the spread of contamination.

Decontamination of the boat will be completed at the end of each work day. Cockpit and crew areas will be rinsed down with water to minimize the accumulation of sediment.

5.3 SUPPORT ZONE

The support zone is any work area beyond the sampling work zone and decontamination zone boundaries where sample collection and processing do not occur. Activities in this zone include boat operations (e.g., piloting the boat and remotely controlling sampling equipment), administrative work (e.g., observing the field effort, taking notes, filling out paperwork, communicating with project managers, and directing field staff), and rest breaks. Prior to entering the support zone, personnel are required to decontaminate or dispose of soiled PPE or equipment to limit the spread of contamination into the clean area.

5.4 ACCESS CONTROL

Security and control of access to the boat will be the responsibility of the FC/HSO and boat captain. Boat access will be granted to necessary project personnel and authorized visitors only. Any security or access control problems will be reported to the client or appropriate authorities.

6 Communications and Safe Work Practices

Communications at the job site will occur by verbal direction, use of hand signals, radio, or a combination of all three. Site personnel will carry cellular telephones and a list of emergency telephone numbers included in this HSP. These telephone numbers are listed in Section 14.3 of this HSP and in the front matter of the document. Boat operators will have VHF radios that are capable of communicating with USCG emergency services and with other vessels operating in the immediate work area. An air horn will be staged at each work area to initiate an evacuation of the site in an emergency, should other means of communication (i.e., radio, telephone, etc.) fail. Site personnel will be informed of site emergency procedures and communication protocols during their initial site orientation.

Following common sense will minimize the risk of exposure or accidents at this work site. The following general safety rules will be adhered to on-site:

- ◆ Do not climb over or under obstacles of questionable stability (e.g., docks, piers).
- ◆ Do not eat, drink, smoke, or perform other hand-to-mouth transfers in the work zone.
- ◆ Work only in well-lighted spaces.
- ◆ Never enter a confined space without the proper training, permits, and equipment.
- ◆ Make eye contact with vessel/sampling equipment operators when moving within the range of their equipment.
- ◆ Be aware of the movements of shipboard equipment when not in the operator's range of vision.
- ◆ Get immediate first aid for all cuts, scratches, abrasions, or other minor injuries.
- ◆ Use the established sampling and decontamination procedures.
- ◆ Always use the buddy system.
- ◆ Be alert to your own and other workers' physical conditions.
- ◆ Report all accidents, no matter how minor, to the FC/HSO.
- ◆ Do not do anything dangerous or unwise even if ordered by a supervisor.

7 Personal Protective Equipment and Safety Equipment

Appropriate PPE will be worn as protection against potential hazards. In addition, a PFD will be required when working onboard the boat. Prior to donning PPE, the field crew will inspect their PPE for any defects that might render the equipment ineffective.

Fieldwork will be conducted in Level D or modified Level D PPE, as discussed in Sections 7.1 and 7.2. Situations requiring PPE beyond modified Level D are not anticipated. Should the FC/HSO determine that PPE beyond modified Level D is necessary, the HSM will be notified and an alternative selected. This HSP also acknowledges that site conditions may change during implementation of the work, possibly leading to a change in exposure pathways or chemicals of concern. If changes are observed, evaluation for potential changes in PPE needs will be completed.

New personnel or visitors will be informed of PPE requirements during their initial site briefing (see Section 3).

7.1 LEVEL D PERSONAL PROTECTIVE EQUIPMENT

Workers performing general activities during which skin contact with contaminated materials is unlikely will wear Level D PPE. Level D PPE includes the following:

- ◆ Protective clothing
- ◆ Chemical-resistant steel-toed boots
- ◆ Chemical-resistant gloves
- ◆ Safety glasses
- ◆ High-visibility vests
- ◆ Hard hats

7.2 MODIFIED LEVEL D PERSONAL PROTECTIVE EQUIPMENT

Workers performing activities during which skin contact with contaminated materials is possible, and during which inhalation risks are not expected, will be required to wear an impermeable outer suit. The type of outerwear will be chosen according to the types of chemical contaminants that might be encountered. Modified Level D PPE includes the following:

- ◆ Impermeable outer garb such as rain gear
- ◆ Waterproof and chemical-resistant steel-toed boots
- ◆ Waders and wader boots
- ◆ Chemical-resistant outer gloves
- ◆ Heavy-duty waterproof gloves

- ◆ High-visibility vests
- ◆ Hard hats
- ◆ Safety glasses
- ◆ Protective face mask (as needed)

When the ability to remain socially distant (i.e., minimum 6 ft apart) is limited (on boats), workers will be expected to don safety glasses and protective fabric or disposable face masks during field activities to comply with the Phase 1 Construction Restart COVID-19 Job Site Requirements (Inslee 2020b), the General Coronavirus Prevention Under Stay at Home-Stay Healthy guidelines (L&I 2020a), and CDC recommendations for reducing exposure to COVID-19 in public spaces. Workers will be provided with safety glasses and disposable medical face masks designed to reduce the transfer of saliva and respiratory droplets to others and to help block potentially infectious materials from reaching the skin, eyes, mouth, or nose of the wearer during daily activities. Workers will be expected to change disposable masks at least halfway through each work day and as frequently as necessary (i.e., when soiled or damaged). Face shields will also be available as additional or alternate options for protection from COVID-19 exposure.

7.3 SAFETY EQUIPMENT

In addition to PPE that will be worn by shipboard personnel, basic emergency and first aid equipment will be provided. Equipment for the field team will include:

- ◆ A copy of this HSP
- ◆ A first aid kit adequate for the number of personnel
- ◆ Emergency eyewash
- ◆ Sunscreen
- ◆ Fire extinguisher

The FC/HSO will ensure that the safety equipment is onboard. Equipment will be checked daily to ensure its readiness for use.

8 Monitoring Procedures for Site Activities

A monitoring program that addresses the potential site hazards will be maintained. For this project, air, dust, and noise monitoring will not be necessary. The sampled media will be wet and will not pose a dust hazard, and none of the equipment will emit high-amplitude (> 85 dBA) sound. For this project, the monitoring program will consist of all workers monitoring themselves and their co-workers for signs that might indicate physical stress or illness.

All personnel will be instructed to look for and inform each other of any deleterious changes in their physical or mental condition during the performance of all field activities. Examples of such changes are as follows:

- ◆ Headaches
- ◆ Dizziness
- ◆ Nausea
- ◆ Fever
- ◆ Coughing
- ◆ Shortness of breath (difficulty breathing)
- ◆ Muscle pain
- ◆ Sore throat
- ◆ Loss of sense of taste or smell
- ◆ Symptoms of heat stress
- ◆ Blurred vision
- ◆ Cramps
- ◆ Irritation of eyes, skin, or respiratory system
- ◆ Changes in complexion or skin color
- ◆ Changes in apparent motor coordination
- ◆ Increased frequency of minor mistakes
- ◆ Excessive salivation or changes in papillary response
- ◆ Changes in speech ability or speech pattern
- ◆ Shivering
- ◆ Blue lips or fingernails

If personnel develop any of these conditions, work will be halted immediately and the affected person(s) evaluated. If further assistance is needed, personnel at the local hospital will be notified, and an ambulance will be summoned if the condition is

thought to be serious. If the condition is the direct result of sample collection or handling activities, procedures will be modified to address the problem.

9 Decontamination

Decontamination is necessary to prevent the migration of contaminants from the work zone(s) into the surrounding environment, and to minimize the risk of exposure of personnel to contaminated materials that might adhere to PPE. The following sections discuss personnel and equipment decontamination. The following supplies will be available to perform decontamination activities:

- ◆ Wash buckets
- ◆ Rinse buckets
- ◆ Scrub brushes
- ◆ Clean water sprayers
- ◆ Paper towels
- ◆ Plastic garbage bags
- ◆ Alconox® or similar decontamination solution

9.1 MINIMIZATION OF CONTAMINATION

The first step in addressing contamination is to prevent or minimize exposure to biological hazards and existing contaminated materials and the spread of those materials. During field activities, the FC/HSO will enforce the following measures:

Personnel:

- ◆ Limit field staff to minimum number required to safely complete the work.
- ◆ Wash hands frequently and thoroughly. Use alcohol-based sanitizer with at least 60% alcohol if soap and running water are not readily available.
- ◆ Follow proper coughing and sneezing etiquette.
- ◆ Avoid sharing personal items.
- ◆ Avoid group gatherings in enclosed spaces.
- ◆ Maintain proper social distance (i.e., minimum 6 ft) to extent possible.
- ◆ Follow the same prevention guidelines off site including while traveling, at a hotel, and participating in other activities in order to address potential exposures outside the workplace.
- ◆ Do not walk through areas of obvious or known contamination, if avoidable.
- ◆ Do not handle, touch, or smell contaminated materials directly.
- ◆ Make sure PPE has no cuts or tears prior to use.
- ◆ Fasten all closures on outer clothing, covering with tape if necessary.

- ◆ Protect and cover any skin injuries.
- ◆ Stay upwind of airborne dusts and vapors.
- ◆ Do not eat, drink, chew tobacco, or smoke in the work zones.

Sampling equipment and boat:

- ◆ Avoid or minimize handling of equipment, tools, and supplies by multiple people.
- ◆ Clean or disinfect touch surfaces, handheld equipment, tools, and supplies frequently.
- ◆ Place clean equipment on a plastic sheet or aluminum foil to avoid direct contact with contaminated media.
- ◆ Keep contaminated equipment and tools separate from clean equipment and tools.
- ◆ Clean boots before entering the boat.

9.2 PERSONNEL DECONTAMINATION

The FC/HSO will ensure that all site personnel are familiar with personnel decontamination procedures. Personnel will perform the following decontamination procedures, as appropriate, before eating lunch, taking a break, or leaving the work location:

1. If outer suit is heavily soiled, rinse it off.
2. Remove outer suit.
3. Wash and rinse outer gloves and boots with soapy water.
4. Remove outer gloves; inspect and discard if damaged.
5. Remove inner gloves and discard.
6. Wash hands.

Before returning to work, personnel will re-don all necessary PPE. If leaving for the day, personnel will dispose of soiled, expendable PPE.

9.3 SAMPLING EQUIPMENT DECONTAMINATION

Sampling equipment will be decontaminated, as described in Section 4.6 of the QAPP, to minimize sample contamination and worker exposure to contamination from samples and potential exposure to the SARS-CoV-2 virus. The following practices will be followed:

- ◆ Shared equipment or supplies and workspaces will be disinfected frequently or between uses, as appropriate.

- ◆ Safety glasses and face shields will be assigned to a single user, and will be disinfected frequently, at the end of the day, or between uses, and be stored in a clean sealable bag.
- ◆ All utensils or equipment used directly in handling sediment (e.g., such as the grab sampler, hand corers, shovels, spoons and bowls) will be scrubbed with Alconox® detergent, rinsed with deionized water, and stored wrapped in aluminum foil until use.
- ◆ Sample processing surfaces will be cleaned and lined with aluminum foil to prevent direct contact with samples.
- ◆ Ice chests will be scrubbed with Alconox® detergent and rinsed with deionized water prior to any sampling activities. Lids and handles will be cleaned frequently throughout each day.
- ◆ Wet ice used for sample storage during field activities will be contained in separate plastic bags, and samples will be placed in resealable, waterproof plastic bags to avoid contamination from melting ice.
- ◆ Sampling equipment will be free from contaminants such as oils, grease, and fuels.

10 Disposal of Contaminated Materials

Contaminated materials that may be generated during field activities include PPE and excess sample material. These contaminated materials will be disposed of as an integral part of the project.

10.1 PERSONAL PROTECTIVE EQUIPMENT

All disposable sampling materials and PPE – such as disposable coveralls, gloves, and paper towels used in sample processing – will be placed in heavyweight garbage bags. Filled garbage bags will be placed in a normal refuse container for disposal as solid waste.

10.2 EXCESS SAMPLE MATERIALS

At each sampling location, excess or unwanted sediment collected will be returned to the collection site.

11 Training Requirements

Individuals performing work at locations where potentially hazardous materials and conditions may be encountered must meet specific training requirements. It is not anticipated that hazardous concentrations of contaminants will be encountered in sampled material, so training will consist of site-specific instruction for all personnel and oversight of inexperienced personnel by an experienced person for one working day. The following sections describe the training requirements for this fieldwork.

11.1 PROJECT-SPECIFIC TRAINING

In addition to HAZWOPER training, as described in Section 3.6 of the QAPP, field personnel will undergo training specifically for this project. All personnel and visitors must read this HSP and be familiar with its contents before beginning work or providing oversight. They must acknowledge reading the HSP by signing the HSP review form (see front matter). The signed form will be kept in the project files.

The boat captain and FC/HSO will also be required to have the US Coast Guard (USCG) Auxiliary Boating Safety certification. The boat captain or a designee will provide project-specific training prior to the first day of fieldwork and whenever new workers arrive. Field personnel will not be allowed to begin work until project-specific training has been completed and documented by the FC/HSO. Training will address the HSP and all health and safety issues and procedures pertinent to field operations. Training will include, but not be limited to, the following topics:

- ◆ Activities with the potential for exposure to chemicals
- ◆ Activities that pose physical hazards, and actions to control the hazards
- ◆ Ship access control and procedures
- ◆ Use and limitations of PPE
- ◆ Decontamination procedures
- ◆ Emergency procedures
- ◆ Use and hazards of sampling equipment
- ◆ Location of emergency equipment on the vessel
- ◆ Vessel safety practices
- ◆ Vessel evacuation and emergency procedures

11.2 DAILY SAFETY BRIEFINGS

The FC/HSO or a designee and the boat captain will present safety briefings before the start of each day's activities. These safety briefings will outline the activities expected for the day, update work practices and hazards, verify that medical screening has been

completed, explain protective measures, address any specific concerns associated with the work location, and review emergency procedures and routes. Social distancing will be maintained during safety briefings, and COVID-19 safety requirements will be visibly posted at the work site (Inslee 2020b; L&I 2020a).

The FC/HSO or designee will document all safety briefings using the daily safety briefing form included in Attachment 2.

11.3 FIRST AID AND CPR

At least two members of the field team must have first aid and cardiopulmonary resuscitation (CPR) training. Documentation of which individuals possess first aid and CPR training will be kept in the project health and safety files.

12 Medical Surveillance

A medical surveillance program conforming to the provisions of 29 CFR 1910.120(f) is not necessary for field team members on this project, because they do not meet any of the following four criteria outlined in the regulations for implementation of a medical surveillance program:

- ◆ Employees who are or may be exposed to hazardous substances or health hazards at or above permissible exposure levels for 30 days or more per year (1910.120(f)(2)(I)).
- ◆ Employees who must wear a respirator for 30 days or more per year (1910.120(f)(2)(ii)).
- ◆ Employees who are injured or become ill as a result of possible overexposures involving hazardous substances or health hazards from an emergency response or hazardous waste operation (1910.120(f)(2)(iii)).
- ◆ Employees who are members of HAZMAT teams (1910.120(f)(2)(iv)).

Specific attention will be given to the requirement to screen all workers at the beginning of their shifts by taking their temperatures and asking them if they have a fever, cough, shortness of breath, fatigue, muscle aches, or new loss of taste or smell. Thermometers used shall be 'no touch' or 'no contact' models to the greatest extent possible. If a 'no touch' or 'no contact' thermometer is not available, the thermometer will be properly sanitized between each use. Any worker with a temperature of 100.4°F or higher will be considered to have a fever and will be sent home.

As described in Section 8, employees will monitor themselves and each other for any deleterious changes in their physical or mental conditions during the performance of all field activities.

Regarding monitoring exposures to the SARS-CoV-2 virus, there are three possible scenarios:³

- ◆ Primary exposure: when an employee has tested positive for the virus
- ◆ Secondary exposure: when an employee has had direct contact with someone diagnosed with COVID-19 within the last 14 days
- ◆ Tertiary exposure: when an employee has had direct contact with someone who has been quarantined due to close contact with someone else who has been diagnosed with or is being screened for COVID-19 within the last 14 days

The FC/HSO (or designee) will also act as the on-site COVID-19 Supervisor, and shall monitor the health of employees and enforce the measures established to minimize

³ Adapted from (Anchor 2020).

exposure to the SARS-CoV-2 virus. Workers are expected to inform the FC/HSO if they develop symptoms of or have been exposed to anyone with COVID-19.

12.1 COVID-19 PRIMARY EXPOSURE

If an employee has tested positive for COVID-19, the FC/HSO will immediately take the following actions:

- ◆ The employee will be immediately sent away for isolation (i.e., 14-day self-quarantine) if they are at the site.
- ◆ The employee's steps will be traced to identify work areas with which the individual may have been in contact.
- ◆ All identified areas will be quarantined and marked as off limits to all site personnel, until a decontamination/ disinfection process following CDC guidelines has been implemented.
- ◆ Employees who have been in direct contact with the infected individual may be asked to seek medical testing.

12.2 COVID-19 SECONDARY EXPOSURE

If an employee has had direct contact with someone who has been diagnosed with COVID-19 within the last 14 days, the FC/HSO will immediately take the following actions:

- ◆ Immediately send the employee home for medical testing or 14-day self-quarantine.
- ◆ Consult with the Washington State Department of Health for additional guidance if the employee is diagnosed with COVID-19 and has been instructed to self-quarantine.
- ◆ Inform the CHSMs and PMs immediately.
- ◆ Follow up with the field team after test results for the potentially exposed employee have been received.
- ◆ Continue cleaning common touch areas with recommended disinfectants.
- ◆ Follow primary exposure scenario (Section 12.1) if an employee is confirmed as positive for COVID-19.

12.3 COVID-19 TERTIARY EXPOSURE

It is more difficult to manage tertiary exposure because there is innately less control in a situation wherein an employee may have had direct contact with an acquaintance who has been quarantined due to close contact with someone else who has been diagnosed with or is being screened for COVID-19 within the last 14 days. The FC/HSO will

request that all site workers provide any relevant exposure information. If an employee is believed to have been subject to tertiary exposure, take the following actions:

- ◆ Consult with the Washington State Department of Health for additional guidance if the acquaintance who is diagnosed with or screened for COVID-19 has been instructed to self-quarantine.
- ◆ Inform the CHSMs and PMs immediately.
- ◆ Follow up with the field team after test results for the potentially exposed employee have been received.
- ◆ Continue cleaning common touch areas with recommended disinfectants.
- ◆ Follow secondary exposure scenario (Section 12.2) if the acquaintance is confirmed as positive for COVID-19.

13 Reporting and Record Keeping

Each member of the field crew will sign the HSP review form (see front matter). If necessary, accident/incident report forms and Occupational Safety and Health Administration (OSHA) Form 200s will be completed by the FC/HSO.

The FC/HSO or a designee will maintain a health and safety field logbook with daily records of health- and safety-related details for the project. The logbook will utilize daily safety briefing forms (Attachment 2) and must be bound and the pages must be numbered consecutively. Entries will be made with indelible ink. At a minimum, each day's entries must include the following information:

- ◆ Project name or location
- ◆ Names of all personnel onboard
- ◆ Weather conditions
- ◆ Type of fieldwork being performed

The person maintaining the entries will initial and date the bottom of each completed page. Blank space at the bottom of an incompletely filled page will be lined out. Each day's entries will begin on the first blank page after the previous workday's entries.

Additionally, for COVID-19 tracking purposes, a record of all site workers and visitors and their contact information (i.e., phone numbers and e-mail addresses) will be kept on file for a minimum for four weeks from the last day they were on site.

14 Emergency Response Plan

As a result of the hazards onboard the sampling vessels and the conditions under which operations will be conducted, the potential exists for an emergency situation to occur. Emergencies may include personal injury, exposure to hazardous substances, fire, explosion, or release of toxic or non-toxic substances (spills). OSHA regulations require that an emergency response plan be available for use onboard to guide actions in emergency situations.

Onshore organizations will be relied upon to respond to emergency situations. Given the location of the site, the local fire department and ambulance service can provide timely response. Field personnel will be responsible for identifying an emergency situation, providing first aid if applicable, notifying the appropriate personnel or agency, and evacuating any hazardous area. Shipboard personnel will attempt to control only very minor hazards that could present an emergency situation, such as a small fire; otherwise, all personnel will rely on outside emergency response resources.

The following sections identify the onboard individual(s) who should be notified in case of emergency, provide a list of emergency telephone numbers, offer guidance for particular types of emergencies, and provide directions and a map for getting from any sampling location to a hospital.

14.1 PRE-EMERGENCY PREPARATION

Before the start of field activities, the FC/HSO will ensure that preparation has been made in anticipation of emergencies. Preparatory actions include the following:

- ◆ Meeting between the FC/HSO and equipment handlers concerning emergency procedures in the event that a person is injured
- ◆ A training session given by the FC/HSO informing all field personnel of emergency procedures, locations of emergency equipment and its uses, and proper evacuation procedures
- ◆ A training session given by senior staff on operating field equipment to apprise field personnel of operating procedures and specific risks associated with that equipment
- ◆ Ensuring that field personnel are aware of the existence of the emergency response plan in the HSP, and ensuring that a copy of the HSP including all attachments accompanies the field team

14.2 PROJECT EMERGENCY COORDINATOR

The FC/HSO will serve as the project emergency coordinator in the event of an emergency. He will designate his replacement during those times when he is not onboard or is not serving as the project emergency coordinator; the designation will be

noted in the logbook. The project emergency coordinator will be notified immediately when an emergency is recognized. The project emergency coordinator will be responsible for evaluating the emergency situation, notifying the appropriate emergency response units, coordinating access with those units, and directing interim actions onboard before the arrival of emergency response units. The project emergency coordinator will notify the HSM and the PMs as soon as possible after initiating an emergency response action. The PMs will have responsibility for notifying the client.

14.3 EMERGENCY RESPONSE CONTACTS

All onboard personnel must know whom to notify in the event of an emergency situation, even though the FC/HSO has primary responsibility for notification. Table C-3 lists the names and phone numbers for emergency response services and individuals.

Table C-3. Emergency response contacts

Contact	Telephone Number
Emergency Numbers	
Ambulance	911
Police	911
Fire	911
Harborview Medical Center	206.323.3074
Emergency Responders	
US Coast Guard Emergency General information	206.286.5400 206.442.5295 VHF Channel 16
National Response Center	800.424.8802
US Environmental Protection Agency	800.424.8802
Washington State Department of Ecology – Northwest Region Spill Response (24-hour emergency line)	206.649.7000
Emergency Contacts	
<i>Anchor QEA Project Manager</i>	
Tom Wang	206.903.3314
<i>Windward Project Manager</i>	
Kathy Godfredsen	206.812.5413
<i>Corporate Health and Safety Manager</i>	
David Templeton	206.910.4279
Gloria Palermo	315.622.3723
<i>Field Coordinator/ Field Health and Safety Officer</i>	
Thai Do (Windward)	206.812.5407
Matt Woltman (Anchor QEA)	206.903.3327

14.4 RECOGNITION OF EMERGENCY SITUATIONS

Emergency situations will generally be recognizable by observation. An injury or illness will be considered an emergency if it requires treatment by a medical professional and cannot be treated with simple first aid techniques.

14.5 DECONTAMINATION

In the case of evacuation, decontamination procedures will be performed only if doing so does not further jeopardize the welfare of site workers. If an injured individual is also heavily contaminated and must be transported by emergency vehicle, the emergency response team will be informed of the type of contamination. To the extent possible, contaminated PPE will be removed from the injured individual, but only if doing so does not exacerbate the injury. Plastic sheeting will be used to reduce the potential for spreading contamination to the inside of the emergency vehicle.

14.6 FIRE

Field personnel will attempt to control only small fires, should they occur. If an explosion appears likely, personnel will follow evacuation procedures specified during the training session. If a fire cannot be controlled with the onboard fire extinguisher that is part of the required safety equipment, personnel will either withdraw from the vicinity of the fire or evacuate the boat as specified in the training session.

14.7 PERSONAL INJURY

In the event of serious personal injury, including unconsciousness, possibility of broken bones, severe bleeding or blood loss, burns, shock, or trauma, the first responder will immediately do the following:

- ◆ Designate an individual to call 911 and administer first aid, if qualified.
- ◆ If not qualified, seek out an individual who is qualified to administer first aid, if time and conditions permit.
- ◆ Notify the project emergency coordinator of the incident, the name of the injured individual(s), the location of the individual, and the nature of the injury.

The FC/HSO or designee will immediately do the following:

- ◆ Notify the boat captain and the appropriate emergency response organization.
- ◆ Assist the injured individual(s).
- ◆ Follow the emergency procedures for retrieving or disposing of equipment reviewed in the training session, and leave the site en route to the predetermined land-based emergency pickup.
- ◆ Designate someone to accompany the injured individual to the hospital.

- ◆ If a life-threatening emergency occurs (i.e., injury where death is imminent without immediate treatment), the FC/HSO or boat captain will call 911 and arrange to meet the ambulance unit at the nearest accessible dock.
- ◆ If a non-life-threatening emergency occurs (i.e., broken bones, minor lacerations, etc.), the project emergency coordinator will follow the procedures outlined above and proceed to the Harbor Island Marina, or to an alternative location of his choice if that would be more expedient.
- ◆ Notify the HSM and the PM.

If the project emergency coordinator determines that an emergency response is not necessary, he may direct someone to decontaminate and transport the individual by vehicle to the nearest hospital. Directions showing the route to the hospital are in Section 14.11.

If a worker leaves the boat to seek medical attention, another worker should accompany him to the hospital. When in doubt about the severity of an injury or exposure, always seek medical attention as a conservative approach, and notify the project emergency coordinator.

The project emergency coordinator will be responsible for completing all accident/incident field reports, OSHA Form 200s, and other required follow-up forms.

14.8 OVERT PERSONAL EXPOSURE OR INJURY

If an overt exposure to toxic materials occurs, the first responder to the victim will initiate actions to address the situation. The following actions should be taken, depending on the type of exposure.

14.8.1 Skin contact

- ◆ Wash/rinse the affected area thoroughly with copious amounts of soap and water.
- ◆ If eye contact has occurred, rinse the eyes for at least 15 minutes using the eyewash that is part of the onboard emergency equipment.
- ◆ After initial response actions have been taken, seek appropriate medical attention.

14.8.2 Inhalation

- ◆ Move victim to fresh air.
- ◆ Seek appropriate medical attention.

14.8.3 Ingestion

- ◆ Seek appropriate medical attention.

14.8.4 Puncture wound or laceration

- ◆ Seek appropriate medical attention.

14.9 SPILLS AND SPILL CONTAINMENT

No bulk chemicals or other materials subject to spillage are expected to be used during this project. Accordingly, no spill containment procedure is required for this project. If crew members encounter a spill created by any others, they will immediately notify the contractor in charge of the spill areas so they can initiate a cleanup action.

14.10 BOATING EMERGENCY HAZARDS

Emergency responses to boating hazards are described in Table C-4. Boat operators will have VHF radios that are capable of communicating with US Coast Guard emergency services and with other boats operating in the immediate work area. USCG monitors channel 16.

Table C-4. Potential boat emergency hazards and responses

Potential Emergency Hazard	Response
Fire or explosion	If manageable, attempt to put out a small fire with a fire extinguisher. Otherwise, call the USCG or 911, evacuate the area (by life rafts, rescue boat, or swimming), and meet at a designated location. The HSO will take roll call to make sure everyone has evacuated safely. Emergency meeting locations will be determined in the field during the daily safety briefings.
Medical emergency/ personal injury	At least two people with current first aid and CPR training will be onboard the vessel at all times. This person will attempt to assess the nature and critical path of the injury, call 911 immediately, and apply first aid/CPR if necessary. Stop work and wait for medical personnel to arrive. Fill out a site accident report.
Falling into an open hatch	Stop work and rescue the person, if safe and necessary. Assess the nature of the injury, and follow the response for medical emergency/personal injury.
Person overboard	Immediately throw a life ring to the person in the water. Have one onboard person (a spotter) keep an eye on the victim and shout the distance (boat lengths) and direction (o'clock) of the victim from the vessel. Stop work and use the vessel to retrieve the person in the water. Approach the person from downstream.
Sinking vessel	Call the USCG immediately. If possible, wait for a rescue boat to arrive to evacuate vessel personnel. See fire/explosion section (above) for emergency evacuation procedures. The HSO will take roll call to make sure everyone has evacuated safely.
Hydraulic oil spill or leak	If the leak/spill is small, immediately apply absorbent pads to control the leak and continue work. If the leak/spill is uncontainable, stop work, call 911 immediately, and wait for assistance. The vessel operator will assess the personal safety hazard associated with the leak/spill and begin evacuation procedures if necessary.
Lack of visibility	If navigation visibility or personal safety is compromised because of smoke, fog, or other unanticipated hazards, stop work immediately. The vessel operator and HSO will assess the hazard and, if necessary, send out periodic horn blasts to notify other vessels potentially in the area of the sampling vessel's location. Move to a secure location (i.e., berth) and wait for visibility to clear.
Loss of power	Stop work and call the USCG for assistance. Vessel personnel should watch for potential collision hazards and notify vessel operator if hazards exist. Secure vessel to a berth, dock, or mooring as soon as possible.
Collision	Stop work and call the USCG for assistance. HSO and vessel operator will assess damage and potential hazards. If necessary, vessel will be evacuated and secured until repairs can be made.

CPR – cardiopulmonary resuscitation

HSO – health and safety officer

USCG – US Coast Guard

14.11 EMERGENCY ROUTES TO THE HOSPITAL

The name, address, and telephone number of the hospital that will be used to provide medical care is as follows:

Harborview Medical Center
325 - 9th Avenue
Seattle, WA
206.323.3074

Directions from the vicinity of the LDW to Harborview Medical Center are as follows (Figure A-ii):

From the Duwamish River boat ramp (at South River Street, beneath the 1st Avenue South bridge):

- ◆ Drive east on South River Street.
- ◆ Turn left on Occidental Avenue South.
- ◆ Turn left on East Marginal Way South.
- ◆ Turn right on South Michigan Street.
- ◆ Look for entrance ramps to I-5 Northbound.
- ◆ Drive north on I-5.
- ◆ Take the James Street exit.
- ◆ Drive east on James Street to 9th Avenue.
- ◆ Turn right on 9th Avenue.
- ◆ Emergency entrance will be two blocks south on the right.

From the Harbor Island Marina (1001 Southwest Klickitat Way):

- ◆ From marina parking lot, turn sharp right onto Klickitat Way Southwest.
- ◆ Turn slight right onto Southwest Spokane Street
- ◆ Turn slight left to take the ramp toward WA-99 N/I-5/Columbian Way.
- ◆ Keep left at the fork in the ramp.
- ◆ Stay straight to go onto West Seattle Bridge.
- ◆ Merge onto I-5 North via the ramp on the left.
- ◆ Take the James Street exit.
- ◆ Head east on James Street to 9th Avenue.
- ◆ Turn right on 9th Avenue.
- ◆ Emergency entrance will be two blocks south on the right.

From South Park Marina (8604 Dallas Ave South):

- ◆ From marina parking lot, turn right onto Dallas Avenue South.
- ◆ Turn right onto 16th Avenue South.
- ◆ Turn left on East Marginal Way South.
- ◆ Look for entrance ramps to I-5 Northbound.
- ◆ Drive north on I-5.
- ◆ Take the James Street exit.
- ◆ Drive east on James Street to 9th Avenue.
- ◆ Turn right on 9th Avenue.
- ◆ Emergency entrance will be two blocks south on the right.

15 References

- Amec, DOF, Ramboll, Floyd | Snider, GeoSyntec, Stephen Frost. 2015. Site-specific health and safety plan. Enhanced natural recovery/activated carbon pilot study. Lower Duwamish Waterway. Final. Amec Foster Wheeler Environment & Infrastructure, Inc., Dalton, Olmsted & Fuglevand, Inc., Ramboll-Environ, Floyd | Snider, Geosyntec Consultants, and Stephen Frost & Associates.
- Anchor. 2020. Field program COVID-19 management plan. Anchor QEA.
- CDC. 2018. Heat stress [online]. Centers for Disease Control and Prevention. Updated June 6, 2018. Available from:
https://www.cdc.gov/niosh/topics/heatstress/#_Heat_Stroke.
- CDC. 2020. Coronavirus (COVID-19) [online]. Centers for Disease Control and Prevention. [Cited March 25, 2020.] Available from:
<https://www.cdc.gov/coronavirus/2019-ncov/>.
- Inslee J. 2020a. Implementation of Phase 1 construction restart - Proclamation 20-25. Office of the Governor, State of Washington, Olympia, WA.
- Inslee J. 2020b. Phase I construction restart COVID-19 job site requirements. Governor Jay Inslee's Construction Working Group, Olympia, WA.
- L&I. 2020a. DOSH Directive. General coronavirus prevention under Stay Home-Stay Healthy order. Washington State Department of Labor and Industries, Olympia, WA.
- L&I. 2020b. Washington coronavirus hazard considerations for employers (except hospitals/clinics). Face coverings, masks, and respirator choices. Washington State Department of Labor and Industries, Olympia, WA.
- OSHA. 2020. Guidance on preparing workplaces for COVID-19. OSHA 3990-03 2020. US Department of Labor, Occupational Safety and Health Administration, Washington, DC.

ADDENDUM TO THE FINAL HEALTH AND SAFETY PLAN (DATED MAY 19, 2020) FOR SEDIMENT SAMPLING OF THE UPPER REACH

In response to the US Environmental Protection Agency's (EPA's) May 26, 2020, comments on the health and safety plan (HSP)¹, this addendum presents additional precautions and clarifications to minimize the risk of field staff exposure to SARS-CoV-2, the virus that causes Coronavirus Disease 2019 (COVID-19). These measures are in compliance with Governor Inslee's Construction Working Group Recommendations and the Washington Department of Labor and Industries Coronavirus Directive, as discussed in and attached to the HSP.

1. During the daily health and safety tailgate meeting:
 - a. Any field staff member who does not want to participate in the COVID-19 screening will not be allowed to work and will be sent home.
 - b. Screening results will be monitored and recorded by only one person (i.e., the COVID-19 supervisor) per vessel.
2. If an field staff member develops symptoms consistent with COVID-19 during the course of the work day, she or he will be sent home and the area(s) where she or he has worked or stayed more than 10 minutes will be immediately disinfected.
3. If a field staff member is determined to have symptoms consistent with COVID-19 and is not able to drive home or to seek treatment, 911 will be called, and the Corporate Health and Safety Manager (CHSM) will be notified. The CHSM will notify the staff member's emergency contact as part of the follow-up response.
4. A field staff member who is sent home due to potential COVID-19-related illness will not be allowed to return to the field until she or he has been tested for COVID-19 and cleared to return to work by her or his health care provider.
5. If the field staff member does not want to be tested, she or he will not be allowed to return to the work site.
6. If a field staff member is confirmed positive for COVID-19, she or he will notify the employer.
 - a. All persons from the ill staff member's vessel who have been in contact with that employee will be notified.

¹The HSP is Appendix C to the *Lower Duwamish Waterway Quality Assurance Project Plan for Remedial Design of Upper Reach: Pre-Design Investigation, Final*.

- b. Those persons must self-quarantine for a minimum of 14 days or be tested and cleared to resume work by their health care providers.
- 7. Routine cleaning and disinfecting of common-touch surfaces, equipment, and other elements of the work environment will be performed at the beginning of the work day, at the end of the work day, and as frequently as necessary. In particular, common-touch surfaces and equipment will be disinfected when:
 - a. There is a change in staffing
 - b. There is a change in gloves
 - c. Different people come into contact with a given work area
- 8. Measures will be taken to limit the frequency and duration of staff exposure to SARS-CoV-2 at pinch-points within a sampling vessel and between vessels, particularly while samples are being transferred from one vessel to another and during bathroom breaks. Such measures will include:
 - a. Remaining socially distant from each other on the vessel to the extent possible at all times
 - b. Keeping boat captains isolated within the wheelhouse to the extent possible
 - c. Maintaining a consistent set of crew members for each vessel (i.e., not switching vessel teams)
 - d. Changing gloves before sample transfer between boats
 - e. Using hand sanitizer before entry to and after exit from the portable toilet structure
 - f. Disinfecting surfaces in the portable toilet structure after each use
 - g. Keeping the door to the portable toilet structure ajar when not in use to increase air circulation

**ATTACHMENT 1. MODIFICATION TO HEALTH
AND SAFETY PLAN FORM**

Modification to Health and Safety Plan

Date: _____

Project No: 180067-02.01 _____

Project Name: Lower Duwamish Waterway Remedial Design _____

Modification: _____

Reason for Modification: _____

Site Personnel Briefed

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Name: _____ **Date:** _____

Approvals

Field Lead: _____
Printed Name Signature Date

Project Manager: _____
Printed Name Signature Date

**ATTACHMENT 2. DAILY SAFETY BRIEFING
FORM AND JOB SAFETY ANALYSIS SHEETS**

Job Safety Analysis



Field Activities

Project Name: Lower Duwamish Waterway Remedial Design	Project Number: 180067-02.01	JSA Number: 001	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: K. Gross	Analysis Date: May 29, 2020
Work Operation: Field activities	Superintendent/Competent Person: M. Woltman	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE): <ul style="list-style-type: none"> Modified Level D—Long pants, long sleeves, and/or Tyvek coveralls if handling potentially contaminated media, and steel-toed footwear conforming to ASTM International (ASTM) F2412-05/ASTM F2413-05, safety glasses/splash goggles, nitrile gloves, high-visibility safety vest, and protective face mask Depending on activity, the following PPE may also be required: hard hat, outer gloves, face shield, and, if boating, U.S. Coast Guard-approved personal flotation device (PFD; see cold stress section for cold-weather PFD information) 		Reviewed by: M. Woltman	Reviewed Date: May 29, 2020
		Approved by: T. Shaner	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
General	COVID-19	<ul style="list-style-type: none"> Refer to Health and Safety Plan (HSP). 	Refer to HSP.
If boating		<ul style="list-style-type: none"> Follow the Job Safety Analysis (JSA) for boating activities. 	
Outdoor, physical activity	Slips, trips, and falls	<ul style="list-style-type: none"> Avoid walking while writing or texting—maintain a heads-up posture. Be aware of potentially slippery surfaces and tripping hazards. Use handrails where available. Wear footwear that has sufficient traction. Maintain good housekeeping practices. Clean up all spills immediately. Be aware of weather effects on the work area, including wet and/or frozen ground. Jumping, running, and horseplay are prohibited. Keep all areas clean and free of debris to prevent any trips and falls. Be aware of and limit loose clothing or untied shoelaces that may contribute to slips, trip, and falls. Notify the field team members of any unsafe conditions. 	<ul style="list-style-type: none"> Routinely inspect work area for unsafe conditions.

Job Safety Analysis



Field Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Outdoor, physical activity (continued)	Heat stress	<ul style="list-style-type: none"> Adjust work schedules, as necessary, to avoid the hottest part of the day. Take rest breaks as warranted. Provide shelter (air-conditioned, if possible) or shaded areas to protect personnel during rest periods. Maintain body fluids at normal levels. Train workers to recognize the symptoms of heat-related illness. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Monitor workers' physical conditions. Monitor outside temperature versus worker activity.
	Cold stress	<ul style="list-style-type: none"> Provide shelter (enclosed, heated environment) to protect personnel during rest periods. Educate workers to recognize the symptoms of frostbite and hypothermia. Use appropriate cold-weather gear, up to and including Mustang-type bib coveralls or jacket/bib combinations. Consider additional precautions if working near water in cold weather. Have a dry change of clothing available. Train workers to recognize the symptoms of cold-related illness. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Monitor workers' physical conditions and PPE. Monitor outside and water temperature versus worker activity and PPE.
	Rain or snow	<ul style="list-style-type: none"> Wear appropriate PPE (rain gear). Be aware of slip hazards, puddles, and electrical hazards when working in wet conditions. If extremely cold conditions are forecast, consider additional precautions or postponing work activity. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Inspect PPE daily prior to use. Routinely inspect work area for deteriorating conditions.
	Sunshine	<ul style="list-style-type: none"> Have sunscreen available for ultraviolet protection. Have abundant water available to prevent dehydration. Consider wearing wide-brimmed headwear and light-colored, lightweight, sun-blocking clothing. 	<ul style="list-style-type: none"> Ensure that sunscreen and water are available.
	Lightning	<ul style="list-style-type: none"> Do not begin or continue work until lightning subsides for at least 30 minutes. Disconnect and do not use or touch electronic equipment. Immediately head for shore if on the water and lightning is observed. If not able to get to shore, disconnect and do not use or touch the major electronic equipment, including the radio, throughout the duration of the storm. 	<ul style="list-style-type: none"> Obtain weather forecast and updates as needed.

Job Safety Analysis



Field Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Outdoor, physical activity (continued)	High winds	<ul style="list-style-type: none"> Wear goggles or safety glasses if dust or debris are visible. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Ensure that goggles or safety glasses are available.
	Biological hazards (flora [e.g., poison ivy and poison oak] and fauna [e.g., bees, spiders, and mosquitoes])	<ul style="list-style-type: none"> Be aware of likely biological hazards in the work area. Wear appropriate clothing (i.e., hat, long-sleeve shirt, long pants, leather gloves, boots, and Tyvek coveralls, as appropriate), and apply insect repellent. Wear hand and arm protection when clearing plants or debris from the work area. Be aware of potential wildlife and defensive behavior (e.g., nesting birds, or animals with young). 	<ul style="list-style-type: none"> Ensure that insect repellent is available. Inspect clothing and skin for insects (e.g., ticks) after working in insect-prone areas.
	Noise exposure	<ul style="list-style-type: none"> Wear hearing protection in high noise environments or when working around heavy machinery or equipment (action level of 85 decibels averaged over an 8-hour day). 	<ul style="list-style-type: none"> Ensure that hearing protection is available.

Training Requirements:

- All personnel working on hazardous waste sites must receive appropriate training as required by 29 Code of Federal Regulations (CFR) 1910.120(e), including but not limited to initial 40-hour, 8-hour supervisor, and annual 8-hour refresher trainings.
- Medical clearance must be received on an annual basis as required by 29 CFR 1910.120(f).
- If boating is involved, and a professional captained vessel is not in use, boat operators must take the appropriate state or provincial boater safety courses.
- All assigned employees are required to familiarize themselves with the contents of this JSA before starting a work activity and review it with their supervisor during their daily safety meeting.

Job Safety Analysis



Sediment Sampling

Project Name: Lower Duwamish Waterway Remedial Design	Project Number:	JSA Number: 002	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: T. Do	Analysis Date: May 29, 2020
Work Operation: Sediment sampling	Superintendent/Competent Person: T. Do	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE):		Reviewed by: S. McGroddy	Reviewed Date: May 29, 2020
<ul style="list-style-type: none"> Modified Level D—Long pants, long sleeves, and/or Tyvek coveralls if handling potentially contaminated media, steel-toed footwear conforming to American Society for Testing and Materials International (ASTM) F2412-05/ASTM F2413-05, safety glasses/splash goggles, hard hat, high-visibility safety vest, medical face mask, and nitrile gloves Depending on activity, the following personal protective equipment (PPE) may also be required: waders and wader boots, face shield, and, if boating, U.S. Coast Guard-approved personal flotation device (PFD). 		Approved by: S. McGroddy	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
General	COVID-19	<ul style="list-style-type: none"> Refer to Health and Safety Plan (HSP) (Appendix C). 	Refer to HSP (Appendix C).
If boating		<ul style="list-style-type: none"> Follow the Job Safety Analysis (JSA) for boating activities. 	
If using glassware		<ul style="list-style-type: none"> Follow the JSA for handling glassware. 	

Job Safety Analysis



Sediment Sampling

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Sediment sample retrieval and processing	Injury from hand and power tool operation (e.g., spatula or drill)	<ul style="list-style-type: none"> • Be aware of sharp edges on hand tools (e.g., spatulas, knives, drill bits, and saw blades). • Be aware of electrical connections and water hazards when working with electric or battery-operated tools. • Ensure that all tools are working properly; repair or replace defective tools. Repair any defective tools when unplugged and off. • Keep guards on power tools when not in use. • Corrective actions may involve installing guards over exposed, rotating parts; isolating or de-energizing equipment; establishing exclusion zones around high-hazard areas; and constructing guardrails around mechanical equipment to prevent inadvertent contact. 	<ul style="list-style-type: none"> • Inspect tools to ensure that they are in good working order. • Inspect electrical connections (if applicable). • Inspect tools periodically to ensure dry and clean operation. • Identify potential pinch, grab, crush, and struck-by hazards.
Sediment sample retrieval and processing (continued)	Noise exposure	<ul style="list-style-type: none"> • Wear hearing protection in high-noise environments or when working around heavy machinery or equipment (action level of 85 decibels averaged over an 8-hour day). 	<ul style="list-style-type: none"> • Ensure that hearing protection is available.
	Slips, trips, and falls	<ul style="list-style-type: none"> • Avoid walking while writing or texting—maintain a heads-up posture. • Be aware of potentially slippery surfaces, including boat decks, riprap, muddy or algae-covered rocks, shoreline plants/seaweed, thick mud, and tripping hazards. Use handrails where available. Wear footwear that has sufficient traction. • Maintain good housekeeping practices. Clean up all spills immediately. • Be aware of weather effects on the work area, including wet and/or frozen ground. • Jumping, running, and horseplay are prohibited. • Be cautious when entering or exiting the vessel, and load/unload items onto/off of the pier or shore once boarded. • Keep all areas clean and free of debris to prevent any trips and falls. • Notify the field team members of any unsafe conditions. 	<ul style="list-style-type: none"> • Routinely inspect work area for unsafe conditions.
	Ingestion of contaminants, or skin or eye contact with contaminants	<ul style="list-style-type: none"> • Wear appropriate PPE to prevent/reduce exposure. • Contact 911, as necessary; perform CPR if breathing stops. • Move exposed person away from source of contamination and rinse mouth. If exposure to skin occurs, promptly wash contaminated skin using soap or mild detergent and water. Rinse eyes with large amounts of water. • Follow decontamination procedures as outlined in the HSP. 	<ul style="list-style-type: none"> • Ensure that decontamination procedures are on hand and are reviewed. • Ensure that PPE and rinsing water are available.
	Muscle strain or injuries from improper lifting	<ul style="list-style-type: none"> • Use proper lifting techniques or ask for assistance with heavy objects. • If boating, avoid carrying objects directly onto or off of the boat; rather, load/unload objects while on the boat to/from the pier/shore. 	<ul style="list-style-type: none"> • Evaluate weight and center of gravity of heavier items prior to lifting or moving.

Job Safety Analysis



Sediment Sampling

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
	Pinch points	<ul style="list-style-type: none"> • If boating, secure any unsecured objects on deck; unsecured items may shift on deck quickly in wave, current, or engine acceleration conditions. • Maintain a safe distance from closing mechanisms and moving parts on sampling gear. • Avoid placing hands or self between boat and dock/piles. 	
Sediment sample retrieval and processing (continued)	Wading	<ul style="list-style-type: none"> • Be aware of potentially slippery surfaces and tripping hazards such as fallen brush, logs, rocks, and other debris. Wear footwear that has sufficient traction. • Be aware of water depth and potential drop-offs. • Be aware of existing and projected river flows. • Wear knee or chest waders as appropriate for traction and to protect against cold water. • Keep extra dry clothes on hand, including socks. • Consider carrying a walking staff for balance. • Always wear a PFD, even if water looks shallow or slow; drop-offs occur and water is often moving faster than it looks. 	<ul style="list-style-type: none"> • Inspect work area for tripping hazards visible from streambank. • Inspect waders for leaks. • Check depths and flows before wading. • Ensure that a change of dry clothes is available if wading in cold weather or cold water conditions. • Inspect PFDs for integrity, particularly the cartridge charge on inflatable PFDs.
	Diving	<ul style="list-style-type: none"> • Follow safety checklists for diving operations. • Assign responsibilities for all dive team members. • Comply with all applicable requirements of Washington Department of Labor & Industry Standards for Commercial Diving Operations (Washington Administrative Code [WAC] 296-37). • Provide a safe practices manual for each diving mode per WAC 296-37-530 before beginning dive operations. 	<ul style="list-style-type: none"> • Contractor will produce a site-specific dive plan for each diving operation; the plan will specify the means and methods that will be used to comply with all required elements of Washington State's diving standards.
Working outdoors	Heat stress	<ul style="list-style-type: none"> • Adjust work schedules, as necessary, to avoid the hottest part of the day. • Take rest breaks as warranted. • Provide shelter (air-conditioned, if possible) or shaded areas to protect personnel during rest periods. • Maintain body fluids at normal levels. • Train workers to recognize the symptoms of heat-related illness. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Monitor workers' physical conditions. • Monitor outside temperature versus worker activity.

Job Safety Analysis



Sediment Sampling

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Working outdoors (continued)	Cold stress	<ul style="list-style-type: none"> • Provide shelter (enclosed, heated environment) to protect personnel during rest periods. • Educate workers to recognize the symptoms of frostbite, hypothermia, and other cold-related illness. • Use appropriate cold-weather gear, up to and including Mustang-type bib coveralls or jacket/bib combinations. • Consider additional precautions if working near water in cold weather. • Have a dry change of clothing available. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Monitor workers' physical conditions and PPE. • Monitor outside and water temperature versus worker activity and PPE.
	Rain or snow	<ul style="list-style-type: none"> • Wear appropriate PPE (rain gear). • Be aware of slip hazards, puddles, and electrical hazards when working in wet conditions. • If extremely cold conditions are forecast, consider additional precautions or postponing work activity. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Inspect PPE daily prior to use. • Routinely inspect work area for deteriorating conditions.
	Sunshine	<ul style="list-style-type: none"> • Have sunscreen available for ultraviolet protection. • Have abundant water available to prevent dehydration. • Consider wearing wide-brimmed headwear and light-colored, lightweight, sun-blocking clothing. 	<ul style="list-style-type: none"> • Ensure that sunscreen and water are available.
	Lightning	<ul style="list-style-type: none"> • Do not begin or continue work until lightning has ceased for 30 minutes. Disconnect and do not use or touch electronic equipment. • Immediately head for shore if on the water and lightning is observed. If not able to get to shore, disconnect and do not use or touch the major electronic equipment, including the radio, throughout the duration of the storm. 	<ul style="list-style-type: none"> • Obtain weather forecast and updates as needed.
	High winds	<ul style="list-style-type: none"> • Wear goggles or safety glasses if dust or debris are visible. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Ensure that goggles or safety glasses are available.
	Biological hazards (fauna [e.g., ticks, bees, spiders, and mosquitoes])	<ul style="list-style-type: none"> • Be aware of likely biological hazards in the work area. • Wear appropriate clothing (i.e., hat, long-sleeve shirt, long pants, leather gloves, boots, and Tyvek coveralls, as appropriate), and apply insect repellent. 	<ul style="list-style-type: none"> • Ensure that insect repellent is available. • Inspect clothing and skin for insects (e.g., ticks) after working in insect-prone areas.

Job Safety Analysis



Sediment Sampling

Training Requirements:

- All personnel working on hazardous waste sites must receive appropriate training as required by 29 Code of Federal Regulations (CFR) 1910.120(e), including but not limited to initial 40-hour, 8-hour supervisor, and annual 8-hour refresher trainings.
- If boating is involved, and a professional captained vessel is not in use, boat operators must take the appropriate state or provincial boater safety courses.
- All assigned employees are required to familiarize themselves with the contents of this JSA before starting a work activity, and to review it with their supervisor during their daily safety meeting.

Job Safety Analysis



General Boating Activities

Project Name: Lower Duwamish Waterway Remedial Design	Project Number: 180067-02.01	JSA Number: 003	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: K. Gross	Analysis Date: May 29, 2020
Work Operation: General boating activities	Superintendent/Competent Person: M. Woltman	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE): <ul style="list-style-type: none"> U.S. Coast Guard (USCG)-approved personal flotation device (PFD; see cold stress section for cold-weather PFD information) 		Reviewed by: M. Woltman	Reviewed Date: May 29, 2020
		Approved by: T. Shaner	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
General	COVID-19	<ul style="list-style-type: none"> Refer to Health and Safety Plan (HSP). 	<ul style="list-style-type: none"> Refer to HSP.
Walking on deck	Pinch points	<ul style="list-style-type: none"> Secure any unsecured objects on deck; they may shift quickly in wave, current, or engine acceleration conditions. Maintain a safe distance from closing mechanisms and moving parts, such as on sampling gear. Avoid placing your hands or yourself between the boat and the dock or piles. 	<ul style="list-style-type: none"> Docks, piers and shoreline areas should be approached slowly.

Job Safety Analysis



General Boating Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
	Slips, trips, and falls	<ul style="list-style-type: none"> • Avoid walking while writing or texting—maintain a heads-up posture. • Be aware of potentially slippery surfaces, including boat decks, riprap, muddy or algae-covered rocks, shoreline plants or seaweed, thick mud, and tripping hazards. Use handrails where available. • Wear footwear that has sufficient traction. • Maintain good housekeeping practices. • Clean up all spills immediately. • Be aware of weather effects on the work area, including wet and/or frozen ground. • Jumping, running, and horseplay are prohibited. • Be cautious when entering or exiting the vessel, and load/unload items onto/off of the pier or shore once boarded. • Keep all areas clean and free of debris to prevent any trips and falls. • Notify the field team members of any unsafe conditions. • Keep rope lines neatly coiled and stowed. Avoid stepping on or over lines. 	<ul style="list-style-type: none"> • Routinely inspect work area for unsafe conditions. • All crew members should watch for hazards such as approaching vessels or wakes. It should never be assumed that other crew members see such hazards.
	Exceeding boat capacity	<ul style="list-style-type: none"> • Keep the number of passengers and equipment as posted on boat placards within limits at all times. If conditions warrant, reduce capacity to maintain boat stability. 	<ul style="list-style-type: none"> • Ensure that field team is aware of limits and adheres accordingly.
Walking on deck (continued)	Noise exposure	<ul style="list-style-type: none"> • Wear hearing protection in high noise environments or when working around heavy machinery or equipment (action level of 85 decibels averaged over an 8-hour day). 	<ul style="list-style-type: none"> • Ensure that hearing protection is available.
Working outdoors	Heat stress	<ul style="list-style-type: none"> • Adjust work schedules, as necessary, to avoid the hottest part of the day. • Take rest breaks as warranted. • Provide shelter (air-conditioned, if possible) or shaded areas to protect personnel during rest periods. • Maintain body fluids at normal levels. • Train workers to recognize the symptoms of heat-related illness. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Monitor workers' physical conditions. • Monitor outside temperature versus worker activity.
	Cold stress	<ul style="list-style-type: none"> • Provide shelter (enclosed, heated environment) to protect personnel during rest periods. • Educate workers to recognize the symptoms of frostbite and hypothermia. • If the combined air and water temperature is below 90 degrees Fahrenheit (°F), wear a USCG-approved float coat, Mustang-type bib coveralls, or one-piece survival suit. • Have a dry change of clothing available. • Train workers to recognize the symptoms of cold-related illness. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Monitor workers' physical conditions and PPE. • Monitor outside and water temperature versus worker activity and PPE.

Job Safety Analysis



General Boating Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
	Rain or snow	<ul style="list-style-type: none"> Wear appropriate PPE (rain gear). Be aware of slip hazards, puddles, and electrical hazards when working in wet conditions. If extremely cold conditions are forecast, consider additional precautions or postponing work activity. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Inspect PPE daily prior to use. Routinely inspect work area for deteriorating conditions.
	Sunshine	<ul style="list-style-type: none"> Have sunscreen available for ultraviolet protection. Have abundant water available to prevent dehydration. Consider wearing wide-brimmed headwear and light-colored, lightweight, sun-blocking clothing. 	<ul style="list-style-type: none"> Ensure that sunscreen and water are onboard.
	Fog	<ul style="list-style-type: none"> Wait for fog to lift for adequate visibility. 	<ul style="list-style-type: none"> Review weather forecast prior to field work.
Working outdoors (continued)	Lightning	<ul style="list-style-type: none"> Do not begin or continue work until lightning subsides for at least 30 minutes. Disconnect and do not use or touch electronic equipment. Immediately head for shore if on the water and lightning is observed. If not able to get to shore, disconnect and do not use or touch the major electronic equipment, including the radio, throughout the duration of the storm. If the time between seeing the lightning and hearing thunder is 3 seconds or less, the boat should be moved near a tall structure such as a bridge and remain there until 30 minutes after the last thunder is heard. 	<ul style="list-style-type: none"> Obtain weather forecast and updates as needed.
	High river flows or high waves	<ul style="list-style-type: none"> Be aware of waves and forecasts and recent rainfall in your watershed. 	<ul style="list-style-type: none"> Have forecast available.
	High winds	<ul style="list-style-type: none"> Wear goggles or safety glasses if dust or debris are visible. Stow or secure loads or equipment that could be moved by wind, particularly when underway. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Ensure that goggles or safety glasses are onboard.
	Biological hazards (e.g., mosquitoes)	<ul style="list-style-type: none"> Wear appropriate clothing (i.e., hat, long-sleeve shirt, long pants, leather gloves, boots, and Tyvek coveralls, as appropriate), and apply insect repellent. 	<ul style="list-style-type: none"> Ensure that insect repellent is onboard.

Job Safety Analysis



General Boating Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Vessel emergencies	Person overboard	<p>If you witness someone fall overboard:</p> <ul style="list-style-type: none"> • Yell, "Person overboard!" • Throw a flotation device immediately. • If the engine is running, take it out of gear and swing the stern clear to keep from hitting the person. • Call 911 or USCG as appropriate. • Assign a spotter to keep the person in sight at all times. • Contact nearby vessels for assistance. • Recover the person from the water. <p>If you fall overboard:</p> <ul style="list-style-type: none"> • Hold your mouth and nose closed and protect your head. • When you reach the surface, look for movement, listen for sounds, and call for help. Use the whistle attached to the PFD and activate the beacon light. • It is only sensible to swim if there is reason to believe you have a chance of reaching your destination. Too much movement in cold water causes hypothermia. 	<ul style="list-style-type: none"> • Ensure that flotation devices are available. • Ensure that team wears PFDs. • Inspect PFDs for integrity, particularly the cartridge charge on inflatable PFDs. • All crew members must be trained so that they know the location and use of onboard safety equipment.
Vessel emergencies (continued)	Fire, abandon ship	<ul style="list-style-type: none"> • Be prepared to abandon ship in case of major fire (too large to control with a fire extinguisher), or other emergency. • Only the boat captain can order abandon ship. • Communicate intent to abandon ship to all personnel onboard. • Notify USCG and nearby vessels of intent to abandon ship. • Call 911. • Notify the Project Manager and Field Lead, if time permits. • Be aware of the propeller position before abandoning ship. • Identify a rally point for all personnel. • Know the dangers of hypothermia. • Use the buddy system to support injured personnel. 	<ul style="list-style-type: none"> • For vessels less than 25 feet long, at least one fire extinguisher must be onboard. For vessels greater than 26 feet in length but less than 40 feet, at least two fire extinguishers must be onboard. • Review abandon ship procedures with field team prior to work.
Navigation	Boat traffic	<ul style="list-style-type: none"> • Maintain a safe operating distance from shoreline and other vessels. 	<ul style="list-style-type: none"> • Be aware of on-water surroundings. • The VHF radio must be turned on and monitored.

Job Safety Analysis



General Boating Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Motor vehicle operation and trailering	Boat not secured properly	<ul style="list-style-type: none">• Ensure that latches, straps, antennas, and onboard gear are secure. Ensure that motor is up and lights are plugged in for driving.• Follow Job Safety Analysis (JSA) for motor vehicle operation.• Crew members should not untie mooring lines until instructed to do so by the vessel operator.	<ul style="list-style-type: none">• Inspect around entire boat before driving.

Training Requirements:

- All personnel working on hazardous waste sites must receive appropriate training as required by 29 Code of Federal Regulations (CFR) 1910.120(e), including but not limited to initial 40-hour, 8-hour supervisor, and annual 8-hour refresher trainings.
- Medical clearance must be received on an annual basis as required by 29 CFR 1910.120(f).
- If professional captained vessel is not in use, boat operators must take appropriate state or provincial boater safety courses.
- All assigned employees are required to familiarize themselves with the contents of this JSA before starting a work activity and review it with their supervisor during their daily safety meeting.

Job Safety Analysis



Decontamination Activities

Project Name: Lower Duwamish Waterway Remedial Design	Project Number:	JSA Number: 004	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: T. Do	Analysis Date: May 29, 2020
Work Operation: Decontamination activities	Superintendent/Competent Person: T. Do	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE):		Reviewed by: S. McGroddy	Reviewed Date: May 29, 2020
<ul style="list-style-type: none"> Modified Level D—Long pants, long sleeves, and/or Tyvek coveralls if handling potentially contaminated media, steel-toed footwear conforming to American Society for Testing and Materials International (ASTM) F2412-05/ASTM F2413-05, safety glasses/splash goggles, high-visibility safety vest, medical face mask, and nitrile gloves Depending on activity, the following personal protective equipment (PPE) may also be required: hard hat, face shield, and, if boating, U.S. Coast Guard-approved personal flotation device (PFD). 		Approved by: S. McGroddy	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
General	COVID-19	<ul style="list-style-type: none"> Refer to Health and Safety Plan (HSP) (Appendix C) 	Refer to HSP (Appendix C).
If boating		<ul style="list-style-type: none"> Follow the Job Safety Analysis (JSA) for boating activities. 	
Decontamination area set up	Vehicle, heavy equipment traffic, or boat traffic in work area	<ul style="list-style-type: none"> Wear high-visibility safety vest and hard hat PPE. Be alert when working around heavy equipment and/or other boats, especially if wearing hearing protection. 	<ul style="list-style-type: none"> Ensure that safety vests are available for staff and visitors.
	Muscle strain or injuries from improper lifting	<ul style="list-style-type: none"> Use proper lifting techniques or ask for assistance with heavy objects. If boating, avoid carrying objects directly onto or off of the boat; rather, load/unload objects while on the boat to/from the pier/shore. 	<ul style="list-style-type: none"> Evaluate weight and center of gravity of heavier items prior to lifting or moving.
	Biological hazards (fauna [e.g., ticks, bees, spiders, and mosquitoes])	<ul style="list-style-type: none"> Be aware of likely biological hazards in the work area. Wear appropriate clothing (i.e., hat, long-sleeve shirt, long pants, leather gloves, boots, and Tyvek coveralls, as appropriate), and apply insect repellent. 	<ul style="list-style-type: none"> Ensure that insect repellent is available. Inspect clothing and skin for insects (e.g., ticks) after working in insect-prone areas.

Job Safety Analysis



Decontamination Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Decontamination activities	Injury from hand and power tool operation (e.g., spatula or drill)	<ul style="list-style-type: none"> • Be aware of sharp edges on hand tools (e.g., spatulas, knives, drill bits, and saw blades). • Be aware of electrical connections and water hazards when working with electric- or battery-operated tools. • Ensure that all tools are working properly; repair or replace defective tools. Repair any defective tools when unplugged and off. • Keep guards on power tools when not in use. 	<ul style="list-style-type: none"> • Inspect tools to ensure that they are in good working order. • Inspect electrical connections (if applicable). • Inspect tools periodically to ensure dry and clean operation.
	Noise exposure	<ul style="list-style-type: none"> • Wear hearing protection in high noise environments or when working around heavy machinery or equipment (action level of 85 decibels averaged over an 8-hour day). 	<ul style="list-style-type: none"> • Ensure that hearing protection is available.
	Slips, trips, and falls	<ul style="list-style-type: none"> • Avoid walking while writing or texting—maintain a heads-up posture. • Be aware of potentially slippery surfaces and tripping hazards. Use handrails where available. Wear footwear that has sufficient traction. • Maintain good housekeeping practices. Clean up all spills immediately. • Be aware of weather effects on the work area, including wet and/or frozen ground. • Jumping, running, and horseplay are prohibited. • Keep all areas clean and free of debris to prevent any trips and falls. • Notify the field team members of any unsafe conditions. 	<ul style="list-style-type: none"> • Routinely inspect work area for unsafe conditions.
	Ingestion of contaminants or decontamination fluids, or skin or eye contact with contaminants or decontamination fluids	<ul style="list-style-type: none"> • Wear appropriate PPE to prevent/reduce exposure. • Contact 911, as necessary; perform CPR if breathing stops. • Move exposed person away from source of contamination and rinse mouth. If exposure to skin occurs, promptly wash contaminated skin using soap or mild detergent and water. Rinse eyes with large amounts of water. • Follow decontamination procedures as outlined in the HSP. 	<ul style="list-style-type: none"> • Ensure that decontamination procedures are on hand and are reviewed. • Ensure that PPE and rinsing water are available.
Working outdoors	Heat stress	<ul style="list-style-type: none"> • Adjust work schedules, as necessary, to avoid the hottest part of the day. • Take rest breaks as warranted. • Provide shelter (air-conditioned, if possible) or shaded areas to protect personnel during rest periods. • Maintain body fluids at normal levels. • Train workers to recognize the symptoms of heat-related illness. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Monitor workers' physical conditions. • Monitor outside temperature versus worker activity.

Job Safety Analysis



Decontamination Activities

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Working outdoors (continued)	Cold stress	<ul style="list-style-type: none"> • Provide shelter (enclosed, heated environment) to protect personnel during rest periods. • Educate workers to recognize the symptoms of frostbite, hypothermia and other cold-related illness. • Use appropriate cold-weather gear, up to and including Mustang-type bib coveralls or jacket/bib combinations. • Consider additional precautions if working near water in cold weather. • Have a dry change of clothing available. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Monitor workers' physical conditions and PPE. • Monitor outside and water temperature versus worker activity and PPE.
	Rain or snow	<ul style="list-style-type: none"> • Wear appropriate PPE (rain gear). • Be aware of slip hazards, puddles, and electrical hazards when working in wet conditions. • If extremely cold conditions are forecast, consider additional precautions or postponing work activity. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Inspect PPE daily prior to use. • Routinely inspect work area for deteriorating conditions.
	Sunshine	<ul style="list-style-type: none"> • Have sunscreen available for ultraviolet protection. • Have abundant water available to prevent dehydration. • Consider wearing wide-brimmed headwear and light-colored, lightweight, sun-blocking clothing. 	<ul style="list-style-type: none"> • Ensure that sunscreen and water are available.
	Lightning	<ul style="list-style-type: none"> • Do not begin or continue work until lightning has ceased for at least 30 minutes. Disconnect and do not use or touch electronic equipment. 	<ul style="list-style-type: none"> • Obtain weather forecast and updates as needed.
	High winds	<ul style="list-style-type: none"> • Wear goggles or safety glasses if dust or debris are visible. 	<ul style="list-style-type: none"> • Review weather forecast prior to field work. • Ensure that goggles or safety glasses are available.

Training Requirements:

- All personnel working on hazardous waste sites must receive appropriate training as required by 29 Code of Federal Regulations (CFR) 1910.120(e), including but not limited to initial 40-hour, 8-hour supervisor, and annual 8-hour refresher trainings.

Job Safety Analysis



Decontamination Activities

- If boating is involved, and a professional captained vessel is not in use, boat operators must take the appropriate state or provincial boater safety courses.
- All assigned employees are required to familiarize themselves with the contents of this JSA before starting a work activity, and to review it with their supervisor during their daily safety meeting.

Job Safety Analysis



Anchor QEA Motor Vehicle Operation

Project Name: Lower Duwamish Waterway Remedial Design	Project Number: 180067-02.01	JSA Number: 006	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: K. Gross	Analysis Date: May 29, 2020
Work Operation: Anchor QEA motor vehicle operation	Superintendent/Competent Person: Vehicle Driver	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE): <ul style="list-style-type: none"> Wear seat belt at all times Make sure that clothing will not interfere with driving 		Reviewed by: M. Woltman	Reviewed Date: May 29, 2020
		Approved by: T. Shaner	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Anchor QEA motor vehicle operation	Unfamiliar with the vehicle	<ul style="list-style-type: none"> Allow yourself some time to get familiar with an Anchor QEA vehicle, a rental vehicle, or one not used often. Test the lights, windshield wipers, hazard lights, horn, parking brake, and other important functions. Review the dashboard controls, steering radius, and overhead and side clearances. Allow extra side, front, and back space around the vehicle while driving or parking an unfamiliar vehicle. Adjust mirrors and the seat while the vehicle is in park. Drive slowly in confined locations, as in a parking garage, parking lots, or industrial settings. Confirm adequate clearances by sight before turning or backing up in tight or unfamiliar locations. Use a second person to be a spotter outside the vehicle if needed in tight spaces. 	<ul style="list-style-type: none"> Inspect fluid levels and air pressure in tires, adjust mirrors and seat positions appropriately, monitor the fuel level, and fill up when the fuel level is low

Job Safety Analysis



Anchor QEA Motor Vehicle Operation

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
	Speed and braking	<ul style="list-style-type: none"> • Fasten and properly adjust the seat belt. • Obey all posted and designated speed limits. • Radar detectors are prohibited in all company-owned, leased, or rented vehicles. • Reduce travel speed during hazardous conditions (e.g., rain, fog, or snow). • Identify whether your vehicle has Anti-Lock Brakes (ABS). If it does, DO NOT pump the brakes to stop when the vehicle has begun to skid. Apply steady pressure to the brakes. If the vehicle does not have ABS, pump the brakes to stop during slippery conditions. 	<ul style="list-style-type: none"> • Seatbelt • Identify designated speed limits • Determine if vehicle has ABS
Anchor QEA motor vehicle operation (continued)	Distance spacing	<ul style="list-style-type: none"> • Continually check your rear and side view mirrors. • Use the 3-second rule to keep a safe distance between vehicles. • Increase the 3-second rule as necessary during hazardous travel conditions. • Regularly scan the area you will be entering in the next 10 to 12 seconds. • Always leave yourself an “out” during travel. • When stopping, make sure that you leave enough distance between you and the car in front of you. You should be able to see the rear tires of the vehicle in front when stopped. • Obey the speed limit and traffic regulations. • When at a red light and it turns green, use the “delayed start” technique, by counting to three before you take your foot off the brake. • DO NOT TAILGATE. • Keep headlights (and running lights, if available) on for maximum visibility. 	<ul style="list-style-type: none"> • Seatbelt
	Skids	<ul style="list-style-type: none"> • If the vehicle has begun to skid out of control, turn the steering wheel in the direction of the skid and re-adjust the wheel, as necessary. • Reduce speed during hazardous travel conditions. • Use 4-wheel drive, if available, when driving vehicles off-road, on steep inclines, or in muddy conditions. • Do not take vehicles off-road if they cannot be operated safely in such conditions. 	<ul style="list-style-type: none"> • Seatbelt
	Blind spots	<ul style="list-style-type: none"> • Become familiar with any blind spots associated with your vehicle. • Adjust mirrors to give the maximum viewing area. • Use your directional devices to signal all turns and when changing lanes; check rear and side view mirror and glance over your shoulder to check that the lane is clear. • Avoid other driver’s blind spots; slow down and let the other vehicle pass. • If parked for an extended period and staying in the vehicle, be sure to inspect the area for changed conditions (e.g., a car that moved in behind you) before leaving. 	<ul style="list-style-type: none"> • Seatbelt • Mirrors

Job Safety Analysis



Anchor QEA Motor Vehicle Operation

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
	Backing	<ul style="list-style-type: none"> • Back into parking spaces upon arrival whenever possible. • Perform a 360-degree walk around the vehicle before backing to identify any new conditions or obstructions. • Use a spotter when backing whenever possible. • Understand hand signals. • Sound the horn prior to backing. • Check the rear and side view mirrors prior to backing. • Back slowly in areas of obstructed vision. • Anticipate others who may be backing out into your pathway and adjust accordingly. 	<ul style="list-style-type: none"> • Seatbelt • Mirrors
Anchor QEA motor vehicle operation (continued)	Distractions (e.g., cell phones, reading maps or directions, eating)	<ul style="list-style-type: none"> • Do not engage in distracted driving—focus on operating the vehicle, and on your surroundings (e.g., road conditions and other drivers). • Obey state or local laws regarding cell phone use, at a minimum. • Certain clients prohibit cell phone use regardless of the state you are operating in—know your client’s policy. • Use hands-free devices (not hand-held cellular phones) while driving. • Pull over to the side of the road when making a call or checking directions. 	<ul style="list-style-type: none"> • Seatbelt • Hands-free devices connected and ready for use
	Accidents	<ul style="list-style-type: none"> • In the event of an accident, use the following procedures: <ul style="list-style-type: none"> – Stop, call for medical assistance, notify police, and complete an accident report and submit it to your supervisor. – Notify the Project Manager (PM) and Field Lead (FL). – Complete the appropriate incident investigation reports. – Contact Sara Weiskotten, Operations Liaison, at (857) 445-4987. – Contact Diana Reynolds, Insurance Liaison, at (302) 236-8403. 	<ul style="list-style-type: none"> • Seatbelt
	Influenced by drugs or alcohol	<ul style="list-style-type: none"> • NEVER DRIVE UNDER THE INFLUENCE OF DRUGS OR ALCOHOL. • Keep in mind that the person in another vehicle may be under the influence of controlled substances, and be prepared for erratic or sudden driving changes on their part. 	<ul style="list-style-type: none"> • Seatbelt
	Driver attitude	<ul style="list-style-type: none"> • Do not operate any vehicle when abnormally tired, temporarily disabled (i.e., injured), or under the influence of drugs or alcohol. • Keep an even temper when driving. Do not let the actions of others affect your attitude. • Do not allow yourself to become frustrated, rushed, distracted, or drowsy. 	<ul style="list-style-type: none"> • Seatbelt

Job Safety Analysis



Anchor QEA Motor Vehicle Operation

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
	Fatigue	<ul style="list-style-type: none"> Stop and rest if fatigued. Exit the road and enter a safe area. Rest until fully refreshed. Be aware that certain medications (such as cold or allergy medicines) may make you drowsy when driving a vehicle. 	<ul style="list-style-type: none"> Seatbelt
	Vehicle loading	<ul style="list-style-type: none"> DO NOT OVERLOAD the vehicle. Secure all equipment and supplies within the body of the vehicle using proper tie-downs. Do not block side view mirrors with the load. Do not transport U.S. Department of Transportation (DOT)-manifested hazardous materials. Dispatch all equipment and personnel with proper forms and identification. 	<ul style="list-style-type: none"> Seatbelt
Anchor QEA motor vehicle operation (continued)	Equipment failure	<ul style="list-style-type: none"> Perform daily inspections of your vehicle. Maintain vehicle safety equipment (e.g., mirrors, alarms, horns, wipers, lights, and brakes). Maintain the vehicle (e.g., tire pressure and fluid levels). Any vehicle with mechanical defects that may endanger the safety of the driver, passengers, or the public shall not be used. Ensure that appropriate safety equipment is in the vehicle. Safety equipment should include a spare tire, jack, first-aid kit, fire extinguisher, and flashlight. Flares and/or reflective triangles should be available in larger trucks. Ensure that the proper documentation is in the vehicle. Documentation should include an operations manual for the vehicle, insurance card, vehicle registration, and accident forms. 	<ul style="list-style-type: none"> Inspect and maintain the vehicle

Training Requirements:

- All drivers are required to have a valid driver’s license, and all vehicles must have appropriate state vehicle registration and inspection stickers. The use of hand-held wireless devices is prohibited while driving any vehicle for business use at any time, for personal use during business hours, and as defined by law.
- If operating a vehicle or vehicle and trailer with a capacity greater than 10,000 pounds, U.S. Department of Transportation regulations may apply. Contact the PM prior to any travel in this configuration.**

Job Safety Analysis



Anchor QEA Motor Vehicle Operation

- All assigned employees are required to read, familiarize themselves with the contents of this Job Safety Analysis, and sign the signature page before the operation of an Anchor QEA vehicle, and review it with their supervisor during their daily safety meeting.
- All assigned employees are required to enroll and complete the Smith System Virtual Driving training programs (*Distracted Driving* and *Small Vehicle Forward - Five Keys to Safe Driving*) prior to driving an Anchor QEA vehicle.

Job Safety Analysis



Investigation-derived Waste Management

Project Name: Lower Duwamish Waterway Remedial Design	Project Number:	JSA Number: 007	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: T. Do	Analysis Date: May 29, 2020
Work Operation: Investigation-derived waste management	Superintendent/Competent Person: T. Do	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE): <ul style="list-style-type: none"> Modified Level D— Long pants, long sleeves, and/or Tyvek coveralls if handling potentially contaminated media, steel-toed footwear conforming to American Society for Testing and Materials International (ASTM) F2412-05/ASTM F2413-05, safety glasses/splash goggles, high-visibility safety vest, medical face mask, and nitrile gloves Depending on activity, the following personal protective equipment (PPE) may also be required: hard hat, face shield, and, if boating, U.S. Coast Guard-approved personal flotation device (PFD). 		Reviewed by: S. McGroddy	Reviewed Date: May 29, 2020
		Approved by: S. McGroddy	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
IDW management – general	Splash	<ul style="list-style-type: none"> Wear the required PPE at all times. Use care to minimize splashing or smearing of IDW during handling and containerization. 	<ul style="list-style-type: none"> Inspect PPE upon donning and periodically during tasks.
	COVID-19	<ul style="list-style-type: none"> Refer to Health and Safety Plan (HSP) (Appendix C) 	<ul style="list-style-type: none"> Refer to HSP (Appendix C)
Containerizing investigation-derived waste (IDW) at the source	Lifting	<ul style="list-style-type: none"> Use care when lifting IDW to redistribute from one container (e.g., bowls and buckets) to another at the source. Seek assistance if loads are too heavy, or if you are experiencing fatigue. Fill containers only to the degree that will be manageable in the future (e.g., half full) and to limit weight. 	<ul style="list-style-type: none"> Inspect containers for competency (i.e., no cracks, and handles in good repair).
	Pinch points	<ul style="list-style-type: none"> Wear hand protection when closing containers. 	<ul style="list-style-type: none"> Inspect containers for rust or sharp edges prior to opening or closing.

Job Safety Analysis



Investigation-derived Waste Management

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Relocating or staging IDW containers	Lifting	<ul style="list-style-type: none"> Use task-specific tools whenever possible to move full containers (i.e., hoists, dollies, and vehicles). When task-specific tools are not available, use the buddy system to move containers that are reasonable to lift. Stage containers in areas protected from heavy traffic and weather, if possible. 	<ul style="list-style-type: none"> Ensure tools are in good repair. Assess IDW container weight prior to moving.
Relocating or staging IDW containers (continued)	Pinch points or crushing	<ul style="list-style-type: none"> Use tools to achieve the final arrangement when staging containers—do not place hands on the edges of containers while moving them into place. Stand well clear of containers being moved in case they become dislodged from their handling tool during transport. Do not stack IDW containers, as this poses a risk for container toppling and damage. Place containers on a wooden pallet for easy transfer using a pallet jack, if possible. 	<ul style="list-style-type: none"> Inspect containers for evidence of cracks or rust.

Training Requirements:

- All personnel working on hazardous waste sites must receive appropriate training as required by 29 Code of Federal Regulations (CFR) 1910.120(e), including but not limited to initial 40-hour, 8-hour supervisor, and annual 8-hour refresher trainings.
- All assigned employees are required to familiarize themselves with the contents of this JSA before starting a work activity, and to review it with their supervisor during their daily safety meeting.

Job Safety Analysis



Structure and Bank Inspection

Project Name: Lower Duwamish Waterway Remedial Design	Project Number: 180067-02.01	JSA Number: 008	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: K. Gross	Analysis Date: May 29, 2020
Work Operation: Inspection of structures and banks	Superintendent/Competent Person: M. Woltman	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE): <ul style="list-style-type: none"> Modified Level D—Long pants, long sleeves, and/or Tyvek coveralls if handling potentially contaminated media, and steel-toed footwear conforming to ASTM International (ASTM) F2412-05/ASTM F2413-05, safety glasses/splash goggles, hard hat, nitrile gloves, high-visibility safety vest, and protective face mask If boating, U.S. Coast Guard-approved personal flotation device (PFD; see cold stress section for cold-weather PFD information) 		Reviewed by: M. Woltman	Reviewed Date: May 29, 2020
		Approved by: T. Shaner	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
General	COVID-19	<ul style="list-style-type: none"> Refer to Health and Safety Plan (HSP). 	Refer to HSP.
If boating		<ul style="list-style-type: none"> Follow the Job Safety Analysis (JSA) for boating activities. 	
Walking and working in natural environments	Slips, trips, and falls	<ul style="list-style-type: none"> Avoid walking while writing or texting—maintain a heads-up posture. Be aware of potentially slippery surfaces, including boat decks, riprap, muddy or algae-covered rocks, shoreline plants or seaweed, thick mud, and tripping hazards such as vines and logs. Use handrails where available. Wear footwear that has sufficient traction. Maintain good housekeeping practices. Clean up all spills immediately. Be aware of weather effects on the work area, including wet and/or frozen ground. Jumping, running, and horseplay are prohibited. Be cautious when entering or exiting the vessel, and load/unload items onto/off of the pier or shore once boarded. Keep all areas clean and free of debris to prevent any trips and falls. Notify the field team members of any unsafe conditions. 	<ul style="list-style-type: none"> Routinely inspect work area for unsafe conditions.

Job Safety Analysis



Structure and Bank Inspection

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Walking and working in natural environments (continued)	Wading	<ul style="list-style-type: none"> • Be aware of potentially slippery surfaces and tripping hazards such as fallen brush, logs, rocks, and other debris. Wear footwear that has sufficient traction. • Be aware of the water depth and potential drop-offs. • Be aware of existing and projected river flows. • Wear knee or chest waders as appropriate for traction and to protect against cold water. • Keep extra dry clothes on hand, including socks. • Consider carrying a walking staff for balance. • Always wear a PFD, even if water looks shallow or slow; drop-offs occur and water is often moving faster than it looks. 	<ul style="list-style-type: none"> • Inspect work area for tripping hazards visible from streambank. • Inspect waders for leaks. • Check depths and flows before wading. • Ensure that change of dry clothes is available if wading in cold weather or cold water conditions. • Inspect PFDs for integrity, particularly the cartridge charge on inflatable PFDs.
	Diving	<ul style="list-style-type: none"> • Follow safety checklists for diving operations. • Assign responsibilities for all dive team members. • Comply with all applicable requirements of Washington Department of Labor & Industry Standards for Commercial Diving Operations (WAC 296-37). • Provide a safe practices manual for each diving mode per WAC 296-37-530 before beginning dive operations. 	<ul style="list-style-type: none"> • Contractor will produce a site-specific dive plan for each diving operation that specifies the means and methods that will be used to comply with all required elements of Washington State's diving standards.
	Biological hazards (flora [e.g., poison ivy and poison oak] and fauna [e.g., bees, spiders, mosquitoes, and snakes])	<ul style="list-style-type: none"> • Be aware of likely biological hazards in the work area. • Wear appropriate clothing (i.e., hat, long-sleeve shirt, long pants, leather gloves, boots, and Tyvek coveralls, as appropriate), and apply insect repellent. • Wear hand and arm protection when clearing plants or debris from the work area. • Be aware of potential wildlife and defensive behavior (e.g., nesting birds, or animals with young). 	<ul style="list-style-type: none"> • Ensure that insect repellent is available. • Inspect clothing and skin for insects (e.g., ticks) after working in insect-prone areas.
	Noise exposure	<ul style="list-style-type: none"> • Wear hearing protection in high noise environments or when working around heavy machinery or equipment (action level of 85 decibels averaged over an 8-hour day). 	<ul style="list-style-type: none"> • Ensure that hearing protection is available.

Job Safety Analysis



Structure and Bank Inspection

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Working outdoors	Heat stress	<ul style="list-style-type: none"> Adjust work schedules, as necessary, to avoid the hottest part of the day. Take rest breaks as warranted. Provide shelter (air-conditioned, if possible) or shaded areas to protect personnel during rest periods. Maintain body fluids at normal levels. Train workers to recognize the symptoms of heat-related illness. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Monitor workers' physical conditions. Monitor outside temperature versus worker activity.
	Cold stress	<ul style="list-style-type: none"> Provide shelter (enclosed, heated environment) to protect personnel during rest periods. Educate workers to recognize the symptoms of frostbite and hypothermia. Use appropriate cold-weather gear, up to and including Mustang-type bib coveralls or jacket/bib combinations. Consider additional precautions if working near water in cold weather. Have a dry change of clothing available. Train workers to recognize the symptoms of cold-related illness. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Monitor workers' physical conditions and PPE. Monitor outside and water temperature versus worker activity and PPE.
	Rain or snow	<ul style="list-style-type: none"> Wear appropriate PPE (rain gear). Be aware of slip hazards, puddles, and electrical hazards when working in wet conditions. If extremely cold conditions are forecast, consider additional precautions or postponing work activity. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Inspect PPE daily prior to use. Routinely inspect work area for deteriorating conditions.
	Sunshine	<ul style="list-style-type: none"> Have sunscreen available for ultraviolet protection. Have abundant water available to prevent dehydration. Consider wearing wide-brimmed headwear and light-colored, lightweight, sun-blocking clothing. 	<ul style="list-style-type: none"> Ensure that sunscreen and water are available.
	Lightning	<ul style="list-style-type: none"> Do not begin or continue work until lightning subsides for at least 30 minutes. Disconnect and do not use or touch electronic equipment. 	<ul style="list-style-type: none"> Obtain weather forecast and updates as needed.
	High winds	<ul style="list-style-type: none"> Wear goggles or safety glasses if dust or debris are visible. 	<ul style="list-style-type: none"> Review weather forecast prior to field work. Ensure that goggles or safety glasses are available.

Job Safety Analysis



Structure and Bank Inspection

Training Requirements:

- All personnel working on hazardous waste sites must receive appropriate training as required by 29 Code of Federal Regulations (CFR) 1910.120(e), including but not limited to initial 40-hour, 8-hour supervisor, and annual 8-hour refresher trainings.
- Medical clearance must be received on an annual basis as required by 29 CFR 1910.120(f).
- If boating is involved, and a professional captained vessel is not in use, boat operators must take the appropriate state or provincial boater safety courses.
- All assigned employees are required to familiarize themselves with the contents of this JSA before starting a work activity and review it with their supervisor during their daily safety meeting.

Job Safety Analysis



Sample and Laboratory Glassware Handling

Project Name: Lower Duwamish Waterway Remedial Design	Project Number:	JSA Number: 009	Issue Date: May 29, 2020
Location: Seattle, Washington	Contractor: Anchor QEA, LLC and Windward Environmental, LLC	Analysis by: T. Do	Analysis Date: May 29, 2020
Work Operation: Sample and laboratory glassware handling	Superintendent/Competent Person: T. Do	Revised by: NA	Revised Date: NA
Required Personal Protective Equipment (PPE): <ul style="list-style-type: none"> Modified Level D—Long pants, long sleeves, and/or Tyvek coveralls if handling potentially contaminated media, steel-toed footwear conforming to American Society for Testing and Materials International (ASTM) F2412-05/ASTM F2413-05, safety glasses/splash goggles, high-visibility safety vest, medical face mask, and nitrile gloves Depending on activity, the following personal protective equipment (PPE) may also be required: hard hat, face shield,, and, if boating, U.S. Coast Guard-approved personal flotation device (PFD). 		Reviewed by: S. McGroddy	Reviewed Date: May 29, 2020
		Approved by: S. McGroddy	Approved Date: May 29, 2020

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
General	COVID-19	<ul style="list-style-type: none"> Refer to Health and Safety Plan (HSP) (Appendix C). 	<ul style="list-style-type: none"> Refer to HSP (Appendix C).
Transporting and using glassware	Breakage of containers during field activities	<ul style="list-style-type: none"> Use appropriately sized tubs or bottle carriers with dividers to prevent bottle-to-bottle contact during transport. Consider using coated glassware, if practicable. Carry oversized bottles in tubs or bottle carriers, using both hands during transfer, to the sampling vessel and whenever the vessel is underway. 	<ul style="list-style-type: none"> Ensure dividers are sufficient and will remain in place during transport.
	Faulty glassware	<ul style="list-style-type: none"> Replace any glassware that is chipped, nicked, or cracked. 	<ul style="list-style-type: none"> Inspect glassware before use.
	Impact with equipment and other objects	<ul style="list-style-type: none"> Use care when loading and unloading sampling equipment. Minimize the handling of individual containers to the extent possible. 	

Job Safety Analysis



Sample and Laboratory Glassware Handling

Work Activity	Potential Hazards	Preventive or Corrective Measures	Inspection Requirements
Filling sample containers	Over-tightening of bottle lids causing breakage	<ul style="list-style-type: none"> Avoid use of excessive force to tighten bottle caps (i.e., finger tight). 	
	Breakage during sample collection	<ul style="list-style-type: none"> Place containers in plastic tubs between aliquots to limit contact with hard surfaces. Place containers on a stable and non-slip surface during collection. Use the buddy system as needed to hold bottles during filling. 	
Filling sample containers (continued)	Contact with sediment sample	<ul style="list-style-type: none"> Wear nitrile gloves and protective eyewear to prevent skin and eye contact if a container is damaged. Do not open preserved bottles until necessary. 	<ul style="list-style-type: none"> Change gloves when damaged or soiled
Packing samples for shipment	Breakage during packing and shipment	<ul style="list-style-type: none"> Use bottle wraps, foam sleeves, or bubble wrap to prevent bottle contact in the cooler. Pack coolers snugly, but do not over pack. 	<ul style="list-style-type: none"> Ensure glass bottles do not touch to minimize potential breakage during transport.

Training Requirements:

- All personnel working on hazardous waste sites must receive appropriate training as required by 29 Code of Federal Regulations (CFR) 1910.120(e), including, but not limited to initial 40-hour, 8-hour supervisor, and annual 8-hour refresher trainings.
- All assigned employees are required to familiarize themselves with the contents of this JSA before starting a work activity, and to review it with their supervisor during their daily safety meeting.

**ATTACHMENT 3. PHASE 1 CONSTRUCTION
RESTART COVID-19 JOB SITE REQUIREMENTS**

Phase 1 Construction Restart

COVID-19 Job Site Requirements

Phase 1: Low-risk construction work resumes.

Any existing construction projects complying with the points below may resume only those work activities that do not require workers to be closer than six-feet together. If a work activity requires workers to be closer than six-feet, it is not considered low-risk and is not authorized. Adherence to the physical distancing requirement and the health and safety points below will be strictly enforced.

Prior to recommencing work all contractors are required to develop and post at each job site a comprehensive COVID-19 exposure control, mitigation, and recovery plan. The plan must include policies regarding the following control measures: PPE utilization; on-site social distancing; hygiene; sanitation; symptom monitoring; incident reporting; site decontamination procedures; COVID-19 safety training; exposure response procedures; and a post-exposure incident project wide recovery plan. A copy of the plan must be available on each job site during any construction activities and available for inspection by state and local authorities. Failure to meet posting requirements will result in sanctions, including the job being shut down.

All Contractors are required to post at each job site written notice to employees, subcontractors and government officials the Phase 1 work that will be performed at that job site and signed commitment to adhere to the requirements listed in this document.

All contractors have a general obligation to keep a safe and healthy worksite in accordance with state and federal law. Failure to follow these requirements will be considered a violation of these duties and be penalized accordingly. Under RCW 49.17.060, “each employer shall furnish to each of their employees a place of employment free from recognized hazards that are causing or likely to cause serious injury or death to his or her employees and shall comply with the rules, regulations, and orders promulgated under this chapter.” The Washington State Department of Labor & Industries’ Division of Occupational Safety and Health (DOSH) is responsible for workplace safety and health, including inspections and enforcement, consultation, technical assistance, training, education and grants.

All contractors are also required to comply with the following COVID-19 worksite-specific safety practices, as outlined in Gov. Jay Inslee’s “Stay Home, Stay Healthy” Proclamation 20-25, and in accordance with the Washington State Department of Labor & Industries General Coronavirus Prevention Under Stay Home-Stay Healthy Order (DOSH Directive 1.70: <https://www.lni.wa.gov/safety-health/safety-rules/enforcement-policies/DD170.pdf>) and the Washington State Department of Health Workplace and Employer Resources & Recommendations at <https://www.doh.wa.gov/Coronavirus/workplace>:

COVID-19 Site Supervisor

1. A site-specific COVID-19 Supervisor shall be designated by the contractor at every job site to monitor the health of employees and enforce the COVID-19 job site safety plan. A designated COVID-19 Supervisor must be present at all times during construction activities, except on single-family residential job sites with 6 or fewer people on the site.

COVID-19 Safety Training

2. A Safety Stand-Down/toolbox talk/tailgate training must be conducted on all job sites on the first day of returning to work, and weekly thereafter, to explain the protective measures in place for all workers. Social distancing must be maintained at all gatherings.
3. Attendance will be communicated verbally and the trainer will sign in each attendee.
4. COVID-19 safety requirements shall be visibly posted on each jobsite.

Social Distancing

5. Social distancing of at least 6 feet of separation must be maintained by every person on the worksite at all times.
6. Gatherings of any size must be precluded by taking breaks and lunch in shifts. Any time two or more persons must meet, ensure minimum 6 feet of separation.
7. Identify “choke points” and “high-risk areas” on job sites where workers typically congregate and control them so social distancing is always maintained.
8. Minimize interactions when picking up or delivering equipment or materials, ensure minimum 6-foot separation.
9. To the extent practical allow only one trade/subcontractor at a time on a jobsite and maintain 6-foot separation social distancing for each member of that trade. If more than one trade/subcontractor must be on the job to complete the job then at a minimum all trades and subcontractors must maintain social distancing policies in accordance with this guidance.

Personal Protective Equipment (PPE) – Employer Provided

10. Provide personal protective equipment (PPE) such as gloves, goggles, face shields and face masks as appropriate, or required, for the activity being performed.
11. Masks, in accordance with Washington Department of Health guidelines, or as required by Washington Department of Labor & Industries (L&I) safety rules, must be worn at all times by every employee on the worksite.
12. Eye protection must be worn at all times by every employee while on worksite.
13. Gloves must be worn at all times by every employee while on worksite. The type of glove worn should be appropriate to the task. If gloves are not typically required for the task, then any type of glove is acceptable, including latex gloves.
14. If appropriate PPE cannot be provided, the worksite must be shut down.

Sanitation and Cleanliness

15. Soap and running water shall be abundantly provided on all job sites for frequent handwashing. Workers should be encouraged to leave their workstations to wash their hands regularly, before and after going to the bathroom, before and after eating and after coughing, sneezing or blowing their nose.
16. When running water is not available, portable washing stations, with soap, are required, per WAC 296-155-140 2(a) – (f). Alcohol-based hand sanitizers with greater than 60% ethanol or 70% isopropanol can also be used, but are not a replacement for the water requirement.
17. Post, in areas visible to all workers, required hygienic practices, including not to touch face with unwashed hands or with gloves; washing hands often with soap and water for at least 20 seconds; use hand sanitizer with at least 60% alcohol; cleaning and disinfecting frequently touched objects and surfaces such as workstations, keyboards, telephones, handrails, machines, shared tools, elevator control buttons, and doorknobs; covering the mouth and nose when coughing or sneezing as well as other hygienic recommendations by the U.S. Centers for Disease Control (CDC).
18. Make disinfectants available to workers throughout the worksite and ensure cleaning supplies are frequently replenished.
19. Frequently clean and disinfect high-touch surfaces on job sites and in offices, such as shared tools, machines, vehicles and other equipment, handrails, doorknobs, and portable toilets. If these areas cannot be cleaned and disinfected frequently, the jobsite shall be shut down until such measures can be achieved and maintained.
20. When the worksite is an occupied home, workers should sanitize work areas upon arrival, throughout the workday and immediately before they leave, and occupants should keep a personal distance of at least 10 feet.
21. If an employee reports feeling sick and goes home, the area where that person worked should be immediately disinfected.

Employee Health/Symptoms

22. Create policies which encourage workers to stay home or leave the worksite when feeling sick or when they have been in close contact with a confirmed positive case. If they develop symptoms of acute respiratory illness, they must seek medical attention and inform their employer.
23. Have employees inform their supervisors if they have a sick family member at home with COVID-19. If an employee has a family member sick with COVID-19, that employee must follow the isolation/quarantine requirements as established by the State Department of Health.
24. Screen all workers at the beginning of their shift by taking their temperature and asking them if they have a fever, cough, shortness of breath, fatigue, muscle aches, or new loss of taste or smell. Thermometers used shall be 'no touch' or 'no contact' to the greatest extent possible. If a 'no touch' or 'no contact' thermometer is not available, the thermometer must be properly sanitized between each use. Any worker with a temperature of 100.4°F or higher is considered to have a fever and must be sent home.

25. Instruct workers to report to their supervisor if they develop symptoms of COVID-19 (e.g., fever, cough, shortness of breath, fatigue, muscle aches, or new loss of taste or smell). If symptoms develop during a shift, the worker should be immediately sent home. If symptoms develop while the worker is not working, the worker should not return to work until they have been evaluated by a healthcare provider.
26. Failure of employees to comply will result in employees being sent home during the emergency actions.
27. Employees who do not believe it is safe to work shall be allowed to remove themselves from the worksite and employers must follow the expanded family and medical leave requirements included in the Families First Coronavirus Response Act or allow the worker to use unemployment benefits, paid time off, or any other available form of paid leave available to the worker at the workers discretion.
28. Any worker coming to work on a construction site in Washington from any state that is not contiguous to Washington must self-quarantine for 14 days to become eligible to work on a job site in Washington.
29. If an employee is confirmed to have COVID-19 infection, employers should inform fellow employees of their possible exposure to COVID-19 in the workplace but maintain confidentiality as required by the Americans with Disabilities Act (ADA). The employer should instruct fellow employees about how to proceed based on the CDC [Public Health Recommendations for Community-Related Exposure](#).

Job Site Visitors

30. A daily attendance log of all workers and visitors must be kept and retained for at least four weeks. The log must include the name, phone number, and email address of all workers and visitors.

No jobsite may operate until the contractor can meet and maintain all requirements, including providing materials, schedules and equipment required to comply.

These Phase 1 COVID-19 job site safety practices are required as long as the “Stay Home, Stay Healthy” Gubernatorial Proclamation 20-25 is in effect or if adopted as rules by a federal, state or local regulatory agency. **All items minus numbers 28 and 30 are subject to enforcement action under L&I’s Division of Occupational Safety and Health (DOSH).**

Workplace safety and health complaints may be submitted to the L&I Call Center: (1-800-423-7233) or via e-mail to adag235@lni.wa.gov. **General questions about how to comply with construction safety practices** can be submitted to the state’s Business Response Center at <https://app.smartsheet.com/b/form/2562f1caf5814c46a6bf163762263aa5>. **All other violations related to Proclamation 20-25** can be submitted via at: <https://bit.ly/covid-compliance>.

DOSH DIRECTIVE

Department of Labor and Industries
Division of Occupational Safety and Health

Keeping Washington Safe and Working

1.70

GENERAL CORONAVIRUS PREVENTION UNDER STAY HOME-STAY HEALTHY ORDER

Date: April 7, 2020

I. Purpose

This Directive provides enforcement policy when evaluating workplace implementation of social distancing, sanitation and sick employee practices as required under the [Governor's Proclamation: Stay Home - Stay Healthy Order](#).

Under the Order, people are required to stay home except for essential activities, which include a wide range of economic and social functions necessary to maintain minimum living conditions. Employers who continue operations under the Order are required to maintain coronavirus prevention practices consistent with DOSH, OSHA and Department of Health guidance. Coronavirus is recognized as a very serious workplace hazard.

II. Scope and Application

- A.** DOSH does not enforce the Governor's Order directly. Under existing DOSH rules, employers are required to protect workers from biological hazards and implement programs to address known hazards in the workplace.
- B.** DOSH staff will not determine whether an employer is engaged in essential activity. If there is no clear rationale for the business operating, this may be referred to the Washington State coronavirus.wa.gov page. (See the Governor's site "What's open and closed" at <https://coronavirus.wa.gov/whats-open-and-closed>).
- C.** DOSH staff will limit actions related to infectious disease only when there is an aspect of exposure that is specific to the relationship between employers and workers. DOSH will do so in a manner consistent with public health orders and issued guidance.
- D.** There are extensive recommendations for healthcare workplaces with specific guidance related to infectious disease prevention. Therefore, this Directive will normally not be used in specific healthcare delivery work task settings.

III. References

- Chapter 296-800 WAC, Safety and Health Core Rules
 - WAC 296-800-11045 Protect employees from biological agents
 - WAC 296-800-140, Accident Prevention Program
 - WAC 296-800-22005, Keep your workplace clean.
 - WAC 296-800-23025, Provide convenient and clean washing facilities

- Proclamation by the Governor: Stay Home - Stay Healthy Order
- CDC: Infection Control in Healthcare Personnel
- CDC Coronavirus (COVID-19) Page
- Washington State Coronavirus Response (COVID-19) Page
- OSHA Publication 3990: Guidance on Preparing Workplaces for COVID-19.pdf (English)
- OSHA Publication 3992: Guidance on Preparing Workplaces for COVID-19.pdf (Spanish)
- Washington State Department of Health Recommendations for Temporary Worker Housing Facilities

IV. **Background**

Staff shall learn and consider the baseline expectations for employers to provide workers a safe workplace during the coronavirus (COVID-19) virus outbreak. Overt workplace specific practices by the employer must be made to implement the Governor's [Executive Order](#). There are four basic categories of prevention elements that must be addressed during the inspection/investigation. Employers must ensure social distancing practices for employees and control customer flow; ensure frequent and adequate employee handwashing and surface sanitation; and ensure sick employees stay home or go home if ill. Employers must also provide basic workplace hazard education about coronavirus and how to prevent transmission in the language best understood by the employee. DOSH staff will need to be thoughtful on how these four elements are addressed based on the challenges that the specific worksite tasks present, but all four elements must be addressed in each operating workplace.

DOSH Staff shall ensure that employers and employees are made aware that it is against the law for any employer to take any adverse action (such as firing, demotion, or otherwise retaliate) against a worker they suspect for exercising safety and health rights such as raising safety and health concerns to their employer, participating in union activities concerning safety and health matters, filing a safety and health complaint or participating in a DOSH investigation. DOSH Staff will ensure workers are informed they have 30 days to file their complaint with L&I DOSH and/or with Federal OSHA.

Employers must institute these prevention program elements or equivalent protections to limit the spread of the disease within the workplace under DOSH rules and in connection to the Governor's Order. These procedures are specific to COVID-19 prevention and the related virus. If a workplace has a concern about exposures to another pathogen, Technical Services must be consulted on procedures specific to that pathogen.

A. Basic Program Elements.

The following **bold program elements are essential** to the program whenever feasible. Employers who can establish work rules consistent with this section are not required to have further active monitoring or ongoing assessment of their workplace.

1. **Educate workers (and customers) about COVID-19 and how to prevent virus spread.**
 - a. Post posters/information from the local health department, state Department of Health, Center for Disease Control and Prevention, and other authorities.
 - b. Inform workers about the steps being taken in the workplace to establish social distancing, increased handwashing, and to prevent the spread of the virus.
2. **Maintain at least 6 feet of spacing at all times.**
 - a. Occupied workstations are separated by 6 feet or have physical barriers
 - b. Only infrequent intermittent passing within 6 feet is allowed between employees without wearing respiratory protection.
 - c. Materials, produce, or work items are transported between workers by mechanical means or by using staging points.
 - Workers may be along a conveyor or production system carrying product.
 - Workers may go to a central point one-at-a-time to drop off or pick up items that transfer between workers.
 - Workers may have mailboxes, bins, or other surfaces at the periphery of their workspace where materials are left for them by other workers.
 - Provisions should be made to clean objects handled extensively by more than one worker when the items are transferred. Physically wiping the object so it is visibly clean (no obvious soiling, smearing, or streaks) is sufficient.
 - Social distancing is maintained during breaks and at shift start and end, while workers are at the employer's worksite.
 - Meetings with workers are limited in less than 10 and maintain 6 foot spacing of all in attendance.
3. **Regular cleaning of area, frequent cleaning of common-touch surfaces.**
 - a. A cleaning schedule must be kept to maintain general housekeeping to prevent buildup of dirt and clutter.
 - b. The first step in cleaning is to remove buildups of dirt and other materials on surfaces. Water and soap or other cleaning fluids are used with wipes, clothes, brushes or other physical means of removing these materials so that there is no visible build-up, smears, or streaks on the surface. Disinfecting is the second step and is primarily needed for high touch surfaces. Bleach solutions or an EPA approved disinfectant **must be used** to make sure this is effective. (See the list of approved disinfectants at <https://www.epa.gov/pesticide-registration/list-n-disinfectants-use-against-sars-cov-2>).

Surfaces that are commonly touched with the hands but difficult to clean (fabric, rough surfaces, and so forth) may need to be covered to make sure the environment is hygienic.

- c. Cleaning supplies need to be available to workers to do spot cleaning when necessary.
 - d. Surfaces that are regularly touched by workers must be cleaned regularly to maintain a visibly clean state (no obvious soiling, smearing, or streaks).
 - For surfaces touched by multiple workers, this can be on a frequent schedule, or between workers.
 - For surfaces touched by a single worker, this should be done periodically, at least once per shift or when unclean.
4. **Workers must have facilities for frequent handwashing readily available**, including hot and cold (or tepid) running water and soap.
- Staff must pay particular attention to transient outdoor and delivery workers and non-fixed worksites where there are no exceptions being granted. Portable wash stations are readily available.
 - To facilitate more frequent cleaning, secondary handwashing or sanitizing stations can be provided with either hand sanitizer, or wipes/towelettes.
 - Workers must be able to wash their hands after touching any surface/tool suspected of being contaminated, before and after eating and using the restroom, and before touching their face.

5. **Sick Employee and Post- employee illness procedures.**

DOSH staff will ensure employers have a program to prevent sick employees from entering the workplace and when recognized, that ill employees are sent home.

- a. Ensure a system for preventing sick employees to be present at work.
- b. Establish a process for deep cleaning after any worker leaves the workplace reporting a suspected or confirmed case of COVID-19.
- c. Thoroughly clean areas where the worker worked or would have stayed more than 10 minutes.
 - Wipe all accessible surfaces
 - Clean up any visible soiling including any smears or streaks.
 - Sanitize common touch surfaces in the vicinity.
- d. Do not allow other workers into these areas until the cleaning is complete.

B. Consider Possible Alternate Strategies.

Some industries may have challenges with basic elements so one or more of the following alternatives may be used to provide protection for workers.

1. Engineering controls can be established and maintained to provide an effective distancing of employees when it is not feasible to fully separate them.

- a. Barriers must block direct pathways from face to face between individuals, and make it so any indirect air pathways are greater than 6 feet. Sneezes and coughs should not be directed into the air above someone within 6 feet.
 - b. Covers can be used on common touch surfaces that cannot be easily cleaned. The covers may create a cleanable surface, or be something that can be changed out between individuals.
 - c. Ventilation that provides a clean air supply to a worker's breathing zone.
2. Job modifications may be necessary to facilitate appropriate social distancing. Although an operation may be overall part of an essential industry or service, there may be portions of the work which can be deferred until a later time. In some cases, reorganizing the work may be necessary to break up tasks in a manner that facilitates social distancing or other protective measures.
 3. Health surveillance can be done to identify early signs of infection, and separate workers who may present a risk to others.
 - a. There will usually be an initial screening and then periodic review (probably daily with COVID-19).
 - b. Initial screening will involve some review of the worker's history that may be relevant to their risk of contracting the disease. This may also include review of the worker's susceptibility to the disease and an education element on the disease and prevention.
 - c. Periodic screening will involve tracking symptoms and ongoing risks for contracting the disease.
 - d. The employer should set up surveillance in consultation with a physician or occupational health nurse and consider having ongoing participation or review by the healthcare professional.
 - e. The employer needs to consult with health professionals and determine whether the program relies on self-reporting by workers or if someone will be actively reviewing worker health on a regular basis.
 4. Personal protective equipment may be helpful to prevent transmission of the disease.
 5. Face shields can prevent direct exposure to expelled droplets and provide protection from disinfectants.
 6. Respirators require care in use and management under a program covered by the Respirator Rule, Chapter 296-842 WAC. Respirators are not normally recommended for social distancing purposes, but may be appropriate where workers must have close proximity to others.
 7. Surgical face masks (loose fitting cloth covers over the mouth and nose) do not prevent respiration of fine aerosols and are not protective in close proximity. The primary purpose for these devices are to prevent exposures to others and may have a use when individuals enter the workplace with a cough or sneeze.

C. Evaluate Special Circumstances.

Two situations where strict social distancing may not be generally feasible are for employer provided housing and businesses with extensive public interaction. The following sections provide additional considerations which are applicable in these situations.

1. Employer provided worker housing is provided by the employer in some circumstances such as agricultural guest workers.
 - a. Workers may have limited control over their environment in some worker housing situations and to the extent that the employer controls conditions, the basic program elements should be maintained as feasible during non-working time.
 - b. Social distancing **must be supported** for occupants during the time workers are housed, which may require additional resources. This includes accommodation of social distancing during cooking, sleeping, and in transportation.
 - c. If strict social distancing is not feasible (including options for dedicated individual or family rooms or offsite accommodations) then health surveillance should be instituted (see above) prior to and during the housing period.
 - d. Housing occupants **must be provided** cleaners and equipment to maintain a hygienic living space.
 - e. **Plans for ill employees must be in place.** If a housing occupant becomes sick:
 - **Employers must provide them with accommodations that are separate from others.**
 - A separate building or room if available, or use barriers or distance to separate them from others.
 - Separate food and bathroom access is also necessary.
 - **Arrangement for medical access.**
 - Telemedicine resources should be utilized first to determine appropriate care.
 - **Provide for transportation**, if necessary in a manner that does not expose others.
 - The employer needs to consult with a physician or public health authority to monitor the situation and provide guidance on treatment and continued housing of all workers.

2. Frequent customer/public interaction may be necessary in some places of employment.
 - a. To the extent feasible, establish social distancing with physical systems.
 - Set up tables that position people away from workers.
 - Place pay stations at a safe distance.
 - Install barriers between people.
 - Place markers and lane dividers to encourage appropriate distancing.
 - b. Have managers or floor leads observing individuals in the workplace and prepared to address behaviors that may put workers at risk.
 - c. Provide supplemental washing facilities to allow additional handwashing when workers handle objects after others, such as:
 - Hand sanitizer stations
 - Wipes or towelettes
 - Tepid water and soap in portable containers.

NOTE: Gloves may be provided, but also must be washed regularly to prevent the spread of the virus. This may help for workers whose hands are bothered by frequent washing.

V. Enforcement Policy

Inspection findings will be reviewed on a case by case basis. Conditions related to COVID-19 and the virus are still emerging. Public health recommendations and orders are being regularly revised, and so any compliance action must take into consideration current understanding of the situation and current rules and guides.

A. Accident Prevention Programs.

1. Employers are not expected to have comprehensive COVID-19 prevention programs at this point. In conducting program reviews, DOSH staff must look at all documents used by the employer to communicate with workers to determine their overall program. Where the employer is clearly implementing recommendations of the public health authorities, they do not need additional documentation of their specific program. Where strict social distancing is not implemented, there needs to be clear communication to workers of the employer's prevention expectations.
2. Violations of the sections of WAC 296-800-140, Accident Prevention Program, should be considered where the employer does not communicate workplace specific expectations to workers or is not effective in implementing those expectations.
3. Serious violations should specifically be considered in cases where the employer adopts practices or policies that clearly contradict the goals of coronavirus prevention practices published by DOSH, OSHA or public health recommendations.
4. Accident prevention program violations must follow instructions in the Compliance Manual.

B. Housekeeping.

Where a workplace is not being cleaned and kept sanitary per public health guidance, a violation of WAC 296-800-22005, *Keep your workplace clean*, may be considered. A serious classification should be strongly considered.

C. Handwashing.

1. There is a requirement for handwashing facilities that applies to all workplaces at all times. A serious and potential willful violation of WAC 296-800-23025, *Provide convenient and clean washing facilities*, will be considered whenever workers do not have basic handwashing facilities available at all or they are grossly inadequate in either number or maintenance.
2. Where employers cannot provide unlimited access to full handwashing facilities at all times, they **must provide alternate means** for frequent hand cleaning. A serious classification should be strongly considered if not adequate to achieve prevention. This is specifically necessary where workers regularly handle or touch objects or surfaces touched by others. Alternate hand cleaning may include:
 - a. Portable wash stations with tepid water and soap.
 - b. Wipes or towelettes with water and soap.
 - c. Hand disinfectant gel.

D. Exposure to Biological Hazards.

1. Workplace conditions which have a direct potential for worker exposure to the COVID-19 virus may be cited under WAC 296-800-11045, *Protect employees from biological agents*. This is the primary WAC code to be used for social distancing practice violations. This may include situations such as ineffective barrier or ventilation systems, or specifically allowing workers to be in close proximity, but where there is no written record of a policy or management decision.
2. Violations of this section are safe place violations in that they must be serious in classification and must follow the Compliance Manual instructions for safe place.

E. Temporary Farmworker Housing.

Temporary worker housing in agriculture is covered under Chapter 296-307 WAC, Part L, *Temporary Worker Housing and Cherry Harvest Camps*. This rule has specific requirements for hygiene facilities and housekeeping. Employers must in general achieve adequate social distancing; frequent handwashing during work; sanitation practices during work; sufficient disinfection supplies in housing; and sick employee practices outlined above. Consult with Technical Services and Compliance Operations on application of these rules when there is a COVID-19 concern.

VI. Point of Contact

DOSH staff should contact Compliance Operations if there are questions about applicability of WISHA rules to an infectious disease in the workplace. Technical Services may be contacted with technical questions about workplace practices.

VII. Review and Expiration

DOSH will review this Directive, and it will remain effective until superseded or canceled.

Approved: 

Anne F. Soiza, L&I Assistant Director
Division of Occupational Safety and Health

Appendix D

D-1 Field Collection Forms

SEDIMENT CORE COLLECTION FORM



Sediment Core Collection Form

Page ___ of ___

Project: _____
Date: _____
Weather: _____
Logged By: _____

Location ID: _____
Attempt No.: _____
Core Type: Intertidal Subtidal Shoaling
Field Staff: _____

Field Collection Coordinates:

Lat/Northing: _____ Long/Easting: _____

A. Water Depth

DTM Depth Sounder: _____
 DTM Lead Line: _____

B. Water Level Measurements

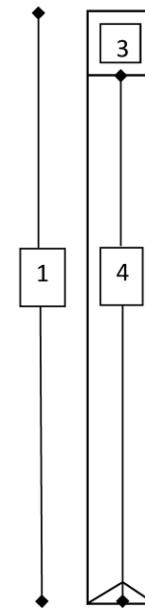
Time: _____
 Height: _____
 Source: _____

C. Mudline Elevation (ft MLLW)

Recovery Measurements (prior to cuts)

Core Collection Recovery Details:

1. Core Tube Length: _____
2. Penetration Depth: _____
3. Headspace Measurement: _____
4. Recovery Depth: _____
5. Recovery Percentage: _____
6. Core Accepted: Yes / No



Core Sections To Process:

- A: _____
 B: _____
 C: _____
 D: _____

Drive Notes:

Shoe Description:

Core Field Observations and Description:

Sediment type, moisture, color, minor modifier, MAJOR modifier, other constituents, odor, sheen, layering, anoxic layer, debris, plant matter, shells, biota

Notes:

SEDIMENT CORE PROCESSING FORM



Sediment Core Processing Form

Project: _____
Date: _____
Processed By: _____
Location ID: _____
Attempt No.: _____

Core Type: Intertidal Subtidal Shoaling
Penetration Depth: _____
Compacted Depth: _____
Compaction-Correction Factor: _____

Recovery Depth	Correction Depth	Sample ID	Sample Description and Notes (Sediment type, moisture, color, minor modifier, MAJOR modifier, other constituents, odor, sheen, layering, anoxic layer, debris, plant matter, shells, biota)

SURFACE SEDIMENT COLLECTION FORM



SURFACE SEDIMENT COLLECTION FORM

Project Name: _____ Project no.: _____

Date: _____ Weather: _____

Sampling Method: _____ Crew: _____

GRAB DATA		Location ID: _____		
Latitude/Northing(Y): _____			Longitude/Easting(X): _____	
Grab time	Water depth (m)	Penetration depth (cm)	Acceptable grab (Y/N)	Comments
SAMPLE DATA		Sample ID: _____		
Pre-homogenization analyses (circle): VOC Sulfides Ammonia AVS/SEM TPH-P Other:				
Sediment type	Sediment color	Sediment odor		Comments:
cobble	brown surface	none	H ₂ S	
gravel	drab olive	slight	petroleum	
sand (F M C)	brown	moderate	other:	
silt	gray	strong		
clay	black			

GRAB DATA		Location ID: _____		
Latitude/Northing(Y): _____			Longitude/Easting(X): _____	
Grab time	Water depth (m)	Penetration depth (cm)	Acceptable grab (Y/N)	Comments
SAMPLE DATA		Sample ID: _____		
Pre-homogenization analyses (circle): VOC Sulfides Ammonia AVS/SEM TPH-P Other:				
Sediment type	Sediment color	Sediment odor		Comments:
cobble	brown surface	none	H ₂ S	
gravel	drab olive	slight	petroleum	
sand (F M C)	brown	moderate	other:	
silt	gray	strong		
clay	black			

BANK SOIL COLLECTION FORM

Project Name/Number: _____

Weather: _____

Date: _____

Crew: _____

Sampling Method: _____

Composite Sample Time: _____

Bank ID: _____

Composite Sample ID: _____

Location ID:	Sample Time:	Sample Depth:
Location Description (coordinates or distances from landmarks; slope, elevation, proximity of three samples):		
Sample Description (i.e., including grain size, color, odor):		
Comments:		

Location ID:	Sample Time:	Sample Depth:
Location Description (coordinates or distances from landmarks; slope, elevation, proximity of three samples):		
Sample Description (i.e., including grain size, color, odor):		
Comments:		

Location ID:	Sample Time:	Sample Depth:
Location Description (coordinates or distances from landmarks; slope, elevation, proximity of three samples):		
Sample Description (i.e., including grain size, color, odor):		
Comments:		

PROTOCOL MODIFICATION FORM

Project Name and Number: _____

Material to be Sampled: _____

Measurement Parameter: _____

Standard Procedure for Field Collection & Laboratory Analysis (cite reference): _____

Reason for Change in Field Procedure or Analysis Variation: _____

Variation from Field or Analytical Procedure: _____

Special Equipment, Materials or Personnel Required: _____

Initiator's Name: _____ Date: _____

Project Officer: _____ Date: _____

QA Officer: _____ Date: _____

D-2 Geotechnical Field Forms

Soil Boring Log Form

Boring Location: _____ Elevation: _____ Datum: _____ Obs. Well Install. <input type="checkbox"/> Yes <input type="checkbox"/> No	Boring _____ Date _____ Sheet _____ of _____ Job _____ Job No. _____ Logged By _____ Weather _____ Drilled By _____ Drill Type/ Method _____ Sampling Method _____ Bottom of Boring _____ ATD Water Level Depth _____
--	---

SIZE (%)			PID or other	DEPTH		SAMPLE		SAMPLE RECOVERY	Penetration Resistance	DESCRIPTION: Den., moist., color, minor, MAJOR CONSTITUENT, NON-SOIL SUBSTANCES: Odor, staining, sheen, scrag, slag, etc.	REMARKS: Drill action, drill and sample procedures, water conditions, heave, etc.	SUMMARY LOG (Water & Date)
G	S	F		From	To	Type	Number					
Max.	Range	Att. Limits										
								0				
								1				
								2				
								3				
								4				
								5				
								6				
								7				
								8				
								9				
								0				
								1				
								2				
								3				
								4				
								5				
								6				
								7				
								8				
								9				
								0				



Soil Boring Log Form (expanded scale)

Boring Location: _____ Elevation: _____ Datum: _____	Boring _____ Date _____ Sheet _____ of _____ Job _____ Job No. _____ Logged By _____ Weather _____ Drilled By _____ Drill Type/ Method _____ Sampling Method _____ Bottom of Boring _____ ATD Water Level Depth _____
Obs. Well Install. Yes <input type="checkbox"/> No <input type="checkbox"/>	

SIZE (%)			PID or other	DEPTH		SAMPLE		SAMPLE RECOVERY	Penetration Resistance	DESCRIPTION: Den., moist., color, minor, MAJOR CONSTITUENT, NON-SOIL SUBSTANCES: Odor, staining, sheen, scrag, slag, etc.	REMARKS: Drill action, drill and sample procedures, water conditions, heave, etc.	SUMMARY LOG (Water & Date)
G	S	F		From	To	Type	Number					
Max.	Range	Att. Limits										
								0				
								1				
								2				
								3				
								4				
								5				
								6				
								7				
								8				
								9				
								0				



Dynamic Cone Penetrometer Field Form



Location ID		Project Name	
Lat/Northing (Y)		Project Number	
Lon/Easting (X)		Date	
Horizontal Datum		Field Staff	
Vertical Elevation			
Vertical Datum		Depth to Water	

Depth		Reading	Depth		Reading	Depth		Reading
cm	ft	blows	cm	ft	blows	cm	ft	Blows
10			190			370		
20			200			380		
30	1		210	7		390	13	
40			220			400		
50			230			410		
60	2		240	8		420	14	
70			250			430		
80			260			440		
90	3		270	9		450	15	
100			280			460		
110			290			470		
120	4		300	10		480	16	
130			310			490		
140			320			500		
150	5		330	11		510	17	
160			340			520		
170			350			530		
180	6		360	12		540	18	

Notes:

D-3 Survey Field Forms

Shoreline Visual Inspection Field Form



Project Name		Field Personnel	
Project Number		Page	of
Date		Time	
General Feature Description			
GPS Location		Location I.D.	

	Description	Water Depth	Feature Height Above Water
Location 1			
Location 2			
Location 3			
Location 4			
Location 5			
Location 6			

Bank Condition	Good Fair Poor	Sloped	Vertical
-----------------------	----------------------	--------	----------

Visible Substrate Type	Riprap Gravel Sand Silt/Clay Debris Vegetation Other_____
-------------------------------	---

Notes

Photograph Log	Description	GPS Location	

FACILITIES CONDITION ASSESSMENT REPORT

Sediment Cleanup of Upper Reach of Lower Duwamish Waterway

Facility Name: example: Grit Tank 1411

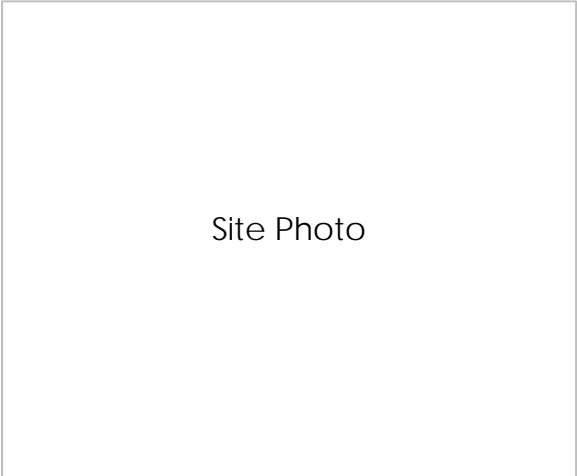
Facility Location: Address

Asset Type: example: Precast Concrete Vaults

Use: XXX

Inspection Date: month dd, yyyy

Inspected By: XXX



General Conditions, Evaluations and Recommendations:

Example Heading – Room, Floor #, etc.

- Item description – per Material Visual Inspection Checklist (photo #-#)
 - Recommendation:
- Item description (photo #-#)

Example Heading

- Item description (photo #-#)
- Item description (photo #-#)

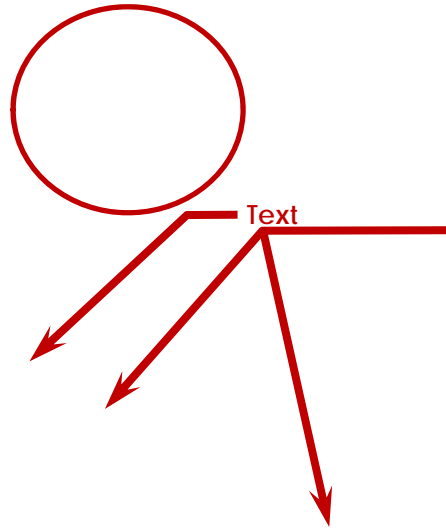
Instructions to User:

1. Complete one Facilities Condition Assessment Report per Facility.
2. Headings specify different elements in the Facility.
3. Bullet points specify Observations and Evaluations. **Use Material Visual Inspection Checklists as Reference.
4. Include Photographs to support Observations, Evaluations, and Recommendations.
5. Recommendations are actions recommended by the Inspector.

PHOTOGRAPHS

Photo 1

Photo 2



Sediment Cleanup of Upper Reach of Lower Duwamish Waterway
Facility:

Date:
Evaluation By:

PHOTOGRAPHS

Photo 3

Photo 4

Sediment Cleanup of Upper Reach of Lower Duwamish Waterway
Facility:

Date:
Evaluation By:

PHOTOGRAPHS

Photo 5

Photo 6

WOOD MATERIAL VISUAL INSPECTION CHECKLIST

1. ENVIRONMENTAL CONDITION	1A – Exposure		1B – Soils (Foundation Conditions)	
		Environment (Marine, Freshwater, Industrial, etc.)		Expansive soil
		Freezing and thawing		Compressive soil (settlement)
		Wetting and drying		Evidence of pumping
		Drying under dry atmosphere		Scour
		Chemical corrosion and attack (Sulfates, Acids, Bases, Chloride, Gases)		Steep or unstable slope/revetment
		Abrasion, erosion, impact		
		Heat from adjacent sources		

2. DISTRESS INDICATORS		Cracking or breakage
		Rot and decay
		Surface deposits
		Termite or Pest Infestation (Borer)

3. PRESENT CONDITION OF STRUCTURE AND POTENTIAL HAZARDS (Tripping, fall, fall through, slippery, impingement, and falling debris)	3A - Overall Apparent Alignment of Structure							
		Settlement		Deflection/Leaning		Expansion		Contraction
	3B – Surface Condition							
	General Condition	<u>Excellent</u>		New or near-new condition: no issues to report. No loss of cross section.				
		<u>Good</u>		Good condition: no reported issues or concerns. Less than 5% loss of cross section.				
		<u>Fair</u>		Average wear; not new but no issues to report. Between 5% - 20% cross section.				
		<u>Poor</u>		Worn from use: Between 20% - 50% loss of cross section.				
		<u>Critical</u>		Extremely worn or damaged: Between 50% - 80% loss of cross section.				
		Finished surfaces – slippery, uneven, or misaligned						
		Cracking						
		Loss of Material						
		Missing or broken members						
		Damage or distress						
		Collapse, partial collapse or structure off foundation						
		Damage or decay of chimney, parapet or other overhead falling hazard						
		Ground or slope movement present						
		Unstable supports – gaps or holes, excessive rotation, loss of bearing, rot						
		Fasteners: Corrosion						
		Soft timber and decay						
		Abrasion						
	Previous Repair							
	Surface Coatings, Protective Systems							
	Debris Buildup							
	Structural Defects							
	Moss							

Instructions to User:

1. Reference to be used to develop Facilities Condition Assessment Reports.
2. May be included, if applicable, as reference for entire Facilities Report Package.

STEEL MATERIAL VISUAL INSPECTION CHECKLIST

1. ENVIRONMENTAL CONDITION	1A – Exposure		1B – Soils (Foundation Conditions)	
		Environment (Marine, Freshwater, Industrial, etc.)		Expansive soil
		Freezing and thawing		Compressive soil (settlement)
		Wetting and drying		Evidence of pumping
		Drying under dry atmosphere		Scour
		Chemical corrosion and attack (Sulfates, Acids, Bases, Chloride, Gases)		Steep or unstable slope/revetment
		Abrasion, impact		
		Heat from adjacent sources		

2. DISTRESS INDICATORS	Member cracking or breakage
	Staining, corrosion
	Surface deposits
	Weld cracking or breakage

3. PRESENT CONDITION OF STRUCTURE AND POTENTIAL HAZARDS (Tripping, fall, fall through, slippery, impingement, and falling debris)	3A - Overall Apparent Alignment of Structure				
		Settlement		Deflection/Leaning	
	3B – Surface Condition				
	General Condition	<u>Excellent</u>		New or near-new condition: no issues to report. No loss of cross section.	
		<u>Good</u>		Good condition: no reported issues or concerns. Less than 5% loss of cross section.	
		<u>Fair</u>		Average wear; not new but no issues to report. Between 5% - 20% cross section.	
		<u>Poor</u>		Worn from use: Between 20% - 50% loss of cross section.	
		<u>Critical</u>		Extremely worn or damaged: Between 50% - 80% loss of cross section.	
		Finished surfaces – slippery, uneven, or misaligned			
		Cracking			
		Rust and scale			
		Loss of Material			
		Missing or broken members			
		Damage or distress			
		Collapse, partial collapse or structure off foundation			
		Damage or decay of chimney, parapet or other overhead falling hazard			
		Ground or slope movement present			
		Unstable supports – gaps or holes, excessive rotation, loss of bearing			
		Stains			
		Corrosion			
	Abrasion				
	Previous Repair				
	Surface Coatings				
	Debris Buildup				
	Structural Defects				
	Moss				

Instructions to User:

1. Reference to be used to develop Facilities Condition Assessment Reports.
2. May be included, if applicable, as reference for entire Facilities Report Package.

CONCRETE MATERIAL VISUAL INSPECTION CHECKLIST

1. ENVIRONMENTAL CONDITION	1A – Exposure		1B – Drainage		1C – Soils (Foundation Conditions)	
		Environment (Marine, Freshwater, Industrial, etc.)		Flashing		Expansive soil
		Freezing and thawing		Joint sealants		Compressive soil (settlement)
		Wetting and drying		Weepholes		Evidence of pumping
		Drying under dry atmosphere		Contour		Scour
		Chemical corrosion and attack		Elevation of drains		Steep or unstable slope/revetment
		Abrasion, erosion, cavitation, impact				
		Heat from adjacent sources				

2. DISTRESS INDICATORS	Cracking or Breakage
	Staining
	Surface deposits and exudations
	Leaking

3. PRESENT CONDITION OF STRUCTURE AND POTENTIAL HAZARDS (Tripping, fall, fall through, slippery, impingement, and falling debris)	3A - Overall Apparent Alignment of Structure							
		Settlement		Deflection/Leaning		Expansion		Contraction
	3B – Surface Condition							
	General Condition	<u>Excellent</u>		New or near-new condition: no issues to report. No loss of cross section.				
		<u>Good</u>		Good condition: no reported issues or concerns. Less than 5% loss of cross section.				
		<u>Fair</u>		Average wear; not new but no issues to report. Between 5% - 20% cross section.				
		<u>Poor</u>		Worn from use: Between 20% - 50% loss of cross section.				
		<u>Critical</u>		Extremely worn or damaged: Between 50% - 80% loss of cross section.				
		Formed and finished surfaces – slippery, uneven, or misaligned						
		Cracking						
		Scaling						
		Spalls, pop outs, and delamination						
		Stains, Efflorescence						
		Exposed Reinforcement: Corrosion						
		Damage or distress						
		Missing or broken members						
		Collapse, partial collapse or structure off foundation						
		Damage or decay of chimney, parapet or other overhead falling hazard						
		Ground or slope movement present						
		Unstable supports – gaps or holes, excessive rotation, loss of bearing						
	Curling and warping							
	Erosion							
	Previous Patching or Other Repair:							
	Surface Coatings, Protective Systems, Linings, Toppings							
	Penetrating Sealers							
	Signs of Past Overflow on Rungs and Walls							
	Debris Buildup							
	Exposed Aggregate							
	Leaks through Walls							
	Structural Defects							
	Moss							

Instructions to User:

1. Reference to be used to develop Facilities Condition Assessment Reports.
2. May be included, if applicable, as reference for entire Facilities Report Package.

Appendix E. Analytical Methods and
Reporting Limits

TABLES

Table E-1	Methods and RL goals for PCB Aroclors, PAHS, metals, SVOCs, and conventionals in sediment/soil	E-1
Table E-2	Method and RL goals for dioxins/furan congeners in sediment	E-6
Table E-3	Accuracy recovery range for individual PAHs and SVOCs	E-7

Table E-1
Methods and RL goals for PCB Aroclors, PAHS, metals, SVOCs, and conventionals in sediment/soil

Analyte	Method	Unit	MDL	RL
PCBs as Aroclors (based on 12.5-g dw sample)				
Aroclor 1016	EPA 8082A	µg/kg dw	1.6 ¹	4.0 ²
Aroclor 1221	EPA 8082A	µg/kg dw	1.6 ¹	4.0 ²
Aroclor 1232	EPA 8082A	µg/kg dw	1.6 ¹	4.0 ²
Aroclor 1242	EPA 8082A	µg/kg dw	1.6 ¹	4.0 ²
Aroclor 1248	EPA 8082A	µg/kg dw	1.6 ¹	4.0 ²
Aroclor 1254	EPA 8082A	µg/kg dw	1.6 ¹	4.0 ²
Aroclor 1260	EPA 8082A	µg/kg dw	1.6 ¹	4.0 ²
PAHs (based on 10-g dw sample)				
Acenaphthene ³	EPA 8270E	µg/kg dw	5.13 ¹	20.0 ²
Acenaphthylene ³	EPA 8270E	µg/kg dw	4.77 ¹	20.0 ²
Anthracene ³	EPA 8270E	µg/kg dw	5.93 ¹	20.0 ²
Benzo(a)anthracene ⁴	EPA 8270E	µg/kg dw	5.18 ¹	20.0 ²
Benzo(a)pyrene ⁴	EPA 8270E	µg/kg dw	6.48 ¹	20.0 ²
Benzo(b)fluoranthene ⁴	EPA 8270E	µg/kg dw	7.02 ¹	20.0 ²
Benzo(k)fluoranthene ⁴	EPA 8270E	µg/kg dw	5.01 ¹	20.0 ²
Total benzofluoranthenes ⁴	EPA 8270E	µg/kg dw	10.2 ¹	40.0 ²
Benzo(g,h,i)perylene ⁴	EPA 8270E	µg/kg dw	5.82 ¹	20.0 ²
Chrysene ⁴	EPA 8270E	µg/kg dw	5.22 ¹	20.0 ²

Table E-1
Methods and RL goals for PCB Aroclors, PAHS, metals, SVOCs, and conventionals in sediment/soil

Analyte	Method	Unit	MDL	RL
Dibenzo(a,h)anthracene ⁴	EPA 8270E	µg/kg dw	6.16 ¹	20.0 ²
Fluoranthene ⁴	EPA 8270E	µg/kg dw	4.52 ¹	20.0 ²
Fluorene ³	EPA 8270E	µg/kg dw	4.95 ¹	20.0 ²
Indeno(1,2,3-cd)pyrene ⁴	EPA 8270E	µg/kg dw	5.99 ¹	20.0 ²
2-methylnaphthalene ³	EPA 8270E	µg/kg dw	5.67 ¹	20.0 ²
Naphthalene ³	EPA 8270E	µg/kg dw	5.25 ¹	20.0 ²
Phenanthrene ³	EPA 8270E	µg/kg dw	4.69 ¹	20.0 ²
Pyrene ⁴	EPA 8270E	µg/kg dw	5.55 ¹	20.0 ²
cPAHs (based on 10-g dw sample)⁵				
Benzo(a)anthracene ⁴	EPA 8270E SIM	µg/kg dw	0.824 ¹	5.0 ²
Benzo(a)pyrene ⁴	EPA 8270E SIM	µg/kg dw	0.614 ¹	5.0 ²
Benzo(b)fluoranthene ⁴	EPA 8270E SIM	µg/kg dw	1.372 ¹	5.0 ²
Benzo(k)fluoranthene ⁴	EPA 8270E SIM	µg/kg dw	0.760 ¹	5.0 ²
Chrysene ⁴	EPA 8270E SIM	µg/kg dw	1.053 ¹	5.0 ²
Dibenzo(a,h)anthracene ⁴	EPA 8270E SIM	µg/kg dw	0.891 ¹	5.0 ²
Indeno(1,2,3-cd)pyrene ⁴	EPA 8270E SIM	µg/kg dw	1.05 ¹	5.0 ²
Metals (based on 1-g ww unless otherwise noted)				
Arsenic	EPA 6020A UCT-KED	mg/kg dw	na ⁶	0.2 ²
Cadmium	EPA 6020A UCT-KED	mg/kg dw	na ⁶	0.1 ^{2,7}
Chromium	EPA 6020A	mg/kg dw	na ⁶	0.5 ^{2,7}

Table E-1
Methods and RL goals for PCB Aroclors, PAHS, metals, SVOCs, and conventionals in sediment/soil

Analyte	Method	Unit	MDL	RL
Copper	EPA 6020A UCT-KED	mg/kg dw	na ⁶	0.5 ^{2,7}
Lead	EPA 6020A	mg/kg dw	na ⁶	0.1 ²
Silver	EPA 6020A	mg/kg dw	na ⁶	0.2 ²
Zinc	EPA 6020A UCT-KED	mg/kg dw	na ⁶	4 ^{2,7}
Mercury (based on 0.2-g ww sample)	EPA 7471B	mg/kg dw	na ⁶	0.025 ²
SVOCs (based on 10-g dw sample)				
2,4-dimethylphenol	EPA 8270E-SIM	µg/kg dw	2.17	20.0
4-methylphenol	EPA 8270E	µg/kg dw	14.7 ¹	20.0 ²
Benzoic acid	EPA 8270E-SIM	µg/kg dw	13.4	100
Benzyl alcohol ⁸	EPA 8270E-SIM	µg/kg dw	12.1	20.0
Bis(2-ethylhexyl)phthalate	EPA 8270E	µg/kg dw	28.8 ¹	50.0 ²
Butyl benzyl phthalate	EPA 8270E	µg/kg dw	8.05 ¹	20.0 ²
Dibenzofuran	EPA 8270E	µg/kg dw	4.61 ¹	20.0 ²
Dimethyl phthalate	EPA 8270E	µg/kg dw	6.44 ¹	20.0 ²
Hexachlorobenzene	EPA 8081B	µg/kg dw	0.145	0.5
n-Nitrosodiphenylamine	EPA 8270E-SIM	µg/kg dw	1.31	5.00
Pentachlorophenol	EPA 8270E-SIM	µg/kg dw	2.13	20.0
Phenol	EPA 8270E	µg/kg dw	8.23 ¹	20.0 ²
1,2,4-trichlorobenzene	EPA 8270E-SIM	µg/kg dw	2.68	5.00

Table E-1
Methods and RL goals for PCB Aroclors, PAHS, metals, SVOCs, and conventionals in sediment/soil

Analyte	Method	Unit	MDL	RL
1,2-dichlorobenzene	EPA 8270E-SIM	µg/kg dw	0.74	5.00
1,4-dichlorobenzene	EPA 8270E-SIM	µg/kg dw	0.6	5.00
Conventionals				
Grain size	PSEP 1986	%	na	0.1
Percent solids	SM 2540 G-97	% dw	na	0.040
TOC (based on 1-g dw sample)	EPA 9060A	% dw	0.018	0.02
Ammonia	SM 4500-NH3 H-97	mg/kg dw	na	0.4
Total sulfides	SM 4500-S2 D-0	mg/kg dw	na	1

Notes:

1. SW 846 no longer requires MDL values. The laboratories have the option to use these values to assess sensitivity for EPA 8000 series methods. ARI has continued to maintain MDL studies for these analytes.
2. RL values are consistent with the LLOQ values required under EPA SW-846.
3. Compound is a component of the LPAH sum.
4. Compound is a component of the HPAH sum.
5. cPAHs will be analyzed by 8270E-SIM for samples that require cPAH analysis and not the full SVOC list (i.e. 0- to 45-cm sediments in Recovery Category 2/3 and beach play areas).
6. SW 846 no longer requires MDL values.
7. Although the RL value is higher than the PQL listed in SCUM II (Ecology 2017), it is lower than the RAO3 cleanup level provided in the ROD (EPA 2014).
8. Because benzyl alcohol is not a CERCLA hazardous substance, benzyl alcohol data will not be included in the data evaluation reports. Benzyl alcohol data obtained through routine SVOC analysis of the PDI sediment samples will be provided to EPA.

CERCLA: Comprehensive Environmental Response, Compensation, and Liability Act

cPAH: carcinogenic polycyclic aromatic hydrocarbon

dw: dry weight

EPA: US Environmental Protection Agency

HPAH: high-molecular-weight polycyclic aromatic hydrocarbon

LLOQ: lower limit of quantitation

FINAL

MDL: method detection limit

LPAH: low-molecular-weight polycyclic aromatic hydrocarbon

na: not available

PCB: polychlorinated biphenyl

PDI: pre-design investigation

PQL: practical quantitation limit

PSEP: Puget Sound Estuary Program

RAO: remedial action objective

RL: reporting limit

ROD: Record of Decision

SCUM II: Sediment Cleanup User's Manual II

SIM: selective ion monitoring

SM: Standard Method

SVOC: semivolatile organic compounds

TOC: total organic carbon

UCT-KED: universal cell technology-kinetic energy discrimination

ww: wet weight

Table E-2
Method and RL goals for dioxins/furan congeners in sediment

Analyte	EPA Method 1613B			
	Sediment (ng/kg dw) Based on 10-g sample		TEQ (ng/kg)	
	EDL ¹	LOQ ²	TEF	TEQ ³
2,3,7,8-TCDD	0.1	1.0	1	0.5
1,2,3,7,8-PeCDD	0.1	1.0	1	0.5
1,2,3,4,7,8-HxCDD	0.1	1.0	0.1	0.05
1,2,3,6,7,8-HxCDD	0.1	1.0	0.1	0.05
1,2,3,7,8,9-HxCDD	0.1	1.0	0.1	0.05
1,2,3,4,6,7,8-HpCDD	0.1	2.5	0.01	0.0125
OCDD	01	10.0	0.0003	0.0015
2,3,7,8-TCDF	0.1	1.0	0.1	0.05
1,2,3,7,8-PeCDF	01	1.0	0.03	0.015
2,3,4,7,8-PeCDF	0.1	1.0	0.3	0.15
1,2,3,4,7,8-HxCDF	0.1	1.0	0.1	0.05
1,2,3,6,7,8-HxCDF	0.1	1.0	0.1	0.05
1,2,3,7,8,9-HxCDF	0.1	1.0	0.1	0.05
2,3,4,6,7,8-HxCDF	0.1	1.0	0.1	0.05
1,2,3,4,6,7,8-HpCDF	0.1	1.0	0.01	0.005
1,2,3,4,7,8,9-HpCDF	0.1	1.0	0.01	0.005
OCDF	0.1	2.5	0.0003	0.000375

Notes:

1. EDL is a sample-specific DL. The value provided here is an estimate, and the sample-specific values will vary based on sample mass and the analytical conditions at the time of analysis.
2. LOQ is ARI's lowest concentration, at or above the LMCL, at which test accuracy (precision and bias) has been demonstrated. Values below the LOQ are J-qualified. The reported LOQ will be adjusted based on the sample mass of each sample
3. TEQ calculated using ½ RL value multiplied by the 2005 WHO TEF.

ARI: Analytical Resources, Inc.

DL: detection limit

dw: dry weight

EDL: estimated detection limit

EPA: US Environmental Protection Agency

HpCDD: heptachlorodibenzo-p-dioxin

HpCDF: heptachlorodibenzofuran

HxCDD: hexachlorodibenzo-p-dioxin

HxCDF: hexachlorodibenzofuran

LMCL: lower method calibration limit

LOQ: limit of quantitation

Table E-3
Accuracy recovery range for individual PAHs and SVOCs

Parameter	LCS/ Spiked Sample ^{1,2}	CRM ^{1,2}
PAHs		
Acenaphthene	45–120%	51–149%
Acenaphthylene	42–120%	52–148%
Anthracene	45–120%	57–143%
Benzo(a)anthracene	10–120%	58–142%
Benzo(a)pyrene	42–120%	54–146%
Total benzofluoranthenes	30–160%	44–156%
Benzo(g,h,i)perylene	38–126%	49–152%
Chrysene	47–120%	58–142%
Dibenzo(a,h)anthracene	30–133%	50–150%
Fluoranthene	53–120%	55–145%
Fluorene	45–120%	54–146%
Indeno(1,2,3-cd)pyrene	42–123%	0–203%
2-methylnaphthalene	43–120%	na
Naphthalene	43–120%	33–167%
Phenanthrene	49–120%	60–140%
Pyrene	48–121%	60–139%
cPAHs³		
Benzo(a)anthracene	42–120%	50–150%
Benzo(a)pyrene	36–120%	45–155%
Benzo(b)fluoranthene	35–127%	51–149%
Benzo(k)fluoranthene	37–129%	51–148%
Chrysene	48–120%	53–147%
Dibenzo(a,h)anthracene	38–120%	48–153%
Indeno(1,2,3-cd)pyrene	40–120%	53–147%
SVOCs		
1,2-dichlorobenzene	36–120%	NR
1,2,4-trichlorobenzene	35–120%	NR
1,4-dichlorobenzene	36–120%	NR
2,4-dimethylphenol	10–120%	NR

Table E-3
Accuracy recovery range for individual PAHs and SVOCs

Parameter	LCS/ Spiked Sample ^{1,2}	CRM ^{1,2}
4-methylphenol	29–120%	NR
Benzoic acid	10–160%	NR
Benzyl alcohol	25–123%	NR
Bis(2-ethylhexyl)phthalate	34–130%	NR
Butyl benzyl phthalate	45–132%	NR
Dibenzofuran	43–120%	NR
Dimethyl phthalate	43–120%	NR
n-Nitrosodiphenylamine	27–120%	NR
Pentachlorophenol	26–120%	NR
Phenol	34–120%	NR

Notes:

1. Values listed are performance-based limits provided by ARI.
2. An LCS may be used to assess accuracy when a CRM is unavailable. CRMs will be analyzed for PAHs, PCB Aroclors, and dioxins/furans only. The satisfactory acceptance limit for CRM recovery will include the uncertainty range around the CRM mean, as well as the uncertainty of the method of measurement: limits listed for Puget Sound Reference Material (PCBs and dioxins/furans), Sigma-Aldrich SQC017-40G (SIM-PAH), and CRM 143 BNA (PAHs). Commercial CRMs may change depending on availability.
3. cPAHs will be analyzed by 8270E-SIM for samples that require cPAH analysis and not the full SVOC list (i.e. 0- to 45-cm sediments in Recovery Category 2/3 and beach play areas).

ARI: Analytical Resources, Inc.

cPAH: carcinogenic polycyclic aromatic hydrocarbon

CRM: certified reference material

LCS: laboratory control sample

na: not applicable

NR: not required

PAH: polycyclic aromatic hydrocarbon

PCB: polychlorinated biphenyl

SIM: selective ion monitoring

SVOC: semivolatile organic compound

References

- Ecology. 2017. Sediment cleanup user's manual II. Guidance for implementing the cleanup provisions of the sediment management standards, Chapter 173-204 WAC. Draft for review and comment through July 7, 2017. Pub. No. 12-09-057. Revised April 2017. Toxics Cleanup Program, Washington State Department of Ecology, Olympia, WA.
- EPA. 2014. Record of Decision. Lower Duwamish Waterway Superfund Site. US Environmental Protection Agency.

Appendix F

Standard Operating Procedures

Contents:

- SOP Number F1 – Surface Sediment Collection
- SOP Number F2 – Subsurface Sediment Collection
- SOP Number F3 – Wet-Sieve Grain Size Determination
- SOP Number F4 – Amphipod Toxicity Test
- SOP Number F5 – Larval Toxicity Test
- SOP Number F6 – Polychaete Toxicity Test
- SOP Number F7 – SPT and Split Spoon Sampling
- SOP Number F8 – Thin Wall Sampling
- SOP Number F9 – Cone Penetrometer Testing
- SOP Number F10 – Dynamic Cone Penetrometer Testing
- SOP Number F11 – Vane Shear Test
- SOP Number F12 – Mercury Cold Vapor Analysis
- SOP Number F13 – Metals Analysis
- SOP Number F14 – SVOC Analysis
- SOP Number F15 – PCB (Aroclor) Analysis
- SOP Number F16 – Ammonia Analysis
- SOP Number F17 – Dioxin/Furan Organic Analysis
- SOP Number F18 – Sulfide by Iodometric Titration
- SOP Number F19 – PAH/PCP Analysis
- SOP Number F20 – Total Organic Carbon Analysis of Soil and Sediment
- SOP Number F21 – Chlorinated Pesticides Analysis

SOP Number F22 – Total Solids Analysis

SOP Number F23 – Particle Size Distribution

SOP Number F24 – Data Validation Process

STANDARD OPERATING PROCEDURE F1

SURFACE SEDIMENT COLLECTION

A Introduction

Surface sediment samples (0- to 10-cm) will be collected from a boat or from land following processing will follow standardized procedures as described in Ecology's Sediment Cleanup User's Manual II (SCUM II) (Ecology 2017) and Puget Sound Estuary Program (PSEP). The SOPs for these procedures are described below.

B Sample Collection by Boat

The primary method for surface sediment sample collection will be to use a pneumatic grab sampler deployed from a sampling vessel. Surface sediment samples will be collected as described in the following steps:

1. Using a differential global positioning system (DGPS)¹ with sub-meter accuracy, maneuver the sampling vessel to the sampling location.
2. Open the decontaminated grab sampler jaws to the deployment position.
3. Guide the sampler overboard until it is clear of the vessel.
4. Using DGPS, position the sampling vessel such that the DGPS receiver (located on top of the sampling frame) is within 3 m (10 feet) of the target sampling location.
5. Lower the sampler through the water column to the bottom at a speed of approximately 0.3 m/s.
6. Record the DGPS location of the boat when the sampler reaches the bottom.
7. Record the water depth and time.
8. Retrieve the sampler, raising it at a speed of approximately 0.3 m/s.
9. Guide the sampler aboard the vessel and place it on the work stand on the deck, taking care to avoid jostling that might disturb the integrity of the sample.
10. Examine the sample using the following sediment acceptance criteria:
 - Sample contains sediment; samples that are predominately gravel, rock, or debris will be rejected.
 - Sediment is not extruding from the upper face of the sampler (indicating sampler was advanced deeper than the target penetration depth).

¹ A Trimble© SPS461 or similar DGPS receiver unit will be employed for the various sampling methods outlined in this QAPP. The DGPS receiver will be calibrated daily to ensure that it is accurately recording positions from known benchmarks and functioning within the individual unit's factory specifications.

- Overlying water is present (indicating minimal leakage).
- Sediment surface is relatively flat (indicating minimal disturbance or winnowing).
- A penetration depth of at least 11 cm has been achieved.

If these sample acceptance criteria are not met, the sample will be rejected. In addition, if there is any indication that the sediment has been recently disturbed then, the grab sample will be rejected. If the initial attempt to collect a sample is not successful due to difficult substrate (e.g., presence of riprap or other debris), up to three subsequent attempts will be made within 10 m (32 feet) of the proposed location. If the initial attempt and three subsequent attempts do not result in a sample that meets the appropriate acceptance criteria, a different sampling location may be selected in consultation with EPA and LDWG.

After sample acceptance, the following observations will be noted in the field logbook or surface sediment collection form:

- Elevation of bed at sampling location
- DGPS location
- Depth as read by the boat's depth sounder and sample collection time
- Maximum penetration depth (nearest 0.5 cm)

C Sample Collection from Shore

For intertidal locations that cannot be sampled from a boat and must be manually sampled from the shoreline during a lower tide, sediment will be collected by directly scooping sediment from the 0- to 10-cm depth with a clean, stainless steel spoon into a clean, stainless steel bowl.

The following observations will be noted in the field logbook or surface sediment collection form:

- Estimated elevation of bed at sampling location
- DGPS location
- Sample collection time

D Sample Processing

After sediment collection and homogenization has been completed, the following steps will be completed to process the sediment samples:

1. **Record information** – Record information regarding the depth of the sample (generally 10 cm), sediment characteristics (e.g., color, smell, grain size, presence of debris, redox layer [if visible], etc.), and any necessary revisions to the sampling location or comments relative

to sample quality, on the sediment collection forms. Take photographs of anything of note and document any deviations from the approved sampling plan on a Protocol Modification Form (Appendix D-1).

2. **Collect and homogenize sample sediment** – The sediment at each location will be transferred directly from the grab sampler (or hole, if collected manually from shore) into a pre-cleaned stainless steel bowl or cauldron and stirred with a clean, dedicated, stainless steel spoon or spatula until texture and color homogeneity have been achieved (Ecology 2017). Any large non-sediment items, such as gravel, shells, wood chips, or organisms (e.g., clams), will be removed prior to homogenization.
3. **Dispense into jars** – Sediment will be dispensed into clean and labelled jars. For any location where toxicity testing is planned, samples will be dispensed from the bowl of homogenized sample material for both toxicity testing and (in separate jars) sulfides and ammonia analysis. These analyses will be expedited in order to have data available prior to the initiation of toxicity testing. Subsamples for sulfides and ammonia will be collected from the homogenized composite sample. The sulfide subsamples will be placed in a 4-oz jar with a Teflon® septa filled with zero headspace. The sample jar will contain 5 mL of 2 Normal zinc acetate per 30 g of sediment as a preservative. The sulfide sample will be placed in the jar, covered, and shaken vigorously to completely expose the sediment to the zinc acetate. The jar will be labeled to indicate that zinc acetate has been added and stored in the dark at 0 to 6°C.
4. **Label jars** – Sample labels will contain the project number, sampling personnel, date, time, and sample ID. A complete sample label will be affixed to each individual sample jar. Labels will be filled out as completely as possible prior to each sampling event.
5. **QC jars and forms** – Thoroughly check all sample containers for proper identification, analysis type, and lid tightness. The FC will be responsible for reviewing sediment sample information recorded on field forms (Appendix D) and will correct any improperly recorded information.
6. **Prepare for delivery to the analytical laboratory** – Pack each container carefully to prevent breakage and place inside a cooler with ice for storage at the proper temperature ($\leq 4 \pm 2^\circ\text{C}$) for delivery to the analytical laboratory.

STANDARD OPERATING PROCEDURE F2

SUBSURFACE SEDIMENT COLLECTION

A Introduction

Subsurface sediment core samples will be collected primarily collected from a sampling vessel (using a vibracorer), or will be manually from shore in intertidal areas where collect from a vessel is not possible. Procedures for these two collection options are described below.

B Sample Collection by Boat

B1 Collect Sediment

When sampling from a boat, the vibracorer will be deployed from the sampling vessel using an A-frame with a hydraulic winch system. The vibracorer consists of a vibrating power head attached to a 4-in.-diameter core barrel (length to be dependent on the target core depth). Sediment core samples will be collected and processed according to the following procedures:

1. The sampling vessel will be maneuvered to the proposed sampling location.
2. The vibracorer and a decontaminated core tube will be deployed.
3. Continuous core samples will be collected to the project depth requirement or until refusal.
4. The depth of core penetration will be measured and recorded.
5. The sample core tube will be extracted, and the assembly will be retrieved aboard the vessel.
6. The core sample will be evaluated at the visible ends of the core tube to verify retention of the sediment in the core tube.
7. If the sediment core is acceptable (see criteria below), the core will be capped, labelled, and held vertically pending transfer to a processing crew.

Acceptance criteria for a sediment core sample are as follows:

- The material is collected to the target depth within the first three attempts.
- Recovery is at least 75% of the penetration depth.
- The core appears to be intact without obstructions or blocking.

If sample acceptance criteria are not achieved, the sample will be rejected. If repeated deployment (i.e., maximum three attempts) does not result in a sample that meets the acceptance criteria, a different sampling location may be selected based on consultation with EPA and LDWG.

Field forms and notes for all core samples will be maintained as samples are collected. The following information will be included in the sediment core collection forms and field notes:

- Water depth and tidal elevation (i.e., raw data), as well as the calculated mudline elevation of each sediment core location relative to MLLW
- Location of each sediment core as determined using a DGPS with sub-meter accuracy
- Date and time of collection for each sediment core
- Names of field supervisor and person(s) collecting and logging the sample
- Core penetration and recovery measurements
- Designation of each coring attempt as "accepted" or "rejected"
- Observations made during sample collection, including weather conditions, complications, ship traffic, and other details associated with the sampling effort
- Core location ID
- Take photographs of anything of note.
- Any deviations from the approved sampling plan on a Protocol Modification Form (Appendix D-1).

B2 *Process Core*

Sediment cores collected from a boat will be processed as soon as possible after a core has been collected that meets the acceptance criteria. The steps for processing the samples are as follows:

1. Prior to processing, evaluate the amount of compaction that may have occurred, and calculate the compaction correction factor (CCF) to be applied during core processing.
 - Measure the core depth (i.e., the compacted depth).
 - To calculate the CCF, divide the compacted depth by the penetration depth (i.e., the depth recorded during core collection and acceptance).
 - Example: If the core depth (i.e., compacted depth) at the time of processing is 2.83 feet (i.e., 2 feet 10 in.), and the core penetration depth (i.e., the core depth recorded at the time of collection) was 3.33 feet (i.e., 3 feet 3 in.), the CCF would be 0.85.
2. Carefully cut along the core tube liner to expose the sediment core for processing and photograph each core.
3. Record the description of each core on the sediment core processing form, including the following parameters, as appropriate, and take photographs of anything of note.

-
- Core penetration depth (from the sediment core collection form)
 - Compacted core depth and calculated CCF
 - Corrected sample depth interval for each sample
 - Odor (e.g., hydrogen sulfide, petroleum)
 - Vegetation
 - Debris
 - Biological activity (e.g., detritus, shells, tubes, bioturbation, live or dead organisms)
 - Presence of oil sheen
 - Any other distinguishing characteristics or features.
4. For each core, separate the material from each target depth interval, applying (i.e., multiplying) the CCF to the target sample depth that will constitute the sample for laboratory analysis. For example, if the CCF for a subtidal sediment core is 0.85, the sample material to collect for a 0- to 60-cm analysis will come from the 0- to 51-cm interval (i.e., $60 \text{ cm} \times 0.85 = 51 \text{ cm}$).
 5. Transfer sample into a separate stainless steel bowl for homogenization.
 - For intertidal sediment cores, the target sample depth interval is 0- to 45- cm.
 - For subtidal sediment cores, the target sample depth interval is 0- to 60- cm.
 - For shoaling areas, the target sample depth interval is dependent on the thickness of the shoaled material (see Appendix G for estimated shoal depths).
 - For samples in the FNC, 1-foot (30-cm) Z-samples will also be collected in shoaling areas and at locations with elevations shallower than -15 feet MLLW.
 6. Homogenize the sediment until texture and color homogeneity have been achieved, removing large non-sediment items such as gravel, shells, wood chips, or organisms (e.g., clams) (Ecology 2017).
 7. Dispense sediment into labeled sample containers. Sample labels will contain the project number, sampling personnel, date, time, and sample ID. A complete sample label will be affixed to each individual sample jar. Labels will be filled out as completely as possible prior to each sampling event.
 8. Thoroughly check all sample containers for proper identification, analysis type, and lid tightness. The FC will be responsible for reviewing sediment sample information recorded on field forms (Appendix D) and will correct any improperly recorded information.
 9. Pack each container carefully to prevent breakage and place inside a cooler with ice for storage at the proper temperature ($\leq 4 \pm 2^\circ\text{C}$) for delivery to the analytical laboratory.

C Sample Collection from Shore

If an intertidal sediment 0- to 45- cm core cannot be collected from the boat due to site access conditions (e.g., too shallow), then the core may be manually collected from shore during a lower tide. At the discretion of the field crew, one of the following two sampling options will be used, whichever is most suitable to the sampling location conditions. In addition, the field crew may use a combined or hybrid approach of the two methods, if necessary.

C1 Option 1: Use Shovel to Dig 45-cm-Deep Hole

The first sampling option is to dig a hole using a shovel and collect the sample directly from the sidewall of the hole. The process for this option is as follows.

1. **Dig hole** – Using a transplanting spade (i.e., a shovel with a narrow blade), dig a 45-cm-deep hole at the identified location. If it is not possible to reach a depth of 45 cm within three attempts, the deepest hole among the attempts will be sampled using the methodology described below, and the depth of refusal will be recorded on the sediment core collection form. At least one side of the hole should be approximately vertical to allow for the collection of the sample. Record any necessary revisions of the sampling location.
2. **Prepare for sampling** – Divide the vertical extent of the hole into three 15-cm sections (i.e., the bottom section 30 to 45 cm below the surface, the middle section 15 to 30 cm below the surface, and the top section from the surface down to 15 cm). If possible, use a spoon to draw a line in the sidewall of the hole at these breakpoints. The bottom section will be sampled first to ensure that the sample is collected prior to the hole filling with water.
3. **Collect and homogenize sample** – Collect the same amount of sediment from each of the three 15-cm subsections along the vertical extent of the hole, sufficient to fill a 16-oz stainless steel measuring cup. When filling the measuring cup (as described in steps 3a-3c), exclude any debris larger than approximately 5 mm in width. If differences pertaining to the diameter of the hole are apparent (e.g., the presence of differently colored material), the resulting sample should proportionally represent all material in the hole.
 - a. Starting with the bottom section of the hole (i.e., 45 to 30 cm), use a small, clean, stainless steel spoon to carefully collect an even amount of sediment from the sidewall by scraping the sidewall from the bottom of the hole to the marked 30-cm line. Fill the 16-oz measuring cup using this method, and dispense the contents into a large, stainless steel bowl.

- b. Repeat process in the middle section of the hole (i.e., scrape the sidewall from the 30-cm to the 15-cm line) to fill the measuring cup, and dispense the contents into the bowl containing the sediment from step 3a.
- c. Repeat process in the top third of the hole (i.e., 15 cm to the surface) to again fill the measuring cup, making sure to capture the full extent of this layer, including the surface material. Dispense the contents into the bowl containing the sediment from steps 3a and 3b.
- d. Homogenize the contents of the bowl with a stainless steel spoon until texture and color homogeneity have been achieved, and dispense the contents into clean and labelled jars.

The procedures for processing shore-collected cores are presented below.

C2 *Option 2: Use Hand-core Tube to Collect 45-cm Core*

The second sampling option is to use a hand-core tube to collect a 45-cm core, extrude the core, and then collect the sample from the interior of the core. This process for this option is as follows:

1. **Collect core** – Drive the pre-cleaned hand-core tube (internal diameter of 7 cm) into the sediment to a depth of 45 cm at the identified location, or as near as possible based on the substrate and debris. Cap the top of the tube and pull core out of the sediment. If it is not possible to reach a depth of 45 cm on the first attempt, up to three attempts should be made in that area (initial attempts will be retained in the core tube or extruded onto a piece of foil). After the third attempt, sample the deepest core using the methodology described below, and record the depth of refusal on the surface sediment collection form (Appendix D-1). Record any necessary movement of the sampling location.
2. **Collect and homogenize sample** – Extrude the contents of the core into a pre-cleaned stainless steel bowl and homogenize with a clean, stainless steel spoon until texture and color homogeneity have been achieved. Any debris wider than approximately 5 mm will be discarded.

The procedures for processing shore-collected cores are presented below.

C3 *Processing Cores Collected from Shore*

After sediment collection and homogenization has been completed, the following steps will be completed to process the sediment cores:

1. **Record information** – Record information regarding the depth of the core (generally 45 cm), sediment characteristics (e.g., color, smell, grain size, presence of debris, etc.), and necessary revisions to the sampling location on the sediment core collection and processing forms. Take photographs of anything of note and document any deviations from the approved sampling plan on a Protocol Modification Form (Appendix D-1).
2. **Dispense into jars** – Sediment will be dispensed into clean and labelled jars. Sample labels will contain the project number, sampling personnel, date, time, and sample ID. A complete sample label will be affixed to each individual sample jar. Labels will be filled out as completely as possible prior to each sampling event.
3. **QC jars and forms** – Thoroughly check all sample containers for proper identification, analysis type, and lid tightness. The FC will be responsible for reviewing sediment sample information recorded on field forms (Appendix D) and will correct any improperly recorded information.
4. **Prepare for delivery to the analytical laboratory** – Pack each container carefully to prevent breakage and place inside a cooler with ice for storage at the proper temperature ($\leq 4 \pm 2^{\circ}\text{C}$) for delivery to the analytical laboratory.

Title: Determining Wet-Sieve Grain Size of Sediment

SOP No.: SAM002.02w

Date: 11/11/19

Page No.: 1 of 2

1.0 SCOPE

This protocol provides a gross field or laboratory measurement of percent fines in a sediment sample.

2.0 SUMMARY OF PROCEDURE

Field collected material from a given sample location is sieved using a USA Standard Testing Sieve #230 (63 μ m) to determine volume of fines. The volume retained in the sieve, subtracted from the original aliquot, provides the volume of fines.

3.0 EQUIPMENT

- Modified ponar grab with line of an appropriate length and accessories. Includes any needed shackles or swivels.
- USA Standard Testing Sieve #230 (63 μ m)
- 50-mL measuring cup
- 100-mL graduated cylinder
- Small plastic funnel
- Plastic spoon
- Squirt bottle filled with water (site water or deionized water)
- A pump-action compression garden sprayer (1 to 2 gallon size)
- Safety glasses or goggles and chemical-resistant gloves (if contamination is suspected to be present)

4.0 PROCEDURE

- 1 Thoroughly rinse the sieve and all other equipment to ensure that no sediment or other detritus is present.
- 2 Collect a homogenized sediment aliquot in a 50-mL cup, removing excess sediment from the top and side of the cup.
- 3 Transfer the 50-mL sediment aliquot from the cup to the sieve using the spoon. Thoroughly rinse the cup and spoon into the sieve with water to ensure the entire aliquot has been transferred.
- 4 Gentle rinse the sieve with running water until the stream of water coming from the bottom of the sieve is clear. Rinse the remaining sediment to one side of the sieve.

Title: Determining Wet-Sieve Grain Size of Sediment

SOP No.: SAM002.02w

Date: 11/11/19

Page No.: 2 of 2

- 5 Place a plastic funnel into the 100-mL graduated cylinder and position the lip of the sieve over the funnel. Using the squirt bottle, rinse the retained sediment into the graduated cylinder, directing the stream of water through the back of the sieve. Continue rinsing until all the sediment has been transferred to the graduated cylinder. If needed, rinse any sediment that may have adhered to the funnel. The rinse water should not overflow the graduated cylinder. If it appears the graduated cylinder will overflow before all sediment has been transferred, discard the sample and repeat the entire procedure.
- 6 Allow the sediment to settle completely in the graduated cylinder (~1-2 minutes) and record the amount of sediment present. This measurement represents the ***volume retained***. Also record any turbidity observed in the overlying water.
- 7 The ***volume retained*** (in mL), subtracted from the original 50-mL aliquot, provides the volume that passed through the sieve, or ***volume of fines***, in the 50-mL sample. Multiplying this remainder by two gives the volume of fines in 100-mL or ***percent fines***. The formula can be stated as:
Percent fines = (50-mL – Volume Retained in mL) × 2.

6.0 SAFETY

The standard safety considerations for aquatic sampling - caution deploying and retrieving equipment, utilizing proper clothing and safety gear, and stepping in the bight of lines or cables - apply to the field crew during sampling. The designated safety officer on the vessel shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an accident or emergency. Particular care should be given to fingers and hands when working with any sampling device. The sediment, soil, and water samples may contain contaminants. Care should be taken to avoid contact with the samples. Protective gloves, glasses and proper clothing should be worn. Waste sample material should be properly disposed.

7.0 PERSONNEL

Persons who will perform this procedure should first read this SOP and then operate under the supervision of an experienced individual for at least one series of grain size determinations.

8.0 REFERENCES

PSEP. 1997. Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound. Puget Sound Estuary Program. Sampling Chapter. April 1997.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

 SOP No.: SED002.09w
 Effective Date: 11/11/19
 Page No.: 1 of 15

1.0 SCOPE

This test determines the short term, adverse effects of potentially contaminated sediment on marine amphipods. Sediment toxicity testing will be conducted according to procedures outlined in **Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**, including modifications from the Sediment Management Annual Review Meeting (SMARM) clarification papers. Other references include **USACE/USEPA (1991) (OTM)** and **USACE/USEPA (1998) (ITM)** (for dredged sediments), **ASTM E 1367**, and **EPA/600/R-94/025**.

2.0 SUMMARY OF TEST

2.1 Approach

Table 1. Conditions for Performing 10-Day Solid Phase Toxicity Testing on Marine Amphipods

Test type	Static Non-renewal*
Test duration	10 Day
Lighting	Ambient and Constant
Test chamber size	1-L glass beaker
Test sediment depth	2 cm (~175 mL)
Test solution volume	775 mL (Chamber Vol. up to 950 mL)
Renewal of test solution	None*
No. of organisms per chamber	20
No. of replicates per treatment	5 test replicates 2 sacrificial chambers (one being the water quality surrogate) recommended minimum
Feeding	None
Test solution aeration	Trickle-flow (sufficient to maintain DO levels above 60% saturation)

* Static renewal, intermittent flow or continuous flow tests may be used where it is necessary to maintain water quality parameters, e.g., dissolved oxygen (DO) or ammonia.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 2 of 15

2.2 Physical Requirements

Table 2. Species Specific Test Condition Summaries

Species	<i>Ampelisca abdita</i>	<i>Rhepoxynius abronius</i>	<i>Eohaustorius estuaries</i>	<i>Leptocheirus plumulosus</i> ⁵
Life Stage Tested	Immature amphipods	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 2-4 mm, mixed sexes
Feeding	Will not be fed	Will not be fed	Will not be fed	Will not be fed
Temperature (°C)	20 ± 1	15 ± 1	15 ± 1	25 ± 2
Salinity (ppt)	28 ± 1	28 ± 1	28 ± 1 or ambient ⁴	20 ± 2
pH	7-9	7-9	7-9	7-9
DO (≥ 60% Saturation)	4.6 mg/L	5.1 mg/L	5.1 mg/L	4.4 mg/L
Grain Size ¹	> 60% fines (> 20% clay fraction) ²	< 60% fines	0 – 99.4% silt-clay; Provided clay fraction < 20% ²	< 70% fines, <70% sand
Total Ammonia (mg/L, pH 7.7)	< 30	< 30	< 60	< 60
Un-ionized Ammonia (mg/L, pH 7.7)	< 0.4	< 0.4	< 0.8	< 0.8
Sulfides	N/A ³	N/A ³	N/A ³	N/A ³

¹ Grain size distributions are recommended guidelines and should not be considered absolute criteria. Species selection generally includes discussion with regulatory agencies and share holders and can be chosen exclusive from grain size characteristics (i.e. comparison to historical data with same species, species availability, etc.)

² SMARM clarification paper: 10/20/99

³ Specific guidance for sulfide sensitivities have not been well established.

⁴ Test salinity for *E. estuarius* may be conducted at the interstitial salinity (ambient) of the test sediments. The target test salinity should be approved by the client or regulatory agency, and will vary agency depending upon the objectives of the testing program.

⁵ Direct guidance for *L. plumulosus* is not given under PSEP guidelines; however, test conditions are similar to that of *E. estuarius* and described in other guidance documents (EPA 1991, 1994).

3.0 TEST ORGANISM

The test organism should be selected based on availability, sensitivity to test materials, tolerance to ecological conditions, ecological importance, and ease of handling in the laboratory. Ideally, organisms with wide geographical distribution should be selected so test results can be compared among laboratories with similar organisms. Test conditions for each amphipod species are summarized in Tables 1 and 2.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 3 of 15

Table 3. Test Organism Suppliers

Species	<i>Ampelisca abdita</i>	<i>Rhepoxynius abronius</i>	<i>Eohaustorius estuaries</i>	<i>Leptocheirus plumulosus</i>
Life Stage Tested	Immature amphipods, or mature females only	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 3-5 mm, mixed sexes	Mature amphipods 3-5 mm, mixed sexes
Sources	John Brezina and Associates, Dillon Beach, CA; Aquatic Research Organisms, Hampton, NH;	Doug Henderson, Puget Sound Organisms; John Brezina and Associates, Dillon Beach, CA	Northwest Aquatic Sciences, Newport, OR	Aquatic BioSystems, Fort Collins, CO; Aquatic Research Organisms, Hampton, NH;

3.1 Test Organism Care

Records will be kept, including the date and location collected, feeding regime, and sediment characteristics.

Holding time for amphipods is standardized to between 2 and 10 days.

4.0 TEST SUBSTANCE

The test sediments will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the facility. The sediments will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 – 6 °C in the dark, in a secure and distinct storage area. Containers should also have as little air as possible over the sediment or be stored with nitrogen gas in the overlying head space.

Test sediments should not be sieved prior to testing unless there is potential concern of similar species, competitors, or predators. Native sediments should always be sieved to remove amphipods from the material to be used as the Control treatment. A 0.5 mm sieve is sufficient to remove the amphipods and sediments should only be dry sieved (manually pushed through the sieve) using only the water present in the sample. These procedures can be performed prior to test set-up and stored under the conditions described above.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 4 of 15

5.0 EQUIPMENT

5.1 Instrumentation/Equipment

Microprocessor-controlled recorder, and a digital thermometer

Light meter

DO meter and probe

Salinity meter and probe

pH meter and probe

Ammonia probe meter and ancillary supplies

Microbalance capable of measuring weights to the nearest 0.0001 mg

Environmental test chamber or water bath capable of maintaining test temperature within 1°C

1 L and 250 mL test chambers

Clean filtered seawater

Deionized water

Pipets

Camel hair brushes

Miscellaneous labware (wash bottles, tally counters, culture bowls, etc.)

500 µm stainless steel sieves

Holding cups (food grade plastic is acceptable)

Stir plate and teflon stir bars

Centrifuge for collecting pore water

5.2 Apparatus

5.2.1 Test Area

The test area consists of a water bath or temperature controlled room with constant monitoring of test temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Overhead lighting will be ambient and continuous (24-hour).

5.2.3 Test Chambers

I-L glass jars with a 10-cm internal diameter, covered with a petri dish.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 5 of 15

6.0 PROCEDURE

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in tap or deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware will also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

Natural seawater will be obtained from North Hood Canal, sand filtered, and filtered to 0.45µm. Seawater will be adjusted as necessary to maintain a target test salinity. Salinity should be lowered with the addition of high purity deionized water or increased with the addition of bioassay grade sea salts or brine.

6.1.3 Test Organism Acclimation

For acclimation, amphipods will be held in control sediment with salinity adjusted dilution water. Gentle aeration will be provided for the duration of the acclimation period. Two to three days are sufficient for acclimation to the test conditions. Organisms may be fed a slurry of ground alfalfa or Tetramin™ if held for an extended period.

Amphipods in holding containers will be checked daily before the initiation of a test. Individuals that emerge from the sediment and appear dead or unhealthy will be discarded. If greater than 10% of the amphipods die or appear unhealthy during 48 hours preceding the test, the health of the batch of organisms should be evaluated for use in the proposed testing. This may include an additional day of holding to determine if mortalities or abnormal behavior are due to shipping or acclimation stress, and not indicative of an overly sensitive population.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 6 of 15

6.2 Primary Task

6.2.1 Pre-Test Analyses

Prior to test initiation, and preferably as soon as sediments are received at the testing facility, pore water should be collected from a homogenized sample from each sediment treatment (including reference and controls). This sample should be analyzed for interstitial salinity, ammonia, and sulfides. The parameters listed in Table 3 are recommendations based upon the tolerance of each species. If conditions within the sediment are outside the tolerance ranges, the project manager and/or client should be notified and possible corrective actions discussed. The most common corrective action involves test chamber overlying water renewal or purging to bring test conditions with tolerance ranges. These procedures are described further in Section 6.2.3.

Table 4. Species Specific Test Condition Summaries

Species	<i>Ampelisca abdita</i>	<i>Rhepoxynius abronius</i>	<i>Eohaustorius estuarius</i>	<i>Leptocheirus plumulosus</i> ²
Total Ammonia (mg/L, pH 7.7)	< 30	< 30	< 60	< 60
Un-ionized Ammonia (mg/L, pH 7.7)	< 0.4	< 0.4	< 0.8	< 0.8
Sulfides	N/A ¹	N/A ¹	N/A ¹	N/A ¹

¹ Specific guidance for sulfide sensitivities have not been well established.

² Direct guidance for *L. plumulosus* is not given under PSEP guidelines; however, test conditions are similar to that of *E. estuarius* and described in other guidance documents (EPA 1991, 1994).

6.2.2 Test Sediment Addition

Test sediment will be prepared using glassware cleaned according to Section 6.1.1, pre-cleaned glassware of a disposable nature, or non-toxic food grade plastic. All test chambers should be labeled accordingly with corresponding random number positions. After setup, the test chambers are distributed throughout the testing area based upon their position numbers. All 5 treatment replicates, including the corresponding Water Quality Surrogate (see Section 6.2.3), should be included in the randomized test matrix.

If necessary, sieving of the control sediment and/or test treatments will be performed (see Section 4.0). On the day before the test begins, each test sediment sample will be thoroughly homogenized within its storage container, and an aliquot added to a test chamber depth of 2 cm.

The sediment within the test chamber will be settled by tapping the test chamber against the side of the hand. Prepared seawater is gently added up to the 950-mL level (about 775 mL). A solid disk attached to a rod is placed inside the chamber to limit the suspension of the sediment into the water column by diffusing the water down the inside of the test chamber. The disc should be maintained just above the water surface as the

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 7 of 15

test chamber is filled. The sample is left overnight with gentle aeration to allow suspended particles to settle and equilibrium to be established between sediment and overlying water before the amphipods are added.

6.2.3 Sample Adjustments

If the water quality conditions in the test chamber are not suitable to support the selected amphipod species, it may be necessary to adjust those conditions to within tolerance limits. The two most common parameters which may require attention include interstitial salinity and ammonia. Water quality conditions (exclusive of contaminants) should be within the tolerance limits of the test species to remove the impact of their interference on the determination of toxic effects. Depending upon the program, manipulations to the test treatments may be performed to correct any deviations. Unfortunately, these manipulations may also alter the level of contaminants through purging or alter their available chemical state (salinity or pH change). Best professional judgment must be employed when deciding to manipulate the sample treatments and should always involve discussion with the client or regulatory agency. If manipulations are performed to the test treatments, the associated Control and Reference sediment should be treated in the same manner.

Generally, adjustments to the interstitial salinity of the sediments are not desirable. Exceptions to this may be sediments with very low interstitial salinities that are destined for open ocean disposal (~32-35 ppt). Salinity may be adjusted by replacing the overlying water within the test chambers with water of salinity equal to, or slightly greater than (or slightly less than if lowering), the target test salinity. The test chamber water should be removed through siphoning or pumping the water out to a level just above the test sediment. Care should be taken not to remove any sediment during this process. Prepared seawater is gently added up to the 950-mL level. A solid disk attached to a rod is placed inside the chamber to limit the suspension of the sediment into the water column by diffusing the water down the inside of the test chamber. The disc should be maintained just above the water surface as the test chamber is filled.

For sediments with pore water ammonia concentrations exceeding those values listed in Table 4, purging may be required to bring the test chambers conditions within acceptable limits. In most cases this should be determined in the pre-test pore water analyses (Section 6.2.1). General procedures for purging of the test chambers are described in further detail in the SMARM clarification paper "Ammonia and Amphipod Toxicity Testing" (SMARM clarification paper: 06/15/02). Additional sacrificial surrogate chambers should be created to monitor pore water ammonia levels during the acclimation process. Overlying water exchanges are conducted in the same manner as the overlying water renewal for salinity adjustment described above. Purging should be conducted twice daily until the pore water ammonia concentrations are below the threshold values. Pore water ammonia levels should be monitored every 1-3 days during the purging process. Overlying ammonia levels should also be measured as part of the monitoring procedure

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 8 of 15

as it gives an estimate of ammonia reduction without the breakdown of a surrogate chamber. Once the pore water ammonia has been reduced below the threshold values, purging should be terminated and the testing period can commence. Depending upon the program, purging may or may not be continued after test initiation. It may be possible in highly biogenic sediment that ammonia may increase again over the course of the test if renewals are discontinued.

6.2.4 Reference Toxicity Test

During this 96-hour toxicity test with marine amphipods and a test substance, five concentrations of a reference substance (ammonium chloride) with 10 test organisms will be used to assess the health of the test organisms. Three test chambers per reference concentration may be used. One concentration will be the 96-hour LC₅₀. The other four concentrations will be selected to bracket the LC₅₀. The LC₅₀ values will be compared with historical data from definitive bioassays with the reference substance. The results of the 96-hour mortality, determined during this study, will be reported and used in combination with control mortality to characterize the health of the test organisms. Table 5 summarizes the test conditions for conducting a 96-hour water-only reference toxicant test.

Table 5. Conditions for Performing 4-Day Water-Only Reference Testing on Marine Amphipods

Test type	Static Non-renewal
Test duration	4 Day
Lighting	Dark and Constant ¹
Test chamber size	250-mL glass beaker (minimum)
Test solution volume	200-mL (minimum)
Renewal of test solution	None
No. of organisms per chamber	10 recommended (minimum of 5)
No. of replicates per treatment	3
Feeding	None
Test solution aeration	None unless needed to maintain DO levels above 60% saturation

¹ In the absence of sediment, amphipods will continue to attempt to bury into the bottom of the chamber. Keeping the amphipods in the dark will lessen this digging behavior thus reducing undue stress on the test organisms.

The results of the ammonia reference-toxicant may be compared to the ammonia concentrations observed within the test samples to assist in correlating any ammonia related effects within a specific batch of organisms. Table 6 summarizes the published threshold ammonia concentrations for each species.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 9 of 15

Table 6. Threshold sediment interstitial ammonia levels for triggering ammonia reference toxicant tests.

Interstitial Ammonia (mg/L @ pH 7.7)	<i>Ampelisca abdita</i>	<i>Rhepoxinius abronius</i>	<i>Eohaustroius estuarius</i>	<i>Leptocheirus plumulosus</i> ¹
Total	>15	>15	>30	>30
Unionized	>0.2	>0.2	>0.4	>0.2

¹ Direct guidance for *L. plumulosus* is not given under PSEP guidelines; however, test conditions are similar to that of *E. estuarius* and described in other guidance documents (EPA 1991, 1994).

6.2.3 Reference and Control Sediment

During this 10-day toxicity test with marine amphipods on project sediment(s), reference sediment(s) will be used to provide a site-specific basis for comparison of potentially toxic and non-toxic conditions. Control sediment, collected during amphipod collection at the same site, will be used to determine the condition of the amphipods.

6.2.5 Water Quality

During routine test observations, a daily record of test room or water bath temperatures and test chamber aeration should be made.

In order to limit the impact of disturbance on the test organisms, all water quality measurements during the testing procedure will be performed in a surrogate water quality only chamber. In addition to the five test treatment replicates, a minimum of three additional surrogate chambers should also be tested; one for use as a water quality surrogate (WQS), and two to be utilized at test initiation and termination for pore water analyses. Surrogate chambers should be treated in the same manner as the test replicates. This includes randomization among the test treatments and addition of test animals. Additional pre-test surrogate chambers may also be required to monitor pore water salinity, ammonia, or sulfide manipulations.

After one day of acclimation after sediment and overlying water layering (test day 0), an initial set of water quality parameters will be measured in the overlying water of the WQS for each test treatment. The water quality parameters include temperature, dissolved oxygen (DO), pH, salinity, total ammonia, and total sulfides. In addition, a surrogate replicate from each test treatment will be sacrificed in order to extract pore water via centrifugation for subsequent analysis of ammonia and sulfides. Prior to test initiation, these initial water quality measurements must be reviewed to ensure that they are within the testing parameters. Test initiation should be postponed until any deviations are addressed and corrected.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 10 of 15

On test days 1 through 9, temperature, DO, pH, and salinity will be measured in the water quality surrogate chamber of each treatment. At test termination (test day 10) the full suite of measurements will be repeated as on day 0.

6.2.6 Test Organism Addition

Amphipods are sieved from the holding sediment (500 µm sieve) and transferred to a sorting tray containing water of the holding temperature and salinity. Active, healthy amphipods are randomly selected from the sorting tray and sequentially distributed among dishes containing approximately 15 mL of dilution seawater until each dish contains 5 individuals. Prior to addition to the test chambers, the number of organisms is verified by recounting the individuals within the dish as well as confirming health and appearance. Unacceptable amphipods are discarded and replaced prior to introduction.

Twenty animals (4 dishes of 5 animals each) are then added to the randomly positioned test chambers. Addition should occur with minimal disruption of the sediment by gently pouring the water and amphipods from the sorting dishes into the test chamber. Any amphipods remaining in the dish should be gently washed into the test chamber. After addition, the test chamber is marked to confirm organism addition, recovered, and aeration restored. Any amphipods that do not bury within 15 minutes will be removed and replaced (*Ampelisca abdita* should be allowed one hour for burial).

6.2.5 Test Initiation

The test is initiated when the test organisms are distributed to each test chamber.

6.2.6 Test Observations

Notes are made on sediment appearance and unusual conditions. This can include fungal and algal growth. The number of amphipods that have emerged from the sediment, either floating on the water surface or lying on top of the sediment is recorded. Amphipods that are floating on the surface can be released from the surface tension by dropping a small drop of water (from the test chamber) with a pipette. Care must be taken not to cross-contaminate beakers. Dead animals either on the water or sediment surface are not removed during the exposure period. A list of observation types and their corresponding codes are detailed in Table 7.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

 SOP No.: SED002.09w
 Date: 11/11/19
 Page No.: 11 of 15

Table 7. Observation Key for Recording Test Observations

Normal	N
No Burrows	NB
Body on surface (mortality). Can indicate a corpse or a molt.	M
Emergence (actively swimming in water column, or walking on sediment surface; not burrowing)	E
Growth. Indicative of fungal, algal, or bacterial mats	G
No Air Flow	D
Floating on surface. Animals caught in surface tension of water.	FOS
Water too cloudy/turbid for observation	TC

6.3 Post-task

The bioassay is terminated on day 10. After final observations are performed, the contents of each test chamber are sieved through a 0.5-mm sieve. A gentle spray of seawater is used to wash the sediment through the sieve. Material retained on the sieve is transferred to a clean sorting vessel containing seawater of a similar salinity and temperature as the test. The numbers of live and dead amphipods are recorded. An amphipod is considered alive if there is any sign of movement (e.g., pleopod twitching or response to gentle prodding). Recoveries may not equal 20 due to the decomposition of dead animals through the test. Although not commonly conducted, there is also a procedure for evaluating the ability of the amphipods (excluding *A. abdita*) to rebury into Control sediment. This sublethal endpoint is discussed in further detail in PSEP 1995.

Results Needed:

- Percent mortality for each treatment
- Mean water quality values by treatment
- LC₅₀ and 95% confidence limits (for ref. tox.)
- Reburial

In screening tests, the responses of amphipods in collected test sediments are compared to control and reference site sediments.

6.4 Reporting

The report may include, but will not be limited to, the following:

- Name and address of the laboratory conducting the study, and dates on which the study was initiated and completed.
 - The name of the Study Director, other scientists or professionals, and supervisory personnel involved in the study.
 - Objectives as stated in the protocol.
 - A description of the methods used.
-

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w
Date: 11/11/19
Page No.: 12 of 15

- Transformations, calculations, or operations performed on the data, a summary and analysis of the data, and a statement of the conclusion drawn from the analysis.
- The test substance identified by code number and the date each sample was used.
- The number of organisms used in the study.
- Concentrations of exposure and exposure method.
- Any circumstances that may have affected the quality or integrity of the data, including deviations from test protocols or Standard Operating Procedures.
- The location where raw data and the final report will be stored.
- Additions or corrections to a final report will be in the form of an amendment by the Study Director. The amendment will clearly identify that part of the final report that is being altered and the reason(s) for the alteration(s). The amendment will be signed and dated by the Study Director.

The master copy of the final report will be signed and dated by the Study Director.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Proper laboratory protection, including lab hood or ventilation system, lab coat, closed-toe shoes, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

Refer to the Port Gamble Laboratory's Chemical Hygiene Plan and Health and Safety Plan at [S:\Health and Safety](#) for procedures to ensure safe operation in the laboratory and for contingency plans in the event of an accident or emergency.

For specific chemical health and safety information, refer to the Safety Data Sheet log.

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures of the Port Gamble Laboratory which are in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w
Date: 11/11/19
Page No.: 13 of 15

Usually tests would be unacceptable if the following conditions occurred:

- More than 10% of the organisms die in the Control treatment.

Test data will need to be evaluated and qualified if:

- All test chambers were not identical.
- Treatments were not randomly assigned to test chambers.
- Test organisms were not randomly or impartially distributed to test chambers.
- All test animals were not from the same population, were not all of the same species, or were not of acceptable quality.
- Reference sediment and controls were not included in the test.
- Amphipods were maintained in the laboratory for less than two days or greater than ten days, unless the effect of prolonged maintenance in the laboratory has been shown to have no significant effect on sensitivity.
- Temperature, DO, pH, salinity, and ammonia were not measured, or were not within acceptable range.
- Test organisms were not acclimated at the test temperature and salinity at least 24 hours before they were placed in test chambers.
- Aeration to the test chamber was off for an extended time such that the DO levels dropped below acceptable limits and was associated with mortality.
- Response criteria were not monitored in a blind fashion.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w

Date: 11/11/19

Page No.: 14 of 15

10.0 REFERENCE DOCUMENTS

Puget Sound Water Quality Authority. Revised July 1995. "Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments." Prepared for U.S. EPA Region 10, Office of Puget Sound. Seattle, W A.

Sediment Management Annual Review Meeting Clarification Paper. Barton, J. "Ammonia and Amphipod Toxicity Testing." June 15, 2002.

Sediment Management Annual Review Meeting Clarification Paper. Kendall, D.R. "Clarification on the Use of the Amphipod, *Eohaustorius estuarius*, Relative to Grain Size and Salinity." October 20, 1999.

Sediment Management Annual Review Meeting Clarification Paper. Warner, L.C. "Reporting Ammonia LC₅₀ Data for Larval and Amphipod Bioassays". October 3, 2001.

Sediment Management Annual Review Meeting Clarification Paper. Michelson, T. "Statistical Evaluation of Bioassay Results". July 25, 1996.

ASTM E 1367. "Standard Test Method for Measuring the Toxicity of Sediment Associated Contaminants with Estuarine and Marine Invertebrates." Annual Book of Standards. Volume 11.06 "Biological Effects and Environmental Fate; Biotechnology." American Society of Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA. 2006.

Norberg-King, T.J. 1998. An interpolation estimate for chronic toxicity: The Icp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

USACE/USEPA (U.S. Army Corps of Engineers/U.S. Environmental Protection Agency). 1991. Evaluation of Dredged Material Proposed for Ocean Disposal - Testing Manual." Office of Water, Washington, DC. EPA/503/8-91/001. February, 1991.

USACE/USEPA. 1994. "Methods for Assessing the Toxicity of Sediment-associated Contaminants with Estuarine and Marine Amphipods." Office of Research and Development, Washington, DC. EPA/600/R-94/025.

USACE/USEPA. 1998. "Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. - Testing Manual." Office of Water, Washington, DC. EPA/823/B-98/004. February, 1998.

Title: 10-Day Acute Sediment Toxicity Test with Marine Amphipods (PSEP)

SOP No.: SED002.09w
Date: 11/11/19
Page No.: 15 of 15

11.0 APPENDIX OF CHANGE

- 08/20/15 Changed test organism acclimation section to reflect a 10% mortality threshold in assessing the organism's health
- 05/23/16 Added "uncontrolled" statement to SOP and updated Health and Safety section
- 05/09/17 Updated health and safety information, removed branding, added review documentation section. Added "proprietary information" statement to footer.

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

 SOP No.: SED005.05w
 Effective Date: 11/11/19
 Page No.: 1 of 12

1.0 SCOPE

To evaluate the chronic toxicity of marine sediments Sediment testing will be conducted as defined in **Dinnel and Stober (1995)**, **Standard Methods (APHA 1985)**, **ASTM (1989)**, and **Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**.

2.0 SUMMARY OF TEST

2.1 Approach

Number of samples	≥ 1
Number of replicates per test sediment	5
Number of controls	1
Number of replicates per control	5
Number of reference sediments	1
Number of replicates per reference sediment	5
Test chambers	1 L glass beaker or comparable wide mouth glass jar (10 cm internal diameter)
Test sediment volume	18 g of sediment per container
Overlying water	900 mL of 28‰ salinity, clean, filtered, seawater with a maximum holding time of 2 days
Renewal of overlying water	None
Number of test organisms per chamber	20,000-40,000 embryos for Bivalves, 25,000 embryos for Echinoderms
Type of biological observations	Survival, Development
Times of biological observations	Post test
Type of physical observations	Room or bath temperature continuous, light daily
Types of water quality analyses	DO, temperature, salinity, pH; ammonia and sulfides (Program Dependent)
Times of water quality samples	DO, temperature, salinity, and pH measured in a surrogate test chamber daily. Ammonia and total sulfide samples taken at the beginning and end of the test.
Aeration	Gentle aeration is applied to all chambers if Dissolved Oxygen levels fall below 6.0 mg/L.
Sediment holding time	Samples must be stored in the dark at 4 ± 2 ° C with no headspace or headspace filled with nitrogen gas.

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 2 of 12

2.2 Physical Requirements

Species	<i>Dendraster excentricus</i>	<i>Strongylocentrotus purpuratus</i>	<i>Mytilus galloprovincialis</i>	<i>Crassostrea gigas</i>
DO (mg/L)*	> 4.8	> 4.8	> 4.8	> 4.6
Temperature (°C)	15 ± 1	15 ± 1	16 ± 1	20 ± 1
Salinity (ppt)	28 ± 1	28 ± 1	28 ± 1	28 ± 1
pH	Ambient	Ambient	Ambient	Ambient
Lighting	14 hours light : 10 hours dark at 50-100 foot-candles	14 hours light : 10 hours dark at 50- 100 foot-candles	14 hours light : 10 hours dark at 50-100 foot-candles	14 hours light : 10 hours dark at 50-100 foot-candles
Ammonia	< 0.14 mg/L unionized	< 0.14 mg/L unionized	< 0.13 mg/L unionized	< 0.13 mg/L unionized
Aeration	Gentle, if D.O. falls below 6.0 mg/L	Gentle, if D.O. falls below 6.0 mg/L	Gentle, if D.O. falls below 6.0 mg/L	Gentle, if D.O. falls below 6.0 mg/L

*60 percent saturation at 15°C and 28 ppt.

2.3 Biological Requirements

Feeding None

Life stage Larval Stage used within 2 hours of fertilization depending on test species.

3.0 TEST ORGANISM

The test organism should be selected based on availability, sensitivity to test materials, tolerance to ecological conditions, ecological importance, and ease of handling in the laboratory. Ideally, organisms with wide geographical distribution should be selected so test results can be compared among laboratories with similar organisms. The organisms for this protocol are *D. excentricus*, *S. purpuratus*, *M. galloprovincialis*, and *C. gigas*.

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 3 of 12

3.1 Test Organism Specifications

Species:	<i>Dendraster excentricus</i>	<i>Strongylocentrotus purpuratus</i>	<i>Mytilus galloprovincialis</i>	<i>Crassostrea gigas</i>
Age:	Larval Stage used within 2 hours of fertilization	Larval Stage used within 2 hours of fertilization	Larval Stage used within 2 hours of fertilization	Larval Stage used within 2 hours of fertilization
Source:	In-house collection; Aquatic Toxicology Support, Bremerton, WA; Dave Guttoff, San Diego, CA	Dave Guttoff, San Diego, CA; In-house collection; Aquatic Toxicology Support, Bremerton, WA	Taylor Shellfish, Shelton, WA; Aquatic Research Organisms, Hampton, NH	In-house collection; Taylor Shellfish, Shelton, WA; Aquatic Toxicology Support, Bremerton, WA

3.2 Test Organism Care

Records of the stock shipments will be kept, including original source, feeding regime, and holding water characteristics

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the Port Gamble Laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client.

The test substance is stored at 0 - 6°C in a secure and distinct storage area.

5.0 EQUIPMENT

5.1 Instrumentation/Equipment

Microprocessor-controlled recorder, and a digital thermometer

Light meter

DO meter and probe

Salinity meter and probe

pH meter and probe

Ammonia probe meter and ancillary supplies

Method of measuring total sulfides

1 L test chambers

Clean filtered seawater

Pipets

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 4 of 12

Miscellaneous labware (wash bottles, tally counters, culture bowls, etc.)
Centrifuge for collecting pore water
20 mL Scintillation or 25 mL shell vials
Syringe (to inject KCl into echinoderms) with 18-22 gauge needle
Pasteur pipets and bulbs
Ice bath or refrigerator
Compound microscope
Neubauer hemocytometer
Sedgwick-Rafter (or equivalent) counting cell (1 mL)
Small siphon hose (2ft. long, 3/16 - 1/4 in diameter)
Laboratory timer
Controlled temperature water bath or room
100-mL graduated cylinder
Perforated plunger

5.2 Reagents

0.5 M KCl
5% Buffered formalin
Copper sulfate
10% hydrochloric acid
Acetone
5% buffered formalin

5.3 Apparatus

5.3.1 Test Area

The test area consists of a room with constant temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.3.2 Lighting

Continuous overhead lighting will be at 50-100 foot-candles (550-1050 Lux).

5.3.3 Test Chambers

I-L glass chambers
20 mL glass scintillation or 25 mL glass shell vials

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 5 of 12

6.0 PROCEDURE

Prior to use, all glassware and plasticware will be thoroughly cleaned.

6.1 Preparation

6.1.1 Glassware Preparation

Glassware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Glassware will be rinsed three times with running deionized water. Glassware will then be rinsed in 10% hydrochloric acid, rinsed three times with deionized water, rinsed once with reagent grade acetone, and finally rinsed three times with deionized water.

6.1.2 Dilution Water Preparation

Filtered seawater collected from North Hood Canal will be diluted to 28 ± 1 ppt salinity using deionized water. Seawater will be held for a maximum of 2 days.

6.1.3 Test Organism Acclimation

Stock cultures will be acclimated in the same dilution water and at the same temperature as in the test procedures. Short-term culture logs will be maintained throughout the holding period.

6.2 Primary Task

6.2.1 Test Sediment Addition

Test sediment will be prepared using glassware cleaned according to Section 6.1.1, pre-cleaned glassware of a disposable nature, or non-toxic food grade plastic.

Eighteen grams of reference or test sediment is added to each chamber. 900 mL of filtered seawater (28 ppt salinity) is added to each test chamber. Two control series are prepared consisting of clean seawater without sediment. One series is used as a duplicate control in order to monitor embryo development. The sediments are suspended by vigorously shaking for 10 seconds. Test chambers will be randomized, and the mixture will be allowed to settle for four hours prior to embryo induction.

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 6 of 12

6.2.2 Reference Toxicant Test

Concurrent with this toxicity test, five concentrations of a reference substance are used to assess the health of the test organisms. Three replicates per reference concentration will be used. Five concentrations will be selected to bracket the 48-hour LC₅₀. The LC₅₀ values will be compared with historical data from definitive bioassays. The results of this survival and development test, conducted during this study, will be reported and used in combination with control survival and development to characterize the health of the test organisms.

6.2.3 Test Organism Spawning and Addition

To collect gametes for testing with bivalve species, the adult organisms are placed in clean seawater and acclimated to the target test salinity (test dependant) and temperature (16°C for *Mytilus* and 20°C for *Crassostrea*) for approximately 20 minutes. The water bath temperature is then increased 5°C over a period of 15 minutes. Bivalves are maintained at this elevated temperature and monitored for spawning individuals. Spawning animals are removed from the water bath and placed in individual containers with seawater. Gametes from at least two males and two females are used to initiate the test. Once sufficient eggs and sperm had been collected, the eggs are screened through 60-µm mesh to remove any detritus or feces and a homogenized sperm solution added to the egg solutions. Egg-sperm solutions are periodically homogenized with a perforated plunger during the fertilization process. Approximately one hour after fertilization, embryo solutions are checked for fertilization and cell division. Only those embryo stocks with >90% cell division are used to initiate the tests. Density of the embryo stock solution is determined by counting the number of embryos in a subsample of stock solution. For bivalve species, approximately 20,000 - 40,000 embryos will be added to test chambers within 2 hours of fertilization.

To collect gametes required for testing echinoderm species, spawning is induced in the adult organisms by the injection of 0.5 to 1.0 mL of 0.5 M KCl into the coelomic cavity through the perisotomal membrane. The injection is performed while the adult animal is out of water. Females will release orange (*S. purpuratus*) or purple (*D. excentricus*) eggs and males of both species will release cream-colored sperm. Once release has been initiated, each adult is inverted over a 50 to 100 mL beaker with filtered seawater at 15 degrees Celsius and gametes are allowed to accumulate for approximately 15 minutes. Once sufficient eggs and sperm had been collected, the eggs are transferred to a larger beaker with cold filtered seawater and a homogenized sperm solution (taken from several males) is added to the egg solutions. Egg-sperm solutions are periodically homogenized with a perforated plunger during the fertilization process. Approximately one half-hour after fertilization, embryo solutions are checked for fertilization. Only those embryo stocks with >90% fertilization are used to initiate the tests. Density of the embryo stock solution is determined by counting the number of embryos in a subsample of stock solution.

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 7 of 12

Approximately 25,000 embryos will be added to test chambers within 2 hours of fertilization.

The test is initiated by randomly allocating an aliquot of the embryo stock solution into each test chamber four hours after sediments are shaken and within two hours of egg fertilization. Embryos are held in suspension during initiation using a perforated plunger. The test chambers are covered and incubated for 48 hours or longer under the conditions specified in Section 2.2.

For embryos/larvae test, a perforated plunger is used to mix the embryos/larvae at the test initiation. Approximately 25,000 echinoderm or 20,000-30,000 bivalve embryos will be added to test chambers within 2 hours of fertilization.

In order to determine the initial embryo concentration, five 10-mL samples should be collected from the control culture and preserved using 1-mL 5% buffered formalin.

6.2.4 Test Initiation

The test is initiated when the first organism enters a test chamber.

6.2.5 Test Substance Renewal

No test substance renewals are required by this protocol.

6.2.6 Test Measurements

Water Quality. All probes will be cleaned thoroughly before initial use. Data collection will be performed on each samples respective surrogate chamber and recorded. The probes will be rinsed with de-ionized water between each sample. DO, temperature, salinity, and pH will be measured from the overlying water in the surrogate chamber daily. Ammonia and total sulfides should be measured in the overlaying water at least at the beginning of the test.

Biological. Larvae will be scored for normal development according to ASTM guidelines.

6.2.7 Test Termination

For echinoderm species, the test is terminated at 48 hours or when greater than 90% of the embryos in the duplicate seawater control have reached normal development (whichever is later and within 96 hours). For bivalve species, the test is terminated at 48 hours or when greater than 95% of the embryos in the duplicate seawater control have reached normal development (whichever is later and within 60 hours).

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 8 of 12

The water and the larvae overlying the settled sediment in each container are carefully mixed in order to suspend larvae and prevent disturbance of the sediment. The overlying water and larvae are then placed into a clean, I-L beaker. The water is then mixed, and three 10-mL aliquots of the sample are removed and placed into 20-mL scintillation vials or shell vials. The contents of each vial are preserved with 1.0-mL of 5% buffered formalin, and the caps are securely replaced on the vials.

Preserved samples are examined on Sedgwick-Rafter cells (if using scintillation vials) or in the shell vials. Normal and abnormal larvae are counted to determine the percent normal development. In addition, percent survival is determined using the appropriate method outlined in **Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**.

6.3 Post-task

- PSEP 1995 Recommendations:

Calculate the percent mortality for each replicate:

$$\text{Mortality} = 100 \times (1 - (\text{No. of surviving test larvae} / \text{No. of control larvae}))$$

Calculate the percent abnormality for each replicate:

$$\text{Abnormality} = 100 \times (1 - (\text{No. of abnormal larvae} / \text{No. of normal and abnormal survivors}))$$

Calculate the combined larval mortality/abnormality:

$$\text{Combined larval mortality/abnormality} = 100 \times (1 - (\text{No. of surviving normal larvae} / \text{No. of embryos inoculated}))$$

- Conventional endpoint calculations typically reported for PSEP testing programs:

Endpoint Calculation	Sample Type	
	Control	Reference and Project
Proportion Normal	No. of surviving normal larvae / No. of normal and abnormal survivors	
Proportion Survival	No. of normal and abnormal survivors / No. of embryos inoculated	
Normal Survivorship (Combined Proportion Normal)	No. of surviving normal larvae / No. of embryos inoculated	No. of surviving normal larvae / Mean No. normal in the Control

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 9 of 12

Results Needed:

- Individual replicate, mean, and standard deviation values for percent survival/mortality, percent normality/abnormality, and combined larval mortality/abnormality
- Plot of dose-response curve at test termination (48 or 72 hours)
- LC₅₀ value for mortality, EC₅₀ value for abnormality
- 95% confidence limits of LC₅₀ value and EC₅₀ value
- Tables showing biological, chemical, and physical data

6.3.1 Method

LC₅₀ and EC₅₀ values and 95% confidence limits will be determined using a computer approach published by Norberg-King (1988) of the U.S. EPA and a commercial statistic software program. The Inhibition Concentration percentage, or ICp, approach to calculating point estimates of toxicity (i.e., LC₅₀ and EC₅₀) is based upon a monotonic smoothing technique of biological response versus concentration. Bootstrapped estimates of mean response at each concentration allow for distribution-free estimates of standard error and confidence intervals. The result is a nonparametric statistical test that requires no assumptions of normality or homogeneous variance and is robust enough to accommodate a wide variety of biological responses.

6.4 Reporting

The report may include, but will not be limited to, the following:

- Name and address of the laboratory conducting the study, and dates on which the study was initiated and completed.
 - The name of the Study Director, other scientists or professionals, and supervisory personnel involved in the study.
 - Objectives as stated in the protocol.
 - A description of the methods used.
 - Information regarding organisms used.
 - All water quality measurements.
 - Transformations, calculations, or operations performed on the data, a summary and analysis of the data, and a statement of the conclusion drawn from the analysis.
 - The test substance identified by code number and the date each sample was used.
 - The number of organisms used in the study.
 - Concentrations of exposure and exposure method.
-

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 10 of 12

- Any circumstances that may have affected the quality or integrity of the data, including deviations from test protocols or Standard Operating Procedures.
- The location where raw data and the final report will be stored.
- Additions or corrections to a final report will be in the form of an amendment by the Study Director. The amendment will clearly identify that part of the final report that is being altered and the reason(s) for the alteration(s). The amendment will be signed and dated by the Study Director.

The master copy of the final report will be signed and dated by the Study Director.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Proper laboratory protection, including lab hood or ventilation system, lab coat, closed-toe shoes, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

Refer to the Port Gamble Laboratory's Health and Safety Plan at <S:\Health and Safety> for procedures to ensure safe operation in the laboratory and for contingency plans in the event of an accident or emergency.

For specific chemical health and safety information, refer to the Safety Data Sheet log.

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures which are in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

Test acceptability criteria are:

- $\geq 90\%$ survival of embryos introduced into control test chambers.
- $\geq 70\%$ of embryos demonstrate normal development in the control.

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 11 of 12

10.0 REFERENCE DOCUMENTS

Dinnel, P.A., J.M. Link, and Q.J. Stober. 1987. Improved methodology for a sea urchin sperm cell bioassay for marine waters. *Arch. Env. Cont. Toxicol.* 16:23-32.

Chapman, G.A., et al. 1995. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms, 1st edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/R-95/136.

Sediment Management Annual Review Meeting Clarification Paper. Warner, L.C. "Reporting Ammonia LC₅₀ Data for Larval and Amphipod Bioassays". October 3, 2001.

Sediment Management Annual Review Meeting Clarification Paper. Kendall, D. "Sediment Larval Test Species Recommended for Toxicity Testing by The DMMP Program". October 17, 2005.

Norberg-King, T.J. 1988. An interpolation estimate for chronic toxicity: The ICp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

USACE/USEPA (U.S. Army Corps of Engineers/U.S. Environmental Protection Agency). 1991. Evaluation of Dredged Material Proposed for Ocean Disposal - Testing Manual." Office of Water, Washington, DC. EPA/503/8-911001. February, 1991.

USACE/USEPA. 1998. "Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. - Testing Manual." Office of Water, Washington, DC. EPA/823/B-98/004. February, 1998.

PTI Environmental Services. 1991. Draft Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments. Prepared for U.S. EPA, PTI Contract C744-12.

Puget Sound Water Quality Authority. Revised July 1995. Recommended Guideline for Conducting Laboratory Bioassays on Puget Sound Sediments. Prepared for U.S. EPA Region 10, Office of Puget Sound, Seattle, WA.

Title: Chronic Larval Sediment Toxicity Test (PSEP Guidelines)

SOP No.: SED005.05w

Date: 11/11/19

Page No.: 12 of 12

11.0 APPENDIX OF CHANGE

- 04/28/16 Updated logo
- 05/26/16 Added “uncontrolled” statement to SOP and updated Health and Safety section
- 05/09/17 Updated health and safety information, removed branding, added review documentation section. Added “proprietary information” statement to footer. Updated organism suppliers. Added the use of shell vials as an alternative to scintillation vials. Removed reference toxicant and retesting time frames from test acceptability criteria in section 9.0. Added clarification papers from Seattle USACE DMMO. Updated post-task calculation options.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

 SOP No.: SED009.08w
 Effective Date: 11/11/19
 Page No.: 1 of 10

1.0 SCOPE

To determine the chronic toxicity of marine sediments on the marine polychaete *Neanthes arenaceodentata*. Sediment toxicity testing will be conducted according to guidelines presented in **ASTM E1611, Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (1995)**, and the various updates presented during the Annual Sediment Management Review meetings (SMARM).

2.0 SUMMARY OF TEST

Table 1 Test Condition Summary

Sample storage conditions	4°C, dark minimal head space
Recommended Sediment Holding Time:	≤8 weeks (56 days)
Test Species	<i>Neanthes arenaceodentata</i>
Age class	Juvenile (2-3 weeks post-emergence)
Test Procedures	ASTM, PSEP 1995 with SMARM revisions
Regulatory program	SMS, DMMP, or other as mandated by the associated program
Test type/duration	20-Day static renewal
Test chamber	1-Liter glass beaker or jar
Exposure volume	175 mL (2cm) sediment/ 775 mL water
Replicates per treatment	5 + 2 surrogate chambers (one used for WQ measurements throughout the test)
Control / Diluent water	North Hood Canal, sand filtered
Test Lighting	Continuous
Aeration	Continuous from test initiation: 100 bubbles per minute
Test temperature	Recommended: 20 ± 1 °C
Test Salinity	Recommended: 28 ± 2 ppt
Test dissolved oxygen	Recommended: > 4.6 mg/L (60% saturation @ 20°C and 28 ppt salinity) ¹
Test pH	Recommended: 7 – 9 ²
Organisms/replicate	5
Feeding	40 mg/jar every other day (8mg/ind every other day)
Water renewal	Water renewed every third day (1/3 volume of exposure chamber)

¹ PSEP guidance is not specific on dissolved oxygen limits. The value of 60% saturation is based on ASTM 2006.

² pH is monitored as a water quality parameter. There are generally no control limits for pH; however measurements of pH may be useful in interpreting results (Ecology 2003).

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w

Date: 11/11/19

Page No.: 2 of 10

2.2 Physical Requirements

DO	>4.6 mg/L (60% Saturation)
Temperature	20 ± 1°C
Salinity	28 ± 2 ppt (PSEP); 28 – 36 ppt (ASTM)
pH	7.0 - 9.0
Lighting	Continuous ambient light at approximately 50-100 foot-candles (550-1050 lux)

2.3 Biological Requirements

Feeding	Organisms will be fed ground TetraMin® on an every-other-day basis. The amount of food provided will be approximately 8 mg (dry weight) per juvenile <i>N. arenaceodentata</i>
Life stage	Juvenile worms (2-3 weeks, 0.25-1.0 mg),

3.0 TEST ORGANISM

The test organism should be selected based on availability, sensitivity to test materials, tolerance to ecological conditions, ecological importance, and ease of handling in the laboratory. Ideally, organisms with wide geographical distribution should be selected so test results can be compared among laboratories with similar organisms. The organism for this protocol is *Neanthes arenaceodentata*.

3.1 Test Organism Specifications

Species:	<i>Neanthes arenaceodentata</i>
Source:	Aquatic Toxicology Support, Bremerton, WA
Age:	Juvenile Worms (2-3 weeks, 0.25-1.0 mg), laboratory cultured

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the Port Gamble Laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 - 6°C in a secure and distinct storage area.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w

Date: 11/11/19

Page No.: 3 of 10

5.0 EQUIPMENT

5.1 Instrumentation/Equipment

Thermometer

Light meter

DO meter and probe

Salinity meter and probe

pH meter and probe

Ammonia probe meter and ancillary supplies

Microbalance capable of measuring weights to the nearest 0.0001 g

Environmental test chamber or water bath capable of maintaining $20 \pm 1^\circ\text{C}$

1000 mL test chambers

Clean filtered seawater

Deionized water

Pipets

Brushes

Miscellaneous labware (wash bottles, tally counters, culture bowls, etc.)

500 μm stainless steel sieves

Aluminum weigh boats

Holding cups (food grade plastic is acceptable)

Stir plate and teflon stir bars

Finely ground TetraMin[®]

Centrifuge and centrifuge Teflon[®] tubes for collecting pore water

Drying oven capable of maintaining 60°C

Muffle furnace capable of 550°C

Desiccator

5.2 Apparatus

5.2.1 Test Area

The test area consists of a water bath or a room with constant temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Continuous overhead lighting will be at 50-100 foot-candles (550-1050 Lux).

5.2.3 Test Chambers

1000 mL glass beakers with a 10 cm internal diameter covered with a petri dish.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w

Date: 11/11/19

Page No.: 4 of 10

6.0 PROCEDURE

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware will also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

Natural seawater will be obtained from North Hood Canal, sand filtered, and filtered to 0.45µm. Seawater will be adjusted as necessary to maintain a target test salinity. Salinity should be lowered with the addition of high purity deionized water or increased with the addition of bioassay grade sea salts or brine.

6.1.3 Test Organism Care and Acclimation

Upon receipt, salinity and temperature of water in shipping containers should be measured. If salinity is more than 2 ppt different from the target test salinity of 28 ppt then the salinity should be adjusted (no more than 3 ppt daily). If salinity is outside the range of 15 to 35 ppt, then test animals may be possibly stressed and the supplier should be notified to provide a new batch of test organisms. Temperature should be allowed to equilibrate to test temperature prior to removing animals from shipping containers. If temperature of shipping containers is outside the range of 15 to 25°C then a new batch of test organisms may be required. Animals should be held for at least 24 hours prior to testing and may be fed during holding period.

If animal health is suspect upon receipt (e.g. over 10% of number received dead, animals behaving strangely or diseased), notify the laboratory manager who will assess whether to notify the supplier and order replacements. If more than 10% of the organisms die in the 48h prior to testing, the entire batch is discarded, and a new batch is ordered. If the acclimation process is repeated with a new group of test organisms and excessive mortality occurs, an alternative source of dilution water should be used.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w

Date: 11/11/19

Page No.: 5 of 10

6.2 Primary Task

6.2.1 Test Sediment Addition

Test sediment will be prepared using labware cleaned according to Section 6.1.1, pre-cleaned labware of a disposable nature, or non-toxic food grade plastic.

If pre-sieving of sediment is required to exclude large material or potential predators they may be press sieved (no water) through a clean stainless steel sieve (2 mm mesh).

One day prior to test initiation test sediment, reference, and control sediment should be added to the test chambers. Sediment should be thoroughly homogenized prior to addition to the test chambers. A subsample should be analyzed for pore water ammonia. Approximately 2 cm of sediment should be added to each of the 5 replicate containers and applicable surrogate chambers. Once sediment has been added, clean filtered seawater should be added up to the 950-mL mark at a salinity of 28 ppt. Water should be added to ensure minimal disturbance of test sediments. Test chambers should be aerated at approximately 100 bubbles/minute under test temperature and photoperiod regime. The system should be left overnight with gentle aeration to allow suspended particles to settle and an equilibrium to be established between sediment and overlying water before the organisms are added.

6.2.2 Reference and Control Sediment Test

During this 20-day toxicity test with *Neanthes arenaceodentata* and a test sediment, a reference substance will be used to provide a site-specific basis for comparison of potentially toxic and non-toxic conditions.

6.2.3 Test Organism Addition

For test initiation, worms should be selected at random from a large culture dish(es) that contains all of the shipped animals. Animals should be added in order of replicate number, not treatment, to ensure an equal distribution of selected animals across treatments (i.e., so that animals selected initially aren't all in a single treatment and animals selected at the end aren't all in a single treatment). Transfer of animals to the test chambers is accomplished by gently drawing one worm into the wide end of a Pasteur pipette and adding the organism directly to the test chamber just above the water's surface to prevent cross-contamination. The number of animals added will be tracked by a cell counter operated by the person adding the worms. As animals are added to the test chamber, test chambers should be marked. Test chambers should be observed within one hour of addition. Worms demonstrating non-burrowing behavior may be replaced, if the observer believes the behavior results from factors other than sediment toxicity.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w

Date: 11/11/19

Page No.: 6 of 10

During test initiation, five worms should be assigned to an additional 3 holding cups for initial calculated individual weight measurements. Worms for these measurements should be selected at random from the culture dish and should be collected at regular intervals during initiation of the test so as not bias the initial size measurements.

6.2.4 Test Initiation

The test is initiated when test organisms are distributed completely to each test chamber.

To make initial weight measurements, individual animals should be gently scooped onto a small brush, rinsed briefly in deionized water, blotted dry on a Kimwipe and transferred onto a pre dried, pre weighed, pre marked (number etched into pan prior to pre weighing) aluminum pan (2x2 cm piece of aluminum foil). All five worms from one holding cup should be placed onto a foil weigh boat. Fold pans over to prevent loss of animals over the course of drying. Oven dry worms and pans at 60°C for 24 hours prior to weighing. Remove pans/worms from the oven and place in a desiccator for approximately 1 hour to cool to room temperature. All weight measurements must be made on a balance that can be measured to the nearest 0.01 mg.

An initial ash-free dry weight (AFDW) measurement may also be desired on the worms if this endpoint is included in the final test weight determinations. After obtaining the dry weight data, each of the weigh boats is then dried in a muffle furnace heated to 550°C for 2 hours in order to determine ashed weights. The ashed boats are again weighed to 0.01 mg and the ashed weight is subtracted from the dry weight to calculate the AFDW.

6.2.5 Test Maintenance

Feed worms every 48 hours. TetraMin® should be provided at approximately 8 mg (dry weight) per juvenile *Neanthes* (40 mg per test chamber).

Overlying water should be renewed every three days (total of six renewals). Approximately one third of the overlying water volume should be exchanged at each renewal.

6.2.6 Test Measurements

Data are recorded on data sheets.

Water Quality. A daily record of test room or water bath temperatures and test chamber aeration should be made. Water quality measurement should be made prior to renewals. Record temperature, salinity, dissolved oxygen, and pH in one randomly selected test chamber per treatment or a designated water quality surrogate chamber.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w

Date: 11/11/19

Page No.: 7 of 10

Biological. Response criteria indicating toxicity of test sediment include mortality, sublethal and chronic effects. A sublethal effect is the emergence from highly toxic sediment during the course of the test. Chronic effects are monitored by comparing the differences in dry weight or AFDW between test sediments and reference sediments (or control treatment when appropriate). Response criteria will be monitored in a "blind" fashion, that is, the observer will have no knowledge of the treatment of the sediment in the test chambers.

Mortality. At test termination (Day 20), all sediment from each individual chamber should be sieved through a 500 μm sieve to collect surviving organisms. Gently rinse sediment through sieve using 26 - 30 ppt salinity seawater. Gently remove animals from the sieve using a camel hair brush taking care not to damage the animal. Once removed, the animal should be placed into a labeled holding container containing clean filtered seawater (26 - 30 ppt) at room temperature. Record whether animal recovered from each test chamber is surviving, dead, or missing (for purposes of calculations all missing animals are assumed to be dead).

Growth (Dry Weight). Growth is measured by the dry weight of the surviving test worms within a replicate. The results are compared with the weight of the worms at the beginning of the test and with the control(s) and the test concentrations of sediment. Each surviving animal is removed from its holding cup, rinsed briefly in deionized water (< 5 seconds) blotted dry on a Kimwipe, and then placed onto a pre dried, pre weighed, pre labeled weigh boat. The aluminum foil boat should be folded over to prevent the loss of the animal during drying. Note weigh boats should be handled with forceps only. Oven dry animals at 60°C for 24 hours, remove animals and boats from oven and allow to come to room temperature in a desiccator prior to weighing on a microbalance to the nearest 0.01 mg. Subtract boat weight from total weight to obtain measured dry weight value of surviving worms.

Growth Modification (Ash-Free Dry Weight). The purpose of this modification is to account for the weight of sediment contained in the gut of the worms during the drying process. Worms reared under similar conditions and life history, but exposed to different grain size sediment, may express significantly different dry weights due to the contribution of heavier gut material of the worms maintained in sandy (heavier particles) sediment. This discrepancy has the potential to lead to Type II errors, where significant differences are found between test treatments, when none actually exist. The procedure below is a tool to estimate the actual contribution of gut content to the overall weight of the animals. A procedure defined as "ashing" is employed to heat the worm tissue at high temperatures until all that is left behind is solid inorganic material.

At the termination of the 20-day survival and growth test, sediment from each test chamber is sieved through a 0.5-mm screen and all recovered polychaetes are transferred into a plastic cup. Survival is recorded and worms are rinsed with deionized water and placed in pre-ashed, pre-weighed aluminum boats and dried in a gravimetric

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w

Date: 11/11/19

Page No.: 8 of 10

oven at 60°C for at least 24 hours. Each weigh-boat is removed from the oven, cooled in a desiccator for approximately 30 minutes, and then weighed on an analytical microbalance to 0.01 mg. Each of the weigh boats is then dried in a muffle furnace heated to 550°C for 2 hours in order to determine ashed weights. The ashed boats are again weighed to 0.01 mg and the ashed weight is subtracted from the dry weight to calculate the AFDW. Both the dry weight and the AFDW are used to determine individual worm weight and growth rates.

The 20-day average individual dry weight (or AFWD) in each exposure chamber is recorded and the mean and standard deviation calculated for each treatment.

6.3 Post-task

Results Needed:

- Percent mortality for each treatment
- Mean dry weight per individual for each treatment
- Ash-Free dry weight (AFDW) per individual for each treatment (program specific, if desired)
- Mean water quality values by treatment
- LC₅₀ and 95% confidence limits (for ref. tox.)
- Tables showing biological, chemical, and physical data

In screening tests, the responses of worms in collected test sediments are compared to control and reference site sediments.

6.4 Reporting

The report may include, but will not be limited to, the following:

- Name and address of the laboratory conducting the study, and dates on which the study was initiated and completed.
- The name of the Study Director, other scientists or professionals, and supervisory personnel involved in the study.
- Objectives as stated in the protocol.
- A description of the methods used.
- Transformations, calculations, or operations performed on the data, a summary and analysis of the data, and a statement of the conclusion drawn from the analysis.
- The test substance identified by code number and the date each sample was used.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w
Date: 11/11/19
Page No.: 9 of 10

- The number of organisms used in the study.
- Concentrations of exposure and exposure method.
- Any circumstances that may have affected the quality or integrity of the data, including deviations from test protocols or Standard Operating Procedures.
- The location where raw data and the final report will be stored.
- Additions or corrections to a final report will be in the form of an amendment by the Study Director. The amendment will clearly identify that part of the final report that is being altered and the reason(s) for the alteration(s). The amendment will be signed and dated by the Study Director.

The master copy of the final report will be signed and dated by the Study Director.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Proper laboratory protection, including lab hood or ventilation system, lab coat, closed-toe shoes, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

Refer to the Port Gamble Laboratory's Health and Safety Plan at [S:\Health and Safety](#) for procedures to ensure safe operation in the laboratory and for contingency plans in the event of an accident or emergency.

For specific chemical health and safety information, refer to the Safety Data Sheet log.

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures which are in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

Usually tests would be unacceptable if one or more of the following occurred:

- More than 10% of the control organisms die.
- All test chambers were not identical.

**Title: 20-Day Chronic Growth and Survival Test with
*Neanthes arenaceodentata***

SOP No.: SED009.08w
Date: 11/11/19
Page No.: 10 of 10

- Treatments were not randomly assigned to test chambers.
- Test organisms were not randomly or impartially distributed to test chambers.
- All test animals were not from the same population, were not all of the same species, or were not of acceptable quality.
- Reference sediment and controls were not included in the test.
- Temperature, DO, pH, salinity, and ammonia were not measured, or were not within acceptable range.
- Aeration to the test chamber was off for an extended time such that the DO levels dropped to less than 4.6 mg/L.
- Response criteria were not monitored in a blind fashion.

10.0 REFERENCE DOCUMENTS

ASTM. 2012. Guide for conducting Sediment Toxicity Test with Marine and Estuarine Polychaetous Annelids. Standard Guide #E-1611-00(Reapproved 2007). American Society for Testing and Materials, Philadelphia, P A.

Puget Sound Water Quality Authority. Revised July 1995. "Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments." Prepared for U.S. EPA Region 10, Office of Puget Sound. Seattle, W A.

11.0 APPENDIX OF CHANGE

- 08/20/15 Hand-written change to reflect criteria: if >5% mortality 48hrs preceding test, organisms should be replaced
- 11/12/15 Updated logo, corrected microbalance to nearest gram, and changed test organism acclimation section to reflect a 10% mortality threshold when assessing the organism's health during rounds
- 05/23/16 Added "uncontrolled" statement to SOP footer and updated Health and Safety section
- 05/09/17 Updated health and safety information, removed branding, added review documentation section. Added "proprietary information" statement in footer. Updated information on animal health upon receipt in section 6.1.3.

STANDARD OPERATING PROCEDURE

SPT AND SPLIT SPOON SAMPLING

Introduction

Split spoon sampling is generally used to collect disturbed soil samples of 18 or 24 inches in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling, providing samples at discrete depth intervals. During discrete sampling, the split spoon is driven to its sampling depth through the bottom of the augured hole and the core extracted. A split-spoon sample is ideal for collecting subsurface geotechnical data, including relative soil strength information through the standard penetration test (SPT). When split spoon sampling is performed to gain geologic information, all work should be performed in accordance with ASTM D1586, "Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils". This SOP describes the SPT and collection of soil samples using the split spoon.

Standard Penetration Test

The SPT is an approximate measure of soil density and consistency. To be useful, the results must be used with engineering judgment in conjunction with other tests. The SPT (ASTM D1586) is used to obtain disturbed soil samples. This test employs a standard 2-inch outside diameter¹ split-spoon sampler. Using a 300-pound hammer, free-falling 30 inches, the sampler is driven into the soil for 18 inches. The number of blows required to drive the sampler the last 12 inches only is the Standard Penetration Resistance. This resistance, or blow count, measures the relative density of granular soils and the consistency of cohesive soils. The blow counts are plotted on the boring logs at their respective sample depths.

Soil samples are recovered from the split-barrel sampler, field classified, and placed into watertight jars or double bagged in ziplock bags. They are then shipped to the geotechnical laboratory for further testing.

In the Event of Hard Driving

Occasionally very dense materials preclude driving the total 18-inch sample. When this happens, the penetration resistance is entered on logs as follows:

¹ Different sized samplers may be used, including oversized split spoons where sample volume requirements dictate collecting more soils. In all cases, the size of the split spoon sampler shall be recorded in field records so that SPT blowcounts can be corrected, if necessary, for non-standard split spoon sizes.

Penetration less than six inches. The log indicates the total number of blows over the number of inches of penetration.

Penetration greater than six inches. The blow count noted on the log is the sum of the total number of blows completed after the first 6 inches of penetration. This sum is expressed over the number of inches driven that exceed the first 6 inches. The number of blows needed to drive the first 6 inches are not reported. For example, a blow count series of 12 blows for 6 inches, 30 blows for 6 inches, and 50 (the maximum number of blows counted within a 6-inch increment for SPT) for 3 inches would be recorded as 80/9.

Required Information on Boring Logs

Logs shall include the following information, at a minimum, to describe the drilling work:

1. The sample station identification
2. Names of field personnel collecting and handling the samples
3. Type of sampling equipment used (i.e. split spoon inside and outside diameter; hammer weight; free fall height; hammer deployment method)
4. Date and time at the start and completion of each boring location
5. Total depth of boring penetration below ground surface or mudline
6. Depth of water and time of measurement for barge-based drilling
7. Date and time of collection of each sample
8. Driller observations regarding changes in subsurface conditions, and depth of drilling equipment at the time of observation (e.g. gravelly drill action, hard penetration, etc.)
9. Observations made during sample collection, including weather conditions, complications, and other details associated with the sampling effort
10. Length and depth intervals of each sample and measured recovery
11. Qualitative notation of apparent resistance during driving
12. Any deviation from the approved SAP

Split Spoon Sample Collection and Processing

The following procedures are used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of barrel and then screwing the drive shoe (with catcher) on the bottom and the head piece on top.
2. Place the sampler in a perpendicular position on the sample material. Where a drill rig is used, this step is performed by the drilling contractor.

3. Use the SPT hammer to drive the tube. Do not drive past the bottom of the sample length. Where a drill rig is used, this step is performed by the drilling contractor.
4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain this depth, in 6-inch depth intervals
5. Withdraw the sampler, and open by unscrewing the bit and head and splitting the barrel. The amount of recovery and soil type should be recorded on the boring log.
 - a. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally.
 - b. The split spoon sampler is typically available in 2- and 3-1/2-inch diameters. A larger barrel may be necessary to obtain the required sample volume.
6. Record soil description on the field log, and place samples in labeled, watertight containers.
7. Store sample in a dry location outside of direct sunlight.

Split Spoon Sample Logging

Split spoon samples will be logged on-site by an experienced field geologist or geotechnical engineer. Prior to sub-sampling, a description of each sample will be recorded on a standard boring log. The following parameters will be noted:

1. Sample recovery
2. Physical soil description in accordance with the Unified Soil Classification System (includes soil type, moisture, density/consistency of soil, color)
3. Odor (e.g., hydrogen sulfide, petroleum)
4. Visual stratification, structure, and texture
5. Vegetation and debris (e.g. woodchips or fibers, concrete, metal debris)
6. Biological activity (e.g., detritus, shells, tubes, bioturbation, live or dead organisms)
7. Presence of oil sheen

Standard terminology for field logs is attached to this SOP.

Sample Description Key

Classification of soils in this report is based on visual field and laboratory observations which include density/consistency, moisture condition, grain size, and plasticity estimates and should not be construed to imply field nor laboratory testing unless presented herein. Visual-manual classification methods of ASTM D 2488 were used as an identification guide.

Soil descriptions consist of the following:

Density/consistency, moisture, color, minor constituents, MAJOR CONSTITUENT, additional remarks.

Density/Consistency

Soil density/consistency in borings is related primarily to the Standard Penetration Resistance. Soil density/consistency in test pits is estimated based on visual observation and is presented parenthetically on the test pit logs.

SAND or GRAVEL Density	Standard Penetration Resistance (N) in Blows/Foot	SILT or CLAY Consistency	Standard Penetration Resistance (N) in Blows/Foot	Approximate Shear Strength in PSF
Very loose	0 - 4	Very soft	0 - 2	< 250
Loose	4 - 10	Soft	0 - 4	250 - 500
Medium dense	10 - 30	Medium stiff	4 - 8	500 - 1,000
Dense	30 - 50	Stiff	8 - 15	1,000 - 2,000
Very dense	>50	Very stiff	15 - 30	2,000 - 4,000
		Hard	>30	> 4,000

Moisture

Dry	Little perceptible moisture
Damp	Some perceptible moisture, probably below optimum
Moist	Probably near optimum moisture content
Wet	Much perceptible moisture, probably above optimum

Minor Constituents





Estimated Percentage

Not identified in description	0 - 5
Slightly (clayey, silty, etc.)	5 - 12
Clayey, silty, sandy, gravelly	12 - 30
Very (clayey, silty, etc.)	30 - 50




Legends

Sampling Test Symbols

BORING SAMPLES

-  Split Spoon
-  Shelby Tube
-  Cuttings
-  Core Run
- * No Sample Recovery
- P Tube Pushed, Not Driven

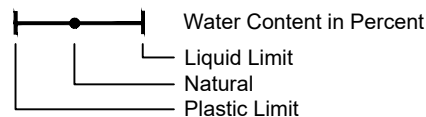
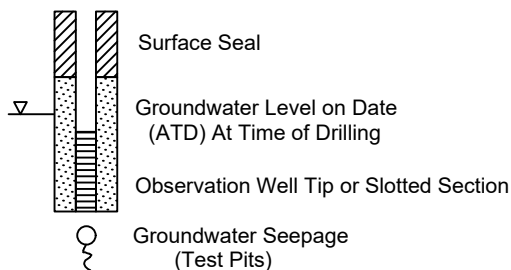
TEST PIT SAMPLES

-  Grab (Jar)
-  Bag
-  Shelby Tube

Test Symbols

- GS Grain Size
- Comp Composite
- Chem Chemistry
- VST Vane Shear Test
- BD Bulk Density
- UU Triaxial Unconsolidated Undrained
- TCU Triaxial Consolidated Undrained
- TCD Triaxial Consolidated Drained
- QU Unconfined Compression
- DS Direct Shear
- K Permeability
- PP Pocket Penetrometer - Approximate Compressive Strength in TSF
- TV Trovane - Approximate Shear Strength in TSF
- AL Atterberg Limits

Groundwater Observations



- PID Photoionization Detector Reading
- Note: additional observation modifiers to be added as appropriate, including approximate amount (e.g. trace debris) at depth interval where encountered

Nov 22, 2019 4:30pm jlaplante K:\Standards\Geotech\KEY TO EXPLORATIONS geotechnical.dwg 1

STANDARD OPERATING PROCEDURE

THIN WALL SAMPLING

Introduction

Undisturbed¹ soil sampling is performed using a thin wall (a.k.a. Shelby tube) sampler advanced by hand, or hydraulically pushed from a land- or water-based drill rig. Thin wall sampling is generally used to collect undisturbed soil cores of 24 to 36 inches in length. A series of consecutive cores may be extracted with a thin wall sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling for a discrete sample interval. In the case of discrete interval sampling, the thin wall sampler is pushed to its sampling depth through the bottom of the augured hole and the core extracted. A thin wall sampler is ideal for collecting relatively undisturbed subsurface geotechnical samples for advanced geotechnical laboratory testing. When thin wall sampling is performed to gain geologic information, all work should be performed in accordance with ASTM D1587, "Thin-Walled Tube Sampling of Soils for Geotechnical Purposes". This SOP describes the collection of soil samples using the thin walled sampler.

Thin Wall Sample Collection and Processing

The following procedures are used for collecting soil samples with a thin-walled sampler:

1. Assemble the sampler by attaching the driving head to the sampling tube.
2. Place the sampler in a perpendicular position on the sample material. Where a drill rig is used, this step is performed by the drilling contractor.
3. Use a smooth continuous push to advance the tube. Do not drive past the bottom of the sample length. Where a drill rig is used, this step is performed by the drilling contractor.
4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, as well as the detailed information described in this SOP.
5. Withdraw the sampler and remove the drive head. The amount of recovery and soil type should be measured recording the depth to soil from both the top and bottom of the sample tube. Note any aberrations such as rocks or other objects visible in the drive end of the sampler, or any visible damage to the sample tube.
6. Fill any voids in the sample tube with packing material such as bubble wrap or wax.
7. Tightly seal both ends of the sample tube, and visually indicate the top of the tube with markings on the outside of the tube.

¹ The term "undisturbed" is relative for soil sampling. All soil sampling induces some disturbance to the sample. Thin-walled sampling induces the least disturbance, compared to other methods such as standard penetration test (SPT) split-spoon sampling.

8. Store sample upright in a protected and dry location outside of direct sunlight.

Required Information on Boring Logs

Logs shall include the following information, at a minimum, to describe the sampling work:

1. The sample station identification
2. Names of field personnel collecting and handling the samples
3. Type of sampling equipment used
4. Date and time at the start and completion of each boring location
5. Total depth of boring penetration below ground surface or mudline
6. Depth of water and time of measurement for barge-based drilling
7. Date and time of collection of each sample
8. Driller observations regarding changes in subsurface conditions, and depth of drilling equipment at the time of observation (e.g. gravelly drill action, hard penetration, etc.)
9. Observations made during sample collection, including weather conditions, complications, and other details associated with the sampling effort
10. Length and depth intervals of each sample and measured recovery
11. Qualitative notation of apparent resistance during driving
12. Any deviation from the approved SAP

Thin Wall Sample Handling

Thin wall tube samples do not allow for direct observation or logging in the field. When recovered from the boring, the tubes will be measured for amount of recovery and checked to ensure the tube was not dented or damaged while driving or removing. The tubes will then be quickly cleaned, sealed with a plastic cap and duct tape on both ends, and labeled with boring name, sample name, date, approximate depth, and the location of the top of the sample with respect to the orientation it was removed from the subsurface. Every effort will be made to store and transport the thin wall sample tubes with minimal disturbance in the upright, vertical position.

Standard terminology for field logs is attached to this SOP.

Sample Description

Classification of soils in this report is based on visual field and laboratory observations which include density/consistency, moisture condition, grain size, and plasticity estimates and should not be construed to imply field nor laboratory testing unless presented herein. Visual-manual classification methods of ASTM D 2488 were used as an identification guide.

Soil descriptions consist of the following:

Density/consistency, moisture, color, minor constituents, MAJOR CONSTITUENT, additional remarks.

Density/Consistency

Soil density/consistency in borings is related primarily to the Standard Penetration Resistance. Soil density/consistency in test pits is estimated based on visual observation and is presented parenthetically on the test pit logs.

Density SAND or GRAVEL	Standard Penetration Resistance (N) in Blows/Foot	SILT or CLAY Consistency	Standard Penetration Resistance (N) in Blows/Foot	Approximate Shear Strength in TSF
Very loose	0 - 4	Very soft	0 - 2	<0.125
Loose	4 - 10	Soft	2 - 4	0.125 - 0.25
Medium dense	10 - 30	Medium stiff	4 - 8	0.25 - 0.5
Dense	30 - 50	Stiff	8 - 15	0.5 - 1.0
Very dense	>50	Very stiff	15 - 30	1.0 - 2.0
		Hard	>30	>2.0

Moisture

Dry	Little perceptible moisture
Damp	Some perceptible moisture, probably below optimum
Moist	Probably near optimum moisture content
Wet	Much perceptible moisture, probably above optimum

Minor Constituents





Estimated Percentage

Not identified in description	0 - 5
Slightly (clayey, silty, etc.)	5 - 12
Clayey, silty, sandy, gravelly	12 - 30
Very (clayey, silty, etc.)	30 - 50




Legends

Sampling Test Symbols

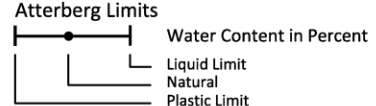
BORING SAMPLES

	Split Spoon
	Shelby Tube
	Cuttings
	Core Run
*	No Sample Recovery
P	Tube Pushed, Not Driven

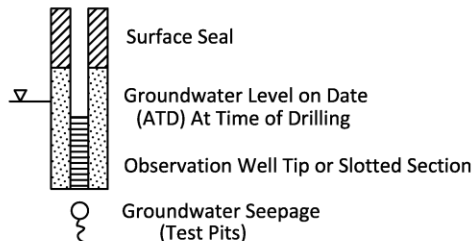
TEST PIT SAMPLES

	Grab (Jar)
	Bag
	Shelby Tube

Test Symbols

GS	Grain Size
Comp	Composite
Chem	Chemistry
NS	No Sheen
SS	Slight Sheen
MS	Moderate Sheen
HS	Heavy Sheen
TCD	Triaxial Consolidated Drained
QU	Unconfined Compression
DS	Direct Shear
K	Permeability
PP	Pocket Penetrometer Approximate Compressive Strength in TSF
TV	Torvane Approximate Shear Strength in TSF
CBR	California Bearing Ratio
MD	Moisture Density Relationship
AL	Atterberg Limits 
PID	Photoionization Detector Reading
CA	Chemical Analysis
DT	In Situ Density Test

Groundwater Observations



STANDARD OPERATING PROCEDURE

CONE PENETROMETER TESTING

Introduction

Cone Penetrometer Testing (CPT) is generally used to develop a continuous profile of subsurface soil/sediment geotechnical characteristics. CPT penetration tip resistance, side friction, and pore water pressure are continuously measured as the instrumented probe is advanced into the subsurface. These three parameters are further processed to develop a range of geotechnical engineering soil classification parameters using industry-standard protocols for interpreting CPT data. This SOP describes subsurface data collection using the CPT.

CPT Data Collection and Processing

The electric piezocone penetrometer test procedure involves hydraulically pushing in instrumented cylindrical rod into the subsurface at a constant rate of two centimeters per second and subsequently monitoring soil and pore fluid response near the conical tip. The cylindrical rod houses a pressure transducer and load cells which, during probing, measure the parameters indicated above. The results are used with engineering judgment in conjunction with other tests, preferably the SPT procedure, which allows soil sample collection for direct comparison purposes. CPT tests are performed in general accordance with procedures outlined in ASTM D 5778, Standard Test Method for Electronic Friction Cone and Piezocone Penetration Testing of Soils.

The cone system is mounted on heavy equipment to provide the necessary reaction for the applied loads. The cone tip has a surface area of about 10 square centimeters (cm^2) and an angle of 30 degrees from the axis. The friction sleeve has a surface area of about 150 cm^2 . Prior to testing, a plastic filter element, which has been saturated under vacuum in glycerin, is placed behind the cone tip. This filter element transmits pore pressures to the transducer. Load cells measure end resistance on the tip and frictional resistance on the friction sleeve. As the cone penetrates the soil, measurements are continuously recorded on a portable computer at depth increments of about 5 centimeters.

The classification method used to develop an interpreted soil profile is based on normalized parameters provided by the piezocone, as there are no soil samples collected with a penetrometer system of this type. The relationship between the cone tip resistance and friction ratio, which has been normalized for soil overburden stresses, can be established to predict soil behavior (e.g. Sabatini et. al. 2002).

Commercial software is often used to process raw CPT data and to provide geologic and geotechnical engineering interpretations of subsurface conditions. Some CPT contractors provide a complete report, with data interpretation as part of their deliverable. In other cases, CPT contractors may provide interpreted data and raw data for independent interpretation.

Independent interpretation of raw CPT data can be performed by commercial software programs. At Anchor QEA, the software package CPeT-IT by Geologismiki is used for raw CPT data interpretation, and CLiq by Geologismiki is used for liquefaction evaluations of CPT data.

Where commercial software is not used to process raw CPT data, the methods described in Sabatini et. al. (2002) will be used to process CPT data for use in geotechnical engineering evaluations.

References

Sabatini, P.J., Bachus, R.C., Mayne, P.W., Schneider, J.A., and Zettler, T.E., 2002. *Geotechnical Engineering Circular No. 5, Evaluation of Soil and Rock Properties, Report No. FHWA-IF-02-034*. U.S. Department of Transportation, Federal Highway Administration, Washington, D.C.

STANDARD OPERATING PROCEDURE

DYNAMIC CONE PENETROMETER TESTING

Introduction

Dynamic Cone Penetrometer (DCP) testing is generally used to develop a continuous profile of subsurface blowcounts indicating relative density of soils, using handheld equipment for locations with difficult access. DCP blowcounts can be correlated to standard penetration test (SPT) blowcounts for further use in classifying site subsurface soils. This SOP describes subsurface data collection using the DCP.

DCP Data Collection and Processing

DCP data collection entails advancing a 10-square-centimeter field point fixed to the end of a drive rod that is driven continuously through a series of hammer blows. The blows are delivered to the top of the 1-meter-long drive rod through the raising and dropping of a 35-pound weight at a consistent fall height of 15 inches. The number of blows is recorded for each 10-centimeter interval for the full drive length. Additional 1-meter drive rods are added as needed until refusal or the desired investigation depth is reached. The blow count data obtained are then correlated to an equivalent SPT N-value for each 10-centimeter interval. The SPT N-values are then used to estimate the geotechnical engineering properties of interest.

EQUIPMENT AND SUPPLIES REQUIRED

- 10-square-centimeter field points (sacrificial)
- 1-meter drive rods with marks at 10-centimeter intervals and thread connections
- Driver hammer attachment with 35-pound weight with minimum 15 inches of throw
- Driving head (threaded connection)
- Mechanical drive rod extractor
- Base plate for drive rod extractor
- Equipment carrying case
- Field logbook, surface soil field collection form, and pens
- Project-specific Field Sampling Plan (FSP) and Health and Safety Plan (HASP)
- Personal protective equipment (safety glasses, steel-toed boots, work gloves, and any other items required by the project-specific HASP)
- Decontamination equipment

PROCEDURES

Performing the Exploration

1. Expose the soil surface by clearing an approximately 1-square-foot area at the sampling site of any surficial detritus that may otherwise create an obstruction
2. Ensure the driving head is threaded onto a 1-meter drive rod
3. Fix the field point to the driving head
4. Place drive rod and field point unit on the ground with field point resting on the desired location of the exploration
5. Connect the driver attachment with the 35-pound hammer
6. Seat the field point by raising and dropping the driver until the field point is fully embedded in the subsurface
7. Begin raising and dropping the driver and count the number of blows required for 10 centimeters of advancement
 - a. Record the blows for each 10-centimeter drive interval; manual adjustments may be needed to maintain verticality of the drive rods
 - b. Record any obstructions/zones of difficult driving or apparent changes in substrate that occur within the 10-centimeter interval, if applicable, on the field data collection form
8. Connect additional drive rods as needed until refusal or the desired drive depth is achieved
 - a. Refusal is assumed to be 50 blows per 10 centimeters or less
 - b. Leave approximately 0.5 meters of stickup of the last rod for extraction
9. After the target depth or refusal is reached, place the base plate near the rod and fix the extractor and begin retrieving the rods
 - a. The drive hammer may need to be removed to allow for extraction of drive rods
 - b. Care must be applied when extracting the rod so as to not drop loose rods back down the hole
10. Decontaminate equipment, if necessary

Data Processing

1. Input the data obtained for each exploration into the data processing spreadsheet, which was developed based on methods described in Triggs and Simpson (1991), attached.
2. The depth, field recorded blow count, and equivalent SPT N-value are reported for the processed data

Quality Assurance and Quality Control

1. Complete all pertinent field quality assurance (QA)/quality control (QC) documentation, logbooks, sample labels, and field data sheets
 - a. Record any deviations from the specified sampling procedures or any obstacles encountered
2. Record actual exploration locations with field measurements from landmarks or a Differential Global Positioning System (DGPS) recording device
3. Photograph the sample location and document it in the logbook
4. Decontaminate all sampling equipment as appropriate

References

Triggs and Simpson, 1991. *A Portable Dynamic Penetrometer for Geotechnical Investigations*. 34th Annual Meeting, Association of Engineering Geologists. Chicago, IL.

Attachment

A PORTABLE DYNAMIC PENETROMETER FOR GEOTECHNICAL INVESTIGATIONS

J. Fred Triggs, P.E.,
Triggs Technologies, Inc., Willoughby Hills, OH 44094

Paul D. Simpson, P.E.,
University of Akron, Akron, OH 44325

INTRODUCTION

Most of us are frustrated by our human inability to "see" into the ground. Without special instruments, we can only see, probe, or squeeze the very surface of the ground. Such looks, probes, and squeezes give little reliable information about its ability to support loads because its supporting properties depend upon the soils' strength, deep within the ground.

The authors have developed and tested a lightweight dynamic cone penetrometer which one person can carry to remote locations where he can readily test for strength properties to deep within the soil. A means of injecting fluid into the cone path annulus to reduce parasitic friction dynamic energy loss is described. A logging program which quickly reduces the penetrometer's blow count data to dynamic cone resistances, plots these resistances, and interprets them, is described and illustrated. Calibration of this dynamic cone penetrometer has been accomplished by the authors' correlations of side-by-side dynamic cone resistances with Standard Penetration Test N values in various soil types. This paper proposes correlations between this penetrometer's dynamic cone resistances and SPT N values.

THE NEED FOR A PORTABLE SOIL EVALUATION INSTRUMENT

The normal commercial structure needs and generally receives a subsurface exploration including test borings with SPT N values and laboratory strength testing of soil samples. But it is often impractical to use test borings to:

- a. preliminarily explore the subsurface in densely wooded, building covered, swampy, or steep terrain sites.
- b. explore the subsurface for single-family residences.
- c. evaluate earth fill compaction.
- d. verify footing bearing capacities during construction.

REQUIREMENTS FOR A PORTABLE PENETROMETER

For such a penetrometer to be most useful, it must be usable by a single person; portable, in that it can be carried to test locations; small enough to travel in the trunk of a

car; versatile enough to test any soil type; sensitive enough to differentiate between weak, medium, and strong soils; and simple to interpret.

DESIGN OF THIS DYNAMIC PENETROMETER

The authors followed these specifications to develop and test a light dynamic cone penetrometer with the characteristics of:

- a. An unmotorized (hand-raised) hammer with a 35 lb weight and a 15 inch drop, to provide the energy for driving a 10 cm² projected area cone. This can be transported in a car trunk, carried by one person, and worked by one person to test all but the most consolidated soils. As testing progresses below the first meter, additional 1 meter long sounding rods are screwed onto the rod string.
- b. A fluid injection system, pumps a cellulose/water mixture into the annulus between the 1.4" diameter cone path and the 1.1" diameter rods, minimizing parasitic friction on the rods. Consequently, undiminished hammer energy is transmitted to the cone, allowing confident use of the Dutch Formula to calculate cone resistance (q_d). The rods slip out of the "lost point" cones to be pulled from the slurry-filled hole by hand. Cellulose slurry biodegrades.
- c. A simple spread-sheet computer program logs the hammer blows per 10 cm; calculates, plots, and tabulates dynamic cone resistances (q_d); and tabulates consistency adjectives.

Unfortunately, this penetrometer, like other dynamic cone penetrometers, does not ascertain the grain size of the tested soils. Consequently, although the data tells much about soils' relative densities, the data does not indicate whether the soils are clay, silt, or sand. Where determination of soil grain sizes is important, that information must be found by some method other than by dynamic cone testing.

REDUCTION AND LOGGING OF DYNAMIC PENETROMETER DATA

In this paper, dynamic cone resistance, q_d , is the cone resistance pressure in Kg/cm², calculated by the "Dutch Formula". In that formula,

$$q_d = \frac{M^2 \times H \times N_d}{A_p(M + M' + P_a)10}$$

where,

M = Mass of the hammer = 35# x 0.453 = 15.89 Kg

H = Height of Drop = 15" x 2.54 = 38.1 cm

N_d = Number of blows per 10 cm of drive

A_p = Projected area of the cone = 10 cm²

M' = Mass of the driven portion of the hammer = 2.49 Kg

P_a = Mass of the rod string = 3.26 Kg x the number of rods.

This means that the dynamic cone resistance, in Kg/cm², is:

4.44 x N_d for 1 sounding rod

3.86 x N_d for 2 sounding rods

3.42 x N_d for 3 sounding rods

3.06 x N_d for 4 sounding rods

2.77 x N_d for 5 sounding rods

2.54 x N_d for 6 sounding rods
2.33 x N_d for 7 sounding rods
2.16 x N_d for 8 sounding rods
2.01 x N_d for 9 sounding rods
1.89 x N_d for 10 sounding rods

The program for logging a dynamic cone penetration test is illustrated in figure 1. The hammer blows per 10 cm are entered. A spread sheet program tabulates these figures, and calculates, tabulates, and plots the dynamic cone resistances. The program also tabulates three columns of consistency adjectives: one for sand, one for silt, and one for clay.

PENETROMETER CALIBRATION BY CORRELATIONS WITH SPT N VALUES

Since many of us in North America are most comfortable evaluating soil strengths from Standard Penetration Test in-situ test results, we have correlated dynamic cone resistance of the dynamic penetrometer with SPT N values by using both test types in close proximity. In the reduction of the correlation test data, we compared the average of three 10 cm long dynamic cone resistances with the corresponding 12 inch SPT N value.

Soil samples are a byproduct of SPT testing, so we took the opportunity to either visually estimate or test for the mean soil particle size of each SPT test sample. These determinations of d_{50} in mm were used in our q_d/N versus d_{50} plot of Figure 2.

(Robertson, Campanella, and Wightman, 1983) in correlating static cone resistances, q_c with SPT N, found that q_c/N increased from approximately 1 for clays to approximately 8 for sands. We have not found a similar increase of q_d/N to be characteristic of dynamic cone resistances. Perhaps because the dynamic cone penetrometer and the Standard Penetration Test both employ a dynamic penetration force, their relationships are more linear than the relationship of static cone and dynamic SPT.

Figure 3 plots our currently available q_d versus N correlations. Each plotted point indicates whether it is a clay, silt, or sand soil type. By plotting q_d directly, rather than the ratio of q_d/N , one can see how at higher blow counts, the q_d/N values increase. We believe that this is caused by the relatively low energy of the dynamic penetrometer, compared to the higher energy of SPT.

CONCLUSIONS

We do believe that this dynamic cone penetrometer, as developed, is a valid instrument for estimating approximate strengths of nearly all soils to reasonable depths. It correlates well with N values of SPT borings. With q_d values up to 90 Kg/cm², q_d/N ratios are approximately 3.5.

Two technical reservations of this penetrometer should be understood. The first reservation is that this penetrometer tells nothing about whether a soil is clay, silt, or sand. The second reservation is that when the q_d values of the cone exceed approximately 90 Kg/cm², SPT N values exceed 25, but are indeterminate.

Most soil evaluation concerns focus on soils with SPT N values less than 15. This penetrometer provides a continuous stream of accurate soil strength data through the entire 0 to 25 range of SPT N values. Consequently, the penetrometer is both usable and most valuable in the soils that require the most concern.

TRIGGS TECHNOLOGIES, INC.
 33977 CHARDON ROAD
 WILLOUGHBY HILLS, OHIO 44094

SHEET #: 1
 FILE #: 1
 STARTED: 4/27/90
 COMPLETED: 4/27/90

 WILDCAT DYNAMIC
 CONE PENETROMETER LOG

CREW: ACT
 TEST #: DEMO
 PROJECT: NONE
 LOCATION: HAYES DRIVE

SURFACE ELEVATION:
 HAMMER WEIGHT: 35 LBS.
 CONE AREA: 10 SQ. CM
 HAMMER DROP: 15"

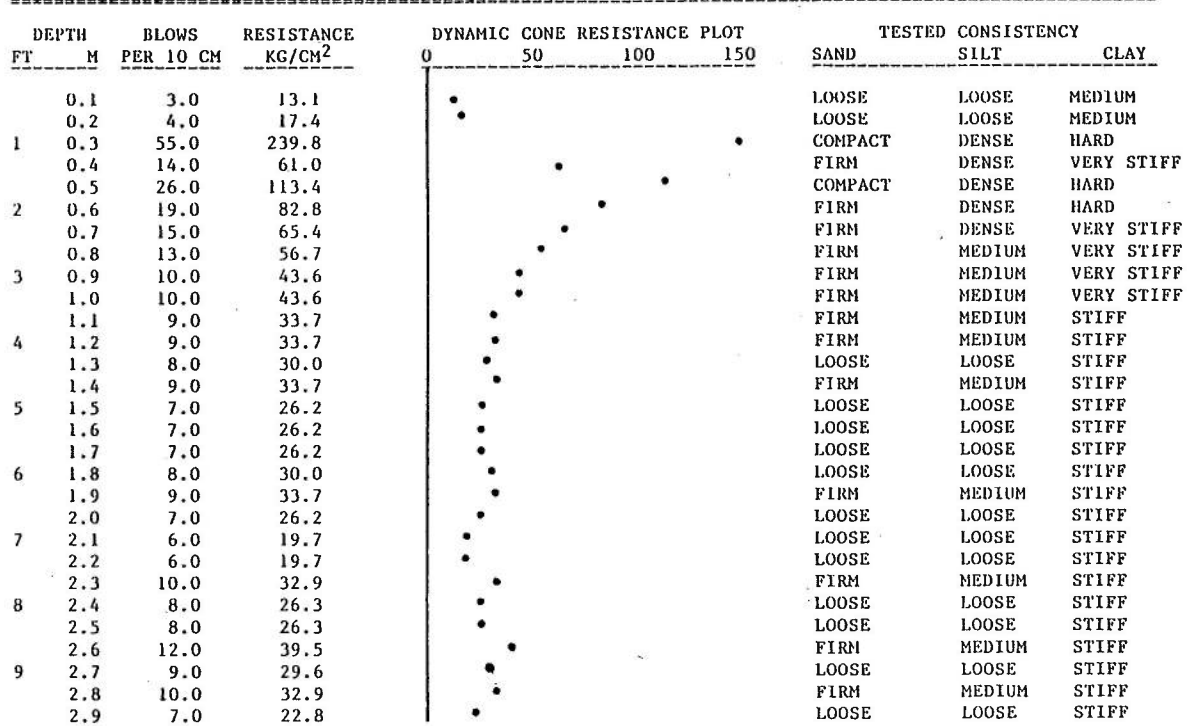


FIGURE 1

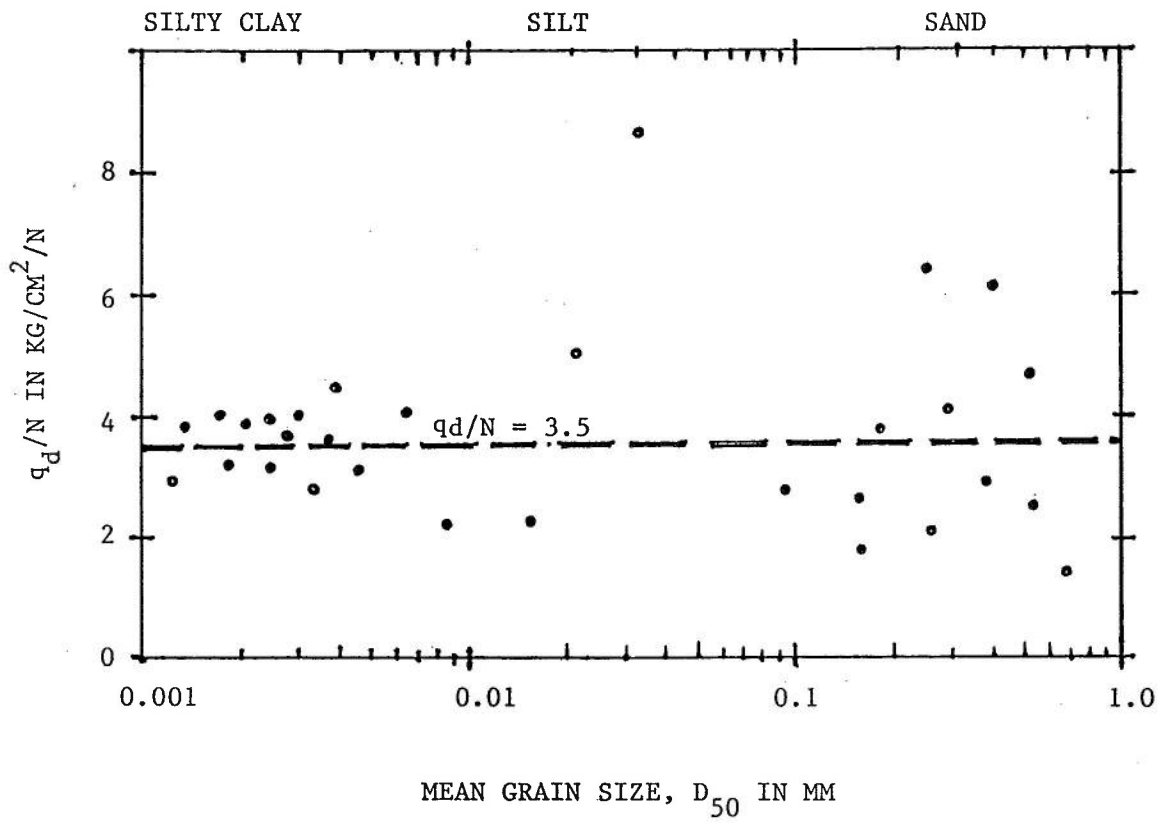


FIGURE 2

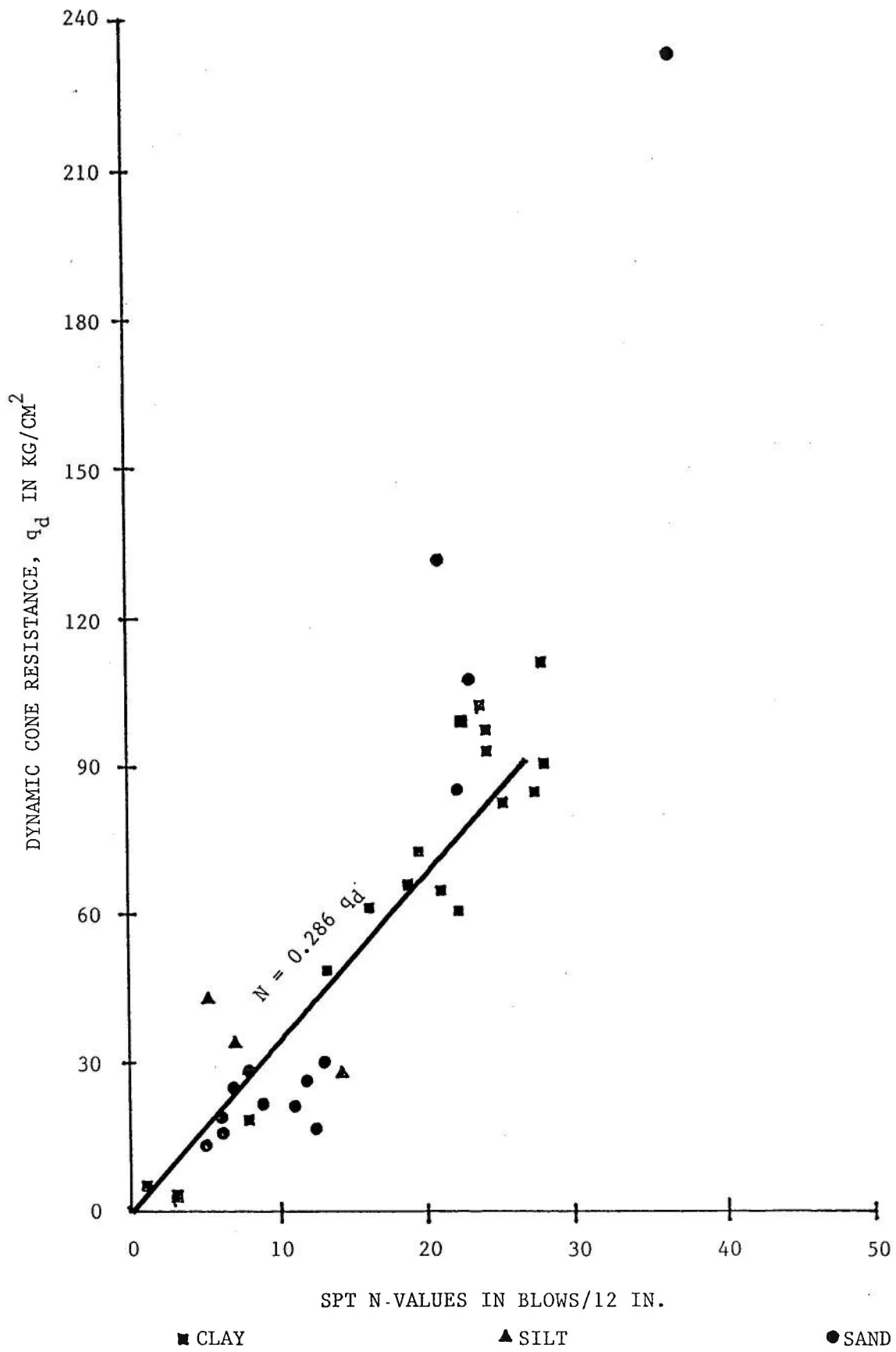


FIGURE 3

REFERENCE

Robertson, P.K.; Campanella, R.G.; and Whitman, A., "SPT-CPT Correlations," Journal of Geotechnical Engineering, Vol. 109, No. 11, (Nov. 1983), 1449-1459.

The information below was presented to the 34th Annual AEG Meeting, but was not included in the Proceedings.

HOW MUCH ENERGY REACHES THE CONE?

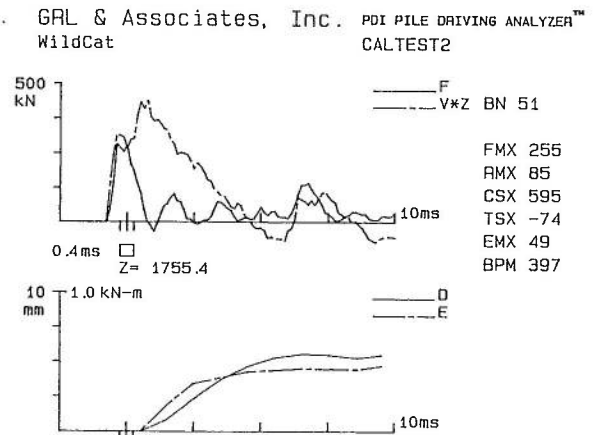
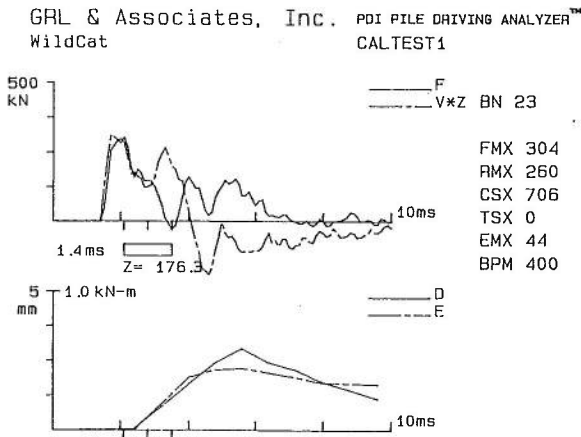
ASTM D 4633-86 specifies a method for measuring the portion of a dynamic penetrometer's kinetic energy that is available to drive the tip. GRL and Associates, Inc. instrumented a WILDCAT DYNAMIC CONE PENETROMETER with two accelerometers and two strain transducers and used a pile driving analyser and their CAPWAP program to estimate the effective energy during both easy and hard driving. For easy driving ($N_d = 7$ blows/10 cm), 82 percent of the kinetic energy was found to be effective. For hard driving ($N_d = 130$ blows/10 cm), the effective energy was measured as 73 percent. In the arena of dynamic penetrometers, these effective energy percentages show the WILDCAT to be exceptionally efficient. The Force, Velocity, and Energy plots of both the hard and easy driving typical blows, and a photograph of the instrumented penetrometer are shown below.

HARD DRIVING

$N_d = 130/10$ cm

EASY DRIVING

$N_d = 7/10$ cm



$$\frac{E_{\max}}{E_{KE}} = \frac{44}{60} = 73\%$$

$$\frac{E_{\max}}{E_{KE}} = \frac{49}{60} = 82\%$$



INSTRUCTION MANUAL

FIELD INSPECTION VANE TESTER

Model H-60

© Roctest Limited, 2005. All rights reserved.

This product should be installed and operated only by qualified personnel. Its misuse is potentially dangerous. The Company makes no warranty as to the information furnished in this manual and assumes no liability for damages resulting from the installation or use of this product. The information herein is subject to change without notification.

Tel.: 1.450.465.1113 • 1.877.ROCTEST (Canada, USA) • 33 (1) 64.06.40.80 (Europe) • www.roctest.com • www.telemac.fr

TABLE OF CONTENTS

1	APPLICATIONS	1
2	PRODUCT	1
2.1	Description	1
2.2	Operation principle	2
3	OPERATION AND READING PROCEDURES.....	2
3.1	Generalities.....	2
3.2	General procedures	2
3.3	Special procedures	4
4	CONVERSION OF READINGS	4
5	MAINTENANCE.....	4
6	CONVERSION FACTORS.....	5

1 APPLICATIONS

The inspection vane borer is used to measure in situ undrained shear strength in clays. It is primarily intended for use in trenches and excavations at a depth not influenced by drying and excavation procedure.

When different sizes of vanes are used, the instrument range is from 0 to 260 kPa. The accuracy of the instrument should be within 10% of the reading.



Figure 1: H-60 vanes in three different sizes

2 PRODUCT

2.1 DESCRIPTION

The vane tester consists in two parts: the vane with its shaft and the measurement part with its handle.

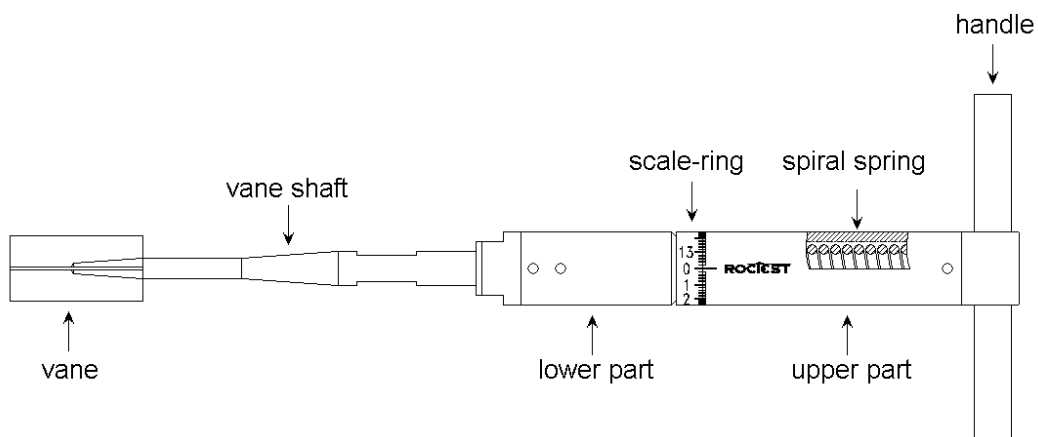


Figure 2: H-60 vane borer

The scale-ring is graduated from 0 to 130 kPa.

Three sizes of four-bladed vanes can be used:

- small: 16 x 32mm
- medium: 20 x 40mm (standard)
- large: 25.4 x 50.8mm

They make it possible to measure shear strength of 0 to 260, 0 to 130 and 0 to 65 kPa respectively.

2.2 OPERATION PRINCIPLE

The measurement part of the instrument is a spiral spring. When the handle is turned, the spring deforms. The upper part and the lower part of the instrument get a mutual angular displacement which depends on the torque applied. The shear strength of the soil is obtained by means of a scale-ring.

The lower and upper halves of the instrument are connected by means of threads. The scale is also supplied with threads and follows the upper part of the instrument by means of two lugs. The zero-point is indicated by a line on the upper part. When torque is applied, the scale-ring follows the upper part of the instrument, and when failure in the soil is obtained, the scale-ring will remain in its position due to the friction in the threads.

3 OPERATION AND READING PROCEDURES

3.1 GENERALITIES

The vane blades are soldered to a shaft which again is extended by one or more 49 cm long rods. The connection between the shaft-rods and the instrument is made by threads. To make the connections as straight as possible, the rods have to be screwed tight together and threads cleaned for dirt.

In clays with shear strength of 260 kPa, a force of about 40 to 50 kilos is required to press the vane down into the soil. The shaft is designed to take this force, but if extension rods are used, precautions against buckling are required.

3.2 GENERAL PROCEDURES

1. Connect required vane and extension rods to the inspection vane instrument.

Note: While screwing vane or rods to instrument, hold onto lower part.

2. Push vane into the ground to the required position.

Note: Do not twist inspection vane during penetration.

3. Make sure that the scale-ring is set to zero-position.

4. Turn handle clockwise.

Note: Turn as slowly as possible with constant speed.

Be careful not to turn the handle over 360°, otherwise the spring inside the instrument may be permanently damaged.

5. When the lower part follows the upper part around or even falls back, failure and maximum shear strength is obtained in the soil at the vane.
6. Holding handle firmly, allow it to return to zero-position.

Note: Do not allow the handle to spring back uncontrolled.

7. Note the reading on the graduated scale.

Note: Do not touch or in any way disturb the position of the graduated ring until the reading is taken.

8. Write down the reading together with position of hole and depth.
9. Turn the graduated scale anti-clockwise back to zero-position.
10. To determine the remoulded shear strength, the following procedure is used:
 - Turn the vane quickly at least 25 revolutions. Do not turn using handle. Turn using wrenches provided.
 - Zero the scale and take at least two measurements by turning the instrument as slowly as possible.
 - The minimum value is considered the correct one.
11. Push the vane down to next position. If necessary, screw on another extension rod.
12. Repeat the above measurement procedure (steps 3 to 10).
13. When the last reading is taken, pull the vane up. If soil is comparatively soft, this can be done by hand, gripping the handle. In harder soils, some mechanical device might be necessary. It is then advisable to connect this device directly to the connection rods (not to the instrument).

3.3 SPECIAL PROCEDURES

When measuring the shear strength at greater depths, the friction between soil and extension rods can be appreciable, and must be taken into consideration.

To measure the friction, extension rods and a vane-shaft without vane (dummy) are pushed into the ground to the depths required for shear force measurements. The torque due to friction is then measured in the same way as when using vanes (steps above from 3 to 9). The friction torque thus obtained is used to evaluate the actual shear strength from the measured shear strength.

To penetrate through firm layers a pre-boring using a rod with the same diameter as the vane may be helpful.

4 CONVERSION OF READINGS

The shear strength depends on the size of vane the instrument is used with. Multiply the reading of the scale-ring by the correct factor in the table below.

$$\text{Shear strength (kPa)} = \alpha \cdot \text{Reading}$$

Vane size in mm	Multiplicative factor α
16 x 32	2
20 x 40	1
25.4 x 50.8	0.5

Table 1: Factors to use for conversions

Note: If a correction on the shear strength should be applied because of friction on the shafts, do the correction on the reading before applying the vane coefficient by subtracting the torque friction. Please refer to the ASTM standard D2573 (volume 04.08) for more information.

5 MAINTENANCE

The H-60 vane borer is simply designed, and does not require much attention. But it is most important to keep it as clean as possible. Periodically, the instrument should be sent back to factory for verification.

6 CONVERSION FACTORS

	To Convert From	To	Multiply By
LENGTH	Microns	Inches	3.94E-05
	Millimetres	Inches	0.0394
	Meters	Feet	3.2808
AREA	Square millimetres	Square inches	0.0016
	Square meters	Square feet	10.7643
VOLUME	Cubic centimetres	Cubic inches	0.06101
	Cubic meters	Cubic feet	35.3357
	Litres	U.S. gallon	0.26420
	Litres	Can-Br gallon	0.21997
MASS	Kilograms	Pounds	2.20459
	Kilograms	Short tons	0.00110
	Kilograms	Long tons	0.00098
FORCE	Newtons	Pounds-force	0.22482
	Newtons	Kilograms-force	0.10197
	Newtons	Kips	0.00023
PRESSURE AND STRESS	Kilopascals	Psi	0.14503
	Bars	Psi	14.4928
	Inches head of water*	Psi	0.03606
	Inches head of Hg	Psi	0.49116
	Pascal	Newton / square meter	1
	Kilopascals	Atmospheres	0.00987
	Kilopascals	Bars	0.01
Kilopascals	Meters head of water*	0.10197	
TEMPERATURE	Temp. in °F = (1.8 x Temp. in °C) + 32 Temp. in °C = (Temp. in °F - 32) / 1.8		

* at 4 °C

E6TabConv-990505

Table 2: Conversion factors



Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Mercury Cold Vapor Analysis

SOP 547S
Version 001

Revision Date: 3/27/19
Effective Date: 3/27/19

Prepared by:

Eric Larson / Tyler Hightower

Approvals:

A handwritten signature in blue ink that reads "Eric Larson".

Eric Larson, Inorganics Division Manager

A handwritten signature in blue ink that reads "David R. Mitchell".

David R. Mitchell, Quality Assurance Manager



digested water, soil, and tissue samples plus the extracts generated from the TCLP and SPLP procedures. The instrument used is a Leeman Labs Hydra II AA.

- 1.2. This method, with modifications to accommodate the use of the Hydra instrument, is consistent with USEPA Methods SW-846 7470A, 7471A and 245.1 and 245.5.
- 1.3. All samples must be digested with the appropriate method prior to analysis. Refer to SOPs 511S and 532S for solids and 535S for waters and aqueous extracts.
- 1.4. The analytical range of this procedure is 0.1 to 10 µg Hg/L. This range can be extended with sample dilution or by increasing or decreasing the sample size.

2. Summary of the Procedure

- 2.1. Cold vapor atomic absorption spectroscopy (CVAAS) is a method based on the absorption of radiation at 253.7 nm by atomic mercury vapor.
- 2.2. The samples are digested then further treated with stannous chloride to reduce the mercury in the samples to the elemental state. The mercury is aerated from the solution to the analyzer by a carrier gas. The vapor passes through the light path of a mercury emission source, absorbing some of the light as it passes. The absorbance is measured and related to the mercury concentration in the sample. Unknown samples are run against a calibration curve generated by standards of known concentration

3. Definitions

- 3.1. CVAAS - Cold Vapor Atomic Absorption Spectroscopy
- 3.2. Detection Limit (DL) - As defined in DoD QSM 5.0; the smallest concentration that can be demonstrated to be different from zero or a blank concentration with 99% confidence.
- 3.3. Limit of Detection (LOD) - As defined in DoD QSM 5.0; the smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence.
- 3.4. Limit of Quantitation (LOQ) - As defined in DoD QSM 5.0; the smallest concentration that produces a quantitative result with known and recorded precision and bias. Often referred to as the reporting limit (RL).
- 3.5. SD - Standard Deviation
- 3.6. RSD - Relative Standard Deviation - The SD divided by the mean, multiplied by 100.
- 3.7. RPD - Relative Percent Difference - The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.
- 3.8. %R - Percent Recovery - The difference between the spike concentration and the original sample concentration divided by the concentration of the spike added multiplied by 100.
- 3.9. LIMS (Element) - Laboratory Information Management System - ARI's computerized sample data and analytical data system.



4. Interferences

- 4.1. Several interferences have been reported for samples containing sulfide, chloride and high amounts of organic material which have a broad absorbance band around 253.7 nm. Because effects from these interferants are difficult to quantitate the sample preparation and quality control procedures must be followed.
- 4.2. Contamination during the preparation and analysis of low-level mercury samples can be very problematic. Proper care should be taken to ensure that all reagents, glassware and equipment are free of mercury sources and samples are not subjected to environmental sources of mercury such as airborne dust.

5. Safety

- 5.1. The mercury samples and reagents contain strong oxidizing and reducing compounds. The mercury reagents are made in excess; that is, the concentration of the reagents is very high to drive the reaction equilibrium equation to one side or the other. Therefore, the solutions must be handled with care and proper safety equipment must be worn at all times. Gloves, safety goggles, and a lab coat for protection are a must.
- 5.2. Mercury compounds are known to be highly toxic if swallowed, inhaled, or absorbed through the skin. Acidification of samples may release toxic gases such as cyanides or sulfides requiring that all sample preparation must be performed in a fume hood.
- 5.3. The work area must be kept clean to eliminate the possibility of contamination, and also as a safety issue to protect the analyst from the hazards of the reagents, as described in section 5.1.
- 5.4. Safety data sheets are available to all employees in hardcopy format located in the file cabinet by the main copier or electronically as linked on the ARI Intranet homepage.

6. Equipment and Supplies

- 6.1. Leeman Labs Hydra II AA, interfaced with a controlling computer running Version 2.1 Software.
- 6.2. Compressed nitrogen gas, "High Purity" grade (99.998% purity), with regulator.
- 6.3. Adjustable air displacement pipettes with disposable tips that have been calibration checked.

7. Reagents and Supplies

- 7.1. Deionized water, ASTM Type I, that is produced with the in-house water system.
- 7.2. 14% Hydroxylamine hydrochloride/sodium chloride solution - Dissolve 144 grams of hydroxylamine hydrochloride (or 144 grams of hydroxylamine sulfate) and 144 grams of sodium chloride in deionized water and dilute to 1000 mL with deionized water. Use reagents that have been certified to be low in mercury. Label the solution bottles with the date of preparation, batch number, and initial.



- 7.3. 10% Stannous chloride solution – To approximately 500 mL of deionized water, with mixing, add 70 ml of concentrated Trace Metal Grade HCl. Add 100 grams of stannous chloride and mix until dissolved. Dilute to 1000 mL with deionized water. Use reagents that have been certified low in mercury. Label the solution bottle with the date of preparation, batch number, and initial. When not in use cap tightly and store in the refrigerator. This solution will need to be made approximately every week. Check bottle for precipitate (cloudy appearance or white layer on the bottom). If solution has precipitated, prepare a fresh batch.
- 7.4. 1% HNO₃/HCl rinse solution – To a clean 2000 mL polybottle add approximately 1000 mL of deionized water. Add, with mixing, 20 mL HNO₃ and 20 mL of HCl. Use only concentrated Trace Metal Grade acids that have been lot certified. Bring to a final volume of 2000 mL. This reagent is non-quantitative, and the volume measurements do not need to be exact but should be consistent.
- 7.5. 30% HNO₃ rinse solution – To a clean 500 mL polybottle add approximately 250 mL of deionized water. Add, with mixing, 150 mL of concentrated Trace Metal Grade HNO₃ that has been lot certified. Bring to a final volume of 500 mL. This reagent is non-quantitative, and the volume measurements do not need to be exact but should be consistent.

8. Sample Collection, Preservation Shipment and Storage

- 8.1. All samples should be received in appropriate collection containers and have been properly preserved by the clients.
- 8.2. Samples are checked for proper preservative and stored refrigerated for a maximum of 28 days prior to sample preparation.
- 8.3. All samples received for dissolved metals analysis that have not been field filtered should be unpreserved at the time of receipt. They should be filtered through a 0.45µm filter prior to preservation to a pH<2 with trace metal grade HNO₃.
- 8.4. All samples requiring preservation in the lab will be allowed to stand with refrigeration for a minimum of 24 hours after preservation before preparation and analysis is performed. In some instances, this may not be possible, and the project manager and client will need to be notified.
- 8.5. Some samples are shared with the organic extractions and or conventional laboratories. Sample receiving places these samples in a share bin in Refrigerator 5. SOP 1008S includes procedures for handling shared samples for the Metals Lab.

9. Quality Control

- 9.1. Documentation: The CVAA summary logbook is filled out during the run. Any event or observation or action that is worth noting should be recorded in the appropriate logbook and on the raw data. When the analytical data is complete, a data package for review consisting of all



raw data, and copies of all related logbook pages, is scanned to the calibration in Element. A text file generated during the run, the name of which is based on the date of analysis, should be included for use in the data loading process.

9.2. Initial Demonstration of Performance.

9.2.1. Before any samples can be analyzed by this method the instrument and analysts' performance must be evaluated. This will require the determination of the instrument calibration range, quantitation limits and the analysis of quality control samples to assess the accuracy and precision of the method.

9.2.2. Quantitation limits (DL, LOD and LOQ) must be established initially according to SOP 1018. Quantitation limits must be verified at least quarterly or whenever major changes are made to the instrument or method. Quantitation data will be maintained by the Quality Assurance Department and analyzed according to SOP 1018.

9.2.3. To demonstrate the initial performance of the instrument and the ongoing ability of each analyst a series of quality control samples must be analyzed. For each new analyst a minimum of four samples of known concentration must be processed and analyzed with calculated recoveries within 10% of the true values. This data will be maintained in individual training records and by the Quality Control Officer.

9.3. Calibration Verification (ICV ICB CCV CCB) – Immediately following calibration the ICV standard must be analyzed followed by the ICB with CCV, CCB repeated after every ten samples and at the end of the analytical run. The ICV must be within 10% of the true value whereas the CCV must be within 20%. The ICB and CCB must be less than the reporting limit. If out of control the analysis should be stopped the problem corrected and all samples not bracketed with in control standards reanalyzed. **Note: For drinking water samples, EPA 245.1 the control limit for the ICV is 5% and the CCV 10%.**

9.4. Detection Limit Standard (CRA): The first sample of the analytic run, immediately following the first CCV/CCB set should be a CRA. The true concentration is 0.1 µg/L and should be recovered within 70-130%. If the standard falls outside of these limits the CRA shall be reanalyzed immediately. If the analysis of the reanalysis is in control no further corrective action is required. If the result is again outside the limits the problem should be corrected and the instrument recalibrated.

9.5. Method Blank (MB / BLK) – At least one method blank / reagent blank will be analyzed for each batch of 20 or fewer prepared samples for each matrix type. The values will be used to determine if contamination exist. The value of the MB should be less than 0.1 µg/L (<1RL) or less than ½ the RL for DOD samples.

9.6. Matrix QC Samples – For each batch of 20 or fewer prepared samples of each matrix type at



least one matrix spike and one laboratory duplicate must be analyzed. The matrix spike is a separate aliquot of a client sample that has been spiked with a known amount of analyte. The calculated recovery should be within 75 - 125% of the true value. The matrix duplicate is a separate aliquot of a client sample that is prepped and analyzed at the same time. The calculated RPD should be less than 20%. If the concentration of the sample is < 5X RL, then the difference must be <1RL.

9.7. Method Blank Spike or Laboratory Control Sample (MBSPK / LCS / BS): Laboratory control samples are analyzed with each batch of 20 or less samples. The true value is 2.0 µg/L with control limits of 80 – 120%. If the control limits are not met, all samples in that batch will need to be re-digested and re-analyzed. A corrective action form needs to be filled out.

10. Calibration and Standardization

10.1. Calibration:

10.1.1. A new calibration is performed with a blank and a minimum of 5 standards at different concentrations each day samples are analyzed, for each Hg prep code, and for all samples requiring extra permanganate additions.

10.1.2. The calibration standards are prepared as described in the individual preparation SOPs. The calibration range is 0.1 to 10 µg/L.

10.1.3. In the “Method” tab, under “Calibration”, select “Clear Calibration” to remove the previous calibration results.

10.1.4. To begin calibration, in the “Sequence” tab right-click “Cal 1 – Blank” and select “Start from here”.

10.1.5. After the calibration has been run, it can be viewed in the “Calibration” section of the “Method” tab. Click “Stop” in the instrument software toolbar before reviewing the calibration.

10.1.6. Review the calibration for precision (<5% SD), and for linearity (Rho > 0.995). One Cal standard may be dropped if its RSD is > 10%, or 30% for the lowest standard, by deselecting all 3 reps for the Cal standard. If more than one standard’s RSD or SD is high, or Rho < 0.995, the instrument should be recalibrated, possibly with different standards.

10.1.7. In the “Calibration Data” box click “Accept” and then print the calibration to include with the data.

11. Procedure

11.1. Instrument and sample setup:

11.1.1. Turn on the instrument and wait 20 minutes for warm-up.

11.1.2. Take 10% SnCl₂ solution (section 7.3) out of the refrigerator and check for precipitate



(cloudy appearance or white layer on the bottom). If the solution has precipitate, prepare fresh solution. Replace the rinse solution with fresh 1% HNO₃ /HCl solution (section 7.5). You will want to make about 2000 mL of this solution for a normal analytic day.

- 11.1.3. Check the waste carboy level; if more than 80% full, dispose.
- 11.1.4. On the peristaltic pump, check the peristaltic pump tubing for flatness, indicating the need to change tubing; if tubing change is necessary, change all 5 tubing as a group. Attach the pump tubing as indicated in the Operator Manual. Clamp the pump tubing in place; no adjustment is usually necessary on the tension.
- 11.1.5. Open the Hydra II software by clicking on Hg Analysis Icon. In the "Method" tab, click open and select "ARI 10ppb"
- 11.1.6. Connect the green "sample gas out" connector to the top of the gas liquid separator (GLS).
- 11.1.7. Open the valve on the nitrogen tank; it is not necessary to adjust the regulator (leave at 25 PSI).
- 11.1.8. Turn on the pump by pressing the "Startup" button in the software toolbar. Put the SnCl₂ line in DI water and check that liquid has begun moving through the pump tubing and the autosampler. In the "Method" tab under "Instrument Control", move the autosampler tip to "Air".
- 11.1.9. Check that liquid and gas are moving through the GLS and draining properly.
- 11.1.10. Check the drain line for good flow.
- 11.1.11. Place the SnCl₂ line in the 30% HNO₃ solution (Section 7.5) and let the system rinse for 10 minutes.
- 11.1.12. After the HNO₃ rinse, rinse for an additional 10 minutes with DI water before placing the line in the SnCl₂ solution. Let aspirate for about 3 minutes, until the solution has moved completely through the instrument.
- 11.1.13. Look for the Hg lamp current on the instrument control page and record this value in the Hydra II Hg Analyzer Instrument Logbook.
- 11.1.14. Prepare the samples and standards for analysis. To each sample and standard add the appropriate amount of hydroxylamine hydrochloride/sodium chloride solution (section 7.1). For water samples prepared in 50 ml HotBlock tubes add 1.05 mL of the solution and for soil samples prepared in 100 ml HotBlock tubes add 2.5 mL. Swirl the tube intermittently. The KMnO₄ will be reduced first to MnO₂, a brown solid, and then will dissolve into solution. The sample is ready for analysis when all the MnO₂ has been dissolved. Make sure no KMnO₄ is left on the lid of the Hot Block tube. This step should be performed just prior to analysis. After the KMnO₄ is reduced the samples should be analyzed within 24 hours.
- 11.1.15. Starting with the first prep code, label 50 mL centrifuge tubes as follows: S0, S0.1, S0.5,



S1.0, S2.0, S5.0, S10.0, CB, CCV (4.0 μ g/L), ICV (8.0 μ g/L). Fill them with the appropriate solution and place in the autosampler standards rack in the designated positions. A diagram of the Cal standard rack can be found under the “Sequence” tab. Note: A separate calibration and sample run is performed for each Hg prep code, and for all samples requiring extra permanganate additions.

11.1.16. On the “Analysis” tab, select “New” and name the analysis as the prep code and analysis date (ex. TWM 01-01-18). Click “View” and select “Latest Chapter”.

11.2. Analysis:

11.2.1. To begin initial QC checks, under the “Sequence” tab right-click the “ICV” and select “Start from here”. Review the CVs, CBs, and CRL for results outside control limits (See section 15). Failing QC samples must be reanalyzed before continuing and recalibration may be necessary.

11.2.2. Type the sample labels into the “Sample ID” column in the “Sequence” tab using the element format: 16A0001-01 (Note: the instrument must be stopped prior to typing in the first sample ID). Sample dilutions are typed into the “Vol.” column. Once finished, click “Update” to add the samples to the run list on the left-hand side. CCVs and CCBs are added automatically to the run list every 9 samples. No more than 10 samples may be run consecutively without a CCV and CCB. More samples can be added to the run list at any time.

11.2.3. Pour the samples into labeled test tubes and load autosampler rack in the positions designated in the run list; take care to avoid particulates--filter with syringe filters if necessary. Note: The autosampler tip has a screen that clogs easily. All soils and any particulate filled liquids should be filtered.

11.2.4. Begin sample analysis by right-clicking the desired sample in the run-list and selecting “Start From Here”. Analysis may be paused at any time by clicking “Stop” in the toolbar.

11.2.5. In the “Analysis” tab, check the run periodically for QC control limits of CCVs, CCBs, MBs, MBSPKs, REFs, DUPs and Matrix Spikes. At the same time check the sample precision, the RSD should be <5% for all samples \geq 5 RL. Also check for samples over the calibration range; these can be diluted and rerun.

11.2.5.1. NOTE: Samples are diluted using the calibration blank for the diluent. An example would be, for a 10X dilution, add 1 part sample and 9 parts calibration blank. All dilutions will be made with QC checked pipettes.

11.3. To Print the Run:

11.3.1. After the sample run has been completed for a prep code group, go to the “Report” tab within the “Analysis” tab. Click “Clear All” to clear the previous report data. Select “Statistics”,



then under “Report Spec” click “Load” and select “Hg Report Temp” from the pop-up window. Click the checkbox next to the analytical run chapter on the left-hand side. Under “Output”, click “Report”, then click “Printer”. Name the file as prep code and date (ex. TWM 01-01-18). Then click “CSV File” and name the file with the same format.

- 11.3.2. Make notes on the printout of %R, RPD, REF mg/kg, prep dilution, etc.
- 11.3.3. Shutdown: Move the autosampler tip to “Air” in the “Instrument Control” screen under the “Method” tab and remove the rinse solution line from the rinse container.
- 11.3.4. Put the SnCl₂ uptake line in 30% HNO₃ (section 7.5) for 10 minutes of rinsing.
- 11.3.5. Remove the uptake line from the 30% HNO₃ and place in deionized water for 10 minutes of rinsing.
- 11.3.6. Remove the SnCl₂ uptake line and allow it to aspirate air until the uptake and drain lines run dry.
- 11.3.7. Turn off the peristaltic pump by clicking the “Stop” button on the toolbar.
- 11.3.8. Release the pump tubing clamps. Turn off the instrument main power using the switch on the back of the instrument.
- 11.3.9. Close the valve on the nitrogen gas tank.
- 11.3.10. Disconnect the green “Sample gas out” connector from the top of the GLS.
 - 11.3.10.1. Dispose standards and samples.
- 11.3.11. All maintenance should be noted in the mercury maintenance logbook. If any maintenance needs to be made during a run, observe the following requirements:
- 11.3.12. For In house CLP runs, the instrument must be recalibrated before continuing with analysis.
- 11.3.13. For Routine runs a CV/CB pair should be run before and after any minor maintenance done during an analytic run. If this cannot be done, the instrument must be recalibrated before continuing with analysis.

12. Data Analysis and Calculations

12.1. The data is reviewed by the analyst during the sample analysis run. For each sample, the instrument operating software graphically displays the peak and prints the mean μ Abs, concentration and %RSD. The analyst reviews the data for high samples, high RSDs, baseline changes, QC samples in or out of control limits, and method blank contamination.

12.1.1. Raw data review

12.1.1.1. Note on the raw data and/or an Analyst Notes Sheet any comments on instrument problems, delays, unusual occurrences, etc. Check for any potential problems and especially check the instrument QC checks (CV %R), matrix duplicates RPD, matrix spike



%R, and reference recoveries, as described in section 13.

12.2. CVAA sample logbook review

12.2.1. Copy the appropriate CVA sample logbook pages that correspond with the raw data. Check every sample label and dilution factor. Highlight the client sample edits and sample analysis deletions so they are not missed during the data loading process. Scan the logbook pages and analysis run pages to the calibration in Element.

12.3. Fill out corrective action forms and analyst notes forms where applicable. Note samples requiring corrective action with "w/CAF" in the log.

13. Method Performance

13.1. Quantitation limit studies are performed for all analytes as described in SOP 1018.

13.1.1. The detection limit must be lower than the limit of quantitation (LOQ) for each analyte. If not, the LOQ will need to be changed or the study replicated.

13.1.2. Quantitation limits shall be re-determined annually or following any change to the sample preparation procedure.

13.2. An Instrument Quantitation Limit Verification Study is performed once each quarter to verify the LOQ and LOD. Summaries are maintained by ARI's QA Section and available for review upon request.

13.3. Analytical accuracy is determined using LCS/MBSPK, SRM or MS analyses. Acceptance limits for spike recovery are specified in the analytical methods and are normally 80 to 120% for LCS and 75 to 125% for matrix spikes. Acceptance limits for SRM analytes are determined by the SRM supplier or manufacturer.

13.4. Laboratory precision is measured by performing replicate analyses. Replicates (sample or matrix spike) acceptance limits are $\pm 20\%$.

13.5. Accuracy and precision acceptance limits are disseminated to the bench chemists and LIMS administrator for use in monitoring method performance in real time.

14. Pollution Prevention

14.1. The primary Pollution Prevention Opportunity for this procedure is to limit the quantity of chemicals purchased and stored on site. Smaller volumes of commercially prepared reagents are being purchased in lieu of in-house preparation from stock salts or crystals. Quantities of reagents purchased and prepared will more closely reflect anticipated usage and stability.

14.2. Wastes known to contain high concentrations of heavy metals are collected and disposed of in the metals solids or aqueous waste streams.

14.3. Corrosive acidic solutions are neutralized prior to sink disposal.



15. Data Assessment and Acceptance Criteria for Quality Control Measures

- 15.1. The correlation coefficient for the calibration, r should be greater than 0.995 (coefficient of determination, $r^2 > 0.990$). Each standard should return a regressed value within 10% of its prepared concentration except for the low standard which should be within 30%
- 15.2. Calibration Verification Standards (ICV/CCV): At the beginning of the mercury run, after every 10 samples, and at the end of the run, a CV standard must be analyzed. Immediately following calibration an ICV must be analyzed. The true concentration of the ICV standard is 8.0 $\mu\text{g/L}$ and must be recovered within 10%. A CCV standard must be analyzed before and after each set of 10 samples and at the end of the run. The true concentration of the CCV standard is 4.0 mg/L and has a control limit of 20%. **Note: For drinking water samples, EPA 245.1 the control limit for the ICV is 5% and the CCV 10%.** If the ICV is out of range, the instrument should be recalibrated. If a CCV is out of control, the problem should be corrected, a new CCV analyzed and all the previous samples run since the last good CCV should be reanalyzed.
- 15.3. Continuing Calibration Blank Standard (ICB/CCB): Immediately after every CV standard, a CB standard must be run. The result of the analysis should be between ± 0.1 mg/L (1 RL). If a CB is outside of these limits, the problem should be corrected, and all previous samples run since the last good CB should be reanalyzed.
- 15.4. Detection Limit Standard (CRA): The first sample of the analytic run, immediately following the first CCV/CCB set should be a CRA. The true concentration is 0.1 $\mu\text{g/L}$ and should be recovered within 70-130 %. If the standard falls outside of these limits the CRA shall be reanalyzed immediately. If the analysis of the reanalysis is in control no further corrective action is required. If the result is again outside the limits the problem should be corrected and the instrument recalibrate.
- 15.5. Spike Recovery (%R): The spike amount for mercury in the digests is equal to 1.0 $\mu\text{g/L}$. To calculate the spike recovery, subtract the background sample result (if the sample is undetected, ± 0.1 $\mu\text{g/L}$, do not subtract anything) from the spiked sample result, divide by the spike added, and multiply by 100:

$$\%R = \left(\frac{\text{spike sample result} - \text{background sample result}}{\text{spike added}} \right) * 100$$

EXAMPLE: Sample 1-SPK has a result of 1.67 $\mu\text{g/L}$. Sample 1 has a result of 0.85 $\mu\text{g/L}$. The spike amount is 1.0 mg/L . The formula to calculate the %R is



$$\%R = \left(\frac{1.67 \mu\text{g} / \text{L} - 0.85 \mu\text{g} / \text{L}}{1.0 \mu\text{g} / \text{L}} \right) * 100 = 82.0\%$$

If the background sample result is 4X greater than the spike added, the %R result has no control limits, otherwise the %R should be between 75-125%. If the spike is out of control a corrective action form must be filled out and the results will be evaluated based on the clients specific project plan. Re-preparation and analysis may be required.

15.6. Duplicates (RPD-Relative Percent Difference): The RPD between a background sample and its duplicate should be no greater than 20%, provided the analysis results are above 0.5 $\mu\text{g}/\text{L}$ (5X the RL). The formula to calculate the RPD of a background sample and its duplicate is

$$RPD = \left[\frac{(\text{background result} - \text{duplicate result})}{(\text{background result} + \text{duplicate result}) / 2} \right] * 100$$

EXAMPLE: Sample 1 has a result of 0.86 $\mu\text{g}/\text{L}$. Sample 1-DUP has a result of 0.99 $\mu\text{g}/\text{L}$. The RPD is:

$$RPD = \left[\frac{(0.86 \mu\text{g} / \text{L} - 0.99 \mu\text{g} / \text{L})}{(0.86 \mu\text{g} / \text{L} + 0.99 \mu\text{g} / \text{L}) / 2} \right] * 100 = 14.1\%$$

If either result is less than 0.5 $\mu\text{g}/\text{L}$ (5X the RL), then the difference between the background sample result and the duplicate result should be no greater than the RL (0.1 $\mu\text{g}/\text{L}$), and the RPD is not used for quality control. If the duplicate is out of control a corrective action form must be filled out and the results will be evaluated based on the client's specific project plan. Re-preparation and analysis may be required.

15.7. Method Blank (MB / BLK): A Method Blank is prepared and analyzed with each job or batch of samples of 20 or less. The blank is used to monitor for possible contamination. The blank results should be < 0.1 $\mu\text{g}/\text{L}$ (<1RL). The DoD-QSM requires that the MB contain $\leq \frac{1}{2}$ the RL. If the blank is detected a corrective action form must be filled out and evaluated based on the clients specific project plan. Re-preparation and analysis of the entire batch may be required if the sample concentrations are less than 10X the blank concentration.

15.8. Method Blank Spike or Laboratory Control Sample (MBSPK / LCS / BS): Laboratory control samples are analyzed with each batch of 20 or less samples. The true value is 2.0 $\mu\text{g}/\text{L}$ with



control limits of 80 – 120%. The % Recovery is calculated the same as a matrix spike except there is no “background sample result” to subtract (see 8.3). If the control limits are not met, all samples in that batch will need to be re-digested and reanalyzed. A corrective action form needs to be filled out.

15.9. Reference Materials (SRM): Reference materials are soil samples that have independently certified concentrations of the analytes of interest. The certificate of analysis accompanying the particular reference material sets the control limits. If the control limits are not met, all samples in that batch will need to be re-digested and reanalyzed. A corrective action form needs to be filled out.

15.10. Any sample with a value above the high calibration standard must be diluted and reanalyzed, see section 11.3.5.1.

16. Corrective Actions For Out of Control Events

16.1. Calibration. If the calibration does not meet the criteria in sections 15.1, then corrective action may need to be taken before proceeding with re-calibration. In these cases all that is required is to recalibrate the instrument again. Instrument problems that require corrective action before recalibration could include gas leaks, worn pump tubing, light source failure, cell misalignment, or incorrect calibration standards preparation.

16.2. The ICV, CCV, ICB, and CCB are considered QC solutions. If a QC solution result is out of control limits, corrective action must be taken before proceeding with analysis. If the ICV is out of range, the instrument should be recalibrated. If a CCV is out of control, the problem should be corrected, a new CCV analyzed and all the previous samples run since the last good CCV should be reanalyzed. A corrective action form must be filled out.

16.3. Instrument malfunctions. When instrument malfunctions occur, consult with other experienced CVAA operators or the supervisor for guidance. Record the event in the mercury instrument maintenance logbook. The maintenance logbook and the service manual could be helpful for troubleshooting.

17. Contingencies for Handling out of Control or Unacceptable Data

17.1. In the event of significant batch QC failure, analysis will stop and the analyst will perform corrective action as discussed above.

17.2. In general, sample data associated with out-of-control batch QC sample results (Method blanks, calibration verification and Laboratory Control Samples) will not be reported. Re-runs will be conducted based upon availability of sample volume. If insufficient sample remains or the remaining sample has been compromised by other withdrawals from the sample bottle or by holding time, the client will be notified to determine an appropriate course of action.



- 17.3. Batch analysis is not controlled by Matrix Specific QC and failing matrix QC does not reflect a failure in the analytical protocol. Failing matrix QC will be reported to the client along with supporting information as may be available to qualify the result.
- 17.4. All corrective actions will be clearly and completely documented on a corrective action form. All maintenance and instrument repairs will be clearly documented in the maintenance log.
- 17.5. In the event of a major instrument failure immediately inform the project managers so all critical samples can be subcontracted if necessary.

18. Waste Management

- 18.1. ARI's Laboratory Chemical Hygiene Plan (CHP) describes internal hazardous waste handling procedures. All analysts must be familiar with these requirements.
- 18.2. ARI properly profiles and disposes all hazardous waste using an EPA registered TSD (Treatment, Storage and Disposal) facility.
- 18.3. Aqueous corrosive waste is neutralized following Elementary Neutralization Procedures in SOP 1201S.
- 18.4. Solid and aqueous samples designating as hazardous for Metals are collected in the "Metals Waste Solids Drum" and the "Metals Waste Solutions Drum", respectively, in the Central Accumulation Area.

19. Method References

- 19.1. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Method 7470A, September 1994
- 19.2. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Method 7471A, September 1994
- 19.3. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Method 7000A, July 1992
- 19.4. USEPA, ILM04.0, Exhibit D, Methods 245.1M and 245.5M
- 19.5. Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Rev 3 May 1994), Method Number 245.1, Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry
- 19.6. Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Rev 3 May 1994), Method Number 245.5, Determination of Mercury in Solids by Cold Vapor Atomic Absorption Spectrometry
- 19.7. DOD Quality Systems Manual for Environmental Laboratories, Version 5.0, July, 2013

20. Appendices

- 20.1. Not Applicable.



Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Metals Analysis

Nexion ICP-MS with Universal Cell Technology

SOP 545S
Version 001

Revision Date: 2/8/16
Effective Date: 2/8/16

Prepared By:

Jay Kuhn / Eric Larson

Approvals:

A handwritten signature in blue ink, appearing to read "Eric Larson".

Eric Larson, Inorganics Division Manager

A handwritten signature in blue ink, appearing to read "David R. Mitchell".

David R. Mitchell, Quality Assurance Manager



1. Scope and Application

- 1.1. This Standard Operating Procedure describes the daily operation, tuning, optimization, and analysis procedures for the analysis of samples on the Nexion® 300D and 350D ICP-MS according to EPA Method 200.8 Version 5.4 and SW-846 Method 6020, 3rd Edition- Final Update IV. See Appendix 10 for a list of isotopes.
- 1.2. Most samples will require some form of sample preparation, preservation, filtration and/or digestion prior to analysis. This procedure is applicable to aqueous samples and acid digestates of solid samples.
- 1.3. Routine operation and maintenance procedures for the Nexion® 300D and 350D ICP-MS may be found in the Nexion® manuals provided by the instrument manufacturer.
- 1.4. Detailed instructions on the use of the Nexion® ICP-MS operating software may be found in a PDF version of the Nexion® Software Manual.
- 1.5. Instructions on the use of the ESI Fast system may be found in the ESI Software Manual.

2. Summary of the Procedure

- 2.1. This method describes the multi-element determination of trace elements by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) using Universal Cell Technology (UCT™). Sample material in solution is introduced by nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio. The separated ions are detected and the ion information processed by a data handling system.
- 2.2. Interferences related to the technique must be recognized and corrected. Such corrections may include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from plasma gas, reagents, or sample matrix.
- 2.3. Instrumental drift, as well as suppressions or enhancements of instrument response, must be corrected by the use of internal standards.

3. Definitions

- 3.1. ICP-MS (Inductively Coupled Plasma - Mass Spectrometer): Refers to an ICP-MS spectrometer or to analytical method(s) that specify the use of an ICP-MS to identify and quantify trace elements in environmental samples.
- 3.2. UCT (Universal Cell Technology): Refers to the different analysis modes of the Nexion 300D and 350D which include KED, DRC, or Standard (STD).



- 3.2.1. DRC (Dynamic Reaction Cell): This mode utilizes ammonia, a reactive gas (NH_3), to carry out gas phase chemical reactions. Interferants are altered (e.g., by proton/electron transfer, oxidation, or dissociation) which causes them to be unstable within the system and eliminated. Analytes of interest do not interact with the NH_3 and thus make it to the detector. It is important to make sure that the analyte of interest/internal standard does not react with the reaction gas (NH_3).
- 3.2.2. KED (Kinetic Energy Discrimination): This mode utilizes helium, an inert gas (He), to collide with interferants to reduce their kinetic energy. A “KED barrier” in the instrument allows only ions with sufficient kinetic energy to pass through it and reach the quadrupole. Care needs to be taken when selecting analytes to monitor in KED mode; common interferants on the analyte of interest should be known and analytes that have a similar cross sectional size as its interferants (i.e. the interferant should be larger than the analyte it interferes with) should not be analyzed in KED.
- 3.3. IDL (Instrument Detection Limit): The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the selected analytical mass(es).
- 3.4. RL (Reporting Limit): The RL is the lowest value at which a given analyte is reported. The RL is based on the IDL, MDL, method efficiency, and analyst’s judgment. The RL will, at minimum, equal the statistical MDL.
- 3.5. MDL (Method Detection Limit): As defined in 40 CFR Appendix E Part 136.
- 3.6. CRDL (Contract Required Detection Limit): Contract specified minimum level of detection.
- 3.7. ICV (Initial Calibration Verification): A mid-range second source standard, run immediately after calibration to verify the accuracy of the calibration.
- 3.8. CCV (Continuing Calibration Verification): A mid-range calibration standard, run after every group of 10 samples and at the end of an analytical sequence to verify calibration accuracy during the analytical run.
- 3.9. ICB (Initial Calibration Blank): A calibration blank run, immediately after the ICV to verify the baseline and to check for carry-over.
- 3.10. CCB (Continuing Calibration Blank): A calibration blank, run immediately after every CCV to verify the baseline and to check for carry-over.
- 3.11. QCS (Quality Control Sample): A QC solution supplied by a source independent from the source of the calibration standards. It is used to verify the accuracy of the newly prepared calibration standards.



- 3.12. IS (Internal Standard): Pure analyte(s) (which is not a sample component) added to a sample, extract, or standard solution in known amounts and used to measure the relative responses of other method analytes that are components of the same sample of solution.
- 3.13. LR (Linear Range): The linear range of an instrument is the upper limit of accurate quantitation with practical rinse-down times. It varies for each isotope and with instrumental conditions.
- 3.14. CRI (Low Check Standard): This low level standard is at 1 RL.
- 3.15. SD: Standard Deviation
- 3.16. RSD (Relative Percent Standard Deviation): The SD divided by the mean, multiplied by 100.
- 3.17. RPD (Relative Percent Difference): The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.
- 3.18. %R (Spike Percent Recovery): The difference between the matrix spike concentration and the background sample concentration divided by the concentration of the spike added multiplied by 100.
- 3.19. Analytical Batch: An analytical batch shall consist of no more than 20 samples.
- 3.20. MB (Method Blank): An aliquot of analyte-free matrix taken through the sample preparation procedure with each analytical batch.
- 3.21. LCS/MBSPK (Laboratory Control Sample, or Method Blank Spike): A reference solution of known concentration processed along with the analytical batch to test the digestion procedure for accuracy. Both soil references and aqueous references (reference solutions or method blank spikes) are LCS's.
- 3.22. SRM (Standard Reference Material): A reference sample of known concentration processed along with the samples to test the digestion procedure for accuracy. For a soil sample the reference used is typically an ERA Soil SRM.
- 3.23. MS (Matrix Spike): A sample prepared by adding a known amount of analyte to a specified amount of sample matrix. Matrix spikes are used to determine the effect of the sample matrix on the method's recovery efficiency.
- 3.24. MSD (Matrix Spike Duplicate): A second replicate matrix spike sample prepared and analyzed as above (Sec. 3.21) to measure precision with respect to a given matrix.
- 3.25. MD (Matrix Duplicate): A second replicate matrix sample prepared and analyzed with a sample batch to measure precision with respect to a given matrix.
- 3.26. ICSA, ICSAB (Interference Check Solutions): The ICSA solution contains interfering elements, at levels often found in samples, to test the efficacy of instrument correction



equations. The ICSAB solution contains the same elements as the ICSA at the same concentrations, plus analytes at moderate levels to test the accuracy of analyte measurement in the presence of interferants.

- 3.27. Carry-over: The effect of a high level sample on a lower level sample which follows. Residual analyte from the high level sample may remain in the uptake lines, nebulizer, spray chamber, cones, or in the torch. The lower concentration sample that follows may show successively decreasing concentrations, which could suggest carry-over. A true test for carry-over is the analysis of a blank, which has either elevated analyte or successively decreasing exposures. Carry-over may also be referred to as memory effect. If carry-over is suspected, the lower level sample should be rerun following a blank, another low level sample, or an extended rinse time.
- 3.28. Set-up (Tuning) Solution: A solution that is used to determine acceptable instrument performance prior to calibration and sample analyses.
- 3.29. Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using high purity solutions purchased from a reputable commercial source (Inorganic Ventures).
- 3.30. Analysis Protocols:
- 3.30.1. Routine or Package: Follows SW-846 6020 and EPA 200.8. If the analysis comment is Package (PKG), a data package will be generated from the routine analytical run and routine QC samples. Other modifications that are necessary for certain quality assurance plans and/or agencies will be detailed in individual sections.
- 3.30.2. CLP-Q: Follows Routine protocol with CLP-type and DOD QC standards analyzed at CLP QC frequency, in order to generate a CLP-type data package.

4. Interferences

- 4.1. Isobaric interference occurs when an isotope of one element is at the same nominal mass as an isotope of another element (e.g., ^{98}Mo and ^{98}Ru). Corrections for isobaric interference may be made by measuring the intensity due to the interfering element at another isotope and using its natural abundance ratios to correct for its presence at the analytical mass of interest. Most commonly used corrections for isobaric interference are already present as default interference equations in the Nexion[®] software. Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample. Correction equations are listed in Appendix 9.
- 4.2. Molecular interferences are caused by molecular species formed in the plasma with argon plasma or matrix ions (examples of common molecular interference include ArCl, ClO, nitrogen



dimer, oxygen dimer, oxide species, double charged species, etc.). Predictions about the type of molecular interference may be made using knowledge about the sample matrix. Molecular interferences are minimized by implementing KED/DRC modes in analytical methods

4.3. Physical interferences are associated with solution viscosity and surface tension differences between standard solutions and samples. These interferences may occur in transfer of solution to nebulizer, at the point of aerosol formation and transport to the plasma, or during the excitation and ionization process within the plasma. Internal standardization is used to compensate for many physical interference effects. Depending on the method, five or six internal standards are chosen to closely match the analytical behavior of the elements being determined.

4.4. Memory Interferences: Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample (Carry-over as defined in Section. 3.26). If memory interference is suspected, the sample should be reanalyzed after a long rinse period.

5. Safety

5.1. The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory technique and safety practices shall be followed at all times.

5.2. Safety glasses shall be worn at all times when handling samples, reagents, or when in the vicinity of others handling these items.

5.3. Liquid argon represents a potential cryogenic hazard and safe handling procedures shall be used at all times when handling liquid argon tanks.

5.4. The Nexion 300D is fully interlocked to protect the user from dangers such as high voltages, radio frequency generators, and intense ultraviolet light. At no time should the operator attempt to disable these interlocks or operate the Nexion 300D if any safety interlock is disabled or malfunctioning.

5.5. Spilled samples, reagents, and water shall be cleaned up from instrument and autosampler surfaces immediately.

5.6. All additional company safety practices shall be followed at all times.

6. Equipment and Supplies

6.1. Perkin-Elmer Nexion ICP-MS system: includes the Nexion[®] instrument, a peristaltic pump, a computer system, Nexion[®] NT software, a printer, and an ESI FAST autosampler.

6.2. Supplies

6.2.1. Peristaltic pump tubing:



- 6.2.1.1. Black/Black PVC - 0.76 mm id used for sample introduction
- 6.2.1.2. 1.30 mm id Gray/Gray Santoprene used for rinse solution
- 6.2.1.3. Orange/Green PVC – 0.38 mm id for internal standard
- 6.2.2. Calibrated mechanical pipettes with metal-free plastic pipette tips
- 6.2.3. 15 mL and 50 mL polypropylene metal-free auto-sampler tubes with caps
- 6.2.4. 100, 200, 500 and 1000 mL polyethylene volumetric flasks
- 6.2.5. Fast supplies: 1.0 mm id sample probe (gray marker), internal standard and carrier solution probes (0.5mm id); sample loops (size varies according to method); and spare valve parts including a stator, rotor, and valve head.

7. Reagents and Standards

7.1. Reagents

- 7.1.1. All reagents may contain impurities that may affect the integrity of the analytical results. Due to the high sensitivity of ICP-MS, high purity reagents, water, and acids must be used whenever possible. All acids used for this method must be of high purity grade. Nitric acid is preferred for ICP-MS in order to minimize polyatomic interference.
- 7.1.2. Nitric acid (HNO₃), concentrated. Trace Metal Grade HNO₃ that has Lot QC documentation to verify that it is acceptable for trace metals use.
- 7.1.3. Hydrochloric acid (HCl), concentrated, Trace Metal Grade HCl that has Lot QC documentation to verify that it is acceptable for trace metals use.
- 7.1.4. Deionized water (DI). Type I reagent water (18.3 megaohm).
- 7.1.5. 1% (vol/vol) nitric acid: Add 10 mL of trace grade nitric acid to a 1 liter volumetric flask containing 900 mL of DI water. Mix well and bring to volume.

7.2. Standards: All standards must be labeled with the analyst's initials, preparation date, expiration date, and standard identification number (from Element). The preparation of all standards and analytic solutions must be documented in Element. Standards are stored in the metals lab either on the standard shelves or near the point of use. All standards are marked with an expiration date derived from the expiration date of the stock from which it is made, or from method requirements.

7.2.1. Single element stock standards of the elements at the highest purity available from Inorganic Ventures. All single element standards and Intermediate Standards are checked by ICP and/or ICP-MS prior to use.

7.2.2. Setup Solution:

7.2.2.1. Setup Solution Intermediate (10 mg/L Be, Mg, Fe, In, ⁶Li, Ce, U and Pb in 1% HNO₃):



Prepare by pipetting 1.0 mL of each 1000 mg/L single element stock standard into a 100 mL volumetric flask containing 90 mL DI water and 1.0 mL concentrated HNO₃. Dilute to 100 mL with DI water and mix well (see Appendix 1 Section 2).

7.2.2.2. Setup Solution (1 µg/L Be, Mg, Fe, In, ⁶Li, Ce, U and Pb in 1% HNO₃): Prepare by pipetting 0.10 mL of Standard Mode Setup Solution Intermediate into a 1000 mL volumetric flask containing 900 mL of DI water and 10 mL of concentrated HNO₃. Dilute to 1000 mL with DI water and mix well.

7.2.3. Internal Standard Solution:

7.2.3.1. Solution Preparation (0.15 mg/L ⁶Li; 0.6 mg/L Ge; 0.12 mg/L Sc; 0.1 mg/L Ga; 0.05 mg/L Y, In, Tb, and 0.2 mg/L Bi): Prepare by pipetting 0.15mL ⁶Li, 0.6mL Ge, 0.12mL Sc, 0.1mL Ga, 0.2mL Bi, and 0.05 mL each Y, In, Tb of the 1000 mg/L individual stock standards into a 1000 mL volumetric flask containing 800 mL DI water and 10 mL concentrated HNO₃. Dilute to 1000 mL with DI water and mix well (see Appendix 1 Section 1).

7.2.3.2. Internal Standard Solution is pumped to all standards and samples via a mixing “T” prior to being introduced into the nebulizer.

7.2.4. Calibration Standard Stocks (see Appendix 2):

7.2.4.1. Calibration Stock 1 (100 mg/L): Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, Th, U, V, and Zn.

7.2.4.2. Calibration Stock 2 (100 mg/L): Mo and Sb.

7.2.4.3. Individual Stock Standards (10,000 mg/L): Al, Ca, Fe, K, Mg, and Na

7.2.5. Calibration Intermediate Standard (Appendix 3) is prepared, as needed, by adding 10.0 mL of each of the Calibration Stock Standards 1 and 2, and the individual elements of Al, Ca, Fe, K, Mg, and Na into a 100 mL volumetric flask containing 10 mL DI water and 1.0 mL of concentrated HNO₃. Bring to volume with DI water and mix well.

7.2.6. Calibration working standards: Prepare fresh every two weeks or as needed at the specified concentrations in Appendix 4. (NOTE: The low standard is the CRI.)

7.2.7. QCS: The QCS, typically an ERA or NIST (National Institute of Standards and Technology) solution, is prepared as recommended by the supplier. It is diluted appropriately and analyzed as a sample when required (see section 15.4.1.1).

7.2.8. Initial Calibration Verification (ICV) Standard: This is a second source calibration verification standard prepared from 2 second source stock solutions purchased from Inorganic Ventures Inc. (see Appendix 5). Prepare by pipetting 20.0 mL of AR-ICVMS-1 stock and 20.0 mL of AR-ICVMS-2 stock into a 1000 mL volumetric flask containing 900 mL of DI water, and 10 mL of



concentrated HNO₃. Dilute to 1000 mL with DI water and mix well.

- 7.2.9. Low Check Solution (CRI): A solution prepared at the RL for each element to check the accuracy at low levels. NOTE: CRI is also used as the first (and lowest) calibration solution.
- 7.2.10. Low Standard/Low Check Intermediate (see Appendix 7): Prepare by pipetting the specified amount of single element stock standard into a 100 mL volumetric flask containing 80 mL DI water and 1.0 mL concentrated HNO₃. Dilute to 100 mL with DI water and mix well.
- 7.2.11. Low Standard/Low Check Solution (levels at 1RL): Prepare by pipetting 0.10 mL of Low Check Intermediate into a 200 mL volumetric flask containing 90 mL of DI water, and 2.0 mL of concentrated HNO₃. Dilute to 200 mL with DI water and mix well.
- 7.2.12. Continuing Calibration Verification: Standard 4 (50 µg/L non-minerals and 5000 µg/L minerals), the mid-range calibration standard, is used.
- 7.2.13. Calibration Blank: A solution containing 1% (v/v) concentrated HNO₃ in DI water. Fill a 1L volumetric flask with approximately 900 mL of DI water. Pipette 10 mL of concentrated HNO₃ into the flask, dilute to 1000 mL with DI water and mix well. NOTE: Cal. Blank is also used as the “carrier solution”.
- 7.2.14. Dual Detector Calibration Solution: contains 200 ug/L each of Al, As, Be, K, Mg, Na, Ni, Pb, Th, Tl, U, Zn, 6Li, Sc, Ge, Y, In, Tb, Bi and 100 ug/L of V, Cr, Co, Mn and 500 ug/L of Ca, Fe and 250ug/L of Mo, Ag, Cd, Cu, Sb, Ba. (see Appendix 6).
- 7.2.15. Dual Detector Calibration Intermediate Solution: Prepare by adding 1.0 mL of each of the above 1000 mg/L elements into a 200 mL volumetric flask containing 150 mL DI water and 2 mL concentrated HNO₃. Dilute to 200 mL with DI water and mix well. Note: There is no need to add Se or additional internal standards to this solution.
- 7.2.16. Dual Detector Calibration Supplementary Elements for Nexion: Prepare by adding 0.01 mL each of 1000 mg/L of V, Cr, Co, Mn; 0.09 mL of Ca and Fe; and 0.04 mL of Mo, Ag, Cd, Cu, Sb, Ba into a 200 mL volumetric flask containing 2.0 mL of Intermediate Standard 1 and 2 mL of concentrated HNO₃. Dilute to 200 mL with DI water and mix well.
- 7.2.17. Interference Check Solutions (ICSA, ICSAB): These solutions are made from Inorganic Ventures multiple element stock standards (see Appendix 8). Prepare as needed.
- 7.2.18. ICSA: Prepare by pipetting 20.0 mL of Inorganic Ventures AR-6020ICS-OA10 stock into a 100 mL volumetric flask containing 70 mL of DI water, and 1.0 mL of concentrated HNO₃. Dilute to 100 mL with DI water.
- 7.2.19. ICSAB: Prepare by pipetting 20.0 mL of Inorganic Ventures AR-6020ICS-OA10 stock and 1.0 mL of ICP-MS ICSAB stock into a 100 mL volumetric flask containing 70 mL of DI water,



and 1.0 mL of concentrated HNO₃. Dilute to 100 mL with DI water.

7.2.20. ICP-MS ICSAB STOCK: Prepare by pipetting 0.10 mL each of 1000mg/L Stock standards Ag, As, Cd, Co, Cr, Cu, Mn, Ni, Zn into a 50 mL volumetric flask containing 20 mL of DI water and 0.5 mL of concentrated HNO₃. Mix well and transfer to a 60 mL clean Nalgene container.

8. Sample Collection, Preservation, Shipment and Storage

8.1. All samples should be received in appropriate collection containers and have been properly preserved by the clients.

8.2. Samples are checked for proper preservation and stored refrigerated for a maximum of 180 days prior to sample preparation.

8.3. Some samples are shared with the organic extractions and/or conventional laboratories. Sample receiving places these samples in a share bin in Refrigerator 5. SOP 1019S includes procedures for handling shared samples.

9. Quality Control

9.1. Documentation

9.1.1. Instrument logbooks

9.1.1.1. Daily analysis: The ICP-MS Sample logbook shall be used as a run sequence log, for sample specific notes, for QC limit notes, and for any notes pertaining to the run.

9.1.1.2. Maintenance logbook: Shall be used for notes of periodic checks of instrument performance and of all maintenance procedures including physical changes (tubing, cones etc.) and operational maintenance routines (i.e. Dual Detector Calibrations)

9.1.2. ICP-MS Files

9.1.2.1. Daily Tuning, Performance, and AutoLens® results are filed daily.

9.1.2.2. Dual detector summary results are filed with that days Tuning, Performance and Autolens®.

9.1.2.3. Standard Certificates: Contains a Certificate of Analysis for all Inorganic Venture Standards as well as standards obtained from other sources.

9.2. Calibration Standards: All standards are prepared every two weeks (or as needed) by dilution from known intermediates and verified by the analysis of certified second-source QC standards (Section 7.4-7.6).

9.2.1. Calibration verification must be performed immediately after calibration with an Initial Calibration Verification Standard (ICV); after every 10 samples and at the end of the analytical run, a Continuing Calibration Verification Standard (CCV) must be run. The ICV is made from a



source other than that used for the preparation of the standard curve. The CCV is the mid-range Calibration Standard.

- 9.2.2. Calibration Verification Blanks (ICB/CCB) are analyzed to confirm the absence of blank contamination, baseline drift and/or carryover. Immediately after the ICV and every CCV a Calibration Verification Blank must be run.
- 9.2.3. Independent QC solutions: This standard is used to check the calibration stock standards stability, concentrations, and preparation. They are analyzed on the day new calibration standards are prepared.
- 9.3. Low Check (CRI) Standard is analyzed following calibration verification for each element. The standard is used to verify the analytical performance at the low end of the calibration or reporting limit.
- 9.4. Interference Check Solutions (ICSA/B) The interference check solutions (See Appendix 8) are analyzed to check the accuracy of correction equations. These standards are analyzed after the Low Check Standard.
- 9.5. Serial Dilution: A five-fold dilution should be performed on any new or unusual sample matrix. This dilution test will help identify a matrix interference if one is present. The dilution is performed on a sample, typically the sample used for matrix QC, from each group of samples of a similar precode for each sample digestion batch. Some projects (including DOD, CLP-Q) require a serial dilution be performed on at least one sample in their batch.
- 9.6. Post Digestion Spike: A post digestion spike should be performed on a new or unusual sample matrix, along with the serial dilution. This sample is intended to help identify matrix interference problems. Some projects, including DOD, require that a post digestion spike be performed on at least one sample in their batch. For CLP type samples this spike is required only for elements that are outside control limits in the Matrix Spike sample. For DOD samples all requested elements must be spiked.
- 9.7. Matrix QC samples: With each preparation batch various matrix QC samples must be analyzed. At a minimum a matrix spike, matrix duplicate, method blank, and a laboratory control sample should be prepared and analyzed. For some projects matrix spike duplicates, laboratory control sample duplicates, and/or certified reference materials may also be required. The analyst must check all paper work to make sure all necessary QC samples have been prepared and analyzed.
- 9.8. All logbooks are reviewed monthly for completeness and accuracy by laboratory personnel.
- 9.9. The QA section will periodically review the standard preparation process, including standard



bottles, logbooks and standard certificates and traceability to standardized sources.

9.10. Initial Demonstration of Laboratory Performance - The following items must be completed before the analysis of any samples is performed by using this method

9.10.1. Instrument Detection Limits (IDLs) shall be determined for all analytes when first putting an instrument into service, and before using this method.

9.10.1.1. IDLs shall be verified following any significant change to the instrument (new detector or different sample introduction system used).

9.10.1.2. Calibrate the instrument, and then run the usual QC sample sequence.

9.10.1.3. Run the blank solution as a series of 10 sequential samples with rinsing in between each sample.

9.10.1.4. Calculate the standard deviation of the 10 blank samples for each isotope.

9.10.2. Method detection limits (MDLs) shall be established for all analytes by the method outlined in 40 CFR Part 136. An MDL check sample must be run on a routine basis to verify detection limits. The check sample is run at ½ the RL.

9.10.2.1. Fortify a reagent blank with a concentration of each analyte that is two to five times the estimated detection limit (the IDL can be used to estimate this). This solution is called the MDL solution.

9.10.2.2. Take eight replicate aliquots of this solution and process through the entire method, including any sample preparation steps. Run these as samples with rinsing between each sample. Calculate the standard deviation of the samples for each isotope. Multiply the standard deviation by 2.998 (student's t value for 99% confidence level and n=8) to obtain the MDL.

9.10.2.3. The MDLs must be lower than in-house RLs. If not, the RLs will need to be changed or the MDL analysis redone.

9.10.2.4. MDLs shall be verified quarterly or following any change to the sample preparation procedure.

9.10.3. Run four LCS or SRM standards and verify the mean concentration is within 10% of the stated value (or within the acceptance limits listed in Table 8 Revision 5.4 EPA METHOD 200.8).

10. Calibration and Standardization

10.1. The instrument must be calibrated using a blank and five calibration standards before analysis. The high concentration standard will contain 100 µg/L of all analytes except for the minerals, which are at a concentration of 5,000 or 10,000 µg/L .

10.1.1. The concentrations of the standards have been entered into the calibration page of the



analytical method in the Nexion® software according to the values of the standards prepared in Section 7.2.6.

10.1.2. Positions of the Standards are entered in the Sampling page of the Method along with any special rinse times needed.

10.1.2.1. A “Linear Through Zero” curve type should be selected for all analytes.

10.1.2.2. The calibration blank should be run as a blank, before the analysis of any calibration standards.

10.1.2.3. The first standard run should be the lowest level standard, followed by standards of increasing concentration in order to minimize cross-contamination and carry-over.

10.2. Before commencing calibration, open a “Blanks” sample table, and run three to five blank samples to ensure the loop is thoroughly rinsed and that the internal standards are stable.

10.3. Load the calibration blank and the calibration standards into the autosampler positions specified on the Sampling page of the analytical method.

10.3.1. Start calibration in the samples table by highlighting the 1st row of the batch labeled “Rinse Sample” with calibration action “Run Blank, Standards, and Samples”. Click on Analyze Batch. Click on Yes to clear the previous calibration.

10.3.2. After calibration has run review the data for acceptable RSDs and internal standard recoveries (see Section 15). View the curve-fit on the Calibration View page for poor curve fit (apparent standard levels >5% from true value), then print a calibration summary. To print a calibration summary, click on the Report tab in the Method Dialog Box., Under Report View, browse to select “**arical.rop**” for the Report Options Template. Click on the Dataset Icon, highlight the latest calibration standard row (rinse sample) and click Reprocess. The method file does not need to be saved at this point, but save the calibration with the name of that run, i.e. mmddy and A, B... for the 1st, 2nd, etc. calibration if re-calibration or re-zeroing is necessary. To reset the usual report options template, click on the Report page, and under Report View, click browse to select “**ariquant.rop**” for the Report Options Template and save the method.

10.3.3. Review the r-values for any that are <0.998

10.3.4. If poor curve fit and/or poor r-value are found, rerun a standard or recalibrate (also see Section 1.1).

10.4. Analyze Required QC Samples

10.4.1. Analyze the ICV and ICB standards. Confirm the standard recovery is within 10% of the known value, and the ICB value is less than the RL. If these conditions are not satisfied the analysis must stop, the problem corrected, the instrument recalibrated and the Initial Standards



rerun.

- 10.4.2. Analyze Low Check Standard (CRI). Confirm the standard is within 50% of the known value (20% for DOD), else the problem must be corrected and the CRI run within limits before samples may be analyzed.
- 10.4.3. Analyze ICSA/B Standards. Confirm the standards return values of less than the RL for all non-spiked elements (unless contamination can be documented), and within 20% of the known value for spiked analytes. (For DOD the absolute value for all non-spiked analytes shall be $<2 \times \text{MDL}$, unless a verified trace impurity from one of the spiked analytes exists.)
- 10.4.4. Analyze the independent QC solution(s) if fresh calibration standards were prepared on this day. This standard serves as an additional check of the calibration solutions. The concentrations should be within the certified limit range provided by the supplier. If the results are outside this range, the analyst should compare the percentages to the nearest CV and rerun the QC solution, recalibrate, or prepare new calibration standard(s).

11. Procedure

- 11.1. Initial Demonstration of Laboratory Performance: The following items must be completed before the analysis of any samples is performed using this method.
 - 11.1.1. Instrument Detection Limits (IDLs) shall be determined for all analytes before using this method. Detection limits established shall be less than or equal to the MDL.
 - 11.1.1.1. Calibrate the Instrument, and then run the usual QC sample sequence.
 - 11.1.1.2. Run the blank solution as a series of 10 sequential samples with rinsing in between each sample.
 - 11.1.1.3. Calculate the standard deviation of the 10 blanks for each isotope.
 - 11.1.1.4. IDLs shall be determined whenever the following occurs:
 - 11.1.1.4.1. When placing a new instrument into service, and before using this method.
 - 11.1.2. Method detection limits (MDLs) shall be established for all analytes by the method outlined in 40 CFR Part 136.
 - 11.1.2.1. Fortify a reagent blank with a concentration of each analyte that is two to five times the estimated detection limit (the IDL can be used to estimate this). This solution is called the MDL solution.
 - 11.1.2.2. Take eight replicate aliquots of this solution and process through the entire method including sample preparation steps. Run these as samples with rinsing between each sample. The resulting values are entered into the spread sheet for MDL calculations.



Following the MDL determination, an MDL verification check sample may be run (spiked at approximately 2XMDL). The MDL check must produce a response at least 3X instrument noise level.

11.1.2.3. The MDLs must be lower than the in-house RLs - If not, the RLs will need to be changed or the MDL analysis redone.

11.1.2.4. MDLs shall be re-determined following any change to the sample preparation procedure.

11.1.3. Linear Range Verification: Linear range limits are determined during the methods development period. Many of them are set below instrument capability, limited by other concerns such as carry-over and rinse-out times. Linear Limits used are verified on an on-going basis and at least every six months. Linear Range standards (LR200, LR300) are analyzed to verify each element is within 10% of expected value and results may be reported to that level.

11.2. Daily Procedure

11.2.1. Preparing the uptake system and interface

11.2.1.1. Open the instrument cover and slide the torch mount door away from the interface using the cone access button on the outside of the instrument. Check the condition of the cones for deposits and clean the outside of the sampler cone using a small amount of DI water on a Kimwipe® or cotton swab. When deposits are severe, change or clean the cones.

11.2.1.2. Attach the three pump tubings to the peristaltic pump. Relative to the instrument, green-orange Tygon® tubing is on the inside channel and is used for the internal standard; black-black Tygon® tubing is located on the second channel from inside and is used for the sample line; gray-gray Santoprene® tubing is used for the spray chamber drain line and is on the outermost channel. Make sure the tubing is not flattened or showing visible signs of wear, otherwise change to new tubing for optimum performance. Place the internal standard probe (green tape) and the carrier probe (blue tape) in a DI container.

11.2.1.3. Initiate the plasma and place the internal standard and carrier probes into a 2% HNO₃ rinse solution and allow instrument to warm-up for 45 minutes. Ensure that the spray chamber is pumping out smoothly. Turn on the Peltier cooling for the spray chamber.

11.2.2. Open the **aridaily_UCT.wrk** workspace to perform the necessary optimization procedures. Verify the active folders and Dataset in use are correct (month and year can be used for the Dataset name).

11.2.3. Open the SmartTune™ window and load the appropriate SmartTune™ wizard file (**aridaily_UCT.swz**). If using KED mode, the KED Autolens® needs to be calibrated (KED



optimize.swz). It is possible to optimize all the parameters at once by clicking “optimize” in the SmartTune™ window, or individually by right clicking (“quick optimize”) on the individual files listed in the SmartTune™ window.

11.2.3.1. Manually aspirate (without the autosampler) the 1 µg/L setup solution by placing the Internal Standard and Carrier Solution probes in the solution. This solution will be continuously aspirated for the torch alignment, mass calibration, AutoLens® calibration and the daily performance checks. **Prior to Tuning and Autolens routines it is helpful to run a Daily performance to check for adequate element intensities.**

11.2.4. Right Click the Daily Performance button to perform the daily performance check.

11.2.4.1. . Continue to aspirate the 1 µg/L setup solution.

11.2.4.2. . Click on the Analyze Sample button in Sample window to start analysis.

11.2.4.3. . Check that the RSDs for five replicates for Be, In, Mg, Pb and U are all ≤5% as required by EPA Methods 6020 and 200.8 (typically all are <3%).

11.2.4.4. Monitor the daily performance measures (as recommended by Perkin Elmer) of Be, Mg, In, Pb and U sensitivity, background, % double charged and % oxide levels:

11.2.4.4.1. Be > 3000 cps, Mg > 20,000 cps, In > 50,000 cps, Pb >20,000cps, and U > 40,000 cps.

11.2.4.4.2. Background at mass 220 < 5 cps

11.2.4.4.3. Ce ⁺² <0.030 (% double charged < 3.0%)

11.2.4.4.4. CeO <0.025 (% oxides < 2.5%).

11.2.5. Right click on **Torch Alignment**. Record the x and y results.

11.2.6. Right Click on the **Calibration and Resolution** button in the SmartTune™ window.

11.2.6.1. After the tuning (mass calibration) has been completed, a tuning report for each of the runs performed will be automatically sent to the printer. Check that the mass calibration for each of the measured masses is ± 0.05 AMU (0.1 AMU ideally) of the true mass. (Methods 6020 and 200.8 require +/- 0.1 AMU).

11.2.6.2. Check that the resolution for all elements is 0.7 ± 0.03 AMU (measured at 10% peak height). EPA Method 6020 requires <0.9 amu at 10% peak height; Method 200.8 requires 0.75 amu at 5% peak height.

11.2.6.3. . If both the resolution and mass calibration are acceptable a report of acceptability will be automatically printed.

11.2.6.4. If any of the tuning parameters do not meet method specifications and the instrument requires adjustment, the instrument will automatically rerun the tuning routine (# of retries



can be set in the method). It is typical to run several tunings to get all 5 elements within specifications.

11.2.7. Right click on the **AutoLens**[®] button to perform the AutoLens[®] calibration.

11.2.7.1. Continue to aspirate the 1 µg/L setup solution.

11.2.7.2. Print an Interactive Graph (add all elements) and save the AutoLens[®] Calibration.

11.2.7.3. Review the AutoLens[®] calibration graphs.

11.2.8. Right Click the Daily Performance button to perform the final daily performance check.

11.2.8.1. . Continue to aspirate the 1 µg/L Set-up solution.

11.2.8.2. Check that the RSDs for five replicates for Be, In, Mg, Pb and U are all ≤5% as required by EPA Methods 6020 and 200.8 (typically all are <3%).

11.2.8.3. Monitor the daily performance measures (as recommended by Perkin Elmer) of Be, Mg, In, Pb and U sensitivity, background, % double charged and % oxide levels:

11.2.8.3.1. Be >3000 cps, Mg > 20,000 cps, In > 50,000 cps, Pb >20,000cps, and U > 40,000 cps.

11.2.8.3.2. Background at mass 220 < 5 cps

11.2.8.3.3. Ce⁺² <0.030 (doubly charged < 3.0%)

11.2.8.3.4. CeO <0.025 (oxides < 2.5%)

11.2.8.3.5. Oxides and doubly charged levels can be reduced by slightly decreasing the nebulizer flow rate or increased by slightly increasing the nebulizer flow rate. To adjust the flow, click on the **Conditions** Icon, **Manual Adjust**, and then adjust the nebulizer gas flow arrows: try using 0.01-0.02 increments to adjust Ce⁺² and CeO levels. Alternately the **Nebulizer adjust routine** can be added to the optimization window and will automatically set the nebulizer flow.

11.2.8.3.6. Other optimization routines are available in the SmartTune™ window by clicking on the Edit button.

11.2.8.3.7. After the Optimization sequence has passed, place the probes in the 2% HNO₃ for 5-10 minutes, and then place the carrier probe (blue tape) and the internal standard probe (green tape) in the appropriate solutions.

11.3. Sample Analysis

11.3.1. Open the ariquant workspace (aridaily_UCT.wrk)and load the applicable method for the analytes required (see the method list at the instrument). In the method window, click on the



report tab. Change the report filename to reflect the run date **mxyymmdd.rep**, where m is the analysis method and x is the instrument number, yy are the last 2 digits of the year, mm is the month and dd is the day of the month). Save the method file.

11.3.2. New sample types can be screened by ICP or the semi-quantitative ICP-MS procedure, Total Quant. Use the report TotalQuantSummary.rop. To screen a sample using Total Quant, first open the **TotalQuantAnalysis.wrk** workspace. Calibrate using the 1% HNO₃ diluent as the calibration blank and standard 50 µg/L non-minerals (5000 µg/L minerals) as the single calibration standard. Run an ICV and an ICB before running samples at an appropriate dilution; new sample types are diluted at least 1/10 (more dilute ~~(1/50 or 1/100)~~ if warranted).

11.3.3. Samples Analysis Setup

11.3.3.1. Edit the “samples” dialog box to enter new samples in the autosampler sequence.

11.3.3.2. The starting sample sequence is: ICV, ICB, CCV1, CCB1, Low Check, ICSA, ICSAB, CCV2, CCB2 and then 10 client samples. Ten samples can be run between CCV/CCB pairs (Low Check, ICSA and ICSAB count as samples). Run the QCS (if necessary) early in the run. Linear range checks, LR200 and LR300, can be run any time after the Low Check, ICSA, ICSAB group. Enter the autosampler sample position in the “A/S Loc” column. Enter the dilution factor in the Batch ID column. REN and RHN preps are run undiluted. SWN preps are diluted 1/20. Enter the sample identification in the Sample ID column (e.g. 16A0001-01). The calibration action for all samples is “Analyze Sample”.

11.3.4. In the method under the samples tab enter peristaltic pump control speeds for all samples: -3 for normal speed. Enter the number of seconds required for sample flush, read delay and wash. (This should all be set and not needed to be done every day.)

11.3.4.1. Check the autosampler positions.

11.3.4.2. Rinse 15 mL polypropylene tubes in groups of five. Rinse with 10% HNO₃ followed by DI water. Prepare the sample dilutions according to sample prep method and knowledge of sample analyte levels. Cap and mix the samples using the small vortexer.

11.3.4.3. Load the samples into the autosampler positions specified in the sample table. Save the sample file (mmdd).

11.3.4.4. Select the samples to be analyzed by highlighting the rows.

11.3.4.5. Click on Analyze Batch. A Pop-up window will ask if you wish to clear the current calibration – Click NO unless you wish to recalibrate. Clicking on Yes will clear the current calibration.

11.3.5. During the run, the instrument condition and sample results are monitored so appropriate



actions can be performed as needed. The CVs, CBs, QC solutions, Linear Range standards, MBs, LCSs, duplicates, matrix spikes, and internal standard recoveries should be checked during the run or soon thereafter. See Section 15 for acceptance criteria.

11.3.6. Analytical Run Order

11.3.6.1. Routine: After acceptable initial QC has been run, every group of 10 samples must be preceded and followed by a CCV, CCB pair. Typically, each group of ten may be started with suspected low level samples, such as matrix blanks and ending with higher level samples such as reference materials, or matrix spikes. In order to facilitate acceptance limit checking samples may be run: matrix duplicate, background sample, matrix spike, reference sample.

11.3.6.2. CLP-Q/DOD The analytical run order is as above plus: a serial-dilution (a fivefold dilution must agree within 10% of the undiluted sample if the analyte levels are >10RL. A post-digestion spike is performed on DOD/CLP-Q samples with recovery outside 75-125% of the expected result.

11.3.7. Monitoring the Analysis

11.3.7.1. Periodically during the run check the sample uptake flow, the level of solution in the autosampler QC vials, the autosampler probe position and the rinse and waste levels. To stop the run, click on "Stop" (to stop immediately) or "Stop after current sample." To pause the run after the current sample, click the "Pause" button in the Run window.

11.3.7.2. Method QC samples such as CV/CB should be monitored closely during the analytical run to check for calibration stability and baseline drift. If the CV and/or the CB are outside or approaching the QC limits, then corrective action should be taken as soon as possible to minimize sample reruns. Corrective action could include recalibrating the blank or extra rinsing time followed by another CV and CB.

11.3.7.3. Monitoring High Levels and carryover: If any sample level within 10% of the linear limit, the sample should be diluted and rerun for the affected element. If high level samples are analyzed, carryover into the following samples may occur. Carryover usually exhibits high SD or RSD in the following samples. If carryover is suspected, the affected sample should be reanalyzed. Note: Some projects (including DOD) require any sample analyte that exceeds the concentration of the high calibration standard be diluted. If required, appropriate instructions will be noted in Element and it is the analyst's responsibility to follow the instructions and document the necessary dilutions on the raw data.

11.3.8. Recalibrating the Calibration Blank: (It is possible to recalibrate the Blank and re-set the internal standards during a run):



11.3.8.1. Stop the run and insert a CV/CB pair in the AS table

11.3.8.2. Right click on the Analyze sample option in the sample table. Choose **Run Blank and Sample** option. This will insert a Calibration Blank in the Run table. After the blank and CV/CB pair has run return to the Batch Sample Mode. **Any recalibration of the Blank must be followed by a CV/CB within QC limits before samples may be run.**

11.3.9. Shut Down

11.3.9.1. Run 5% HNO₃ as a sample 3-4 times followed by DI water 3-4 times. Move the carrier solution and I.S. probes to air to drain the uptake lines and the spray chamber. When the spray chamber drain line is empty, extinguish the plasma by clicking “Stop” in the Instrument window. Loosen the peristaltic pump tubing and turn off the Peltier cooler.

11.3.9.2. Auto-shutdown (unattended shutdown) requires adding a 5% HNO₃ sample (use autosampler position 9) and a DI water sample (use autosampler position 10) to the last autosampler sequence (in the sample window). In the **Run List** window, click on Auto Stop to set shutdown after run is complete. Start the autosampler batch. On the following workday, run the peristaltic pump to completely drain the uptake lines and the spray chamber, then loosen the pump tubing. Allow the pump tubing to relax for at least 1 hour. Alternatively, the tubing can be removed and saved in a bag labeled as “used” and new tubing installed.

12. Data Analysis and Calculations

12.1. Data Entry

12.1.1. To transfer the data file: On the desktop, double click on the Report Output folder. Highlight the filename and drag it to the desired folder (i.e. Element).

12.1.2. To archive raw data files: Every few runs, move the raw sample files (except those from the most recent run) from the C drive the sub-directory Dataset\Default to the “annual” Archive. On the desktop, double click on the Default folder. Highlight the files and drag them to the “annual” folder.

13. Method Performance

13.1. MDL studies are performed for all analytes as described in Section 9.11.

13.1.1. The MDLs must be lower than in-house RLs. If not, the RLs will need to be changed or the MDL study replicated.



- 13.1.2. MDLs shall be re-determined following any change to the sample preparation procedure.
- 13.2. Analytical accuracy is determined using LCS/MBSPK, SRM or MS analyses. Acceptance limits for spike recovery are specified in the analytical methods and are normally 80 to 120% for LCS and 75 to 125% for matrix spikes. Acceptance limits for SRM analyzes are determined by the SRM supplier or manufacturer.
- 13.3. Laboratory precision is measured by performing replicate analyzes. Replicates (sample or matrix spike) acceptance limits are $\pm 20\%$.
- 13.4. Accuracy and precision acceptance limits are disseminated to the bench chemists and LIMS administrator for use in monitoring method performance in real time.

14. Pollution Prevention

- 14.1. All acidified sample waste must first be neutralized prior to sink disposal.
- 14.2. Dispose of expired standards into the designated barrel in the hazardous waste room.
- 14.3. Samples that are designated as hazardous waste by the LIMS "Hazardous Report" must be placed in the designated drum in the Hazardous Waste Storage Area when they are disposed. This process is described in SOP 1003S.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

- 15.1. Precision Criteria: Intensity RSDs should be $\leq 5\%$ for concentrations ≥ 10 RLs, Conc. SD ≤ 1 RL for concentrations < 10 RLs. If a sample has poor precision (RSD or a SD outside these limits), rerun the sample. If the RSDs or SDs are still outside the limits, then the sample may need to be rerun at dilution (if no instrumental precision problems are suspected).
- 15.2. Internal Standard Responses
 - 15.2.1. The internal standard intensities for all internal standards used will be monitored and compared to the intensity in the most recently run calibration blank.
 - 15.2.2. The intensities of the internal standards in all samples, QC, and continuing calibration checks should be 60-125% of the original response in the calibration blank. If the responses are not within the limits, rinse for 10-15 minutes, then run a CCB to check the intensities of the internal standards in the blank. If the intensities are now close to the intensities of the internal standards in the original calibration blank, dilute the sample by a factor of 2 to 5, and reanalyze.
- 15.3. Isotope Selection:
 - 15.3.1. Look for significant differences ($> 2\%$ for concentrations ≥ 50 RLs, or > 1 RL for concentrations < 50 RLs) between isotopes on those elements which have multiple isotopes. If the difference is significant, choose the isotope with the lowest concentration.



15.3.2. Highlight the raw data for the acceptable values of the requested elements. If an isotope other than the first one listed is chosen, make a dash with highlighter pen into the margin to the left of isotope.

15.3.3. For indications of possible interference, refer to the interference information in the Equations window of the method.

15.4. QC Samples Review

15.4.1. Method QC Solutions:

15.4.1.1. QCS analysis should be performed when new standards are prepared to verify the accuracy of the calibration standards.

15.4.1.1.1. Whenever the QCS is analyzed the results should be within the certified QC range. If the limits are not met, rerun the QCS. If the limits are still not met, re-preparation of standards and/or recalibration may be indicated. Notify the supervisor of QCS problems.

15.4.1.2. Calibration Verifications (ICV, CCV): Calibration verification QC samples are run to verify calibration stability. The ICV is run immediately after calibration and the CCV is run before and after groups of up to 10 samples. Both ICV and CCV readings should be $\pm 10\%$ of the true value for all requested elements for each isotope used. If this limit is not met, recalibrate and rerun the samples; or rinsing (10-15 minutes) may correct a matrix carry-over effect, followed by rerunning the CCV, CCB, and the affected samples.

15.4.1.3. Calibration Blanks (ICB, CCB): Calibration blanks are run after every ICV or CCV to verify baseline stability and to check for carry-over. Both ICB and CCB readings should be $< 1\text{RL}$ (DOD projects require that no analyte is detected $> 2\text{x MDL}$). If this limit is not met, recalibrate the blank, rerun the CCV, CCB, and then rerun the samples that were not bracketed by in-control blanks. Rinsing (5-10 minutes) before recalibrating the blank may correct a carry-over effect.

15.4.1.4. Interference Check Solutions: The interference check solutions, ICSA and ICSAB, are run near the start of the run. See Appendix 8 for the concentrations of these solutions.

15.4.1.4.1. ICSA: The ICSA contains the following interferants: Al, C, Ca, Cl, Fe, K, Mg, Mo, Na, P, S, and Ti. The interferants which are analyzed should be $\pm 20\%$ of true values. The analyte (analytes which are spiked in the ICSAB) concentrations should typically run $\pm 2\text{RL}$, although no QC limits are used. DOD requires the absolute value of all non-spiked analytes to be $< 2 \text{ X MDL}$ (unless they are a verified trace impurity from



one of the spiked analytes.

15.4.1.4.2. ICSAB: The ICSAB solution contains the same interferants as the ICSA at the same levels, plus some commonly requested analytes. These analytes are Ag, As, Cd, Co, Cr, Cu, Mn, Ni, and Zn; they are all at 20 µg/L in the ICSAB solution. Both the interferants which are analyzed and the analytes should be $\pm 20\%$ of true values.

15.4.1.5. Low Check Standard: This low level standard verifies the accuracy of the instrument at the RL for all analytes. The limits are $\pm 1/2$ RL. DOD requires limits within 20% of the expected value. If the concentrations are outside this range, the analyst should look for the possible cause (e.g. calibration blank intensities too high, baseline drift, contamination, etc.). Re-preparation of the blank, recalibration of the blank, or rinsing the instrument may be required.

15.4.1.6. Linear Range Solutions: The linear range of an instrument for an isotope is the upper limit of accurate quantitation with practical rinse-down times. It varies for each isotope and with instrumental conditions. Two LR solutions can be analyzed on a daily basis if the samples are expected or found to be above the calibration range. LR200 (200 µg/L non-minerals, 20,000 µg/L minerals) and LR300 (300 µg/L non-minerals, 30,000 µg/L minerals) are the linear range solutions. The LR solution concentration must be within 10% of the true value to extend the calibration range of that isotope. DOD requires samples to be diluted and reanalyzed (if possible) to bring them within the calibration curve.

15.4.2. Digestion / Batch QC Samples

15.4.2.1.1. Method Blank (MB): A method blank (MB) should be run with every batch of samples or every CLP sample delivery group (SDG). A minimum of one MB must be run for every batch of 20 samples of the same matrix. For solid matrix DOD projects, add Teflon boiling chips to the MB.

15.4.2.1.2. MB values greater than the RL indicate laboratory or reagent contamination.

15.4.2.1.3. The method blank concentration should be $< 1RL$ for all requested elements. If a requested element is detected in the method blank at $> 1RL$, then all the associated samples need to be re-digested and reanalyzed unless all samples are > 10 times the detected method blank concentration. The analyst should fill out a corrective action form



and the supervisor should be informed.

15.4.2.2. Laboratory Control Sample, Reference Sample or Method Blank Spike (LCS / REF / MBSPK)

15.4.2.2.1. One LCS, REF or MBSPK (of the same matrix type as the samples), should be analyzed with each batch of samples of the same preparation procedure.

15.4.2.2.2. For an aqueous LCS, a REF sample or an MBSPK, the quality control sample must be carried through all the procedures with which the samples are subjected. The MBSPK is prepared by spiking an aliquot of the method blank at the appropriate levels. The REF sample is prepared by diluting a QC standard to the appropriate levels.

15.4.2.2.3. The percent recovery for an aqueous LCS is calculated according to the following:

$$\% R = \frac{LCS}{s} * 100$$

Where:

%R: Percent Recovery

LCS: LCS, REF, or MBSPK Results

s: True concentration

15.4.2.2.4. The Percent Recovery for the aqueous LCS, REF sample, or MBSPK should be within the required control limits of 80-120% (85-115% for Method 200.8). If the recovery is outside the QC limits, then the source of the problem shall be identified and resolved before re-preparation of the sample batch. The analyst should fill out a corrective action form, and the supervisor should be informed.

15.4.2.2.5. For a soil reference, typically an ERA SRM, the certified ranges are used as recovery limits, though a client may specify other statistical limits. The reference sample concentration must be calculated in mg/kg units. If the recovery is outside the certified range, then the source of the problem shall be identified and resolved before re-preparation of the sample batch. The analyst should fill out a corrective action form, and the supervisor should be informed.



15.4.2.3. Matrix Spike/Matrix Spike Duplicate.

15.4.2.3.1. . A matrix spike should be run with every batch of samples or every CLP sample delivery group (SDG). The laboratory must spike a known amount of analyte into a minimum of one sample per batch not to exceed 20 samples. DOD requires an MS/MSD for each batch of 20 samples.

15.4.2.3.2. Calculate the percent recovery for the matrix spike as follows:

$$\% R = \frac{C_s - C}{s} * 100$$

Where:

%R: Percent Recovery

C_s : Measured concentration in fortified sample matrix

C: Measured concentration in unfortified sample

s: Amount of analyte added to sample matrix

15.4.2.3.3. The recovery of the matrix spike should be within the designated QC limits of 75-125%. If it is not within this range, and the LCS recovery is acceptable, the data user will be informed that the result in the unfortified sample is suspect due to heterogeneity or an uncorrected interference effect. Recovery calculations are not required if the concentration of the analyte added is <25% of the analyte present in the sample. If the matrix spike %R is outside the QC limits, the analyst should fill out a corrective action form and the supervisor should be informed. For DOD spike recovery acceptance criteria is 85-115%. Also, DOD projects require a post digestion spike for out of control analytes.

15.4.2.4. Laboratory Duplicate

15.4.2.4.1. A laboratory duplicate should be run with every batch of samples or every CLP sample delivery group (SDG). There must be at least one laboratory duplicate prepared with each batch of samples not to exceed 20 samples.

15.4.2.4.2. Calculate the RPD as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2) / 2} * 100$$



Where:

RPD: Relative Percent Difference

D1: Measured concentration of first sample

D2: Measured concentration of replicate sample

15.4.2.4.3. A control limit of $\leq 20\%$ shall be used for the RPD if the sample concentration is $> 5RL$. A control limit of $\pm 1RL$ shall be used if either the sample or the duplicate sample concentration is $< 5RL$. If it is not within this range, the analyst should fill out a corrective action form and the supervisor should be informed. The project manager will be informed of the poor duplication, and project specific corrective action will be taken.

16. Contingencies for Handling Out-of-Control or Unacceptable Data

- 16.1. Calibration: If the calibration does not meet the criteria in Section 11.3.3.2, then corrective action shall be taken before proceeding with recalibration. This could involve uptake rate optimization, clog removal, re-preparation of calibration standards, etc.
- 16.2. Instrumental QC checks: If an instrumental QC sample (CV, CB, QCS, etc.) is out of control, then corrective action shall be taken before proceeding with analysis. This could involve recalibration of the blank (resetting the baseline), re-preparation of calibration standards and recalibration, analysis of an alternate QCS, etc.
- 16.3. Instrument malfunctions: When instrument malfunctions occur, consult with other experienced ICP-MS operators or the supervisor for guidance. The maintenance logbook, the ICP-MS hardware manual, or the ICP-MS software manual could be helpful for troubleshooting.
- 16.4. In the event of significant QC failure, analysis will stop and the analyst will perform corrective action as discussed above. In general, out-of-control sample results will not be reported. Reruns will be conducted based on sample availability. If insufficient sample remains the client will be notified to determine an appropriate course of action.

17. Waste Management

- 17.1. Metals analysis results in the generation of two waste streams which must be given special treatment.
 - 17.1.1. Acidic solutions having pH < 2 and little or no trace metal concentrations: These should be neutralized to pH 7 and then sink discharged. A log book for Elementary Neutralization Activities is available in the Neutralization Area of the Lab. The Date, Source, Volume, Initial and Final



pH, and Analyst initials should be recorded each time waste is neutralized.

17.1.2. Samples and sample preparation solutions having pH <2 and Hazardous levels of trace metals. A list of such samples is computer generated from sample analysis data. This list is used to mark all samples and sample solutions requiring segregation and disposal as Hazardous Waste. All such wastes are collected in a polyethylene satellite container in the Metals Instrument Lab or in the Metals Waste Drum in the Hazardous Waste Accumulation site. When the containers are full the Hazardous Materials Coordinator is notified for offsite disposal.

18. Method References

- 18.1. "Methods for the Determination of Metals in Environmental Samples - Supplement 1", "Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry", Revision 5.5, EPA-600/R-94-111, May 1998.
- 18.2. Nexion 300D Hardware Manual, Perkin-Elmer Corporation
- 18.3. Nexion 350D ICP-MS Software Manual, Perkin-Elmer Corporation
- 18.4. EPA SW-846 "Method 6020A Inductively Coupled Plasma – Mass Spectrometry", Revision 1, Feb. 2007

19. Appendices

- 19.1. Appendix 1: Internal Standards and Tuning Solutions
- 19.2. Appendix 2: Calibration Stocks
- 19.3. Appendix 3: Calibration Intermediate
- 19.4. Appendix 4: Calibration Standards and Linear Range Solutions
- 19.5. Appendix 5: Inorganic Ventures ICV
- 19.6. Appendix 6: Dual Detector Solution
- 19.7. Appendix 7: Low Check Solution
- 19.8. Appendix 8: Interference Check Solutions (ICSA, ICSAB)
- 19.9. Appendix 9: Interference Correction Equations
- 19.10. Appendix 10: Analytical Isotopes and Additional Monitored Isotopes
- 19.11. Appendix 11: ICP-MS Reporting Limits
- 19.12. Appendix 12: Troubleshooting
- 19.13. Appendix 13: Instrument Maintenance



Appendix 1

ICP-MS INTERNAL STANDARDS AND TUNING SOLUTIONS

All concentrations in mg/L

1. INTERNAL STANDARD SOLUTION

Use at 1/100 for final levels, all concentrations in mg/L

ELEMENT	STOCK CONC	VOL OF STK IN 1000 ml	FINAL CONC in 1% HNO ₃
⁶ Li	1000	0.15	0.15
Sc	1000	0.12	0.120
Ge	1000	0.6	0.600
Y	1000	0.05	0.050
In	1000	0.05	0.050
Tb	1000	0.05	0.050
Bi	1000	0.2	0.200
Ga	1000	0.1	0.100

2. SETUP SOLUTION

Use at 1/100 for final levels, all concentrations in mg/L

ELEMENT	STOCK CONC	VOL OF STK IN 100 ml	INT CONC	FINAL CONC in 1% HNO ₃
Be	1000	0.10	1.0	0.001
Mg	1000	0.10	1.0	0.001
Fe	1000	0.10	1.0	0.001
In	1000	0.10	1.0	0.001
Li	1000	0.10	1.0	0.001
Ce	1000	0.10	1.0	0.001
U	1000	0.10	1.0	0.001
Pb	1000	0.10	1.0	0.001



Appendix 2

ICP-MS CALIBRATION STOCKS

STOCK #1

Prepare in 1% trace grade HNO₃. All concentrations in mg/L

ELEMENT	STOCK CONC	VOL OF STD IN 100 mL	STOCK CONC
Ag	10000	1.0	100
As	10000	1.0	100
Ba	10000	1.0	100
Be	10000	1.0	100
Cd	10000	1.0	100
Co	10000	1.0	100
Cr	10000	1.0	100
Cu	10000	1.0	100
Mn	10000	1.0	100
Ni	10000	1.0	100
Pb	10000	1.0	100
Se	10000	1.0	100
Tl	10000	1.0	100
Th	10000	1.0	100
U	1000	10.0	100
V	10000	1.0	100
Zn	10000	1.0	100

STOCK #2

Prepare in DI H₂O

Sb	10000	1.0	100
Mo	10000	1.0	100



Appendix 3

ICP-MS CALIBRATION INTERMEDIATE

All concentrations in mg/L
Prepare in 1% trace grade HNO₃

ELEMENT	STOCK CONC	VOL OF STK IN 100 mL	INT CONC
Al	10000	10.0	1000
Ca	10000	10.0	1000
Fe	10000	10.0	1000
K	10000	10.0	1000
Mg	10000	10.0	1000
Na	10000	10.0	1000
STOCK #1	see table 2	10.0	10
STOCK #2	see table 2	10.0	10



Appendix 4

ICP-MS CALIBRATION STANDARDS and LINEAR RANGE SOLUTIONS

Add the intermediate to a 100 mL volumetric flask containing 1.0 mL trace metal grade HNO₃ and bring to volume. Standard 3 is made up to 200 mL with addition of 2.0 mL HNO₃.

NOTE: Standard 1 is a standard at the RL (Low Check Standard) level see Section 7.9 and Appendix 7 for solution preparation.

Standard	mL Intermediate	Concentration $\mu\text{g/L}$ in 1% HNO ₃	
		Non-minerals	Minerals
1 see Note	0.10	RL	RL
2	0.1	10	1000
3	0.2	20	2000
4	1.0	50	5000
5	1.0	100	10000
LR200	2.0	200	20000
LR300	3.0	300	30000



Appendix 5

ICP-MS INORGANIC VENTURES ICV

All concentrations in mg/L

ELEMENT	STOCK CONC	FINAL CONC
Ag	2.5	0.050
Al	250	5.000
As	2.5	0.050
Ba	2.5	0.050
Be	2.5	0.050
Ca	250	5.000
Cd	2.5	0.050
Co	2.5	0.050
Cr	2.5	0.050
Cu	2.5	0.050
Fe	250	5.000
K	250	5.000
Mg	250	5.000
Mn	2.5	0.050
Mo	2.5	0.050
Na	250	5.000
Ni	2.5	0.050
Pb	2.5	0.050
Sb	2.5	0.050
Se	4.0	0.080
Th	2.5	0.050
Tl	2.5	0.050
U	2.5	0.050
V	2.5	0.050
Zn	2.5	0.050



Appendix 6

ICP-MS DUAL DETECTOR CALIBRATION SOLUTION

All concentrations in mg/L
Use Intermediate 1 at 1/200

ELEMENT	STOCK CONC	VOL OF STOCK (Elan) Intermediate 1 in 200mL	VOL OF SUPPLEMENT 1000mg/L individual elements	FINAL CALIB SOL'N CONC $\mu\text{g/L}$ (in 1% HNO_3)
Ag	1000	1.0	0.04	0.250
Al	1000	1.0		0.050
As	1000	1.0		0.050
Ba	1000	1.0	0.04	0.250
Be	1000	1.0		0.050
Bi	1000	1.0		0.050
Ca	1000	1.0	0.09	0.500
Cd	1000	1.0	0.04	0.250
Co	1000	1.0	0.01	0.100
Cr	1000	1.0	0.01	0.100
Cu	1000	1.0	0.04	0.250
Fe	1000	1.0	0.09	0.500
Ge	1000	1.0		0.050
In	1000	1.0		0.050
K	1000	1.0		0.050
^6Li	1000	1.0		0.050
Mg	1000	1.0		0.050
Mn	1000	1.0	0.01	0.100
Mo	1000	1.0	0.04	0.250
Na	1000	1.0		0.050
Ni	1000	1.0		0.050
Pb	1000	1.0		0.050
Sb	1000	1.0	0.04	0.250
Sc	1000	1.0		0.050
Tb	1000	1.0		0.050
Th	1000	1.0		0.050
Tl	1000	1.0		0.050
U	1000	1.0		0.050
V	1000	1.0	0.01	0.100
Y	1000	1.0		0.050
Zn	1000	1.0		0.050



Appendix 7

ICP-MS LOW CHECK SOLUTION

Use Intermediate at 0.05/100 for final levels

ELEMENT	STOCK CONC mg/L	VOL OF STOCK IN 100 mL	INT CONC mg/L	FINAL CONC $\mu\text{g/L}$ (in 1% HNO_3)
Ag	1000	0.04	0.4	0.2
Al	10000	0.4	40	20
As	1000	0.04	0.4	0.2
Ba	1000	0.1	1	0.5
Be	1000	0.04	0.4	0.2
Ca	10000	1	100	50
Cd	1000	0.02	0.2	0.1
Co	1000	0.04	0.4	0.2
Cr	1000	0.1	1	0.5
Cu	1000	0.1	1	0.5
Fe	10000	0.4	40	20
K	10000	0.4	40	20
Mg	10000	0.4	40	20
Mn	1000	0.1	1	0.5
Mo	1000	0.04	0.4	0.2
Na	10000	2	200	100
Ni	1000	0.1	1	0.5
Pb	1000	0.02	0.2	0.1
Sb	1000	0.04	0.4	0.2
Se	1000	0.1	1	0.5
Th	1000	0.04	0.4	0.2
Tl	1000	0.04	0.4	0.2
U	1000	0.04	0.4	0.2
V	1000	0.04	0.4	0.2
Zn	1000	0.8	8	4



Appendix 8

ICP-MS Interference Check Solutions: ICSA and ICSAB

All concentrations in mg/L

* AR-6020ICS-A10 Custom Stock Solution from Inorganic Ventures.

ELEMENT	ICSA STOCK CONC*	ICSA FINAL CONC	ICSAB STOCK CONC	ICSAB FINAL CONC (in 1% HNO ₃)
Ag			2.0	0.02
Al	100	20		20
As			2.0	0.02
C	200	40		40
Ca	100	20		20
Cd			2.0	0.02
Cl	1000	200		200
Co			2.0	0.02
Cr			2.0	0.02
Cu			2.0	0.02
Fe	100	20		20
K	100	20		20
Mg	100	20		20
Mn			2.0	0.02
Mo	2	0.4		0.4
Na	100	20		20
Ni			2.0	0.02
P	100	20		20
S	100	20		20
Ti	2	0.4		0.4
Zn			2.0	0.02



Appendix 9

ICP-MS INTERFERENCE CORRECTION EQUATIONS

ANALYTE	MASS	EQUATION
⁷⁸ Se	77.917	-0.030461*Kr83
⁸² Se	81.917	-1.007833*Kr83
⁹⁸ Mo	97.906	-0.109613*Ru101
¹¹¹ Cd	110.904	-1.073*(MoO 108-(0.712*Pd106))
¹¹⁴ Cd	113.904	-0.027250*Sn118
¹¹⁵ In	114.904	-0.014038*Sn118
¹²³ Sb	122.904	-0.125884*Te125
²⁰⁸ Pb	207.977	Pb206+Pb207



Appendix 10

ANALYTICAL ISOTOPES AND ADDITIONAL MONITORED ISOTOPES

1. ANALYTICAL ISOTOPES			2. ADDITIONAL ISOTOPES	
ELEMENT	ISOTOPE(S)	MODE	ELEMENT	ISOTOPE
Li	6	STD	Ru	101
Be	9	STD	Pd	106
Sc	45	STD	Sn	118
Al	27	STD	Te	125
V	51	DRC		
Cr	52, 53	DRC		
Fe	54, 57	KED		
Mn	55	DRC		
Co	59	KED		
Ge	72	KED		
Ni	60, 62	KED		
Cu	63, 65	KED		
Zn	66, 67, 68	KED		
Ga	71	DRC		
As	75	KED		
Se	78, 82	DRC		
Mo	98	KED		
Y	89	STD		
Kr	83	STD		
Ag	107	STD		
Cd	111, 114	KED		
In	115	KED/STD		
Sb	121, 123	STD		
Ba	135, 137	STD		
Tb	159	STD		
Tl	205	STD		
Pb	208	STD		
Bi	209	STD		
Th	232	STD		
U	238	STD		



Appendix 11

ICP-MS REPORTING LIMITS

ELEMENT	RL µg/L
Ag	0.2
Al	20
As	0.2
Ba	0.5
Be	0.2
Ca	50
Cd	0.1
Co	0.2
Cr	0.5
Cu	0.5
Fe	20
K	20
Mg	20
Mn	0.5
Mo	0.2
Na	100
Ni	0.5
Pb	0.1
Sb	0.2
Se	0.5
Th	0.2
Tl	0.2
U	0.2
V	0.2
Zn	4



Appendix 12

Troubleshooting

1. The following sections describe some commonly occurring problems and proposed solutions:

1.1. Poor Curve Fit

1.1.1. Poor curve fit may require individual standards to be rerun or re-prepared; a complete recalibration may be required.

1.1.2. If the curve fit appears to be off between pulse readings (less than approx. 1.5 million-cps) and analog readings (approx. 2 million to 1 billion cps), then a new dual detector optimization/calibration may be required. Poor Pb or Tl curve fit is a good indicator of when this is necessary (other indicator elements are Mn, Th, U).

1.2. Dual Detector Calibration/Optimization : Edit the Smart Tune file in use by adding Detector Voltage optimization and Dual Detector optimization routines. Or go to **DUALDET.SWZ**

1.2.1. Check the files to be used. For the Detector optimization both a Pulse and Analog method will be listed in the Setup section of the SmartTune window. Perform the Detector optimization by aspirating Blank solution. The results will be automatically printed at the end of the procedure.

1.2.2. Check the files to be used. Make sure the DualDetectorNew.mth is listed. Perform a dual detector calibration. Aspirate the dual detector calibration solution. Click on Calibrate. This calibration will take approximately 10 minutes to run. Save the file. An optimization summary will be automatically printed. Note the range of gain values from the optimization print out; record the range of gain values in the maintenance log and compare with those from several previous dual detector calibrations. On the optimization summary, make a note of any r-values <0.9995 and number of points <10. On the Interactive page, check the individual calibration graphs for good curve fits.

1.2.3. Run a daily performance check to check sensitivity. Compare the sensitivity before and after the dual detector calibration.

1.3. Poor relative standard deviation (precision) on standards and samples: Poor RSDs have many potential causes. Recalibrate if any adjustments are made.

1.3.1. First, check that the peristaltic pump tubing is in good condition and not worn. When a probe is removed and reinserted in the rinse solution an air bubble will be visible in the tubing. Watch the progress of this bubble and check that the flow is smooth without any pulsation. Only adjust the tension on the pump tubing beds if necessary.

1.3.2. Check that the nebulizer is operating properly by first by checking the back pressure in the



instrument window (Diagnostics Tab). The aerosol may be checked with the plasma off and the nebulizer removed from the spray chamber. Turn on the nebulizer gas and the peristaltic pump; there should be a visible aerosol leaving the spray chamber. If there is not, clean or replace the nebulizer. **NOTE: If a clogged nebulizer is suspected use the “Nebulizer Obstruction Removal Kit” to unclog. Do not sonicate the nebulizer as this will render it non-operational.**

1.3.3. Check that the interface cones are in good condition and the orifices of all cones are round and of the proper size.

1.4. Low Sensitivity

1.4.1. First check the x-y adjustment of the torch to sampler cone: this is normally done during the daily optimization routine.

1.4.2. Check the sample uptake as recommended in section 1.3.2. If it is too low, then check the tubing for clogs and check the air bubble progress in the uptake tubing.

1.4.3. With the plasma off, check the sampler cone to torch spacing using the Perkin Elmer spacer tool. Also check the condition of the cones.

1.5 Check the 6-port Valve. **Aspirate DI water, then air until all water is removed from the sample introduction system. Turn off the Plasma.**

1.5.1 See the maintenance section (pp117-120) of the ESI Manual before disassembling the valve. Inspect valve parts and surfaces for cleanliness and clogs. Clean parts as recommended in the ESI manual. Replace the rotor or stator is necessary (check for scratches on the rotor surface).

1.5.2 Note: the sample probe and sample Loop can be removed from the valve for cleaning and flushing while the instrument is running provided the valve is in the **LOAD** position. These should be flushed with ~2% Nitric acid solution, Methanol, followed by DI water and air.



Appendix 13 Instrument Maintenance

1. Daily Maintenance

1.1. Cones: The sample cone is inspected daily for build-up of salts and soot. No cleaning is required for light build-up. Swab lightly with a slightly DI water moistened cotton swab to remove moderate build-up. Allow to air dry for 5 minutes. If the salt build-up is heavy, remove both the sample and the skimmer cone assembly (Skimmer and attached hyper skimmer), and sonicate after the removal of their O-rings (see page 111-121 of the Nexion® Maintenance Manual).

1.1.1. Peristaltic Pump Tubing: Inspect the peristaltic pump tubing daily for flat areas and wear. Typically, they require replacement after 2 to 3 sample runs.

1.1.2. Water Chiller: Check the water chiller daily for the following settings: the temperature display should be 14-16°C. The temperature can be adjusted using the knob below the display (wait 5 minutes between adjustments). Check the coolant level under the small square panel on the top right corner of the chiller. It should be almost full (to the line below the cap threads), if not, fill with appropriate coolant. The pressure gauge on the front panel should be between 54-56 psi. The pressure can be adjusted at the regulator located on the back (see page 5-31 of the hardware guide).

1.1.3. Vacuum Pump: Use the Maintenance section of the Instrument window to check oil change parameters.

1.2. Maintenance as Needed:

1.2.1. Nebulizer: The PFA-ST nebulizer may require maintenance if a lowered uptake rate is suspected. Check all tubing connectors and sample probe for clogs first. To change the nebulizer, extinguish the plasma, and replace the nebulizer with a spare one.

1.2.2. Torch: The torch, which is made up of a quartz torch body, a quartz injector and a lexan adapter/base, requires replacement periodically. Torch body discoloration is acceptable unless performance is affected. If the torch has an arc spot, be aware that it may develop into a crack or hole. Sensitivity losses may necessitate torch maintenance to eliminate it as a possible cause.

1.2.3. Load Coil: The load coil requires replacement periodically. Inconsistent torch lighting may necessitate cleaning of the coil. Replace the coil if the surface becomes pitted from excessive arcing.



Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Semi-Volatile Organic Analysis Gas Chromatography/Mass Spectrometry EPA Method 8270E

**SOP 804S
Version 018**

**Revision Date: 6/06/19
Effective Date: 6/06/19**

Prepared by:

Van Spohn

Approvals:

A handwritten signature in blue ink that reads "Brian N. Bebee".

Brian N. Bebee, Laboratory Section Manager

A handwritten signature in blue ink that reads "Bob Congleton".

Bob Congleton, Quality Assurance, Manager



1. Scope and Application

- 1.1. Method 8270E is used to determine the concentration of semivolatile organic compounds in extracts prepared from various types of sediments, soils, solid waste matrices, tissues, and waters. See Appendix 20.2 for the compounds that may be determined using this method. EPA Method 8270E will be reported for State of California work.
- 1.2. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including the EPA SW-846 methods and the Department of Defense Quality Systems Manual (DoD-QSM). The procedures described also meet the requirements of EPA Method 625.1 (Reference 19.5). The requirements outlined in Appendix 20.7 are used when analyzing samples using EPA Method 625.1. Some text is directly from the referenced documents. The table in Appendix 20.1 outlines ARI's routine procedure. DOD-QSM acceptance criteria are shown in Appendix B of DOD-QSM 5.3. Acceptance criteria for projects requiring modified DOD-QSM criteria are provided by the project manager and are project specific. **Analysts are responsible for determining which QA program is applicable to a set of samples prior to beginning analyzes and complying with all project specific analytical requirements.**
- 1.3. The reference methods for this procedure are listed in Section 19.
- 1.4. Method 8270E may be used to analyze for most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted from a gas-liquid chromatographic system. Such compounds include hydrocarbons, polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, resin acids, phthalate esters, organophosphates, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. Appendix 20.3 includes a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system. Detailed lists of project-specific compounds may be found in the LQAP for a given project. Other compounds may be analyzed if specifically requested.
- 1.5. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration, and its chromatography is poor. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine and pyridine are difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 4-Chloroaniline; 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are active analytes and



subject to erratic chromatographic behavior, especially if the GC system is contaminated.

1.6. Method Reporting Limits

Extraction Type	Extraction Parameters	MRL
In House Soil Extraction	7.5g to 0.5mL	67 to 330µg/Kg
DUAL SCAN Soil Extraction	10g to 1mL	20 to 200µg/Kg-Full scan 5 to 100µg/Kg-Sim scan
Water Extraction	500mL to 0.5mL	1 to 10µg/L
1,4-Dioxane Water Extract	500ml to 1.0ml	0.2µg/L

1.7. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.8. ARI routinely performs Method Detection Limit (MDL) studies for each extraction and analytical method performed using this SOP. The results of these studies help define the reporting limits of data generated. The results are kept by the QA department, and are distributed to the bench chemists and the ELEMENT administrator. For current RLs and MDLs, see the ARI website.

2. Summary of Procedure

2.1. For example, an aliquot of sample (water or soil) is extracted by a matrix appropriate technique. Typically, this will be either continuous liquid-liquid or separatory funnel extraction for aqueous samples and sonication or microwave extraction for solid samples. The extracted sample is subjected to any appropriate cleanup and then concentrated. The extract is then delivered to the refrigerator 15.

2.2. After the instrument lab has assumed custody of the sample, it is injected onto the column of a properly calibrated GC/MS system for chromatographic determination. Analyte identification is performed using the relative time of elution (RRT, relative to the appropriate internal standard) and comparison of mass spectra to a spectral library. Quantitation is performed by comparing the detector responses of each analytes' characteristic mass ion and internal standard characteristic mass ion to the responses of these ions in a calibration curve containing those analytes at known concentrations.

3. Definitions

3.1. Initial Calibration Verification (ICV): A process used to verify that the current instrument calibration is acceptable at the beginning of an analytical sequence

3.2. Continuing Calibration Verification (CCV): A process used to verify that the current instrument calibration is acceptable during or at the end of an analytical sequence.



- 3.3. Decafluorotriphenylphosphine, (DFTTP): used to demonstrate acceptable tuning parameters.
- 3.4. Method Detection Limit (MDL): The lowest result that can reliably be distinguished in a matrix from a blank. Also referred to as Detection Limit (DL)
- 3.5. Extracted Ion Current Profile (EICP): A plot of the abundance of a specific ion as a function of time
- 3.6. Second Source Verification (SCV): A process used to verify that the current instrument verification is acceptable.
- 3.7. Internal Standard (IS): Internal standards are compounds added to each standard, sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of these internal standards.
- 3.8. Blank Spike (BS): A sample matrix, free from the analytes of interest, spiked with verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system.
- 3.9. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, a BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS.
- 3.10. Laboratory Information Management System (LIMS): Software used to compile and report final chromatographic data. The use of the term "Element" refers to the LIMS system.
- 3.11. Limit of Detection (LOD): The lowest result that can be reported while meeting method precision and accuracy requirements.
- 3.12. Method Reporting Limit (MRL): The lowest result that may be reported unqualified based upon the lowest curve point.
- 3.13. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method.
- 3.14. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision.
- 3.15. Method Blank (MB): A sample of a matrix like the batch of associated samples (when available) that is free from the analytes of interest and interferences. It is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures.
- 3.16. Organic-free reagent water (OFW): Organic-free reagent water, all references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.
- 3.17. Method detection Limit Spike (MDL): A matrix spike prepared at the reporting limit and used for preparing MDL studies to calculate the MDL.



- 3.18. Reconstructed Ion Current (RIC): A plot of the total instrument response versus time
- 3.19. Relative Retention Time (RRT): The elution time of an analyte relative to the elution time of its associated internal standard
- 3.20. Instrument Blank (IB): Clean solvent containing internal standards at the appropriate level for the analysis is analyzed using the same conditions as a regular sample. An instrument blank is analyzed to detect and/or remove sample carryover from one analysis to another.
- 3.21. Surrogate (SURR): A substance with properties that mimic analytes of interest. It is unlikely to be found in environment samples and is added to them to monitor extraction efficiency.
- 3.22. Target software (TARGET): Chromatographic analysis software from Thermoquest Thru-Put version 4.14
- 3.23. Dual scan (DS): Dual scan is the synchronous acquisition of both full scan and sim data used to achieve lower reporting limits for all matrices.
- 3.24. Low level calibration verification (LCV): Lowest calibration standard used for an initial calibration.

4. Interferences

- 4.1. Extraction Interferences: Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem. Most commonly this will involve contamination with the phthalate esters.
- 4.2. Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride followed by baking the glassware at 450 degrees centigrade overnight.
- 4.3. High purity reagents must be used to minimize interference problems.
- 4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, or the detector shows saturation due to analytes present in a sample, subsequent samples should be scrutinized for cross contamination.
- 4.5. Matrix interferences may be removed using sample clean-ups depending on the list of target analytes, these may include (but are not limited to) the use of solid phase extraction clean-up, silica gel, absorption chromatography, water washing or gel permeation chromatography. See the appropriate extractions SOPs for clean-up applicability to matrices or target analytes.

5. Safety

- 5.1. The toxicity and carcinogenicity of each reagent used in this method is not precisely defined.

However, all compounds and solutions should be treated as health hazards, and exposure of these



chemicals to skin and clothing should be minimized to the lowest possible level by whatever means available.

- 5.2. Contact with all chemicals should be minimized using nitrile gloves, safety glasses, and laboratory coats.
- 5.3. Standard solutions should be handled in the fume hoods to avoid exposure to fumes.
- 5.4. All GC-MS split vents and vacuum exhaust are connected to an exhaust vent or charcoal filter.
- 5.5. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult with SDS sheets for all chemicals handled. SDS are available on-line at www.msds hazcom.com.

6. Equipment and Supplies

6.1. Gas chromatograph/mass spectrometer system

- 6.1.1. Gas chromatograph - An analytical system with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, autosampler, and gases. The capillary column should be directly coupled to the source of the mass spectrometer.
- 6.1.2. Fused-silica capillary column - 30 m x 0.25 mm ID (or 0.32 mm ID) 0.25 -0.5 μm film thickness coated with cross bonded 5% diphenyl/95% dimethylpolysiloxane stationary phase (Phenomex ZB-5msi or equivalent).
- 6.1.3. Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less. The mass spectrometer must be capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all the criteria in Appendix 20.3 when 1-2 μL of the GC/MS tuning standard is injected through the GC (50 ng or less of DFTPP).
- 6.1.4. GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration for each compound of interest and achieves acceptable tuning performance criteria. For a capillary column, the interface is usually capillary-direct into the mass spectrometer source.

6.2. Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on electronic media of all mass spectra obtained throughout the duration of the chromatographic program.

- 6.2.1. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits.



6.2.2. The data system should be equipped with the most recent version of the EPA/NIST Mass Spectral Library.

6.2.3. The data must be securely stored for at least seven years from date of acquisition in Target.

7. Reagents and Standards

7.1. Stock standard solutions (1000 - 10,000 µg/L) - Standard solutions can be prepared from neat standards or purchased as certified solutions. Certificates of analysis for all purchased neats and solutions are kept electronically in Element

7.2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2.1. All Components and reagents used for any standard preparation are entered in Element

7.2.2. The laboratory should have high purity acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, methanol and other appropriate solvents for preparing standards.

7.2.3. Organic-free reagent water - All references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.

7.2.4. Neat standards are not assigned an expiration day and are considered never expired regardless of what is shown on the standard certificate (COA).

7.3. Stock Standard Preparation

7.3.1. Prepare stock standard solutions by accurately weighing about 0.2500 g of pure material. Dissolve the material in pesticide quality methylene chloride or other suitable solvent and dilute to volume in a 25mL volumetric flask. Larger or smaller volumes can be used at the convenience of the analyst. When compound purity is assayed to be 97% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

7.3.2. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.3.3. Transfer the stock standard solutions into amber bottles with Teflon lined screw-caps. Store at >0 to 6°C and protect from light.

7.3.4. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.3.5. Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

7.3.6. Stock standard solutions must be replaced 1 year after being de-ampullated.



- 7.3.7. A PDF record of analysis must be attached to the standard in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.
- 7.4. Internal Standard Stock Solution - The internal standards employed are 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, di-n-octylphthalate-d4 and perylene-d12. Other compounds may be used as internal standards if the method requirements are met. Dissolve 0.250g of each compound with a small volume of methylene chloride or appropriate solvent. Transfer to a 250mL volumetric flask and dilute to volume with methylene chloride. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d12. The resulting solution will contain each standard at a concentration of 1,000µg/ml.
- 7.4.1. Each 0.1mL aliquot of the sample extract undergoing analysis should be spiked with 2µL of the internal standard solution, resulting in a concentration of 20ng/µL of each internal standard (for example, when preparing a sample aliquot of 0.3ml, spike the extract with 6µl of the internal standard stock). Dual Scan internal standard is at 200µg/mL and is spiked at 4µg/ml.
- 7.5. Surrogate Stock Standards - The surrogate standards employed are phenol-d5, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluorobiphenyl, 2-chlorophenol-d4, 1,2-dichlorobenzene-d4, and p-terphenyl-d14.
- 7.5.1. Prepare a stock solution containing all the acid surrogates (d5-phenol, 2-fluorophenol, d4-2-chlorophenol, and 2,4,6-tribromophenol) by adding 250mg of each into a 50mL volumetric flask. Bring the solution up to volume with methylene chloride. The resulting solution will contain the acid surrogates at 5000µg/ml.
- 7.5.2. Prepare a stock solution containing all the base surrogates (d4-1,2-dichlorobenzene, d5-nitrobenzene, 2-fluorobiphenyl, and d14-p-terphenyl) by dissolving 250mg of each into a 50mL volumetric flask. Bring the solution up to volume with methylene chloride. The resulting solution will contain the base surrogates at 5000 µg/ml.
- 7.6. Working solutions- working standards are prepared from stock standards or purchased as commercially certified mixtures.
- 7.6.1. Working standards expire on the date of expiration of the stock solutions they are made from, on the manufacturer's certified expiration date or within one year from date of preparation, whichever comes first. They must be replaced at this time.
- 7.6.2. Working standard solutions must be replaced 1 year after being de-ampullated.
- 7.6.3. Working standards must be stored at >0 to 6°C and protected from light.
- 7.6.4. Working standards should be checked frequently for signs of concentration or degradation.
- 7.6.5. A PDF record of analysis must be attached to the standard (non-virtual only) in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.



7.7. Surrogate working standards

7.7.1. Surrogate calibration standard- the surrogate calibration standard is prepared by diluting the acid and base surrogate stocks in methylene chloride such that the concentration of each analyte is 500µg/ml. This solution is used to calibrate the instrument to quantitate surrogate concentrations.

7.7.2. Surrogate spiking standard- the surrogate spiking standard is prepared by diluting the acid and base surrogate stocks such the concentrations of the acid surrogates are 150µg/mL and the concentrations of base surrogates are 100µg/ml. This solution is prepared in methanol. This solution is used to spike all extracted samples and QC samples with surrogates.

7.8. Matrix spike working standards- the matrix spiking standards are used to prepare MS/MSD sets as well as BS/BSDs.

7.8.1. The matrix spiking solution is purchased commercially and contains all the analytes in an acetone/methylene chloride mixture. The concentration of each analyte is 100µg/ml.

7.8.2. If alternative matrix spiking solutions are required (for example, a matrix spike containing an extra analyte not contained in the full spike) an appropriate concentration should be determined, and the solution prepared in a water-soluble solvent (usually methanol or acetone) at that concentration.

7.9. Calibration working standards- the standards used to prepare calibration curves are usually purchased as commercially certified mixtures. Working calibration solutions are prepared by diluting these standards in methylene chloride such that the concentration of each analyte is 50 to 1000µg/ml.

7.9.1. Benzoic acid; 2,4-dinitrophenol; and 4,6-dintro-2-methylphenol are augmented in the working calibration solutions such that the concentration of each analyte is 100 to 2000µg/ml.

7.9.2. A selected number of acids and bases are augmented for the Dual Scan working solution from 100 to 225µg/ml.

7.10. GC/MS working tuning standard- a tuning standard should be prepared containing 500µg/mL each of DFTPP (Decafluorotriphenylphosphine); p,p'-DDT, Pentachlorophenol, and Benzidine.

8. Sample Collection, Preservation, Shipment, Storage, Holding time and Disposal.

8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 °C.

8.2. Samples must be stored at ARI, at >0 to 6 °C until final disposal.

8.3. Samples must be extracted within holding times determined from the day of sampling. The standard holding time for water samples is seven days. The standard holding time for solid samples



is 14 days.

8.4. Solid and sediment samples may be stored at -10°C to -20°C to extend the holding time to one year.

8.5. Extracts are delivered to Refrigerator 15 in the instrument laboratory by extractions technicians.

8.5.1. Analysts in the instrument lab assume custody of the sample extracts and then move them into Refrigerator 18 and update the location in Element

8.5.2. Extracts must be stored at >0 to 6 °C and protected from light.

8.5.3. Extracts must be analyzed within 40 days of extraction.

8.5.4. Extracts must be stored in their assigned Element bin.

8.5.5. Extracts may be deposited 40 days after the analysis has been completed and the Element bin will be recycled for future use.

8.5.6. Extracts will be disposed in the large blue barrel in the satellite accumulation area designated for extract vials. Disposed extracts are now marked in Element as disposed.

9. Quality Control

9.1. Quality control requirements related to tuning, initial and continuing calibration are detailed in Section 10 of this document.

9.2. Surrogates

9.2.1. Surrogate standards are added to every sample and associated QA (MB, BS, MS etc.) prior to extraction to monitor extraction efficiency.

9.3. Method Blanks and Instrument Blanks

9.3.1. A method blank is a volume of a clean reference matrix (OFW or sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

9.3.2. Method blank extraction and analysis are performed as follows:

9.3.2.1. MBs must be processed with every batch of 20 or fewer samples of similar matrix

9.3.2.2. Method blanks should be analyzed on each GC/MS system used to analyze associated samples. When a method blank shows contamination the blank should be re-vialed and reanalyzed to confirm the contamination.

9.3.2.3. A method blank for water samples consists of 0.5-1L volume of reagent water. For medium and low level soil/sediment samples, a method blank consists of 1g to 10g of sodium sulfate. Extract, concentrate, cleanup and analyze the method blank according to procedures



used for water; tissue; or solid (soil or sediment) samples.

9.3.2.4. An instrument blank consisting of internal standard and clean solvent is analyzed prior to sample analysis after the ICV when a method blank is not analyzed.

9.4. Blank Spikes (BS)

9.4.1. In order to evaluate the accuracy of the analytical method independent of matrix-related effects, a matrix-specific blank spike (BS) must be included in each preparation batch. The BS must contain all surrogates and target analytes required by the method.

9.4.2. In instances where insufficient sample volumes exist to perform an MS/MSD analysis, an BS/BSD may be performed upon client request to assess the precision of the analytical method. A BSD, when required, is prepared and analyzed identically to the BS.

9.4.2.1. The recovery of each blank spike target must be evaluated and reported

9.4.2.2. The RPDs between the BS/BSD samples must be measured and reported.

9.4.2.3. Evaluate the BS/BSD RPD and note any deviation >30% in the reviewer checklist.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. In order to evaluate the effects of the sample matrix on the methods used for ABN analyses, a mixture of all target compounds is spiked into two aliquots of a sample and analyzed using the same method as all other samples.

9.5.2. A matrix spike and matrix spike duplicate should be extracted and analyzed for every 20 field samples of a similar matrix or whenever samples are extracted by the same procedure.

9.5.2.1. The recovery of each matrix spike must be evaluated and reported.

9.5.2.2. The RPDs between the MS/MSD samples must be measured and reported.

9.5.2.3. the MS/MSD RPD and note any deviation >30% in the reviewer checklist.

9.5.3. As part of a client's QA/QC program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to the laboratory for analysis. The laboratory will not perform MS/MSD analysis on any of the field QC samples.

9.5.4. If a client designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the laboratory shall choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the laboratory shall notify the client that insufficient sample was received and identify the sample selected for the MS/MSD analysis. The rationale for the choice of another sample other than the one designated by the client shall be documented in the narrative.

9.5.5. If there is insufficient sample to perform a requested MS/MSD, the laboratory should contact the client to inform them of the situation. The client will either approve that no MS/MSD is required, require that a reduced sample aliquot be used for the MS/MSD analysis or request that a BS/BSD (See Section 9.4.2) analysis be performed. The laboratory shall document the client's



decision in the narrative.

9.5.6. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.6. Duplicate Analysis

9.6.1. When mandated by project-specific requirements, a duplicate analysis of a given sample may be performed as an independent assessment of method precision. A duplicate consists of an independently prepared second aliquot of a given sample carried through the entire analytical process.

9.6.2. The RPDs between the Sample and Sample duplicate must be measured and reported.

9.6.3. Evaluate the Sample and Sample duplicate RPD and note any deviation >30% in the reviewer checklist.

9.6.4. When mandated by project-specific requirements, an SRM (Standard Reference Material) sample will be analyzed as an independent assessment of method performance.

9.6.5. The recovery of each target in the SRM must be compared to the true value provided by the SRM provider to be evaluated and reported. Any targets not meeting the recovery limits will require corrective action.

9.7. Internal Standard Response (EICP) area and retention time data must be evaluated during and/or immediately after the analysis. The response for the ICV internal standards must be within the inclusive range of -50.0 to +100.0 percent of the response of the internal standards in the most recent mid-point of the initial calibration analysis. The response for each sample, associated batch QC, and the CCV internal standards must be within the inclusive range of -50.0 to +100.0 percent of the response of the internal standards in the most recent ICV. The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the ICV and the last CCV run or from the middle point of the initial calibration. The retention time shift for each of the internal standards must be within ± 0.166 minutes (10 seconds) between the samples/associated batch QC and the ICV.

9.8. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for BS/BSD are statistically generated on a periodic basis. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. All analysts using this SOP must use it in conjunction with Control Limit documentation in order to assess data quality and any possible need for corrective actions. Current control limits may be found in the Element.

9.9. Initial Demonstration of Proficiency- Each analyst must demonstrate initial proficiency with each sample preparation and determinative method combination performed, by generating data of



acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat these procedures whenever new staff is trained or significant changes in instrumentation or procedure are made. See EPA Methods 8000 and 3500 for information on how to accomplish this demonstration.

10. Calibration and Standardization

10.1. Calibration standards

10.1.1. A minimum of six calibration standards should be prepared.

10.1.2. One of the calibration standards must be at the reporting limit, while the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. The lowest calibration point of each individual target analyte becomes the reporting limit for that target. All target analytes quantitated below the lowest calibration point for any target analyte must be qualified with a "J" flag to show the quantitation is below the working range of the curve and therefore is an estimate.

10.1.3. Calibration standards are prepared from the working calibration solutions at concentrations of 0.2 (1,4-dioxane-full scan), 1, 5, 10, 25, 40, 60 and 80 $\mu\text{g}/\text{mL}$

10.1.3.1. Dual Scan Calibration standards are prepared from the working calibration solutions at concentrations of 0.05 to 20 $\mu\text{g}/\text{mL}$

10.1.3.2. Concentrations of specific acids and bases are varied in the Dual Scan calibration standards and tailored to the reporting limits.

10.1.4. The concentrations of Benzoic Acid; 2,4-Dinitrophenol; and 4,6-Dinitro-2-Methylphenol are doubled in the calibration standard solutions, hence their concentrations are 2, 10, 20, 50, 80, 120 and 160 $\mu\text{g}/\text{mL}$

10.1.5. The calibration curve standards are made as needed and the internal standard solution is added prior to analysis.

10.1.6. Each standard must contain all analytes requested for a specific project, and no target analyte may be quantitated without first being calibrated.

10.1.7. All standards should be stored at >0 to 6°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The ICV/CCV standard should be prepared weekly with the preparatory date on the label and stored at >0 to 6°C . If the analyst suspects degradation the standard should be replaced.

10.1.8. The calibration standards are analyzed, and a minimum of six curve points are used to calibrate each analyte as follows:



Compounds that are routinely calibrated (In House) at 80, 60, 40, 25, 10, 5, and 1µg/mL		
Phenol	Naphthalene	Carbazole
Bis (2-Chloroethyl)ether	Hexachlorobutadiene	Di-n-butylphthalate
2-Chlorophenol	2-Methylnaphthalene	Fluoranthene
1,3-Dichlorobenzene	4-Bromophenyl-phenylether	Pyrene
1,4-Dichlorobenzene	2-Chloronaphthalene	Phenanthrene
1,2-Dichlorobenzene	Dimethylphthalate	Butylbenzylphthalate
2-Methylphenol	Acenaphthylene	Benzo(a)anthracene
2,2'-oxybis(1-Chloropropane)	Acenaphthene	Chrysene
4-Methylphenol	Dibenzofuran	Di-n-octylphthalate
Hexachloroethane	Fluorene	Benzo(b)fluoranthene
Nitrobenzene	Diethylphthalate	Benzo(k)fluoranthene
Isophorone	4-Chloropheny-phenylether	Benzo(a)pyrene
Bis (2-Chloroethoxy)methane	N-Nitrosodiphenylamine	Indeno(1,2,3-cd)pyrene
1,2,4-Trichlorobenzene	Hexachlorobenzene	Dibenzo(a,h)anthracene
Anthracene	Benzo(g,h,i)perylene	1-methylnaphthalene
Azobenzene(1,2-DP-Hydrazine)	Butylatedhydroxytoluene	Tributyl phosphate
1,4-Dioxane (0.2)	Benzyl Alcohol	Triphenyl phosphate
Butyl diphenyl phosphate	Dibutyl phenyl phosphate	Bis(2-ethylhexyl)phalate

Compounds that are routinely calibrated (In House) at 80, 60, 40, 25, 10, and 5µg/mL		
All Tetrachlorophenols	Hexachlorocyclopentadiene	2,4-Dinitrotoluene
1,4-Dioxane-d8	2,4,6-Trichlorophenol	4-Nitroaniline
N-Nitroso-Di-N-Propylamine	2,4,5-Trichlorophenol	Pentachlorophenol
2-Nitrophenol	2-Nitroaniline	3,3-Dichlorobenzidine
2,4-Dimethylphenol	2,6-Dinitrotoluene	N-Nitrosodimethylamine
2,4,-Dichlorophenol	3-Nitroaniline	Benzidine
4-Chloroaniline	4-Nitrophenol	Pyridine
4-Chloro-3-Methylphenol	Aniline	1,2-Dichlorobenzene-d4
2-Fluorophenol	2-Fluorobiphenyl	Nitrobenzene-d5
Phenol-d5	Terphenyl-d14	
2-Chlorophenol-d4	2,4,6-Tribromophenol	



Compounds that are routinely calibrated (In House) at 160, 120, 80, 50, 20 and 10µg/mL

Benzoic Acid	2,4-Dinitrophenol	4,6-Dinitro-2-methylphenol.
--------------	-------------------	-----------------------------

10.2. MS tuning- prior to initial calibration, each GC/MS system must be hardware-tuned to meet the criteria in Appendix 20.3 for a 50ng total or less injection of DFTPP. Analyses must not begin until all these criteria are met. Evaluate the ion abundance by using any of the following three scenarios: Use a single spectrum at the Apex of the DFTPP peak, use the mean of the apex and the preceding and following scans (the mean of a symmetric pattern of scans about the apex), or use the average across the entire peak. The tune must satisfy the ion abundance acceptance criteria listed in Appendix 20.3. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. Do not subtract part of the DFTPP peak.

10.2.1. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD must not exceed 20%. DDT percent breakdown is calculated by dividing the sum of the DDD and DDE areas by the sum of the areas of DDT, DDE and DDD and then multiplying this result by 100. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. Peak tailing factors will be calculated using the procedure detailed in Appendix 20.6 using a Target macro to calculate the tailing factor.

10.2.2. Tailing factors must be <2.0 for benzidine and pentachlorophenol. See Section 16 for procedures on how to bring the instrument into compliance for tuning, DDT breakdown, or peak tailing factors.

10.2.3. The mid-level standard ABN may be used as the tuning standard as it contains DFTPP, DDT, pentachlorophenol, and benzidine at 25µg/ml. Providing that the requirements in Section 10.2 are met, the analysis of the initial calibration may continue.

10.2.4. All analyses performed in the sequence following the tune standard must use the same instrument parameters (GC program, MS parameters, etc.)

10.3. Calculate Relative Response Factors (RFs)

10.3.1. Evaluation of the initial calibration begins by calculating response factors (RRFs) for each analyte in each calibration standard. The formula for calculating each response factor involves the areas of the quantitation ion of the analyte and its associated internal standard as well as the concentration of the analyte and internal standard in the calibration standard according to the formula:

$$RRF = (As * Cis)/(Ais * Cs)$$



Where
As = The peak area of the analyte or surrogate
Cis = The concentration of the internal standard in µg/L
Ais = The peak area of the internal standard
Cs = The concentration of the analyte or surrogate in µg/L

10.3.2. The RRF for each analyte should meet the advisory RRF listed for the analyte in Appendix 20.2 for each of the calibration levels. Special care should be taken to monitoring the RRF in the lowest calibration standard to ensure adequate sensitivity at the reporting limit. The minimum RRF for any target for all calibration levels is 0.01.

10.4. Analyte Linearity.

10.4.1. After measuring the relative response factors for each analyte in each of the calibration standards, the linearity of the analyte must be measured.

10.4.2. The average RRF should be calculated for each compound using the formula

$RRF_{av} = \frac{\sum RRF_i}{n}$
Where
RRFi = the RRF of the analyte in each calibration level
n = the number of calibration levels (usually six or five)

10.4.3. The percent relative standard deviation (% RSD) should also be calculated for each compound using the formula

$RSD = \frac{100 * SD}{RF_{av}} = 100 * ((\sum (RRF_i - RRF_{av})^2) / (n-1))^{1/2} / RRF_{av}$
Where
RRFi = the RRF of the analyte in each calibration level
RRFav = the average RRF of the analyte over the entire calibration range
n = the number of calibration levels (usually six or five)

10.4.4. The % RSD should be less than 15% for each compound, in which case the average response factor will be used for quantitation as it is considered constant over the calibration range. Target analytes that exceed 15% RSD will attempt to utilize an alternative calibration option.

10.4.4.1. Before attempting an alternative calibration model the analyst should ensure that the RSD failure is not due to detector or chromatographic system saturation and that the chromatographic system is functioning properly. Should saturation or chromatographic activity



be evident, the analyst should correct the problem and reanalyze the affected calibration standards.

10.4.4.2. A linear fit calibration that does not include the origin and generates a coefficient of determination (R^2) that is greater than or equal to 0.99 is acceptable. ARI will primarily attempt to force calibration curve through zero. Forcing the curve through zero is not the same as including the origin as a point in the calibration. When the curve is forced through zero, the intercept is set to 0 before the regression is calculated, thereby setting the bias to favor the low end of the calibration range by “pivoting” the function around the origin to find the best fit and resulting in one less degree of freedom.

10.4.4.3. Next the analyst may attempt a quadratic non-linear calibration which may be used with target analytes that have six or more calibration points only. An additional initial calibration point may be considered for target analytes that require non-linear calibration if only five calibration points are available.

10.4.4.4. An analyte is determined to meet the calibration criteria found in Section 10.4.4, even if its RSD exceeds 15% if the analyte has an acceptable linear or quadratic fit curve with a coefficient of determination (R^2) greater than 0.99.

10.4.4.5. See EPA Method 8000C Section 11 for reference to linear fit and non-linear (quadratic) calibration.

10.4.5. Targets requiring either a linear or quadratic fit will be documented in the reviewer checklist.

10.4.6. Individual targets that are unable to meet the above requirements in Section 10.4.4.4 must be documented in the reviewer checklist

10.4.7. Special care should be taken to monitor the RRF in the lowest calibration standard to ensure adequate sensitivity at the method reporting limit. In addition, the lowest calibration point should be recalculated (not reanalyzed) using the final calibration curve in which the standard is used. The recalculated concentration, especially where linear and quadratic fits are used, should be within $\pm 50\%$ of the standard's true concentration. The recalculated concentration of the standards above the low point should be $\pm 30\%$. If a failure occurs in the lowest calibration point and it is equivalent to the method reporting limit (MRL), the analyte should be reported as estimated near that concentration or the MRL should be reestablished at a higher concentration. Following examination of the ICAL and any corrective action, all compounds not meeting the calibration acceptance criteria must be documented on the reviewer's checklist.

10.5. Calibration Acceptance

10.5.1. A calibration for an analyte is deemed valid when it meets the RSD criteria found in 10.4.4 and 10.4.4.4

10.5.2. Due to the large number of analytes that may be assayed using this SOP, some analytes



may fail to meet the calibration acceptance criteria. The method allows some flexibility in dealing with such cases.

10.5.2.1. A calibration curve may be considered valid even with some analytes failing the criteria so long as the number of analytes failing the acceptance criteria found in Section 10.5.1 is equal to or less than 10% of the total number of analytes calibrated including surrogates (e.g. a calibration with sixty analytes may have up to six analytes exceed the acceptance criteria.)

10.5.2.2. Quantitated values for analytes which fail calibration acceptance criteria must be flagged with a "Q" qualifier for all detected analytes and noted on the Reviewer checklist.

10.6. Evaluation of retention times - The relative retention time (RRT) of each target analyte in the calibration standard should agree within 0.05 RRT units. Late-eluting target analytes usually have much better agreement. The RRT is calculated by dividing the retention time of the target analyte/surrogate by the retention time of its assigned internal standard.

10.6.1. The internal standards selected should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards.

10.7. Calibration curve verification - Prior to use for sample analysis, the acceptability of a calibration curve must be verified through analysis of a second source calibration verification (SCV) obtained from a second source. The SCV must be derived from a different manufacturer than the stock standard used to prepare the calibration curve when available. The SCV should show 70 - 130% (80 - 120% for DoD-QSM analyses) recovery for all compounds when compared to the initial calibration curve. Due to the large number of analytes that may be assayed using this SOP, some analytes may fail to meet the calibration acceptance criteria. Up to 10% of analytes may exceed the SCV criteria if they show a recovery within 50-150% of the true value for in-house analyses. No exceptions for DOD-QSM are allowed.

10.8. The reference mass spectrum used to verify the identity of analytes should be updated from the mid-point of the initial calibration.

10.9. Daily GC/MS calibration verification - Performed at the beginning of each 12-hour analytical shift.

10.9.1. The GC/MS tuning standard is not required for GC/MS calibration verification

10.9.2. Analysis of an initial calibration verification (ICV) at mid-concentration (25 ng/μL), containing each compound of interest, including all required surrogates, must be performed daily before analysis. Next, a continuing calibration verification (CCV) must be run after every 12 hours of analysis time and at the end of the analytical sequence, using the introduction technique used for the initial calibration. The results from the ICV analysis must meet the acceptance criteria detailed below. See section 10.9.2.7 and 10.9.2.8 for CCV acceptance criteria.

10.9.2.1. Calculate Relative Response Factors- A system performance check must be made at the start of every 12-hour shift. This is the same check that is applied during the initial



calibration. Calculate the RRF for each analyte. Each compound should meet the advisory minimum relative response factor found in Section 20.2. If the minimum relative response factors are not met, the system must be evaluated, and corrective action should be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the guard column/analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins. See Section 16.5 for procedures for dealing with RRF failures.

10.9.2.2. Analyte linearity- The response factors calculated in Section 10.9.2.1 are used to measure the validity of the initial calibration by using them to calculate the percent difference (for average RRF calibrations) or percent drift (for linear fit or quadratic fit calibrations.)

10.9.2.2.1. Calculate the percent difference using:

$\% \text{ Difference} = \frac{\text{RRF}_i - \text{RRF}_c}{\text{RRF}_i} * (100)$
Where:
RRFi = Average relative response factor from initial calibration.
RRFc = Relative response factor from current verification check standard.

10.9.2.3. If the percent difference for each analyte is less than or equal to 20% the initial calibration verification (ICV) is valid. Problems similar to those listed under the minimum response factors could affect this criterion. See Section 16.6 for procedures for dealing with %D failure.

10.9.2.4. The responses and retention times in the calibration check standard must be evaluated immediately after data acquisition. Chromatography system maintenance (shortening the column, etc) may change retention times. Corrective action is required when:

10.9.2.4.1. Relative retention times change.

10.9.2.5. The response (EICP) of any internal standard (IS) is in the acceptable range of -50% to +200% using the IS in the mid-point standard level (25ng/μl) from the most recent initial calibration as the reference.

10.9.2.6. Much in the manner that a certain number of analytes may fail the initial calibration criteria, the method allows a certain number of analytes to fail the criteria set above for initial calibration verification. In the case of the initial calibration verification (ICV), a number of analytes less than or equal to 20% of the total number of calibrated analytes (including surrogates) may exceed the criteria set in Sections 10.9.2.1 and 10.9.2.2.



10.9.2.6.1. Reported values for the analytes failing the acceptance criteria must be flagged with a "Q" qualifier and noted in the Reviewer checklist.

10.9.2.7. A continuing calibration verification may be used as an initial calibration verification to extend the analytical sequence if the CCV meets all requirements as required for the ICV.

10.9.2.8. (CCV criteria) If the percent difference for each analyte is less than or equal to 50% the continuing calibration verification (CCV) is valid. Problems similar to those listed under the minimum response factors could affect this criterion. See Section 16.6 for procedures for dealing with %D failure.

10.9.2.9. (CCV criteria) The response (EICP) of any internal standard (IS) is in the acceptable range of -50% to +200% using the IS reference from the ICV.

11. Procedure

11.1. Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods.

11.2. Sample Preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580
Tissue	3540, 3545, 3550

11.3. Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640
Anilines and aniline derivatives	3620
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640



Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

11.4. The recommended GC/MS operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration).

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 3.5 minutes
Temperature program:	40-320°C at 12/15C°/min
Final temperature:	320°C, hold until benzo[g,h,i]perylene is eluted
Injector temperature:	250°C
Transfer line temperature:	300°C
Source temperature:	According to manufacturer's specifications(230-250°C for MSD)
Injector:	Grob-type, splitless/split
Sample volume:	1-2 µL
Carrier gas:	Helium at 30 cm/sec.

11.5. Dual Scan Analysis requires a 5975C XL Inert GC/MS with synchronous sim/scan mode which allows for selective SIM acquisition while also acquiring full scan data.

11.6. Prior to sample analysis the GC/MS system must be tuned as described in Section 10.2, and must have an acceptable initial calibration curve (the requirements for the calibration curve are in Sections 10.3 and 10.4).

11.7. Prior to sample analysis the initial calibration verification must be analyzed, and this ICV must meet the criteria found in Sections 10.9.2. If time remains in the 12-hour QC period begun with the initial calibration, the midpoint calibration standard from the initial calibration may be used as the ICV provided it meets the requirements found in Section 10.9.2.

11.8. Next, A method blank or an instrument blank must be analyzed after the ICV and prior to sample analysis to ensure the system is free of contaminants. If the method blank shows contamination, then it may be appropriate to analyze an instrument blank to demonstrate the source of contamination is not the result of carryover from standards or samples.

11.9. GC/MS analysis

11.9.1. It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds and may show high background



- samples. Highly concentrated samples should be extracted using a medium/high level extraction.
- 11.9.2. Spike a 0.3ml aliquot of the 0.5-1ml extract obtained from sample preparation with 6 μ L of the internal standard solution just prior to analysis. This is the equivalent internal standard concentration of 20 μ g/mL (4 μ g/mL for dual scan) of each standard in the sample. This aliquot should be prepared in an amber glass autosampler vial and sealed with a PTFE crimp cap.
- 11.9.3. Analyze the 0.3ml aliquot by GC/MS. The volume to be injected should ideally contain 25 μ g/mL (5 μ g/mL dual scan) of base/neutral and 37.5 μ g/mL (7.5 μ g/mL dual scan) of acid surrogates. The injection volume must be the same volume used for the calibration standards. The recommended GC/MS operating conditions to be used are specified in Section 11.4.
- 11.9.4. When the response for any target analyte exceeds the high point of the initial calibration curve, then extract dilution must take place. See section 16.12 for guidance on dilutions.
- 11.10. Perform all qualitative and quantitative measurements as described in Section 11. Store the extracts at >0 to 6°C, protected from light in screw-cap vials equipped with un-pierced Teflon® lined septa.

12. Data Analysis and Calculations

- 12.1. An analyte is identified by comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this SOP. These standard reference spectra may be obtained through analysis of the calibration standards and should be updated with every initial calibration. The characteristic ions are defined as the three ions of greatest intensity, or any ions over 30% intensity relative to the base ion, if less than three such ions occur in the reference spectrum. Two criteria must be satisfied to verify identification: (1) elution of sample component at or near the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component mass spectrum and the standard component mass spectrum.
- 12.2. The intensities of the characteristic ions must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.
- 12.3. The sample component RRT must compare within ± 0.05 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12-hour QC period as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted, ion-current profiles for ions unique to the component of interest.
- 12.4. All ions present in the standard mass spectra at a relative intensity greater than 10% (the most



abundant ion in the spectrum is equal to 100% intensity) should be present in the sample spectrum. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Spectral enhancement can sometimes create these discrepancies

12.5. The relative intensities of ions specified in Appendix 20.2 must agree within plus or minus 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample abundance must be between 20 and 80 percent.) If not, the compound may be flagged with an "M" if the analyst determines that the identification is valid (favors false positive).

12.6. Structural isomers that produce very similar mass spectra should be identified as individual isomers, if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Typically, structural isomers not meeting the 50% resolution requirement are identified and integrated as a whole peak and reported as a total analyte. (Total Benzofluoranthenes)

12.7. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes co-elute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

12.8. Tentatively Identified Compounds (TICS)

12.8.1. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for qualitative identification are:

12.8.1.1. Relative intensities of major ions in the reference spectrum (ions >10 % of the most abundant ion) should be present in the sample spectrum.



- 12.8.1.2. The relative intensities of the major ions should agree within $\pm 30\%$.
- 12.8.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.
- 12.8.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- 12.8.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- 12.8.1.6. Sample spectrum will be searched against the unknown spectral library with the top three matches identified for each TIC. The spectra is reviewed and assigned a general chemical classification in the following style: Unknown Hydrocarbon, Unknown PNA, Unknown Acid Ester, etc. The general classification prevents the assignment of a specific CAS number when importing into the ELEMENT database. Sample TIC spectrum that does not appear to be of any general chemical classification may be presented simply as "Unknown".

12.9. Quantitative analysis

- 12.9.1. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of a given analyte. If secondary ion quantitation is necessary due to interference, then a short quantitation report list is generated. This quantitation contains the integrated areas of the affected compounds, based on the secondary ion(s) for that compound, and of the relevant internal standards. Identical reports must be generated for the sample with interference and for the relevant continuing calibration. The report for the continuing calibration is used to generate a relative response factor for the affected compound based on its secondary ion. This relative response factor is then used in the calculations for that compound in the affected sample. Note that the source of the relative response factor for the aforementioned situation differs from quantitation using the primary characteristic ion (when free of interference). All quantifications using the primary characteristic ion use the average relative response factor from the initial calibration. The short quantitation report may be hand calculated by the analyst if it is signed and dated by the analyst. The report must be included with the data file PDF in Element.
- 12.9.2. Calculate the concentration of each identified analyte in the sample as follows:

12.9.3. Water

Concentration ($\mu\text{g/L}$) =	$\frac{(A_x)(I_s)(V_t)(D)}{(A_{is})(RRF)(V_o)(V_i)}$
---	--



where:
D = Dilution Factor
A _x = Area of characteristic ion for compound being measured
I _s = Amount of internal standard injected (ng)
V _t = Total volume of the extract
A _{IS} = Area of characteristic ion for the internal standard
RRF = Relative response factor for compound being measured
V _o = Volume of water extracted (ml)
V _i = Volume of extract injected (μL)

12.9.4. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)

Concentration (μg/kg) =	$\frac{(A_x)(I_s)(V_t)}{(A_{IS})(RRF)(V_i)(W_s)(D)}$
where:	
A _x = Area of characteristic ion for compound being measured	
I _s = Amount of internal standard injected (ng).	
V _t = Volume of total extract, taking into account dilutions (i.e. for a 1 to 10 dilution of a 1 ml extract V _t = 10,000 μL)	
A _{IS} = Area of characteristic ion for the internal standard	
RRF = Relative response factor for compound being measured	
V _i = Volume of extract injected (μL)	
W _s = Weight of sample extracted or diluted in grams	
D = % Dry weight of sample = 1.0 on an as received basis	

12.9.4.1. Where applicable, an estimate of concentration for tentatively identified compounds (TICS) in the sample should be made. The formula given above should be used with the following modifications: The area A_x and A_{IS} should be from the total ion chromatograms (RIC) and the RRF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration.

12.9.4.2. Use the nearest internal standard free of interferences. Free of interferences means <10% of internal standard RIC is from any co-eluting interferences present in the sample matrix.

12.9.4.3. Quantitation is performed using the total ion chromatograms (RIC) for both the internal standard and the TICs.

12.9.4.4. In cases where all the internal standards show RIC interference >10% contribution from



the sample matrix the internal standard showing the least amount of interference shall be used to quantify all the unknowns

12.9.4.5. TICS that elute before the first target 1,4-Dioxane or N-Nitrosodimethylamine will not be included as their identifications are more appropriately made from the GC/MS volatile analysis.

12.9.4.6. TICS that are less than 10% area of the closest internal standard free of interferences are discarded.

12.9.4.7. A maximum of 20 TICS for any individual sample are quantified.

12.9.4.8. The method blank associated with the samples is also evaluated for TICS and any unknowns found are compared to those quantified in the samples and “B” flagged when the spectra and retention times match closely. The analyst will use their best judgment to make this determination.

12.9.4.9. Project specific requirements may require more (or less) TICS to be quantified for each individual sample.

12.9.5. Quantitation of multi-component compounds (e.g. Toxaphene, Aroclors) is beyond the scope of this method. Normally, quantitation is performed using a GC/ECD by Method 8081 or 8082. However, this SOP may be used to confirm the identification of these compounds, when the sample extract concentrations are 10µg/mL or greater.

12.9.6. Manual Integration – see SOP 1021S for guidance when manual integration is required.

13. Method Performance

13.1. The QA department measures method performance using a combination of continuing MDL studies, quarterly LOD verifications, performance evaluation samples, standard reference materials, and the monitoring of surrogate and spike recoveries.

13.1.1. Detection limits- the LOD for all analytes quantitated using this SOP are set using the MDL studies. The detection limit indicates the lowest result that can reliably be distinguished in a matrix from a blank.

13.1.2. LOD verifications are performed each quarter for each analyte by each preparatory and analytical method.

13.1.3. MDL, LOD and MRL values may be found for each analyte in Element.

13.2. Laboratory precision and bias measurements are performed by monitoring surrogate and spike recoveries in samples and quality control samples.

13.2.1. Control limits are calculated from these recoveries.

13.2.2. These control limits are disseminated to the bench chemists and ELEMENT administrator for use in monitoring method performance in real time.



13.2.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found in Element

13.3. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in Section 12.3 and Appendix 2.2 of ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC is kept on record in SharePoint.

13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.

13.5. The experience of the analyst must weigh heavily in the interpretation of the chromatogram.

14. Pollution Prevention

14.1. All syringe rinsing must be performed over charcoal to minimize the exposure of the environment to solvent or extract.

14.2. Charcoal containers must be covered when not in use to prevent fugitive vapors from escaping.

14.3. All GC split vents will be connected to an exhaust vent and charcoal filter.

14.4. All MS vacuum pumps will be connected to an exhaust vent.

14.5. All spent vials are placed into the blue waste drum for proper disposal after analysis is finished.

14.6. Open solvent containers should only be present when actively preparing samples.

14.7. Wherever possible the final sample extract volume should be as small as possible to minimize the generation of waste.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 of this document.

15.2. Method Blanks and Instrument Blanks- The blank must contain less than 1/2 the reporting limit (MRL) of the targeted analytes or corrective action is required.

15.3. Internal Standards- All samples and associated QC samples internal standard EICP areas following the ICV must meet the technical acceptance criteria listed in Section 9.1

15.4. Surrogate Recoveries

15.4.1. All method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates, SRMs or other samples must have acceptable surrogate recoveries. Surrogate recoveries are considered unacceptable when:

15.4.1.1. Any surrogate has a recovery less than 10.0 percent

15.4.1.2. More than one base/neutral surrogate or more than one acid surrogate have recoveries outside of the applicable surrogate acceptance windows.



- 15.4.1.3. Note: ARI uses a surrogate solution containing 8 surrogates rather than the method recommended six.
- 15.4.1.4. Recoveries outside of the In-House QC limits should not necessarily be used to reject batch data but will require corrective action.
- 15.4.2. These requirements do not apply to subsequent dilutions of samples where a prior analysis of the diluted sample extract shows acceptable surrogate recovery.
- 15.4.3. Project specific recovery limits may be applied to surrogate recoveries. Corrective actions must be performed in response to failure to meet project specific surrogate acceptance criteria, even when the criteria are labeled as advisory in the reference method or the recoveries meet in house criteria.
- 15.4.4. Surrogate recovery acceptance windows are ideally determined statistically from method and matrix specific laboratory data updated on a periodic basis. Certain methods or clients may specify project specific surrogate recovery acceptance windows.
- 15.4.5. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.
- 15.4.6. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.
- 15.5. Blank Spikes (BS)
- 15.5.1. The BS recovery values should fall within the specified recovery acceptance limits. If a BSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.
- 15.5.2. BS recovery acceptance windows are ideally determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Project or method specific limits may supersede laboratory acceptance criteria.
- 15.5.2.1. The RPDs between the BS/BSD samples must be measured and reported.
- 15.5.2.2. Evaluate the BS/BSD RPD and note any deviation >30% in the reviewer checklist.
- 15.5.2.3. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.
- 15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)
- 15.6.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified recovery acceptance limits.
- 15.6.1.1. The RPDs between the MS/MSD samples must be measured and reported.
- 15.6.1.2. Evaluate the MS/MSD RPD and note any deviation >30% in the reviewer checklist.



15.6.1.3. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.

15.7. Holding Times

15.7.1. Samples must be extracted within holding times (7 days for water samples and 14 days for solid samples).

15.7.2. Extracts must be analyzed within the extract holding time (40 days from the initial date of extraction.)

15.7.3. In the event that re-extraction due to an out of control event requires that samples be re-extracted after their extraction holding time has elapsed (7 days for water and 14 days for tissues/solids) the analyst should analyze and report both extraction sets, whenever practical, distinguishing between the initial extraction and re-extraction on all deliverables. This will document that the samples were originally extracted within holding times and may allow for comparisons that will determine whether any of the more volatile analytes were lost in the interval between extractions.

15.7.4. If any extracts are analyzed after the 40-day extract holding time has elapsed, the analyst will document this in the analytical notes accompanying the data so that it may be included in the reviewer checklist.

16. Corrective Actions for Out of Control Events

16.1. Corrective actions may include any, but are not limited to, the following:

16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the reviewer checklist.

16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.3. Repreparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.4. Reanalysis – the extract aliquot that was originally prepared is reinjected and run on the gas chromatograph again.

16.1.5. Reextraction – a reextraction request is filled out (Form 0030F). Copies of the form are provided to the extractions department, the project manager, the QA manager and the lab manager. The remaining sample is extracted.

16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in ELEMENT.

16.1.7. Recalibration – a new initial calibration is evaluated and the associated samples reanalyzed.

16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error



was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.

16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.

16.2. Mass Spectrometer Tuning

16.2.1. When the MS does not produce an acceptable mass spectrum when injected with 25µg/mL of DFTPP, re-inject the DFTPP. If the spectrum again fails to meet the criteria found in Appendix 20.3, the MS may need to be re-tuned.

16.2.2. If the re-tuned mass spectrum still fails to meet the criteria found in Appendix 20.3, the MS may require maintenance. The MS should be vented, and maintenance may include: replacing the filaments, cleaning the MS source, cleaning the MS lenses, cleaning the MS mass selective filter, or replacing the electron multiplier. All maintenance must be documented in Element.

16.3. If Peak tailing factors and or DDT breakdown exceed the limits found in Section 10, the chromatographic system may need maintenance. Inspect and perform maintenance on the chromatographic system. This maintenance may include, but is not limited to: replacing the inlet liner and liner packing, cleaning the inlet liner, cleaning or replacing the inlet seal, cleaning or replacing the inlet body, replacing the split line, cleaning the split arm, clipping a length from the front of the column, or replacing the column. All maintenance must be documented in Element.

16.4. When an Initial Calibration RSD for an analyte exceeds 15%

16.4.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option, and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

16.5. RRF failure- If the minimum RRF of 0.01 is not met for all analytes and calibration points perform



any appropriate corrective actions found in Section 16.1.

16.6. When an Initial Verification (ICV) fails:

16.6.1. At the discretion of the analysts, a second ICV may be immediately run after the failing ICV.

If the second ICV meets all ICV criteria then the sequence may begin.

16.6.2. If the second injection of the ICV fails, perform the appropriate corrective action(s) from Section 16.1 and re-calibrate the instrument.

16.6.3. DoD-QSM requires that %D for all analytes in the ICV is $\leq 20\%$. For DOD analysis, immediately analyze two additional consecutive ICVs.

16.6.3.1. When both ICVs meet acceptance criteria the analytical sequence may be continued.

16.6.3.2. If either fails or if two consecutive ICVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.6.4. If a CCV is used both as an ICV and CCV (in the middle of an analytical sequence) then the ICV requirements must be applied.

16.7. When a Continuing Calibration Verification (CCV) fails:

16.7.1. Perform any appropriate corrective action(s) from Section 16.1 if not a DOD-QSM project.

16.7.2. DoD-QSM requires that %D for all analytes in the CCV be $\leq 50\%$. For DoD analyses, immediately analyze two additional consecutive CCVs.

16.7.2.1. When both CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.7.2.2. If either fails or if two consecutive CCVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.8. Internal Standards

16.8.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8.1.1. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.

16.8.1.2. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.

16.8.1.3. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.8.1.4. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".

16.9. Surrogates

16.9.1. Examine the bench sheet to verify spiking levels are correct.

16.9.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.



16.9.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.10. Method Blanks and Instrument Blanks-

16.10.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.10.2. Corrective action for a method blank which fails acceptance criteria may involve re-extraction and reanalysis of all associated samples and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager.

16.10.3. Corrective action for an Instrument blank which fails acceptance criteria may involve re-preparation of the Instrument blank and re-analyzing the instrument sequence.

16.11. Blank Spikes (BS)

16.11.1. Examine the bench sheet to verify spiking levels are correct.

16.11.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.12. Matrix Spike/Matrix Spike Duplicates

16.12.1. Examine the bench sheet to verify spiking levels are correct.

16.12.2. Recoveries are advisory and should not necessarily result in re-extraction.

16.12.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.13. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve, a dilution must be performed such that the analyte's quantitated value is within the curve range.

16.13.1. Additional internal standard must be added to the diluted extract to maintain the required 20µg/mL of each internal standard in the extracted volume.

16.13.2. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

16.13.3. When peaks from an analyte saturate the detector:

16.13.3.1. The analyst must note the saturation in the reviewer checklist.

16.13.3.2. The analyst should analyze an Instrument Blank consisting of clean solvent and internal standard until the system has been decontaminated.

16.14. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.

16.14.1.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst



should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)

16.14.1.2. All QC limit issues (including continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Section 16.2 for guidance on dealing with out-of-control tuning events.

17.2. See section 16.3, 16.4 and 16.5 for guidance on dealing with out-of-control events related to initial calibrations (RRF or RSD), peak tailing factors, or DDT breakdown.

17.3. See Section 16.6 for guidance on dealing with ICV out-of-control events.

17.4. See Section 16.7 for guidance on dealing with CCV out-of-control events.

17.5. See Section 16.8 for guidance on dealing with internal standard out-of-control events.

17.6. See Section 16.9 for guidance on dealing with surrogate out-of-control events.

17.7. See Section 16.10 for guidance on dealing with method blank and instrument blank related out-of-control events.

17.8. See Section 16.11 for guidance on dealing with blank spikes related out-of-control events.

17.9. See Section 16.12 for guidance on dealing with MS/MSD related out-of-control events.

17.10. See Section 16.13 for guidance on dealing with over range value related out-of-control events.

17.11. See Section 16.14 for guidance on dealing with particular circumstances out-of-control events.

18. Waste Management

18.1. All extract vials must be disposed of by placing them in the blue hazardous waste drum in the lab set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.

18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.

18.3. All spent charcoal must be disposed of by placing it in the charcoal disposal bin located in the waste storage area.

18.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

19.1. "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Method 8270E, Test Methods for Evaluating Solid Waste (SW-846), Revision 6, June, 2018.

19.2. USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media,



Multi-Concentration Revision OLM03.1, August, 1994.

- 19.3. "Determinative Chromatographic Separations": Method 8000D, (SW-846), Revision 5, March, 2018.
- 19.4. "Department of Defense (DOD) Department of Energy (DOE) Consolidated Quality Systems Manual for Environmental Laboratories", Version 5.3, 2019.
- 19.5. "EPA Method 625.1 – Base/neutrals and acids", Appendix A to CFR Part 136, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. December 2016.

20. Appendices

- 20.1. Appendix 20.1: ARI Acceptance Criteria
- 20.2. Appendix 20.2: 8270E target analyte list
- 20.3. Appendix 20.3: DFTPP Key ion and ion abundance criteria
- 20.4. Appendix 20.4: Chromatogram of calibration standard - Acid/Base/Neutral
- 20.5. Appendix 20.5: Example pages from GC/MS semivolatile organics virtual logbook
- 20.6. Appendix 20.6: Peak tailing factor calculations
- 20.7. Appendix 20.7 Method 625.1 requirements
- 20.8. Appendix 20.8 SIM 1,4-dioxane analysis



Appendix 20.1. ARI ACCEPTANCE CRITERIA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method (see ARI SOP 1017S)	QC acceptance criteria published by DoD, if available; otherwise method specified criteria.	1) Recalculate results 2) Locate and correct the source of the problem and repeat the test for all parameters of interest.	Not applicable (NA)	This is a demonstration of ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., BS or PT sample) as described in ARI SOP 1017S. Analysis is not allowed by analyst until she/he has completed a successful demonstration of capability.
Method detection limit (MDL) study	At initial set-up and subsequently once per 12 month period; otherwise quarterly MDL verification checks shall be performed (see box D-18)	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or reconduct MDL study	NA	Samples should not be analyzed without a valid MDL.
Tuning	Prior to the initial calibration	Refer to method for specific ion criteria.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
DDT breakdown check	Prior to the initial calibration	Degradation < 20% for DDT. Benzidine and PCP peak tailing must be <2.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
Retention time (RT) window calculated for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	RT width is ± 3 times standard deviation for each analyte RT from 72-hour study.	NA	NA	
Evaluation of Relative retention times (RRT)	With each standard	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.	After maintenance is performed which may affect relative retention times the RRT may be updated based on the ICV
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	1) Analytes' RRFs must meet 0.01 across calibration range. 2) Analytes' RSDs must be less than or equal to 15%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (R^2) greater than 0.99. 3) Up to 10% of the total analytes may fail 1 and 2 above.	Correct problem then repeat initial calibration.	Analytes which fail the RRF or RSD/ R^2 limits must have their values flagged with Q qualifiers to mark the values as estimates.	Problem must be corrected. No samples may be run until ICAL has passed.



Appendix 20.1. ARI ACCEPTANCE CRITERIA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Second source calibration verification	Once after each initial calibration	Value of second source for all analytes within $\pm 30\%$ of expected value (initial source). Up to 10% of analytes may exceed the SCV criteria if they show a recovery within 50-150% of the true value	Correct problem, verify second source standard. Rerun verification. If that fails, correct problem and repeat ICAL	Flagging criteria are not appropriate.	Historic data shows that some analytes will very seldom meet $\pm 20\%$ when purchased from different vendors. Second sources may not be available for all analytes.
Retention time established for all analytes and surrogates	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	NA	NA	
Initial and continuing Calibration verification (ICV/CCV)	Daily, before sample analysis (ICV); after every 12 hours of analysis time; and at the end of the analytical batch run (CCV).	1. Average RRFs for analytes must meet 0.01 2. ICV %Difference/Drift for analytes: $\leq 20\%D$ Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the ICVS are Q flagged. 3: CCV %Difference/Drift for analytes $\leq 50\%$.	ICV FAILURE: Correct problem, then rerun ICV. If that fails, repeat initial calibration. CCV FAILURE: Perform corrective action from section 16.1	Apply Q-flag to reported target analytes exceeding criteria.	
Internal standards verification	All ICV	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or most recent ICV. ICV EICP area within - 50% to + 100% of ICAL midpoint standard.	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	Flagging criteria are not appropriate	Sample results are not acceptable without a valid IS verification.
Internal standards verification for samples, batch QC and CCV	All samples, batch QC, and the CCV	Retention time ± 10 seconds from retention time of the ICV. EICP area within - 50% to + 100% of ICV.	Rerun affected samples.	If corrective action fails in field samples, associated batch QC, or the CCV apply *-flag to the non-compliant IS.	
Method blank and Instrument blank	One per preparatory batch	No analytes detected $> \frac{1}{2}$ MRL. For common laboratory contaminants, no analytes detected \geq MRL.	Correct problem, if required, re-prep then reanalyze method blank. Perform corrective action from section 16.1	Apply B-flag to all results for the specific analyte(s) reported above the MRL to all samples in the associated preparatory batch for method blanks exceeding criteria. Flagging criteria are not appropriate for instrument blanks.	



Appendix 20.1. ARI ACCEPTANCE CRITERIA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Blank Spike control sample (BS) containing all reported analytes & surrogates	One BS per preparatory batch	QC acceptance criteria specified by ARI LQAP.	Correct problem, then re-prepare and reanalyze the BS. Perform corrective action from section 16.1	Apply *-flag to the specific analytes if acceptance criteria are not met to BS results.	
Blank spike duplicate (BSD)	Project specific	RPD \leq 30% (between BS and BSD or sample and sample duplicate)	Perform corrective action from section 16.1	Apply *-flag to the specific analytes if acceptance criteria are not met to BSD results.	The data shall be evaluated to determine the source of difference.
Matrix spike (MS)	One MS per preparatory batch per matrix	For matrix evaluation, use QC acceptance criteria specified by ARI LQAP for MS. MS recoveries are advisory.	Perform corrective action from section 16.1.	Apply *-flag to the specific analytes if acceptance criteria are not met to MS results.	For matrix evaluation only. If MS results are out of control, data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	RPD \leq 30% (between MS and MSD or sample and sample duplicate) Limits are advisory.	Perform corrective action from section 16.1	Apply *-flag to the specific analytes if acceptance criteria are not met to MSD results.	The data shall be evaluated to determine the source of difference.
Surrogate spike	All field and QC samples	Method-specified criteria or laboratory's own in-house criteria (No more than 1 acid surrogate or 1 base surrogate is allowed out of control, all surrogate recoveries must be > 10%.)	For QC and field samples, correct problem then re-prepare and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Apply *-flag to the specific analytes if acceptance criteria are not met to surrogate results.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Results reported between MDL and MRL	When requested	Peak integration should meet signal to noise ratio of 3:1	NA	Apply J-flag to all results between MDL and MRL.	



Appendix 20.2
ARI's Routine Method 8270E Target Analytes
Internal Standards, Quantitation Ions, and Calibration Criteria

Internal Standard Associated Analyte ¹	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
1,4-Dichlorobenzene-d4 (IS)¹	106-46-7	152	150,115	--	--	--
1,4-Dioxane	123-91-1	88	58,57	NA	15	20
d8-1,4-Dioxane (SS)	17647-74-4	64	96,62	NA	15	20
Aniline ²	62-53-3	93	66,65	NA	15	20
Benzyl alcohol ²	100-51-6	108	79,77	NA	15	20
<i>bis</i> (2-chloroethyl) ether	111-44-4	93	63,95	0.7	15	20
<i>bis</i> (2-chloroisopropyl) ether	108-60-1	45	77,121	0.01	15	20
2-Chlorophenol	95-57-8	128	64,130	0.8	15	20
1,3-Dichlorobenzene	541-73-1	146	148,111	NA	15	20
1,4-Dichlorobenzene	106-46-7	146	148,111	NA	15	20
1,2-Dichlorobenzene	95-50-1	146	148,111	NA	15	20
2-Fluorophenol (SS) ¹	367-12-4	112	--	NA	15	20
d4-2-chlorophenol (SS) ¹	93951-73-6	132	134	NA	15	20
d4-1,2-dichlorobenzene (SS) ¹	2199-69-1	152	150	NA	15	20
Hexachloroethane	67-72-1	117	201,199	0.3	15	20
2-Methylphenol	95-48-7	108	107,77,79,90	0.7	15	20
4-Methylphenol	106-44-5	108	107,77,79,90	0.6	15	20
N-Nitrosodimethylamine ²	62-75-9	74	42	NA	15	20
N-Nitroso-di-n-propylamine	621-64-7	70	42,101,130	0.5	15	20
Phenol	108-95-2	94	65,66	0.8	15	20
Phenol-d5 (SS)	108-95-2	99	42,71	NA	15	20
Pyridine ²	110-86-1	79	52	NA	15	20
Naphthalene-d8 (IS)¹	91-20-3	136	68	--	--	--
Benzoic acid ²	65-85-0	122	105,77	NA	15	20
Bis(2-chloroethoxy)methane	111-91-1	93	95,123	0.3	15	20
4-Chloroaniline ²	106-47-8	127	129,65,92	0.01	15	20
4-Chloro-3-methylphenol	59-50-7	107	144,142	0.2	15	20
2,4-Dichlorophenol	120-83-2	162	164,98	0.2	15	20
2,4-Dimethylphenol	105-67-9	107	121,122	0.2	15	20
Hexachlorobutadiene	87-68-3	225	223,227	0.01	15	20
Isophorone	78-59-1	82	95,138	0.4	15	20



Internal Standard Associated Analyte ¹	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
2-Methylnaphthalene	91-57-6	142	141	0.4	15	20
1-Methylnaphthalene	90-12-0	142	141,143	NA	15	20
Naphthalene	91-20-3	128	129,127	0.7	15	20
Nitrobenzene	98-95-3	77	123,65	0.2	15	20
Nitrobenzene-d5 (SS) ¹	98-95-3	82	128	NA	15	20
2-Nitrophenol	88-75-5	139	109,65	0.1	15	20
1,2,4-Trichlorobenzene	120-82-1	180	172,145	NA	15	20
Acenaphthene-d10 (IS)¹	83-32-9	164	162,160	--	--	--
Acenaphthene	83-32-9	154	153,152	0.9	15	20
Acenaphthylene	208-96-8	152	151,153	0.9	15	20
2-Chloronaphthalene	91-58-7	162	127,164	0.8	15	20
4-Chlorophenyl Phenyl Ether	7005-72-3	204	206,141	0.4	15	20
Dibenzofuran	132-64-9	168	139	0.8	15	20
Diethyl phthalate	84-66-2	149	177,150	0.01	15	20
Dimethyl phthalate	131-11-3	163	77,164	0.01	15	20
2,4-Dinitrophenol	51-28-5	184	63,154	0.01	15	20
2,4-Dinitrotoluene	121-14-2	165	63,89	0.2	15	20
2,6-Dinitrotoluene	606-20-2	165	63,89	0.2	15	20
Fluorene	86-73-7	166	165, 167	0.9	15	20
2-Fluorobiphenyl (SS) ¹	321-60-8	172	171	NA	15	20
Hexachlorocyclopentadiene	77-47-4	237	235,272	0.05	15	20
2-Nitroaniline ²	88-74-4	138	65,92	0.01	15	20
3-Nitroaniline ²	99-09-2	138	65,92	0.01	15	20
4-Nitroaniline ²	100-01-6	138	65,92	0.01	15	20
4-Nitrophenol	100-02-7	139	109,65	0.01	15	20
1,2,4,5-Tetrachlorophenol		232	230,234	NA	15	20
2,3,5,6-Tetrachlorophenol	935-95-5	232	230,234	NA	15	20
2,4,6-Tribromophenol (SS) ¹	118-79-6	330	332	NA	15	20
2,4,6-Trichlorophenol	88-06-2	196	198,200	0.2	15	20
2,4,5-Trichlorophenol	95-95-4	196	198,200	0.2	15	20
Phenanthrene-d10 (IS)¹	85-01-8	188	94,80	--	--	--
Anthracene	120-12-7	178	176,179	0.7	15	20
4-Bromophenyl phenyl ether	101-55-3	248	250,141	0.1	15	20
Di-n-butyl phthalate	84-74-2	149	150,104	0.01	15	20
4,6-Dinitro-2-methylphenol ²	534-52-1	198	51,105	0.01	15	20
1,2-Diphenylhydrazine	122-66-7	77	105,182	NA	15	20
Fluoranthene	206-44-0	202	101,200	0.6	15	20
Hexachlorobenzene	118-74-1	284	142,249	0.1	15	20
N-Nitrosodiphenylamine	86-30-6	169	168,167	0.01	15	20
Pentachlorophenol	87-86-5	266	264,268	0.05	15	20
Phenanthrene	85-01-8	178	179,176	0.7	15	20



Internal Standard Associated Analyte ¹	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
Chrysene-d12 (IS)¹	218-01-9	240	120,236	--	--	--
Benzidine ²	92-87-5	184	92,185	NA	15	20
Benzo(a)anthracene	56-55-3	228	229,226	0.8	15	20
Butyl benzyl phthalate	85-68-7	149	91,206	0.01	15	20
Chrysene	218-01-9	228	226,229	0.7	15	20
3,3'-Dichlorobenzidine ²	91-94-1	252	254,126	NA	15	20
Pyrene	129-00-0	202	200,101	0.6	15	20
Terphenyl-d14 (SS) ¹	84-15-1	244	122,243	NA	15	20
Di-n-octylphthalate-d4 (IS)¹	117-84-0			--	15	20
Bis(2-ethylhexyl) phthalate	117-81-7	149	167,279	0.01	15	20
Di-n-octylphthalate	117-84-0	149	167,279	0.01	15	20
Perylene-d12 (IS)¹	198-55-0	264	260,132	0.01	15	20
Benzo(b)fluoranthene	205-99-2	252	253,126	0.7	15	20
Benzo(k)fluoranthene	207-08-9	252	253,126	0.7	15	20
Benzo(g,h,i)perylene	191-24-2	276	138,277	0.01	15	20
Benzo(a)pyrene	50-32-8	252	253,126	0.7	15	20
Dibenz(a,h)anthracene	53-70-3	278	139,279	0.5	15	20
Benzo(g,h,i)perylene	191-24-2	276	138,274	0.5	15	20
Indeno(1,2,3-cd)pyrene	193-39-5	276	138,227	0.5	15	20

1 – Compound designations: IS = Internal Standard, SS = Surrogate Standard; 2 – Active analytes



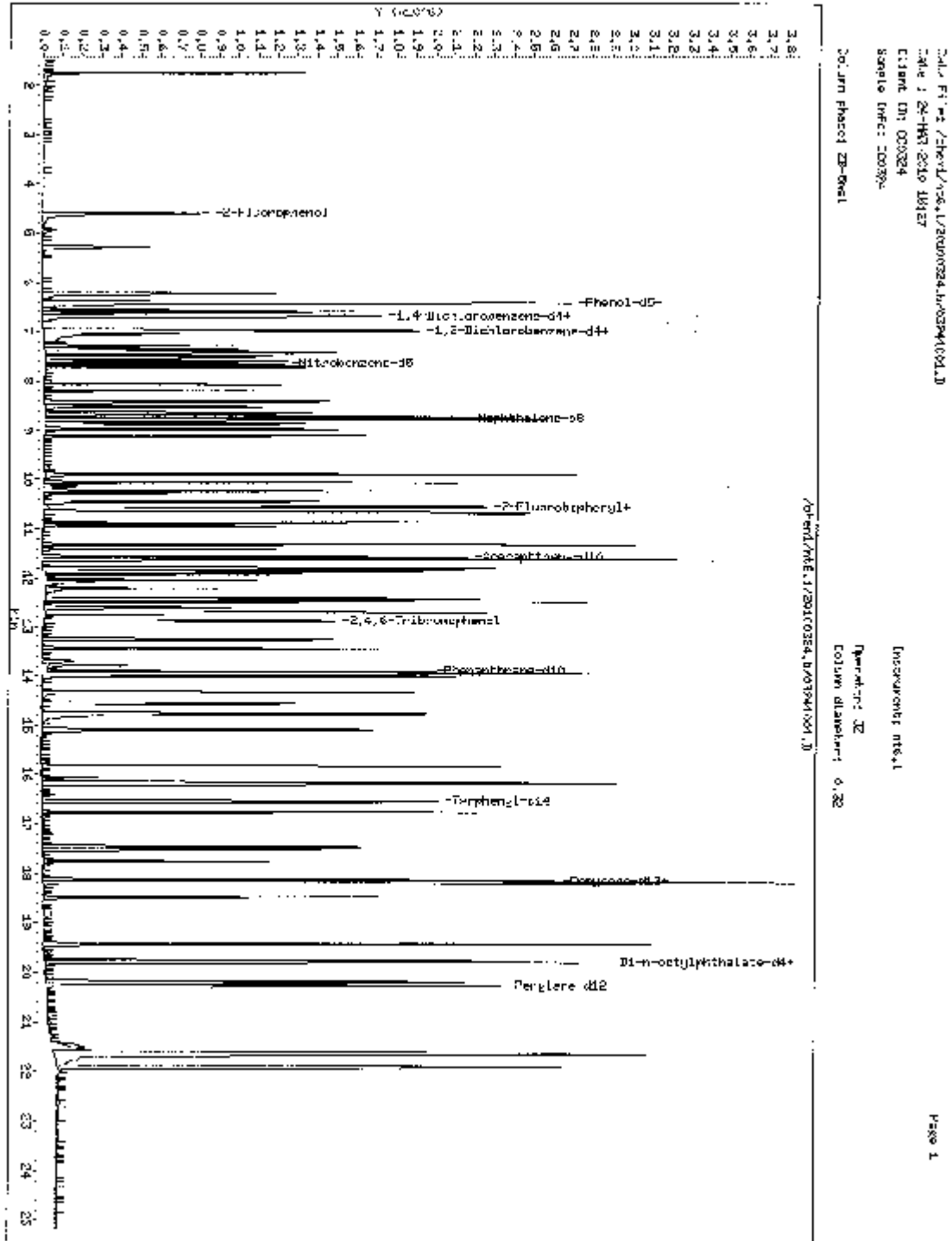
Appendix: 20.3
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR
METHOD 8270E

Mass	Ion Abundance Criteria
68	< 2% of mass 69
69	Present
70	< 2% of mass 69
197	< 2% of mass 198
198	Base peak or Present
199	5-9% of mass 198
365	> 1% of base peak
441	< 150% of mass 443
442	Base peak or Present
443	15-24 % of mass 442



Appendix 20.4

Chromatogram of calibration standard - Acid/Base/Neutral





Appendix 20.5 GC/MS Semivolatile Organics Logbook



Analytical Resources, Incorporated
Analytical Chemists and Consultants

ANALYSIS SEQUENCE
SP00000

Printed: 01/17/2017 9:58:25AM

Instr Model: NT11 Element Column ID: EOC6480
Calibration File: ZL00000 Tune File: 161216.D
EOD Voltage: 2300

Lab Number	Sample Name	Analysis	Container	Order	SYNID	MSID	Comments
SP00000-T171	OTTP	GC		1	EOC6480		
SP00000-CV1	nickel (3) 1000	GC		2	EOC6480	E000000	
RE00000-ELK1	Blank	GC		1		E000000	
RE00000-ELK2	Blank	GC		4		E000000	
161216-01	161216-122116	SEMIPAH LOW (0.01 ug/L - D)	E D1	5		E000000	
161216-07	161216-122116	SEMIPAH LOW (0.01 ug/L - D)	E D1	6		E000000	
SP00000-CV1	SEMIPAH	GC		7	EOC6480	E000000	

INTERNAL STANDARD SUMMARY FOR DATAFILE - \\target\share\chem\nt11.i\20170117.D

NUM	NAME	RT	CONC	IS
1	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1.157	0.0000	1
2	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1.157	1.0000	1
3	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1.157	1.0000	1
4	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1.157	1.0000	1
5	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1.157	1.0000	1
6	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1.157	1.0000	1
7	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1.157	1.0000	1

INTERNAL STANDARD SUMMARY FOR DATAFILE - \\target\share\chem\nt11.i\20170117.D

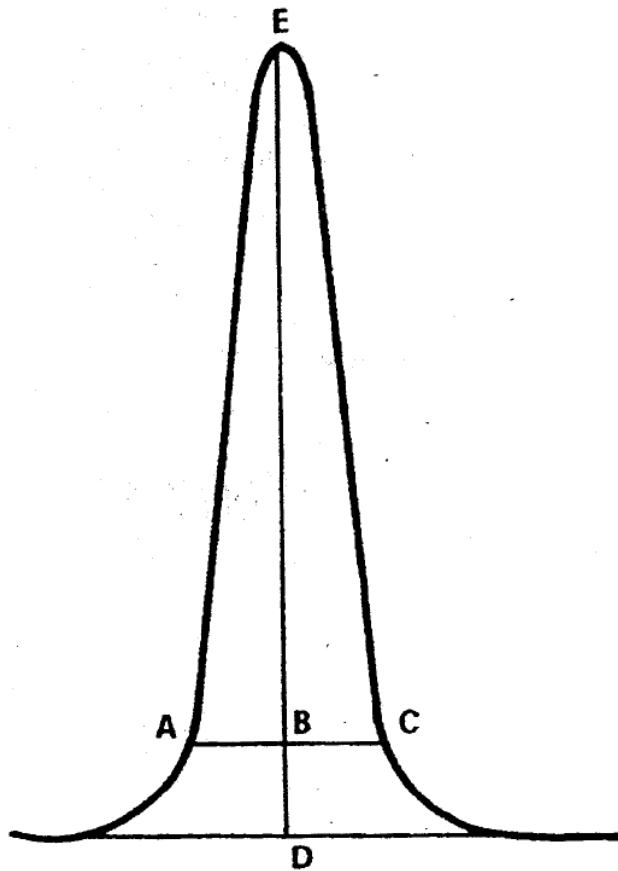
AKI Job No.: SP00 Method: OTTP.n Instrument: nt11.i Date: 16-JAN-2017

Time	Retention	Label	IS	Identify Integrated Compounds
1.157	1.157	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1	NO IDENTIFICATION
1.157	1.157	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1	NO IDENTIFICATION
1.157	1.157	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1	NO IDENTIFICATION
1.157	1.157	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1	NO IDENTIFICATION
1.157	1.157	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1	NO IDENTIFICATION
1.157	1.157	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1	NO IDENTIFICATION
1.157	1.157	1,2,4,5-TETRAHYDRO-1,4-DIOXINE	1	NO IDENTIFICATION



Appendix 20.6 Peak Tailing Factor Calculations

$$RF = \frac{(A_2)(C_2)}{(A_1)(C_1)}$$



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$



Appendix: 20.7

20.7 Modification Required for EPA Method 625.1 (These modifications are only implemented when specifically requested by a client, otherwise Method 625.1 is analyzed as described in previously in this SOP)

20.7.1 The following DFTPP key ions and ion abundance criteria for Method 625.1 are substituted for those listed in Appendix 20.3 used for Method 8270E.

Mass	Ion Abundance Criteria
51	30 – 60 % of mass 198
68	< 2 % of mass 69
70	< 2 % of mass 69
127	40 – 60 % of mass 198
197	< 1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	> 1% of mass 198
441	Present, but < mass 443
442	40 -100% of mass 198
443	17-23 % of mass 442

20.7.2 The Initial Calibration for Method 625.1 is a minimum of 5 points for averaged fit and 6 points for a quadratic fit.

20.7.3 Initial calibration RSD for Method 625.1 must be $RSD < 35\%$ or $R^2 < .990$ with no exceptions.

20.7.4 ICV/CCV %D for Method 625.1 must be fall within the limits shown in appendix 20.7.6. Note that these limits are not in Element as shown on table 6 -QC acceptance criteria for method 625.1-and must be evaluated manually.

20.7.5 Blank spike and matrix spike recoveries verification %D for Method 625.1 must be fall within the limits shown in appendix 20.7.6. Note that these limits are not in Element as shown on table 6 -QC acceptance criteria for method 625.1-and must be evaluated manually.

20.7.6 Table 6 as shown below includes control limits for the ICV/CCV (%Q), the blank spike/blank spike duplicate (X), and matrix spike/matrix spike duplicate (P_1P_2). Note that these limits are not in Element as shown in table 6 and must be evaluated manually for quality control.



Table 6 – QC Acceptance Criteria – Method 625¹

Analyte	Range for Q (%) ²	Limit for s (%) ³	Range for \bar{X} (%) ³	Range for P ₁ , P ₂ (%) ³	Limit for RPD (%)
Acenaphthene	70-130	29	60-132	47-145	48
Acenaphthylene	60-130	45	54-126	33-145	74
Aldrin	7-152	39	7-152	D-166	81
Anthracene	58-130	40	43-120	27-133	66
Benzo(a)anthracene	42-133	32	42-133	33-143	53
Benzo(b)fluoranthene	42-140	43	42-140	24-159	71
Benzo(k)fluoranthene	25-146	38	25-146	11-162	63
Benzo(a)pyrene	32-148	43	32-148	17-163	72
Benzo(ghi)perylene	13-195	61	D-195	D-219	97
Benzyl butyl phthalate	43-140	36	D-140	D-152	60
beta-BHC	42-131	37	42-131	24-149	61
delta-BHC	D-130	77	D-120	D-120	129
bis(2-Chloroethyl)ether	52-130	65	43-126	12-158	108
bis(2-Chloroethoxy)methane	52-164	32	49-165	33-184	54
bis(2-Chloroisopropyl) ether	63-139	46	63-139	35-166	76
bis(2-Ethylhexyl) phthalate	43-137	50	29-137	8-158	82
4-Bromophenyl phenyl ether	70-130	26	65-120	53-127	43
2-Chloronaphthalene	70-130	15	65-120	60-120	24
4-Chlorophenyl phenyl ether	57-145	36	38-145	25-158	61
Chrysene	44-140	53	44-140	19-165	87
4,4'-DDD	D-135	56	D-135	D-145	93
4,4'-DDE	19-130	46	19-120	4-136	77
4,4'-DDT	D-171	81	D-171	D-203	135
Dibenz(a,h)anthracene	13-200	75	D-200	D-227	126
Di-n-butyl phthalate	52-130	28	8-120	1-120	47
3,3'-Dichlorobenzidine	18-213	65	8-213	D-262	108
Dieldrin	70-130	38	44-119	29-136	62
Diethyl phthalate	47-130	60	D-120	D-120	100
Dimethyl phthalate	50-130	110	D-120	D-120	183
2,4-Dinitrotoluene	53-130	25	48-127	39-139	42
2,6-Dinitrotoluene	68-137	29	68-137	50-158	48
Di-n-octyl phthalate	21-132	42	19-132	4-146	69
Endosulfan sulfate	D-130	42	D-120	D-120	70
Endrin aldehyde	D-189	45	D-189	D-209	75
Fluoranthene	47-130	40	43-121	26-137	66
Fluorene	70-130	23	70-120	59-121	38
Heptachlor	D-172	44	D-172	D-192	74
Heptachlor epoxide	70-130	61	71-120	26-155	101
Hexachlorobenzene	38-142	33	8-142	D-152	55
Hexachlorobutadiene	68-130	38	38-120	24-120	62
Hexachlorocyclohexane	55-130	32	55-120	40-120	52



Table 6 – QC Acceptance Criteria – Method 625¹

Analyte	Range for Q (%) ²	Limit for s (%) ³	Range for \bar{X} (%) ²	Range for P ₁ , P ₂ (%) ³	Limit for RPD (%)
Indeno(1,2,3-cd)pyrene	13-151	60	D-151	D-171	99
Isophorone	52-180	56	47-180	21-196	93
Naphthalene	70-130	39	36-120	21-133	65
Nitrobenzene	54-158	37	54-158	55-180	62
N-Nitrosodi-n-propylamine	59-170	52	14-198	D-230	87
PCB-1260	19-130	77	19-130	D-164	128
Phenanthrene	67-130	24	65-120	51-120	39
Pyrene	70-130	30	70-120	52-120	49
1,2,4-Trichlorobenzene	61-130	30	57-130	44-142	50
4-Chloro-3-methylphenol	68-130	44	41-128	22-147	73
2-Chlorophenol	55-130	37	36-120	23-134	61
2,4-Dichlorophenol	64-130	30	53-122	39-135	50
2,4-Dimethylphenol	58-130	35	42-120	32-120	58
2,4-Dinitrophenol	39-175	79	D-173	D-191	132
2-Methyl-4,6-dinitrophenol	56-130	122	53-130	D-181	203
2-Nitrophenol	61-165	33	45-167	29-182	55
4-Nitrophenol	35-130	79	13-129	D-132	131
Pentachlorophenol	42-152	52	38-152	14-176	86
Phenol	48-130	39	17-120	5-120	61
2,4,6-Trichlorophenol	69-130	35	52-129	37-144	58

¹ Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 1625. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.

² Test concentration = 100 µg/ml.

³ Test concentration = 100 µg/l.

Q – Calibration verification (Sections 7.3.1 and 13.4)

s – Standard deviation for four recovery measurements in the DOC test (Section 8.2.4).

\bar{X} – Average recovery for four recovery measurements in the DOC test (Section 8.2.4).

P₁, P₂ – MS/MSD recovery (Section 8.3.2, Section 8.4.2).

RPD – MS/MSD relative percent difference (RPD; Section 8.3.3)

D – Detected; result must be greater than zero.



Appendix 20.8 1,4-Dioxane sim analysis

Internal Standard Associated Analyte ¹	CAS Number	Primary Ion	Secondary Ion	Min RRF	Max %RSD	Max %D
1,4-Dichlorobenzene-d4 (IS)¹	106-46-7	152	150	--	--	--
1,4-Dioxane	123-91-1	88	58	NA	15	20
d8-1,4-Dioxane (SS)	17647- 74-4	96	64	NA	15	20

20.8.1. A seven-point calibration from 0.1-20µg/ml is performed for the initial calibration.

20.8.2. The initial and continuing calibration verification is prepared at 5.0µg/ml.

20.8.3. The method MRL for waters is 0.2µg/L.

20.8.4. The instrument acquisition is done in SIM(Selected ion monitoring) mode.

20.8.5. All method and quality control requirements as described in this SOP apply to SIM 1,4-Dioxane analysis.



Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Polychlorinated Biphenyls (Aroclor) Analysis

SOP 403S
Revision 26

Revision Date: 2/11/2020
Effective Date: 2/11/2020

Prepared by:

Josh Rains, Van Spohn

Approvals:

A handwritten signature in blue ink, reading "Brian N. Bebee".

Brian N. Bebee, Laboratory Section Manager

A handwritten signature in blue ink, reading "David R. Mitchell".

David R. Mitchell, Quality Assurance Mgr.



Annual Review

SOP Number: _____

Title: _____

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____



1. Scope and Application

1.1. This procedure summarizes ARI's protocol for identifying and quantifying mixtures of Polychlorinated Biphenyls (PCBs), known as Aroclors, in a variety of matrices including sediments, soils, solids, tissues, waters, and waste products (oils, etc.) The procedures described meet the requirements of EPA Method 8082A (Reference 19.1) and EPA Method 608 for PCB Aroclors only (Reference 19.2). The following Aroclors may be determined using this protocol:

Table 01: Aroclor Analytes	
PCB Mixture	CAS Number
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5
Aroclor-1262	37324-23-5
Aroclor-1268	11100-14-4

1.2. Detection limits- depending on the volume of sample extracted, the detection limits range from 0.01 to 10ug/L for aqueous samples and from 4 to 800ug/kg (based on dry weight) for solid samples.

Table 02: Aroclor Reporting Limits			
Sample Matrix	Extract Volume or Weight	Final Volume	Reporting Limit
Aqueous	500 mL	5 mL	1 ppb
	500 mL	1 mL	0.1 ppb
	1000 mL	0.5 mL	0.01 ppb
(TCLP)	100 mL	10 mL	10 ppb
Solids	12 g	4 mL	33 ppb
	12.5 g	2.5 mL	20 ppb
	12.5 g	2.5 mL	10 ppb
	12.5 g	2.5 mL	4 ppb
	1 g	40 mL	800 ppb
	5 g	40 mL	800 ppb



Tissue	10 g	5 mL	50 ppb
	25 g	5 mL	20 ppb
	25 g	1 mL	4 ppb

1.3. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including the EPA SW-846 methods, EPA Contract Laboratory Program (CLP), NELAP and the Department of Defense Quality Systems Manual (DoD-QSM). The table in Appendix 21.1 outlines ARI's routine procedure. Please refer directly to DOD-QSM 5.3 for guidance on the special requirements of the DoD-QSM. Analysts are responsible for determining which QA program is applicable to a set of samples prior to beginning analyzes and complying with all project specific analytical requirements.

1.4. The reference methods for this procedure are listed in Section 19.

2. Summary of the Procedure

2.1. Surrogate standards are added to a measured volume or weight of sample which is extracted using an appropriate organic solvent and extraction technique. The resulting extract is concentrated to a specified final volume. Project or Protocol required Quality Assurance Samples are prepared and analyzed using identical techniques.

2.1.1. A variety of cleanup steps may be applied to the extracts, depending on the nature of any co-extracted matrix interferences and the requested target analytes. All cleanup techniques must be applied to all sample extracts including QC samples (MB, BS, MS, MRL, and DUP).

2.1.1.1. Following any cleanup, the extract is concentrated to a designated final effective volume and delivered to ARI's Gas Chromatography Laboratory for identification and quantification of polychlorinated biphenyls.

2.1.1.1.1. Following addition of internal standards 1-2 μL of the extract is injected onto a GC using an auto-sampler and splitless injection technique.

2.1.1.1.1.1. The injected sample is split onto two columns by passing through a glass Y connector. Analytes are detected and quantified using ECD detectors.

2.1.1.1.1.2. Identified Target analytes are quantified using an internal standard procedure as described in Sections 10 and 11

3. Definitions

3.1. Aroclors- mixtures of polychlorinated biphenyl congeners

3.2. BNB (1-Bromo-2-Nitrobenzene): Internal standard.

3.3. Initial Calibration Verification (ICV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable.



- 3.4. Continuing Calibration Verification (CCV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable.
- 3.5. Continuing Calibration Verification Standard (CCVS): The standard prepared at the mid-point concentration of the initial calibration prepared from the same source as the initial calibration used to perform the ICV and CCV.
- 3.6. DCBP (Decachlorobiphenyl): Surrogate standard.
- 3.7. ECD (Electron Capture Detector): A detector with a high specificity and sensitivity to organic molecules with highly electronegative functional groups. An ECD is especially suitable for identifying and quantifying organochlorine compounds including Aroclors and selected pesticides and herbicides.
- 3.8. HBBP (2,2',4,4',5,5'-Hexabromobiphenyl): Internal standard.
- 3.9. Second source Calibration Verification (SCV): An instrument calibration standard purchased from a secondary vendor is used to verify that the current instrument calibration is acceptable.
- 3.10. Instrument Blank (IB): A QC sample made by adding surrogates to clean solvent used to measure instrument background.
- 3.11. Internal Standard (IS): internal standards are compounds added to each standard, sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of these internal standards.
- 3.12. Blank Spike (BS) – A sample matrix, free from the analytes of interest, spiked with verified amounts of analytes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system. Aroclor 1660 (Section 7.1) is the routine BS analyte.
- 3.13. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, an BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS. Aroclor 1660 (Section 7.1) is the routine BSD analyte.
- 3.14. ELEMENT (Laboratory Information Management System): Software used to compile and report final chromatographic data.
- 3.15. MDL (Method detection Limit): The lowest result that can reliably be distinguished in a matrix from a blank. Also referred to as the limit of Detection (LOD)
- 3.16. MRL (Method Reporting Limit)–The lowest result that may be reported unqualified based on the lowest curve point.
- 3.17. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a



specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method. Aroclor 1660 (Section 7.1) is the routine MS analyte.

- 3.18. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision. Aroclor 1660 (Section 7.1) is the routine MSD analyte.
- 3.19. Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
- 3.20. PCBs - polychlorinated biphenyls- biphenyl molecules with varying degrees of chlorination
- 3.21. MRL (Method Reporting Limit): A matrix spike prepared at reporting limit, used to determine MDL(LOD) and MRL.
- 3.22. Solvent Blank (SB) – Clean solvent is analyzed using the same conditions as a regular sample. A solvent blank is analyzed to detect and/or remove sample carryover from one analysis to another.
- 3.23. Surrogate – A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.
- 3.24. Target Software: Software used to integrate and reduce raw chromatographic data.
- 3.25. TCMX (Tetra chloro-m-Xylene): Surrogate standard

4. Interferences

- 4.1. Extraction Interferences: Data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.
 - 4.1.1. Method interferences are reduced by washing all glassware with hot soapy water, a weak HCL acid bath, and finally OFW before being baked at 500 degrees centigrade overnight.
 - 4.1.2. Recycled glassware method interferences are reduced by washing all glassware with hot soapy water, a weak HCL acid bath, OFW, acetone, and methylene chloride in the order listed.
 - 4.1.3. High purity reagents must be used to minimize interference problems.
- 4.2. Co-extraction of analytes which respond to the ECD detector may cause interferences. These co-extracted contaminants may be removed by an appropriate clean-up technique.
 - 4.2.1. Typical clean-up procedures include silica gel clean-up, removal of elemental sulfur, and sulfuric acid treatment as described in SOP 3327S.



- 4.3. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a solvent blank to check for cross contamination (if needed).
- 4.4. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to assure proper qualitative and quantitative analysis. In these cases, PCB congener analysis may be more appropriate.

5. Safety

- 5.1. The toxicity and carcinogenicity of each reagent used in this method is not precisely defined. However, all compounds and solutions should be treated as health hazards, and exposure of these chemicals to skin and clothing should be minimized to the lowest possible level by whatever means available.
- 5.2. Wear nitrile gloves, safety glasses, and laboratory coats when working with reagents, standards and sample extracts to minimize exposure to chemicals.
- 5.3. Standard solutions should be handled in the fume hoods to avoid exposure to fumes.
- 5.4. All GC split vents are connected to an exhaust vent
- 5.5. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult with SDS website for all chemicals handled. www.msds-haz.com

6. Equipment and Supplies

- 6.1. Gas chromatograph
- 6.1.1. Gas chromatograph - An analytical system with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including:
- 6.1.2. ECD detectors
- 6.1.3. Autosampler
- 6.1.4. Analytical columns Fused-silica capillary columns - Columns used may vary depending on currently available technology (other column pairs may be used so long as they generate equivalent data):
- 6.1.4.1. Standard pair - Column 1: ZB-5, 30m, 0.53mm ID, 0.5 μ m film. Column 2: ZB-35, 30m, 0.53mm ID, 0.5 μ m film.
- 6.1.4.1.1. Alternate pair - Column 1: Rtx CLP1 30m, 0.32mm ID, 0.5 μ m film. Column 2:



Rtx CLP2, 30m, 0.32mm ID, 0.25 μ m film.

6.1.4.2. Guard Column 5m IP deactivated.

6.1.4.3. Y-connectors

6.1.5. High Purity Gases

6.2. Chemstation Data system - A computer system capable of collecting chromatographic data must be connected to the GC. The system must allow the recording of instrument response as a function of time

6.3. Syringes - 10 μ L, 25 μ L, 50 μ L, 100 μ L, 250 μ L, 500 μ L, and 1000 μ L

6.4. Volumetric flasks, Class A - 5mL to 1000mL.

6.5. Bottles – 5, 10, 25, 50, and 100 mL glass with Teflon-lined screw caps or crimp tops.

6.6. Balance - Analytical, readable to 0.0001 g

6.7. Autosampler vials- clear 2 ml autosampler vials with PTFE crimp caps.

7. Reagents and Standards

7.1. Stock standard solutions (100 - 10,000 μ g/L) - Standard solutions can be prepared from neat standards or purchased as certified solutions. Certificates of analysis for all purchased neat and stock solutions are attached as a pdf file to the standard registry in Element.

7.2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2.1. The laboratory should have acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, methanol and other appropriate solvents for preparing standards.

7.2.2. Organic-free reagent water - All references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.

7.2.3. Neat chemicals do not have an expiration date regardless of what is shown on the certificate of analysis.

7.2.4. All reagents and chemicals used in any preparation must be documented in Element.

7.3. Stock Standard Preparation

7.3.1. Prepare stock standard solutions by accurately weighing about 0.2500g of pure material. Dissolve the material in pesticide quality methylene chloride or other suitable solvent and dilute to volume in a 25mL volumetric flask. Larger or smaller volumes can be used at the convenience of the analyst. When compound purity is assayed to be 97% or greater, the weight may be used without correction to calculate the concentration of the stock standard.



- 7.3.2. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.
- 7.3.3. Transfer the stock standard solutions into amber bottles with Teflon lined screwcaps. Store at >0 to 6°C and protect from light.
- 7.3.4. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.
- 7.3.5. Stock standard solutions must be re-assayed or replaced after six months or sooner if comparison with quality control check samples indicates a problem.
- 7.4. Aroclor 1660- is a mixture of Aroclors 1016 and 1260 used to prepare the instrument calibration curve and as the spike in blank spikes and matrix QC - Purchased commercially as a $1000\ \mu\text{g}/\text{mL}$ in Hexane stock solution.
- 7.4.1. Prepare an BS and MS spike solution by diluting 2.0 mL of the Aroclor 1660 stock to 100 mL using Acetone.
- 7.5. Standardized solutions (100 to $1000\ \mu\text{g}/\text{mL}$ in Hexane) of Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268 are purchased from a commercial vendor.
- 7.6. Aroclor 2162 – A mixture of Aroclors 1221 and 1262 used for instrument calibration and as a non-routine BS or MS spike. The mixture is prepared by mixing equal volumes of the purchased Aroclor 1221 and 1262 standard solutions and therefore has each Aroclor at $500\ \mu\text{g}/\text{mL}$.
- 7.7. Aroclor 3268 – is a mixture of Aroclors 1232 and 1268 used for instrument calibration and as a non-routine BS or MS spike. The mixture is prepared by mixing equal volumes of the purchased Aroclor 1232 and 1268 standard solutions and therefore has each Aroclor at $500\ \mu\text{g}/\text{mL}$.
- 7.8. 1-Bromonitrobenzene (BNB) the first eluting internal standard, Aroclors 1016, 1221, 1232, 1242, 1248, and 1254 are quantified using its response.
- 7.9. 2,2',4,4',5,5'-Hexabromobiphenyl (HBBP) the second eluting internal standard. Aroclors 1260, 1262, and 1268 are quantitated using its response.
- 7.10. Tetrachloro-m-xylene (TMCX) - the surrogate (CAS # 877-09-8) purchased as a neat compound.
- 7.11. 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl (DCBP) - the surrogate (CAS # 2051-24-3) purchased as a neat compound.
- 7.12. Internal Standard Stock Solution – Prepared by diluting the commercially prepared stocks $1000\ \mu\text{g}/\text{mL}$ solutions of the internal standards BNB and HBBP in hexane.
- 7.13. Internal Standard Working Solution- Prepare an internal standard working standard (IS) with $8\ \mu\text{g}/\text{mL}$ BNB and HBBP in hexane.



- 7.13.1. Each 0.1 mL aliquot of the sample extract undergoing analysis should be spiked with 1 μL of the IS Working Solution, resulting in a concentration of 80ng/mL BNB and HBBP (for example, when preparing a sample aliquot of 0.3ml, spike the extract with 3 μL of the internal standard stock).
- 7.14. Surrogate Stock Standards- Prepared Stock 1000 $\mu\text{g/mL}$ solution of the surrogate standards TCMX and DCBP by dissolving 0.10g of each in a small amount of hexane in a 100mL volumetric flask and diluting to volume with hexane.
- 7.15. Surrogate spiking standard- Prepare a surrogate working standard with 2 $\mu\text{g/mL}$ TCMX and DCBP by diluting 0.08mL of the surrogate stock solutions with acetone.
- 7.16. Blank Spike (BS) Stock Standards – Typically, a 1000 $\mu\text{L/mL}$ solution of Aroclor 1660 in Hexane is used to spike BS and MS samples. The spike is purchased as a commercially certified working solution and diluted to volume with acetone.
- 7.17. BS Spike Working Standard contains Aroclor 1660 at 80 $\mu\text{g/mL}$. Prepare the standard by adding 0.8mL of the BS Spike Stock Standard and dilute to volume with hexane.
- 7.18. MRL spike working standards made from certified solutions are used to prepare MRL spikes. Aroclor 1660 is used in the preparation of the MRL spike.
- 7.19. Calibration working standards Prepared as outlined in Section 10.
- 7.20. The SCV must be derived from a different manufacturer than the stock standard used to prepare the calibration curve.
- 7.20.1. Two sources from different manufacturers are obtained when feasible or at least two different lot numbers from the same manufacturer.
- 7.20.2. Standards produced by two different manufacturers may be purchased from the same vendor.

8. Sample Collection, Preservation, Shipment, Storage, Holding times and Disposal.

- 8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 $^{\circ}\text{C}$.
- 8.2. Samples must be stored at ARI, at >0 to 6 $^{\circ}\text{C}$ until final disposal.
- 8.2.1. Samples must be extracted with holding times determined from the day of sampling. The standard holding time for water samples is 7 days. The standard holding time for solid samples is 14 days.
- 8.2.2. A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected from preservation, storage and analyses performed



outside the recommended holding times.

8.2.3. Solid and sediment samples may be stored frozen at -10 to -20 °C to extend the holding time to one year.

8.2.4. Water samples being analyzed under the MTCA program stored at >0 to 6 °C have an extended holding time of one year

8.3. Extracts

8.3.1. Extracts are delivered to Refrigerator 15 in the instrument laboratory by extractions technicians.

8.3.2. Analysts in the instrument lab assume custody of the sample extracts and then move them into Refrigerator 17 and place them in a bin assigned in Element.

8.3.3. Extracts must be stored at >0 to 6 °C and protected from light.

8.3.4. Extracts must be analyzed within 40 days of extraction except for MTCA waters which have an extract holding time of one year.

8.3.5. Extracts must be stored in their assigned Element bin.

8.3.6. Extracts may be disposed 40 days after the analysis has been completed and the Element bin will be recycled for future use.

8.3.7. Extracts will be disposed in the large blue barrel in the satellite accumulation area designed for extract vials.

9. Quality Control

9.1. Quality control requirements are available in the table in Appendix 21.1.

9.1.1. Criteria for ARI's routine analyses are listed in Appendix 21.1

9.1.2. When DoD-QSM acceptance criteria are required, please refer to DoD-QSM 5.1 for further guidance.

9.2. ARI routinely checks the effect of the matrix on both method precision and bias. At a minimum, this check should include the analysis of at least one matrix spike and one duplicate unspiked sample, or one MS/MSD pair with each preparation batch of up to 20 samples of the same matrix.

9.2.1. ARI will not perform MS/MSD analysis on any of the field QC samples delivered as part of a client's QA/QC program (water rinsate samples, field/trip blanks etc.)

9.2.2. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.3. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for matrix spike and matrix spike duplicates are statistically generated on a periodic basis.



- 9.3.1. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation.
- 9.3.2. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. Current control limits are listed in Element.
- 9.3.3. All analysts using this SOP must use it in conjunction with the Control Limit documentation in Element to assess data quality and any possible need for corrective actions.
- 9.4. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC must be documented in SharePoint.
- 9.5. Each reagent and standard preparation are recorded in Element standard registry and assigned a unique identification for traceability to the certificate of analysis of the source chemical. See ARI SOP 1013S for details.

10. Calibration and Standardization (Calibration criteria and verification apply to both chromatographic columns)

- 10.1. ARI uses single injection dual column GC-ECD systems for analysis of Aroclors. Analysis must not proceed until both columns meet initial calibration criteria.
- 10.2. The Aroclor 1660 mixture contains many of the congeners present in other Aroclors, an acceptable calibration performed with this Aroclor mixture serves to demonstrate the linearity of the detector for the other Aroclors.
- 10.3. Prepare six calibration solutions by diluting the stock of the 1660 calibration solution described in Sections 7.1 through 7.4 as outlined in Table 03.

Table 03 - Calibration Standard Concentration							
Stock Calibration Dilution		1X	2X	4X	10X	20X	50X
Used for:		ICAL	ICAL	ICAL ICV CCV	ICAL	ICAL	ICAL
Aroclor	Component	Calibration Standard Concentration (ng/mL)					
1660	1016	1000	500	250	100	50	20
	1260	1000	500	250	100	50	20
2162	1221	-	-	250 ¹	-	-	-
	1262	-	-	250 ¹	-	-	-
3268	1232	-	-	250 ¹	-	-	-
	1268	-	-	250 ¹	-	-	-



Table 03 - Calibration Standard Concentration							
Stock Calibration Dilution		1X	2X	4X	10X	20X	50X
Used for:		ICAL	ICAL	ICAL ICV CCV	ICAL	ICAL	ICAL
Aroclor	Component	Calibration Standard Concentration (ng/mL)					
1242	1242	-	-	250 ¹	-	-	-
1248	1248	-	-	250 ¹	-	-	-
1254	1254	-	-	250 ¹	-	-	-

1) Working standards prepared at 250ng/ml do not require dilution.

10.4. Add surrogate standards to the calibration working solutions so that the final concentration of each surrogate is 40ng/mL.

10.5. Spike each calibration solution with 1µL Internal Standard solution per 100µL of each standard.

10.6. Analyze each calibration solution using the same conditions and instrument setting to be used for sample extract analyzes.

10.7. For each Aroclor, select 3 or more characteristic peaks on each column to represent that Aroclor. The area of selected peaks should be ≥ 25% of the area of the largest Aroclor peak. An effort should be made to make sure that the peaks selected for quantitation in one Aroclor are not used for quantitation in other Aroclors.

10.8. Calculate the Relative Response Factor (RRF) for each Aroclor peak selected in Section 10.7 using the following formula:

$RRF = (A_x C_{IS}) / (A_{IS} C_x)$
where:
A_x = Peak area for the quantitation peak being measured
A_{IS} = Peak area of the internal standard
C_{IS} = Concentration of the IS associated with the peak
C_x = Concentration of the analyte

10.9. Calculate the Average RRF for each peak.

$Average\ RRF = \Sigma\ RRF_i / n$
where:
RRF_i = the peak response factor for each quantitation peak in the calibration standard



N = the total number of standards (usually 5)

10.10. Calculate the Relative Standard Deviation (RSD) for each peak. (These calculations are normally performed by the chromatographic data system).

$$\text{RSD} = \text{SD} / (\text{Ave RRF}) = ((\sum (\text{RRF}_i - \text{Ave RRF})^2) / (n-1))^{1/2}$$

10.11. When the average RSD for each compound is $\leq 20\%$, the calibration is acceptable and the average RRF is used to calculate analyte concentration.

10.12. When the %RSD for any Aroclor peak is not $\leq 20\%$ the analyst will:

10.12.1. Determine that there is no detector or chromatographic peak saturation and that the chromatographic system is functioning properly, then:

10.12.2. Use a linear or quadratic regression to calibrate for the Aroclor.

10.12.2.1. The analyst will first attempt to use a linear fit requiring at least five calibration points.

10.12.2.2. Next, a Quadratic non-linear calibration requires six calibration points may be used.

10.12.3. See EPA Method 8000C Section 11 for reference to linear or quadratic regression calibration.

10.12.4. When specifically required by a project or QAP, the other Aroclors may be curved along with or in lieu of Aroclor 1660.

10.12.5. The DoD-QSM requires that all Aroclors be quantified using a five-point calibration curve for each specific Aroclor quantified in a sample.

10.13. The average RSD for the quantitation peaks for each Aroclor must be less than or equal to 20% for the initial calibration to be valid. Quantitation is performed using the average RRF from the initial calibration. Surrogates may use the linear calibration model discussed in Section 11.5 of Method 8000C so long as the coefficient of determination is greater than 0.99.

10.14. Retention time windows- Retention times for each analytical batch are established by the first calibration verification in each analytical sequence.

10.14.1. ARI uses a default retention time window width of ± 0.05 minutes. Retention time studies suggested by the method often result in windows of 0.01 minutes or less.

10.14.2. ARI's experience indicates that allowing the chromatographic data system to identify analytes based on narrow statistically derived retention times may lead to false negative results. This happens often when analyzing extracts from difficult matrices that contained oily material or high background contamination. For this reason, ARI sets retention time windows



to ± 0.05 minutes and requires the analyst to manually screen for and eliminate resulting false positives.

10.14.3. Retention time criteria may change during an analytical sequence if the RT shift is explainable (a column was shortened and all RT shift equally) and CCVs confirm that the calibration is valid. All such deviations must be explained on the reviewer checklist.

10.15. The instrument initial calibration (ICAL) must be verified prior to use by analysis of a second source calibration verification standard (SCV).

10.15.1. The SCV standard is prepared at the same concentration as the mid-point ICAL standard as noted in Table 3.

10.15.2. Analyze the SCV using the same conditions as the initial calibration.

10.15.3. The SCV must be derived from a different manufacturer than the stock standard used to prepare the calibration curve.

10.15.3.1. Two sources from different manufacturers are obtained when feasible or at the very least two different lot numbers from the same manufacturer.

10.15.3.2. Standards produced by two different manufacturers may be purchased from the same vendor.

10.15.4. Calculate the percent difference using the formula:

$\%D = 100(\text{Conc} - \text{Concmp}) / \text{Concmp}$
where:
Concc = the quantitated concentration in the CVS
Concmp = the concentration of the midpoint in the ICal (500)

10.16. Initial and Continuing Calibration Verification (ICV/CCV): The performance of the instrument over time is monitored by analyzing initial and continuing calibration verifications.

10.16.1. The ICV/CCV standards are prepared from the same source as the ICAL standards. ICV/CCV standards are analyzed at the concentration of the mid-point ICAL standard (250ng/ml).

10.16.2. Each set of ICV/CCV analyses should include an Aroclor 1660 standard and one other Aroclor standard (1242, 1248 or 1254) on a rotating basis. When requested, ARI may vary the concentration of ICV/CCVs to include several standards from the calibration range or use different Aroclor pairs in the ICV/CCV sets.

10.16.3. The ICV/CCV standards are prepared from the same source as the ICAL standards. CCV standards are analyzed at the midpoint ICAL concentration as noted in Table 3.

10.16.4. An ICV is analyzed at the beginning of the analytical bracket and CCVs must be



analyzed at the end of an analytical bracket.

- 10.16.5. A CCV pair must be analyzed after every 10 field samples.
- 10.16.6. No more than 12 hours may pass between ICV/CCVs.
- 10.16.7. The retention times of all analytes in all daily ICV/CCVs must fall within the retention time windows established during initial calibration.
- 10.16.8. The Aroclors in the ICV/CCVs are quantified using the average response of 3 to 5 representative PCB congener peaks.
- 10.16.9. Calculate the RRF for each group of peaks in the ICV/CCV using the formulae used for the ICAL.
- 10.16.10. Calculate the %D between the CCV RRF and the average ICAL RRF.
- 10.16.11. Each ICV/CCV must have an average concentration of these peaks within $\pm 20\%$ of the true value when quantified using the ICAL.
- 10.16.12. All peaks used for quantitation should be at least 25% in height when compared to the height of the largest aroclor peak.
- 10.16.13. A minimum of three quantitated peaks need to be included to average an Aroclor and determine its percent difference from the ICAL.

11. Procedure

- 11.1. Prior to using this method, the samples must be prepared for chromatography using the appropriate sample preparation and cleanup methods.
- 11.2. Examine the project requirements in Element for each Work order.
 - 11.2.1. Work order documents and the project version may contain information affecting the analysis such as unusual analytes, control limits, project specific MRL standard requests, and project required data quality objectives.
 - 11.2.2. Organic extraction documents may contain useful sample or extract specific information and may include screening to which may be used to adjust extract concentration prior to analysis.
- 11.3. The recommended GC operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration.)

Initial temperature:	160°C, hold for 1 minute
Temperature program:	160-310°C at 15C°/min
Final temperature:	310°C, hold for 4 minutes
Injector temperature:	220°C



Detector temperatures:	330°C
Detector make-up gas flows	40 mL/min (front) and 35 mL/min (back)
Column initial flow	3.6 mL/min (hold for 12 minutes)
Column flow ramp	3.6-5 mL/min at 1 mL/min
Column flow final hold	5 minutes at 5 mL/min
Injector:	Grob-type, splitless/split
Injector Pulse	20 psi at 0.45 minutes
Split flow	20 mL/min at 0.5 minutes
Sample volume:	2 µL
Carrier gas:	Helium at 30cm/sec.

11.4. Prior to sample analysis the GC system must have an acceptable initial calibration curve (the requirements for the calibration curve are found in Section 10)

11.5. Prior to sample analysis an initial calibration verification must be analyzed and this ICV must meet the criteria found in Section 10.11.

11.6. Rinses before CCVs are not allowed unless rinses are placed before all injections in the analytical sequence. Rinses are permitted before the ICV analyses.

11.7. Screen extracts as necessary

11.7.1. It is highly recommended that the extract be screened on a GC/ECD using the same type of capillary column. This will minimize contamination of the GC system from unexpectedly high concentrations of organic compounds and may show high background samples that should be analyzed using a medium/high level extraction. If the screening chromatograms indicate the presence of elemental sulfur, remove the sulfur using elemental Mercury as described in Appendix 20.3.

11.8. Remove sample extracts from refrigerator 15 and change the location to refrigerator 17 in Element under batch or sequence.

11.9. GC analysis

11.9.1. Measure a 0.3-0.5ml aliquot of the sample extract obtained from sample preparation. Use a 10µL syringe to add 1µL of Internal Standard spiking solution for each 0.1 mL of extract. This results in a concentration of 80ng/µL of each internal standard in the extract. This aliquot should be prepared in a clear glass auto-sampler vial and sealed with a crimp cap. Store the remaining extract volume at >0 to 6°C, protected from light in screw-cap vials equipped with unpierced Teflon lined septa.

11.9.2. Load autosampler with the aliquots prepared in Section 11.8.1.

11.9.3. Enter the analytical sequence into the chromatography data system.



- 11.9.4. Begin the analytical sequence.
- 11.9.5. The injection volume must be the same volume used for the calibration standards. Recommended GC operating conditions are specified in Section 11.3.
- 11.9.6. The computer system will collect and process the chromatography data and export it to “Target” software.
- 11.9.7. The “Target” software assigns the chromatographic baseline and integrates the electronic signal producing a chromatogram.
- 11.9.8. Examine the chromatogram for the presence of elemental sulfur.
 - 11.9.8.1. If the presence of sulfur is suspected a Mercury cleanup must be performed on the affected extract and all associated QA sample extracts. The clean-up procedure is outlined in Appendix 20.3. Following clean-up, the sample extracts must be re-analyzed starting at Section 11.8.2.
- 11.9.9. Verify that the computer has correctly identified the chromatographic baseline and integrated all peaks correctly.
 - 11.9.9.1. If corrections are required, manually re-integrate the data file following guidelines in SOP 1021S “Manual Integration of Chromatographic Peaks”.
 - 11.9.9.2. Manual integrations must be identified and explained in the reviewer checklist associated with each analytical sequence loaded into Element.
 - 11.9.9.3. The final raw data report includes a before manual integration chromatogram and an after manual integration chromatogram for all manual integrations performed. This manual integration report is attached to the data file .PDF.
- 11.9.10. Perform all qualitative and quantitative measurements as described in Section 12.
- 11.9.11. Replace the punctured septum on the auto-sampler vial with a new one.
- 11.9.12. Store the extracts at >0 to 6°C, protected from light in Refrigerator 17.
- 11.9.13. Following the data analysis, upload the data into Element using data tool.
- 11.9.14. Attach PDF’s of all bracketing CCVs, raw data for all the samples and associated QC, the ELEMENT report, and an analyst’s note form in the project folder.
- 11.9.15. Attach a .pdf of the virtual logbook to the sequence associated with the data.
 - 11.9.15.1. Make sure the Reviewer Checklist(s) include all deviations from standard procedure and any other noteworthy information concerning the project analyzes.
- 11.9.16. The analyst initials as loaded into Element should reflect the analyst who reduced and uploaded the data if different from the analyst who initiated the analytical sequence.



12. Data Analysis and Calculations

12.1. Aroclor Identification- A sample is tentatively determined to have Aroclor content when the Aroclor peaks fall within the retention time windows for the Aroclor peaks that are used to calibrate the Aroclor and the pattern ratios are consistent with one or more of the Aroclor standards.

12.1.1. The Aroclor detection must be confirmed by examining the data from the second analytical column. Should the second column also show detection of Aroclor peaks within the RT windows, the hit has been confirmed.

12.1.2. Choose the Aroclor standard whose pattern most closely resembles that of the sample chromatogram. Carefully examine the patterns on both columns.

12.1.3. When samples appear to contain weathered PCBs, treated PCBs, or mixtures of various Aroclors, use of Aroclor standards may not be straightforward (or technically appropriate). In such cases, the analyst must decide which Aroclor or Aroclors most closely represent the range of PCBs present and will quantify total PCBs by quantifying and averaging those congener peaks with the most consistent ratios based on the analyst's opinion. When samples appear to contain multiple Aroclors, the analyst should attempt to quantify the individual Aroclors using peaks that are unique to each Aroclor or are significantly larger in one of the Aroclors. Weathered patterns and difficult mixtures should be noted in the reviewer checklist. The analyst should also attempt to report the total PCB content as accurately as possible and avoid "double counting" of Aroclors.

12.1.4. All Aroclor peaks should show consistent RT shifting in comparison to the initial calibration (i.e. all peaks should elute earlier or later compared to the initial calibration, and by the same amount.) Large chromatographic interferences may cause inconsistent shifting by moving some of the peaks more than others. The chromatographs of samples should be examined to ensure that false negatives aren't created by this manner of chromatographic overload.

12.2. All peaks for each Aroclor should show quantitative agreement. Again, interferences can elevate the quantitation number for some of the peaks. Analysts are expected to average the peaks that best represent a given Aroclor in a specific chromatogram. Should some of the quantitation peaks be interfered with, these peaks may be removed from the average Aroclor concentration calculation, so long as at least three peaks remain for averaging. The peaks removed from the calculation, as well as the corrected average concentration need to be noted on the raw data.

12.3. Sample Quantitation (Calculation performed by Target and verified with Element software)

12.3.1. Water



Concentration (µg/L) = $\frac{(A_x)(I_s)(V_t)(DF)}{(A_{IS})(RRF)(V_o)(V_i)}$
where:
A_x = Peak of the quantitation peak for the compound being measured
I_s = Amount of internal standard injected (ng).
V_t = Volume of total extract
A_{IS} = Peak area of the internal standard
RRF = Relative response factor for compound being measured
C_x = Concentration of the analyte
V_o = Volume of water extracted (ml)
V_i = Volume of extract injected (ul)
DF = Sample Dilution Factor (1 for undiluted samples)

12.3.2. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)

Concentration (µg/kg) = $\frac{(A_x)(I_s)(V_t)(DF)}{(A_{IS})(RRF)(V_i)(W_s)(D)}$
where:
A_x = Peak of the quantitation peak for the compound being measured
I_s = Amount of internal standard injected (ng).
V_t = Volume of total extract
DF = Sample Dilution Factor (1 for undiluted samples)
A_{IS} = Peak area of the internal standard
RRF = Relative response factor for compound being measured
V_i = Volume of extract injected (ul)
W_s = Weight of sample extracted or diluted in grams
D = % Dry weight of sample = 1.0 on an as received basis

12.4. ARI will report the higher of the Aroclor results as per Method 8000B. This approach is conservative relative to protection of the environment. In certain instances, or for project specific requirements, it may be appropriate to report the lower result as per Method 8000C. This approach is only valid under the discretion of an experienced analyst and must be noted in the reviewer checklist and in the project narrative.

13. Method Performance

13.1. The QA department measures method performance using a combination of quarterly MRL studies, performance evaluation samples, and the monitoring of surrogate and spike recoveries.



- 13.1.1. Detection limits- the LOD for all analytes quantitated using this SOP are set using the low point of the initial calibration curve and validated by MRL studies.
- 13.1.2. MRL studies are performed each quarter for each analyte by each preparatory and analytical method.
- 13.1.3. LOD and MRL values may be found for each analyte in Element.
- 13.2. Laboratory precision and bias measurements are performed by monitoring surrogate and spike recoveries in samples and quality control samples.
 - 13.2.1. Control limits are calculated from these recoveries.
 - 13.2.2. These control limits are disseminated to the bench chemists and Element administrator for use in monitoring method performance in real time.
 - 13.2.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found in Element.
- 13.3. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. See ARI SOP 1017S.
- 13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.
- 13.5. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to assure proper qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation (weathering) or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards. In these cases, PCB peak analysis may be more appropriate.
- 13.6. **The experience of the analyst must weigh heavily in the interpretation of the chromatogram.** In the case of multi-component analytes such as Aroclors the analyst should rely primarily on pattern recognition.

14. Pollution Prevention

- 14.1. All syringe rinses are discharged into activated charcoal. Spent charcoal is properly disposed of as "Solvent Contaminated Solids" by ARI's designated Treatment, Storage and Disposal Facility.
- 14.2. Charcoal containers must remain covered when not attended to prevent fugitive vapors.
- 14.3. Expired standards are disposed into the designated barrel in the hazardous waste room.
- 14.4. Auto-sampler vials containing sample extracts are placed in the satellite accumulation station in the GC storeroom for eventual removal by an EPA approved Treatment, Storage and Disposal Facility.



- 14.5. All GC split vents are connected to an exhaust vent and the filter is changed biannually.
- 14.6. Open solvent containers should only be present when actively preparing samples.
- 14.7. Wherever possible the final sample extract volume should be as small as possible to minimize the generation of waste.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

- 15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 and Appendix 21.1 of this document.
- 15.2. Requirements for Method Blanks are tabulated in Appendix 21.1.
- 15.3. Internal Standards- All samples' internal standard peak areas must meet the technical acceptance criteria listed in Appendix 21.1 of this SOP.
- 15.4. Surrogate Recoveries
 - 15.4.1. All method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates, or other samples must have acceptable surrogate standard recoveries. Surrogate recoveries are acceptable when they are within ARI's statistically generated control limits or limits set by ARI's client or a specific quality systems protocol such as the DoD-QSM.
 - 15.4.2. Any surrogate recovery that is "out-of-control" required that a corrective action be initiated.
 - 15.4.2.1. These requirements do not apply to subsequent dilutions of samples where a prior analysis of the diluted sample extract shows acceptable surrogate recovery.
 - 15.4.2.2. When mandated by contract-specific requirements, corrective actions must be performed for unacceptable surrogate recovery even when the criteria are labeled as advisory in the reference method.
 - 15.4.3. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.
- 15.5. Blank spikes (BS)
 - 15.5.1. Blank Spike recovery must fall within specified recovery acceptance limits or corrective action is required.
 - 15.5.1.1. Blank Spike recovery acceptance criteria are determined statistically from historic laboratory data. Criteria specified by a method, ARI's client or a particular quality system (i.e. DoD-QSM) may supersede ARI's historic values.
 - 15.5.1.2. When mandated by a particular quality system or contract-specific requirements, corrective actions are required in response to unacceptable BS criteria, even when the criteria are labeled as advisory in the reference method.



15.5.1.3. Spike acceptance criteria are method, matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no specific acceptance criteria are available, the closest approximation of available acceptance criteria may be used for advisory purposes only.

15.5.2. When an BSD is analyzed, relative percent difference (RPD) acceptance limits also apply, if specified by contract or quality system.

15.5.3. The RPD between spiked Aroclor concentrations in an BS and an BSD should be $\leq 30\%$. If the RPD exceed 30%, examine the surrogate recovery of the BS/BSD. Since the surrogate is a measure of extraction efficiency, if the RPD between the surrogate recoveries of the BS/BSD is $\leq 30\%$ then no corrective action is necessary. If the surrogate RPD also exceeds 30%, submit the BS and all associated samples for re-extraction and reanalysis.

15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.6.1.1. MS spike recovery must fall within specified recovery acceptance limits or corrective action is required.

15.6.1.2. MS recovery acceptance criteria are determined statistically from historic laboratory data. Criteria specified by a method, ARI's client or a particular quality system (i.e. DoD-QSM) may supersede ARI's historic values.

15.6.1.3. When mandated by a particular quality system or contract-specific requirements, corrective actions are required in response to unacceptable MS criteria, even when the criteria are labeled as advisory in the reference method.

15.6.1.4. Spike acceptance criteria are method, matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no specific acceptance criteria are available, the closest approximation of available acceptance criteria may be used for advisory purposes only.

15.6.2. When an MSD is analyzed, relative percent difference (RPD) acceptance limits also apply, if specified by contract or quality system.

15.6.2.1. The RPD between spiked Aroclor concentrations in an MS / MSD must be $\leq 30\%$. If the RPD exceed 30%, examine the surrogate recovery of the MS/MSD. Since the surrogate is a measure of extraction efficiency, if the RPD between the surrogate recoveries of the MS/MSD is $\leq 30\%$ then no corrective action is necessary. If the surrogate RPD also exceeds 30%, submit the BS and all associated samples for re-extraction and reanalysis.

15.7. Holding Times

15.7.1. Extracts should be analyzed within the extract holding time (40 days from the date of



extraction.)

15.7.2. If re-extraction due to an out of control event requires that samples be re-extracted after their extraction holding time has elapsed (seven days for water and fourteen days for tissues/solids) the analyst should analyze and report both extraction sets, whenever practical, distinguishing between the initial extraction and re-extraction on all deliverables. This will document that the samples were originally extracted within holding times and may allow for comparisons that will determine whether data quality was affected by the samples being analyzed out of holding.

15.7.3. If any extracts are analyzed after the 40-day extract holding time has elapsed, the analyst shall document this in the reviewer checklist accompanying the data so that it may be included in the narrative.

15.8. Analytical sequences

15.8.1. For GC and GCMS analysis; Analysts should not intersperse instrument blanks between samples and closing calibrations or method blanks. If instrument blanks are run between samples and QC samples or standards, then every sample in the job or the bracket must be preceded by an instrument blank. Also, QC samples should be run with their associated samples and; specifically, running all method and spike blanks at the beginning of an analytical queue prior to samples is strongly discouraged.

16. Corrective Actions for Out of Control Events

16.1. Corrective actions may include any, but are not limited to, the following:

16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the reviewer checklist.

16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.3. Repreparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.4. Reanalysis – the extract aliquot that was originally prepared is reinjected and run on the gas chromatograph again.

16.1.5. Reextraction – a reextraction request is filled out (Form 0030F). PDF Copies of the form are provided to the extractions department, the project manager, the QA manager and the lab manager. The remaining sample is extracted.

16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's



- experience and a description of the maintenance performed will be documented in Element.
- 16.1.7. Recalibration – a new initial calibration is evaluated, and the associated samples reanalyzed.
- 16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.
- 16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.
- 16.2. When an Initial Calibration (ICAL) RSD for an analyte exceeds 20%
- 16.2.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.
- 16.2.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all the data.
- 16.3. When an Initial or Continuing Calibration Verification (ICV/CCV) %D exceeds 20%
- 16.3.1. At the discretion of the analyst, a second ICV may be run after the failing ICV. If the second ICV meets all ICV criteria, then the sequence may begin.
- 16.3.2. If the second injection of the ICV fails, perform the appropriate corrective action(s) from section 16.1 and re-calibrate the instrument
- 16.3.3. DoD-QSM requires that %D for all analytes in both the ICV and CCV be $\leq 20\%$. For DoD analyses immediately analyze two consecutive ICVs or CCVs. This is not required; the analyst may default to Section 16.3.1.
- 16.3.3.1. When both ICVs/CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued



16.3.3.2. If either fails or two consecutive ICVs/CCVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.4. Internal Standards

16.4.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.2. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.

16.4.3. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.

16.4.4. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.4.5. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".

16.5. Surrogates

16.5.1. Examine the bench sheet to verify spiking levels are correct.

16.5.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.5.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.6. Method Blanks- Corrective action for a method blank which fails acceptance criteria may involve re-extraction and reanalysis of all associated samples and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.7. Blank spike/Blank spike duplicate Samples

16.7.1. Control limits for this method and defined in Element for all PCB analysis. Verify that the correct and appropriate control limits have been applied. Blank spikes and blank spike duplicates that do not meet the control limits must not be used solely to reject data.

16.7.2. Examine the bench sheet to verify spiking levels are correct.

16.7.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8. Matrix Spike/Matrix Spike Duplicates

16.8.1. Examine the bench sheet to verify spiking levels are correct.

16.8.2. Recoveries are advisory and should not necessarily result in re-extraction.

16.8.3. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.

16.9. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve; a dilution must be performed such that the analyte's quantitated value is within the curve



range.

16.9.1. Additional internal standard must be added to the diluted extract to maintain the required 80 ng/mL of each internal standard in the extracted volume.

16.9.2. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

16.9.3. When peaks from an analyte saturate the detector:

16.9.3.1. The analyst should analyze an Instrument Blank consisting of clean solvent until the system has been decontaminated.

16.10. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.

16.10.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)

16.10.2. All QC limit issues (including continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

16.11. If contaminants (including target and non-target compounds) continue to cause significant interference, even after all relevant cleanups have been performed; the sample should be re-extracted at a level appropriate to the amount of contamination. The particular re-extraction level should be based on the initial analysis or pre-analysis GC-ECD screen. The experience and discretion of the analyst and section supervisor will be relied upon for re-extraction decisions. The PM will be notified if re-extraction at a different level is required.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Section 16.2 for guidance on dealing with initial calibration out-of-control events.

17.2. See Section 16.3 for guidance on dealing with initial and continuing calibration verification out-of-control events.

17.3. See Section 16.4 for guidance on dealing with internal standard out-of-control events.

17.4. See Section 16.5 for guidance on dealing with surrogate out-of-control events.

17.5. See Section 16.6 for guidance on dealing with method blank related out-of-control events.

17.6. See Section 16.7 for guidance on dealing with blank spike and blank spike duplicate related



out-of-control events.

17.7. See Section 16.8 for guidance on dealing with MS/MSD related out-of-control events.

17.8. See Section 16.9 for guidance on dealing with over range related out-of-control events.

17.9. See Section 16.10 for dealing with particular circumstances out-of-control events.

17.10. See Section 16.11 for dealing with out-of-control events concerning contamination.

18. Waste Management

18.1. All extract and standard vials must be disposed of by placing them in the blue hazardous waste drum in the lab set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.

18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.

18.3. All spent charcoal must be disposed of by placing it in the charcoal disposal bin located in the hazardous waste room.

18.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

19.1. "Polychlorinated Biphenyls by Gas Chromatography": Method 8082A, Test Methods for Evaluating Solid Waste (SW846), Revision 1, February 2007

19.2. EPA Method 608.3—Organochlorine Pesticides and PCBs by GC/HSD December 2016

19.3. USEPA Contract Laboratory Program, Statement of Work for Organics Superfund methods SOM02.4, October 2016.

19.4. "Determinative Chromatographic Separations": Method 8000D, (SW-846), Revision 5, March 2018.

19.5. Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 5.3, June 2019

20. Appendices

20.1. Appendix 21.0: In-house PCB Quality Control Requirements

20.2. Appendix 21.1: Sulfur cleanup procedure

20.3. Appendix 21.2: Congener analysis by ECD

20.4. Appendix 21.3: Method 608 modifications



21. Appendix 21.0: In-House PCB Quality Control Requirements

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	Corrective Action (see Section 17)	Flagging Criteria
Demonstration of capability (DOC). DOC requirements are outlined in ARI SOP 1017S.	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method.	ARI spike recovery QA limits	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria.	Not applicable (NA)
Method detection limit (MDL) study	At initial set-up and subsequently once per 12-month period; otherwise quarterly MDL verification checks shall be performed.	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study.	NA
Retention time (RT) window width for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	ARI uses a default retention time window of 0.05 minutes	NA	NA
Breakdown check (Endrin and DDT)	Run DDT's to check for possible DDT's in samples	NA	NA	Note possible DDT's in reviewer checklist
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	One of the options below: Option 1: RSD for each analyte \leq 20% Option 2: non-linear regression: coefficient of determination (COD) $r^2 \geq 0.99$ (6 points required)	Correct problem then repeat initial calibration.	Flagging criteria are not appropriate.
Second source initial calibration verification	Once after each initial calibration	Value of second source for all analytes within \pm 20% of expected value (initial source)	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat initial calibration.	Flagging criteria are not appropriate.
Retention time window position established for each analyte and surrogate	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	NA	NA
Retention time Window verification for each analyte and surrogate	Each calibration verification standard	Analyte within established window	Correct problem, then reanalyze all samples analyzed since the last acceptable retention time check. If they fail, redo ICAL and reset retention time window.	Flagging criteria are not appropriate for initial verification.



QC Requirement	Minimum Frequency	ARI Acceptance Criteria	Corrective Action (see Section 17)	Flagging Criteria
Calibration verification (initial [ICV] and continuing [CCV])	ICV: Daily, before sample analysis CCV: After every 10 field samples and at the end of the analysis sequence	All analytes within $\pm 20\%$ of expected value from the ICAL	ICV: Correct problem, rerun ICV. If that fails, repeat initial calibration. See section 5.5.10 and box 55. CCV: Correct problem then repeat CCV and reanalyze all samples since last successful calibration verification.	ICV: Flagging criteria are not appropriate. CCV: Flagging criteria are not appropriate.
Method blank	One per preparatory batch	No analytes detected	Correct problem, if required re-prepare then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-qualifier to all results for the specific analyte(s) in all samples in the associated preparatory batch
Blank Spike (BS) containing all analytes and surrogates to be reported	One BS per preparatory batch	ARI BS control limits	Correct problem, then re-prepare and reanalyze the BS and all samples in the associated preparatory batch, if sufficient sample material is available.	If corrective action fails and there is insufficient sample material; report and discuss in the case narrative.
Matrix spike (MS)	One MS per preparatory batch per matrix.	ARI MS control limits	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the MS sample, apply *-qualifier if acceptance criteria are not met.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	ARI MS and %RPD control limits	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the MSD, apply *-qualifier if acceptance criteria are not met.
Surrogate spike	All field and QC samples	ARI control limits	For QC and field samples, correct problem then re-prepare and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	For the specific analyte(s) in all field samples collected from the same site matrix as the parent, apply *-qualifier if acceptance criteria are not met.
Confirmation of positive results (second column or second detector)	All positive results must be confirmed.		NA	Apply p1-qualifier if RPD > 40%. Discuss in the case narrative.
Results reported between LOD and MRL	NA		NA	Apply J-qualifier to all results between LOD and MRL.



21.1. Sulfur Clean-up

- 21.1.1. Elemental Sulfur is precipitated from the sample extract using elemental Mercury which forms the insoluble salt HgS.
- 21.1.2. This procedure is performed only when the presence of elemental sulfur is indicated in initial sample analyzes and is performed by GC analysts in addition to the Sulfur removal using TBAS performed in the Organic Extractions Laboratory following ARI SOP 334S "Sulfur Removal".
- 21.1.3. Using a syringe insert a drop (~0.05 mL) of elemental Mercury into the autosampler vials containing the sulfur contaminated extract(s) and all associated QA sample extracts.
- 21.1.4. Shake the vials for approximately 30 seconds each using a "Vortex" type shaker.
- 21.1.5. Let the vial stand for 15 to 20 minutes to allow the precipitate to settle.
- 21.1.6. Repeat steps 20.2.3 through 20.2.5 until no additional dark precipitate is produced.
- 21.1.7. When the precipitate has settled, the vial may be placed in the autosampler tray for re-analysis.
- 21.1.8. Following analysis, dispose of the Mercury contaminated vial in the designated container in Fume Hood 34.



21.2. Appendix 20.3 - PCB Congeners by GC/ECD - ARI Method based on 8082A

21.2.1. This procedure summarizes ARI's protocol for identifying and quantifying specific Polychlorinated biphenyl congeners that in technical mixture compose PCB Aroclors. A variety of matrices may be analyzed including soils, solids, waters, tissues, and waste products (oils, sludges)

Congener*	BZ#
2,4'-Dichlorobiphenyl	8
2,2',5'-Trichlorobiphenyl	18
2,4,4'-Trichlorobiphenyl	28
	31
	33
2,2',3,5'-Tetrachlorobiphenyl	44
	49
2,2',5,5'-Tetrachlorobiphenyl	52
	60
2,3',4,4'-Tetrachlorobiphenyl	66
	70
	74
3,3',4,4'-Tetrachlorobiphenyl	77 ^t
	87
	95
	97
	99
	56
2,2',4,5,5'-Pentachlorobiphenyl	101
	105
2,3,3',4,4'-Pentachlorobiphenyl	110
2,3',4,4',5-Pentachlorobiphenyl	118
3,3',4,4',5-Pentachlorobiphenyl	126 ⁱ
2,2',3,3',4,4'-Hexachlorobiphenyl	128
	132
2,2',3,4,4',5'-Hexachlorobiphenyl	138
	141
	149
	151
2,2',4,4',5,5'-Hexachlorobiphenyl	153



	156
	158
2,2',3,3',4,4',5-Heptachlorobiphenyl	170
	174
	177
2,2',3,4,4',5,5'-Heptachlorobiphenyl	180
	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	187
	194
2,2',3,3',4,4',5,6-Octachlorobiphenyl	195
	201
	203
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	206
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	209/

† These compounds not currently analyzed for.

* This is ARI's standard list of PCB congeners. Other congeners are available upon client request.

21.2.2. Congener analysis is recommended for samples containing multiple Aroclors that are indistinguishable from the patterns used in method 8082A

21.2.3. Detection limits-will depend on the amount of sample extracted and the final effective volume.

SAMPLE MATRIX	SAMPLE BASIS	FINAL VOLUME	MRL
Solid	12.5grams	2.5mL	1µg/kg

21.2.4. The congeners are quantitated from a 6-point curve ranging from 5ng/mL to 100ng/mL on column.

21.2.5. The curve points are 5, 10, 25, 50,75, and 100ppb

21.2.6. Compound identification is based on a dual column analysis.

21.2.7. The columns used are Restek STX CLP1 0.32mm ID x 30m x 0.32µm and STX CLP2 0.32mm ID x 30m x 0.25µm.



21.3. Modifications Required for EPA Method 608

21.3.1. Modification Required for EPA Method 608

21.3.2. **(These modifications are only implemented when specifically requested by a client, otherwise Method 608 is analyzed as described in previously in this SOP)**

21.3.3. The Initial Calibration for Method 608 is a minimum of 3 points instead of 5 points required in Method 8082A.



Standard Operating Procedure

Ammonia, Auto-phenate

SOP 615S
Version 006

Revision Date: 3/29/17
Effective Date: 3/29/17

Prepared by:

Mike Perkins

Approvals:

A handwritten signature in blue ink, appearing to read "Casey English".

Casey English, Laboratory Supervisor

A handwritten signature in blue ink, appearing to read "Eric Larson".

Eric Larson, Inorganics Division Manager



Annual Review

SOP Number: 615S

Title: Ammonia, Auto-phenate

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____



Standard Operating Procedures: Ammonia, Auto-phenate

1. Scope and Application

1. This method is for the determination of ammonia nitrogen ($\text{NH}_3\text{-N}$) in drinking, surface, domestic and industrial wastes and saline (2M KCl) soil extracts using automated phenate, flow injection analysis (FIA). The procedure is based upon the requirements of Standard Methods 4500- NH_3 H-97.
2. The automated phenate method is applicable to the measurement of 0.04 mg/L to 1.00 mg/L $\text{NH}_3\text{-N/L}$ in potable and surface waters and domestic and industrial wastes. The range may be extended by diluting samples for analysis.
3. While Standard Methods states that “sample distillation is unnecessary”, the method is not applicable for NPDES reporting without a preliminary distillation (40 CFR 136.3, 2012 Method Update Rule, Table IB). The same is true for all NPDES ammonia methods. Footnote 6 to Table IB indicates that distillation is not required if comparability studies indicate that distillation is not required for the test effluent.
4. ARI does not normally distill samples for ammonia analysis by either ISE or the automated phenate procedure. Clients requesting ammonia analysis by either procedure should be aware of this potential limitation in the use of the data.

2. Summary of the Procedure

1. Ammonia (NH_3) in natural waters derives largely from the microbial breakdown of organic materials (deamination of organic nitrogen (R-NH_2), hydrolysis of urea (H_2NCONH_2), etc.) and, under anaerobic conditions, the reduction of nitrate (NO_3). Ammonia exists either as a dissolved gas (NH_3 aq) or as the ammonium ion (NH_4^+), primarily dependent upon pH (temperature and dissolved solids also affect the speciation). At $\text{pH} < 7$, NH_4^+ predominates and as the medium becomes more basic ($\text{pH} > 7$) gaseous NH_3 predominates (approximately 50% at $\text{pH} 9$ and 100% at $\text{pH} > 11$). The approximate speciation of ammonium and ammonia is shown in figure 1 below.

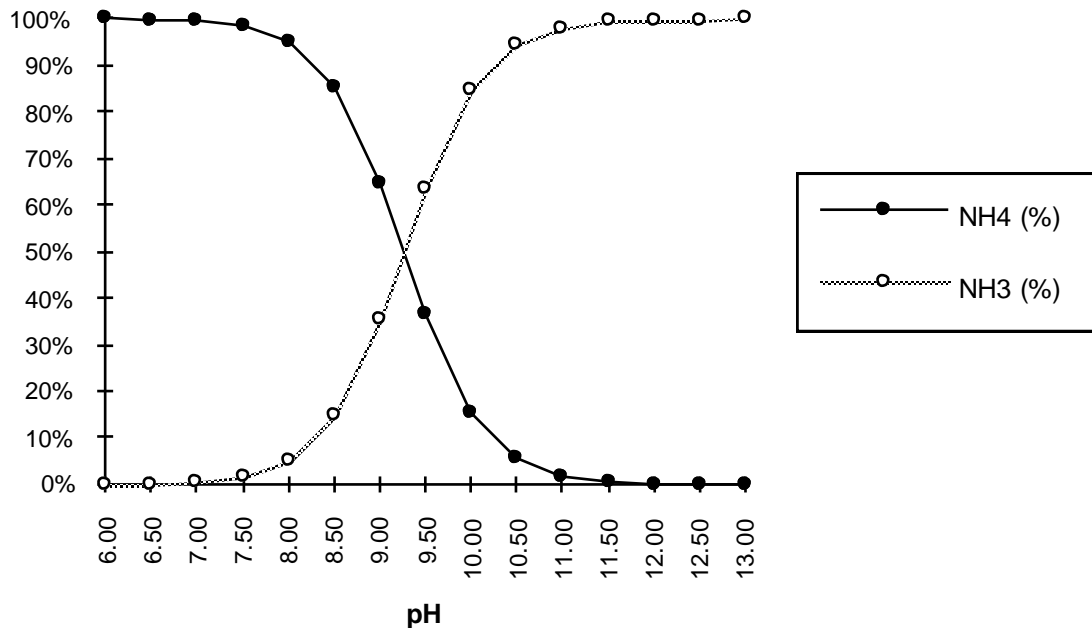


Figure 1. Approximate speciation of ammonium (NH₄) and ammonia (NH₃)

2. Two procedures are used for the analysis of ammonia in our laboratory, the automated phenate (this SOP) and ion-specific electrode (SOP ARI 616S). Both procedures measure ammonia as NH₃-N under alkaline conditions. The phenate procedure allows for rapid analysis of large numbers of relatively clean low level samples (<10 mg/L) but is more subject to interference related to color, turbidity and dissolved solids. This is the procedure of choice for routine analysis. For samples which are highly turbid, colored, or have high TDS/Conductivity (>500 mg/L, >770 μ S) or have an ammonia concentration requiring a dilution greater than 1:100 (>100 mg/L) the ISE procedure should be used.
3. Soil/Sediment will be extracted following MSA 33.3.
 - 2.3.1. 1:10 Extraction with 2N KCl and a shake time of 1 hour.

3. Definitions

1. Method Detection Limit (MDL): Defined as the minimum concentration of an analyte that can be detected as being significantly greater than zero for a given instrument configuration. Defined in ARI SOP 1018S as synonymous with the Detection Limit (DL).



2. Analytical Batch: An analytical batch will consist of no more than 20 samples including one distillation blank, one Laboratory Control Standard, one Method Reporting Limit standard and matrix spikes and duplicates.
3. Method Blank (MB): The Method Blank is treated exactly the same as the samples during preparation. DI water is used for preparation of the method blank, all standards and for sample dilutions.
4. Method Reporting Limit standard (MRL): The MRL is a standard prepared at a concentration equal to the low point of the curve and treated exactly the same as the samples during preparation.
5. Laboratory Control Standard (LCS): The LCS is a standard prepared at a concentration mid-range of the curve from a secondary source and treated exactly the same as the samples during preparation.
6. Calibration Verification Standard (CVS): It is a standard prepared at a concentration mid-range of the standard curve and derived from a source other than that used for calibration. The CVS is used to verify the performance and stability of the standard curve throughout the batch run. Control limits are $\pm 10\%$ of the known concentration.
7. Matrix Spike (MS): A sample prepared by adding a known amount of ammonia to a specified amount of sample matrix. Matrix spikes are used to determine the effect of the sample matrix on a method's recovery efficiency.
8. Matrix Spike Duplicate (MSD): When requested will be analyzed following the MS. An MSD is required for work conducted under the Department of Defense (DoD) Quality Systems Manual. Such projects will be clearly identified by the Project Manager.
9. Matrix Duplicate: A second replicate matrix sample prepared in the laboratory and analyzed to obtain a measure of the precision of the determination with respect to the matrix.
10. Laboratory Information Management System (LIMS): Software program called Element used to track laboratory samples and produce data reports.

4. Interferences

1. Under basic conditions, NH_3 is subject to loss by volatilization hence samples are preserved by acidification which also retards microbial activity.
2. Ammonia will react with residual chlorine to form chloramines (monochloramine, dichloramine and nitrogen trichloride) hence any residual chlorine should be removed immediately upon collection.

5. Safety

1. The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.



2. Use extreme caution when handling phenol. This chemical causes severe burns and is rapidly absorbed into the body through the skin.
3. Consult the SDS for each chemical used in this procedure should questions arise. SDS are available as a hardcopy in the central office area, or online as linked on the ARI intranet.
4. Always wear appropriate PPE (personal protective equipment) when working in the Laboratory. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, etc. are provided for your protection
5. Environmental Samples may contain hazardous waste; treat them as potential health hazards.
6. Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan.
7. All acid and sample waste must be disposed following the ARI Waste Management Plan.
8. Dispose of all unwanted, broken glassware into a broken glassware container. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

6. Equipment and Supplies

1. Lachat Quikchem® 8000 series FIA
2. XYZ Autosampler
3. Reagent Pump and associated tubing
4. Omnion Software on equipped computer and printer.
5. Volumetric Flasks
6. Pipettes
7. Analytical Balance
8. Disposable Glass Tubes, Fisherbrand Cat. No. 14-961-29

7. Reagents and Standards

1. Reagents: Use fresh deionized water (DI) when making reagents and standards. Avoid using any DI which has been stored for appreciable period of time due to the potential for ammonia absorption from the atmosphere. All reagents including DI must be degassed (unless specifically noted) with Helium at 140 kPa (20 psi) with the use of a degassing tube or a fritted glass tube. Record preparation of reagents in Element and affix labels to containers.
 - 7.1.1. Sodium Phenolate: CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin. In a 1L volumetric flask, dissolve 83g crystalline phenol (C₆H₅OH), or 88mL of 88% liquefied phenol, in approximately 600mL DI water. While stirring, slowly add 32 g sodium hydroxide (NaOH). Cool, dilute to the mark, and invert to mix.



Do not degas this reagent. Prepare fresh every 3 to 5 days. Discard when reagent turns brown.

7.1.2. Sodium Hypochlorite: In a 500 mL volumetric flask, dilute 250 mL 5.25% sodium hypochlorite (NaOCl) to the mark with DI water. Invert to mix. Prepare fresh daily.

7.1.3. Sodium Nitroprusside: In a 1L volumetric flask dissolve 3.5g sodium nitroprusside (sodium nitroferrocyanide [Na₂Fe(CN)₅NO.2H₂O]). Dilute to the mark with DI water and invert to mix. Prepare fresh every 1 to 2 weeks.

7.1.4. 1M Sodium Hydroxide Solution: In a 1L volumetric flask dissolve 40.0 g sodium hydroxide (NaOH) in approximately 900mL DI water. Dilute to the mark and mix with a magnetic stirrer until dissolved.

7.1.5. Buffer: In a 1L volumetric flask, dissolve 50.0 g disodium ethylenediamine tetraacetic acid (Na₂EDTA) and 225 mL 1 M sodium hydroxide in approximately 700 mL DI water. Dilute to the mark and mix with a magnetic stirrer until dissolved. Prepare fresh monthly.

7.1.6. 2N KCl: Partially fill a 1L volumetric flask with deionized water and dissolve 149.12g KCl. Let the reagent warm up to room temperature, then dilute to volumetric mark. Prepare fresh monthly.

2. Ammonia Standards. Ammonia standards are prepared from either ammonium chloride salt or from commercially prepared and certified reference standards. In general, the in-house prepared ammonium chloride standards will be used for preparation of standard curves and for matrix spiking. The commercially prepared standard will be used as the independent source for calibration verification. Preparation of any stock standard solution must be documented by entry of preparation data into the LIMS. You must verify that data entry is correct and that ammonia is expressed as elemental nitrogen (i.e. NH₃-N). All standards must be made volumetrically using clean volumetric glassware and pipettes.

7.2.1. Ammonium chloride Stock standard (1,000 mg NH₃-N/L). In a 1 liter volumetric flask dissolve 3.8189 g anhydrous ammonium chloride (NH₄Cl, FW = 53.492, 26.18%N), pre-dried at 100 °C, into approximately 500 mL fresh DI and dilute to 1000 mL. Enter data (exact weight and volume) into LIMS and print a label for the prepared bottle to show the name of the standard, the standard ID Number, the date of preparation and your initials. Use this standard for the preparation of the Intermediate ammonia standard and prepare fresh annually or as needed.

7.2.2. Intermediate NH₃-N Standard (Concentration = 20 mg/L). Dilute 2 mL of the NH₃-N Stock standard to 100 mL with DI. Use this solution for the preparation of the Standard Curve. Prepare this Intermediate Standard weekly.



3. Calibration Standards. Dilute the above Intermediate Standard to 100 mL as indicated in the table below: These standards must be made fresh weekly and should be labeled with the date of preparation and your initials.

Standard #	Final volume (mL)	Volume of Intermediate Std (20 ppm) (mL)	Concentration (mg/L NH ₃ -N)
S0	100	0.0	0.0
S1	100	0.20	0.04
S2	100	0.50	0.10
S3	100	1.00	0.20
S4	100	2.50	0.50
S5	100	4.00	0.80
S6	100	5.00	1.00

4. Method Blank. The Method Blank for preserved samples is prepared by adding 2 mL 9N H₂SO₄ to a 500 mL sample bottle containing DI. The method blank is used to prepare the MRL and LCS. For unpreserved samples the method blank is a DI filter blank. Prepare fresh with each batch.
5. Method Reporting Limit standard (MRL). The MRL is prepared at the low point of the curve by diluting 0.1 mL 20 ppm intermediate to 50 mL with the method blank. Prepare fresh with each batch.
6. Laboratory Control Standard (LCS). The LCS is prepared from a 1000 mg/L NIST traceable independent source stock solution. Dilute 0.05 mL of the 1000 mg/L stock to 100 mL using the method blank for a concentration of 0.50 mg/L. Prepare fresh with each batch.
7. Calibration Verification Standard (CVS). Calibration verification standard is prepared from a 1000 mg/L NIST traceable independent source stock solution. To prepare the working standard add 0.05 ml of the 1000 mg/L stock to a 100 mL volumetric flask containing about 50 mL of DI. Mix well and bring to a 100mL final volume, the concentration is 0.50 mg/L. This standard should be prepared weekly.

8. Sample Collection, Preservation, Shipment and Storage

1. Aqueous samples are collected in 500 ml HDPE containers, preserved with 9N H₂SO₄ to pH <2 and kept cool between 0 – 6 degrees C. Preserved samples can be held up to 28 days, but unpreserved samples must be analyzed within 48 hours from collection.
2. Solid samples are collected in 4 oz wide mouth glass jars and kept cool between 0 – 6 degrees C. The holding time for solid samples is 7 days.

9. Quality Control



1. Demonstration of Capability. Each analyst using this procedure must run an initial "Demonstration of Capability" by preparing and analyzing 4 replicates of the QC Check Solution. The recovery (Accuracy) must be within the range of $\pm 10\%$ (90 to 110 %) with a relative standard deviation (Precision) less than 10 %. An on-going DOC will be provided by the analysis and recording of the QC Check Solution for each batch of ammonia analyses conducted.
2. Detection and quantitation limits are retained in LIMS. See SOP 1018S for additional information on how detection and quantitation limits are calculated.
3. Control charts for trend analysis. Control charts for the Ammonia Low Level Check Standard will be constructed and updated on a periodic basis. Results will be evaluated relative to Warning and Control limits set at 2 and 3 standard deviations of the mean, respectively.
4. The regression coefficient, r should be greater than 0.995.
5. Initial Calibration Verification (ICV) and Calibration Blank (ICB) must be run at the beginning of each batch. Continuing Calibration Verification standards and blanks (CCV, CCB) must be run after every ten samples in the batch and at the end of each run. The calibration verification standards must agree within $\pm 10\%$ of the "true" value and the concentration of the blanks should be less than the absolute value of the reporting limit.
6. Matrix spike and duplicate analyses are run with each batch or as requested by the client.
 - 9.6.1. Duplicate analysis. If both the original and duplicate sample concentrations are greater than 5X the detection limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the detection limit, then the absolute difference between the two should be less than or equal to the detection limit. If these criteria are not satisfied, corrective actions must be taken.
 - 9.6.2. Matrix Spikes. The acceptance limits for matrix spike recoveries are $\pm 25\%$ if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.
7. MRL Check Standard: A standard prepared at the low point of the curve and prepared exactly the same as the samples on the batch. Run immediately following the ICV/ICB.
8. Method Blank: A method blank should be analyzed with each batch after the MRL Standard. This blank should have a value less than the absolute value of the reporting limit.
9. Laboratory Control Standard: A positive control standard prepared with each batch. The LCS must agree within $\pm 10\%$ of the "true" value.

10. Calibration and Standardization

1. A six point calibration curve is prepared weekly, ranging from 0.04 to 1.0 mg/L $\text{NH}_3\text{-N}$, and analyzed with each sequence.



2. Initial Calibration Verification (ICV) and Calibration Blank (ICB) are run at the beginning of each sequence. Continuing Calibration Verification standards and blanks (CCV, CCB) are run after every ten samples in the sequence and at the end of each run.

11. Procedure

1. Preparations

- 11.1.1. If residual chlorine is suspected use Starch-Potassium Iodide paper to test the sample. If detected it can be removed by adding 1 mL of sodium thiosulfate solution (0.35 grams sodium thiosulfate dissolved in 100 mL DI) to 500 mL of sample. Retest for residual chlorine and add additional reagent as necessary. If present and sample treatment was required, document on the Analyst Notes "Green Sheet".
- 11.1.2. Preserved samples should be neutralized before analysis. Adjust samples and batch standards to pH 5-9 with either 6.0 M NaOH or 1+1 H₂SO₄.

2. Operating Procedure (Lachat):

- 11.2.1. Basic Operation and Maintenance of the Lachat is more detailed in SOP 659S, Lachat Instrument Basic Operation and Data Management. Analysts should also consult the Lachat instrument user guides.
- 11.2.2. Note: NH₃ is a heated chemistry. The manifold tubing is attached to the heater after the last 'T' and just prior to the flow cell/detector. To eliminate the possibility of reagents sitting in the tubing, while the heater is on in stand by mode, switch the pump to "MANUAL".
- 11.2.3. Turn on the power to the autosampler, pump and system unit along with the associated computer and printer. Switch the pump to "MANUAL". Note: Prior to running, perform any required maintenance as outlined in the instrument maintenance log. Document the maintenance performed.
- 11.2.4. Open OMNION 3.0 software displayed as an icon on the system computer desktop.
- 11.2.5. Method parameters and conditions including timing, designated pump tubing, sample loop size etc. are already defined within the system and should not be modified without consultation with Conventional's lab supervisor and adequate documentation. Refer to the appendices for the manifold diagram and system parameters.
- 11.2.6. Select 'Run', 'Open' in the toolbar.
- 11.2.7. Choose appropriate ammonia template from the available files (e.g. NH₃.omn) Note: Ensure that proper calibration standard values appear for each corresponding standard ID. Verify ICV/CCV (Sample type = 'Check Standard') concentration is correct.
- 11.2.8. Enter batch QC and sample ID's starting in the cell following the ICB. Sample Type = "Unknown".



- 11.2.9. Enter CCV (Sample Type = "Check Standard")/CCB after every 10 injections including rinse blanks. Enter 0.5 ppm known concentration and $\pm 10\%$ acceptance criteria for the CCV and 0ppm known concentration and \pm MRL acceptance criteria for the CCB. Schedule these as a Data Quality Management (DQM) set to be run after every 10 injections and at the close of the run.
- 11.2.10. Add lines in the sample tray template as needed for samples and QC. Note: CCV's and CCB's will be automatically entered into the tray at the required interval when defined as a DQM set. Adjust the cup numbers to correspond with sample tube placement in the autosampler rack.
- 11.2.11. Record the entries of the sample tray in the Lachat Run Log.
- 11.2.12. Filter all samples including the batch QC standards using a 20mL disposable syringe and 0.45 μ m syringe filters. One filter per sample and rinsing the syringe three times with DI water between samples.
- 11.2.13. Sample duplicates need to be analyzed for each batch of samples.
- 11.2.14. Matrix spikes are prepared at a 0.5 ppm concentration if QC limits stated in Section 9.6.2 are met. For samples requiring dilution the sample is first spiked with standard and then the dilution performed on the 10 mL final volume of spiked sample. "Spike first, then dilute". Add the appropriate spike as stated in the table below and take to a 10 mL final volume with filtered sample, then dilute. Spiking guidelines are as follows:

Required sample dilution	mL Intermediate Standard (20ppm)	mL of Stock Standard (1000ppm)	Final volume of spiked sample
Undiluted	0.250		10mL
1:5		0.025	10mL
1:10		0.05	10mL
1:20		0.10	10mL
1:50		0.25	10mL
1:100		0.50	10mL

- 11.2.15. Load the sample tubes in the exact sequence as indicated in the sample table. **Note:** Samples are loaded and run starting in the lower left-hand corner of the rack and continuing up then starting again at the bottom of the next column. Calibration standards are loaded highest to lowest concentration ending with the blank.
- 11.2.16. Observe pump tubing and manifold lines for jerky motion that indicates a flow problem and/or backpressure. Also check for any leaks at all tees and junctions. Refer to the troubleshooting section of the User's manual if problems are noted.



- 11.2.17. If no flow problems are apparent transfer reagent pump tubing from the DI water to the appropriate reagent containers. Continue pumping (pump speed at 35) until air bubbles are removed and baseline is void of air spikes and appears steady with no drift upward or downward. (Press 'Preview' on the toolbar to monitor current baseline.)
- 11.2.18. Press 'Start' on the toolbar to begin the run. Note: Calibration is run first and upon passing the samples will be analyzed. The methods have been set to halt the tray if the $r < 0.995$.
- 11.2.19. Review the calibration while samples are running and note the peak area of the 1.0 ppm standard. Peak area should be approximately 35-40 V-s (volt-seconds). If this value falls outside this range, the run should be stopped and the cause of the peak area change should be determined. Refer to the User's manual for troubleshooting guidelines.
- 11.2.20. Save the run as MMDDYYXXS.omn where M is a 2 digit code for the month, D is the 2 digits for the day, YY is the 2 digits for the year, X is the 3 letter code for the parameter, S is the sequence letter for the day's runs and 'omn' is the required filename extension needed for the Omnion software to recognize the file. Press 'Enter'. For example, if this is the second Lachat run conducted on February 5, 2004 the file name would be: 020504NH3B.omn.
- 11.2.21. To generate the final report for the run go to 'Tools' in the toolbar, 'Custom Report'. Click the Format icon.
- 11.2.21.1. Under the Table tab de-select 'Rep #', select 'Detection Time', 'Cup #', 'Peak Area' and 'Manual Dilution Factor' if the manual dilution factor was entered in the sample table prior to the sample running.
- 11.2.21.2. Under the Layout tab enter your initials in the 'Author' portion of the Header box and the filename and instrument name in the Right portion of the Footer box.
- 11.2.21.3. Under the Charts tab in the Options section select 'Calibration' and select Channel Data Display. Then select 'Show 10 Peaks per Chart for All Peaks'.
- 11.2.22. Click 'Apply' to incorporate all chosen options to the report then 'Close'.
- 11.2.23. Evaluate all results for the run including: Regression coefficient (r), calibration standard regressed values, initial calibration blank (ICB), initial calibration verification (ICV), batch QC standards, continuing calibration blanks and checks (CCB, CCV), RPD, matrix spike recovery and any off scale samples. If some of these parameters are out of the range, re-run the affected samples. IT IS THE RESPONSIBILITY OF THE ANALYST TO VERIFY ALL DATA.
- 11.2.24. Print out the final report.
- 11.2.25. At the end of the day's analysis. Turn off the heating coil. Place the transmission lines in cleaning buffer (65 g NaOH and 6 g tetrasodiummethylenediamine tetraacetic acid (EDTA) dissolved in 1 L DI water) and pump through the manifold for 10 minutes. After 10 minutes



place the transmission lines in DI water and pump water through for 10 minutes. After the water rinse remove the transmission lines from the water and pump the manifold dry.

11.2.26. Stop pump and remove lines from the pump cartridges. Turn off the power to the autosampler, pump, and system. Turn off computer.

11.2.27. Wipe down all instrument surfaces and wash pump cartridges. Record maintenance in the instrument maintenance log.

3. Operation Notes:

11.3.1. Staining of the pump tubing

11.3.1.1. Ensure the mixed stream between the last tee and the heater is between pH 11 and 12. Higher than 12.3 (usually caused by too much NaOH in the buffer) will contribute to staining.

11.3.1.2. Crystalline phenol is preferred over liquid or solid. The reagent needs to be prepared at least every 3-5 days, sooner if the color turns darker than pale orange.

11.3.1.3. Do not allow the pump to go to STANDBY mode.

11.3.2. Negative peaks

11.3.2.1. This can occur if the carrier and sample matrices are different. For best results neutralize the samples to a pH of 6-9 prior to running and use the non-acidified reagents.

11.3.2.2. Ammonia contamination of the carrier can produce negative peaks. Use fresh DI water and keep covered to prevent ambient ammonia contamination.

11.3.2.3. High metals concentrations within samples will precipitate and create negative peaks. Samples with this characteristic should be diluted to reduce the metals effect.

11.3.3. For high concentration samples, samples requiring >100X dilution, ion specific electrode (ISE) is the preferred method. See the NH3-ISE SOP for details.

11.3.4. Use the KCl extraction procedure for the analysis of soil and sediment samples. See the NH3-ISE SOP for details on the procedures for soils extraction.

12. Review

1. Refer to ARI's Laboratory Quality Assurance Plan for data review procedures.
2. Specifically for Ammonia, the analyst should check instrument output for accuracy and examine chromatograms to ensure all reported peaks are correctly integrated. Any anomalies such as abnormal peak shapes should be recorded in the analyst comments.

13. Data Analysis and Calculations

1. Calibration is done by injecting standards. The data system prepares a calibration curve by plotting response versus standard concentrations. Sample concentration is calculated from the regression equation.



2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

14. Method Performance

1. The reporting limit is set to the lowest calibration curve standard at 0.04 mg/ L NH₃-N.

15. Pollution Prevention

1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
2. The quantity of chemicals purchased should be based on expected usage during their shelf life to reduce disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

16. Data Assessment and Acceptance Criteria for QC Measure

1. The regression coefficient, r should be greater than 0.995.
2. The calibration verification standards must agree within $\pm 10\%$ of the "true" value and the concentration of the blanks should be less than the absolute value of the reporting limit.
3. If both the original and duplicate sample concentrations are greater than 5X the reporting limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the reporting limit, then the absolute difference between the two should be less than the reporting limit. If these criteria are not satisfied, corrective actions must be taken.
4. Matrix Spikes. The acceptance limits for matrix spike recoveries are $\pm 25\%$ if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.
5. The LCS must agree within $\pm 10\%$ of the "true" value.
6. The method blank should have a value less than the absolute value of the reporting limit.

17. Corrective Actions for Out of Control Events

1. If r is less than 0.995, new calibration standards must be prepared and the calibration repeated. All samples associated with the out of control standard curve must be re-run.
2. If Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB) are out of QC limits, new calibration standards or new ICV solution should be made. All samples associated with the out of control condition must be re-run. If the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are out of QC limits, they should be reread to verify. All samples between the last in control condition and the out of control condition must be re-run. All samples in any run must be bracketed by in control verification standards.



3. After the above two corrective actions, if the results are still outside the limits, the supervisor will review the entire procedure with the analyst to verify that correct procedures are being followed or check the instrument to make sure it is working properly.
4. If the method blank or LCS is out of control, it should be reread to verify. If the results are still out of control, stop the run and evaluate the filters and procedure. All samples on the batch will need to be re-filtered and reanalyzed. If results are persistent it may be required that each filter first be rinsed with DI water then with sample before filtering the portion used for analysis.
5. If RPD or matrix spike recoveries are outside the prescribed limits, the analysis will be repeated to confirm the outlying condition.
6. If any of the following situations arises, the supervisor will be immediately notified and the project manager will be informed for resolution with the client:
 - 17.6.1. Samples have exceeded holding times.
 - 17.6.2. Samples have been improperly preserved.
 - 17.6.3. There is insufficient sample to run the analysis.
7. Analyst's notes are recorded on the Analyst's Notes ("green sheet") in the job folder. Sample anomalies such as unusual sample characteristics or sample problems that were not covered on a Corrective Action form are recorded here.
8. As a general rule, all corrective actions taken during the course of an analysis must be described on the analysts comment sheet (i.e. the green sheet) and a Corrective Action Sheet must be submitted to the PM. It must be clearly evident to the data reviewer and PM exactly how a sample was handled during analysis.

18. Contingencies for Handling Out-of-Control or Unacceptable Data

1. Any out-of-control events (i.e. failed spike, high RPD, failed CCV) will be noted on a Corrective Action form including the recommended corrective action and corrective action taken. The form is generated and completed by the analyst. It is turned in for review with the affected data and signed by the supervisor.
2. Analyst's notes are recorded on the Analyst's Notes ("green sheet") in the job folder. Sample anomalies such as unusual sample characteristics or sample problems that were not covered on a Corrective Action form are recorded here.

19. Waste Management

1. The phenol hypochlorite waste generated as a result of this analysis is considered a hazardous waste mixture for the characteristic of toxicity (phenol in excess of 1%). These wastes must be collected during the run and transferred to the phenol/ammonia waste accumulation container located in the laboratory.



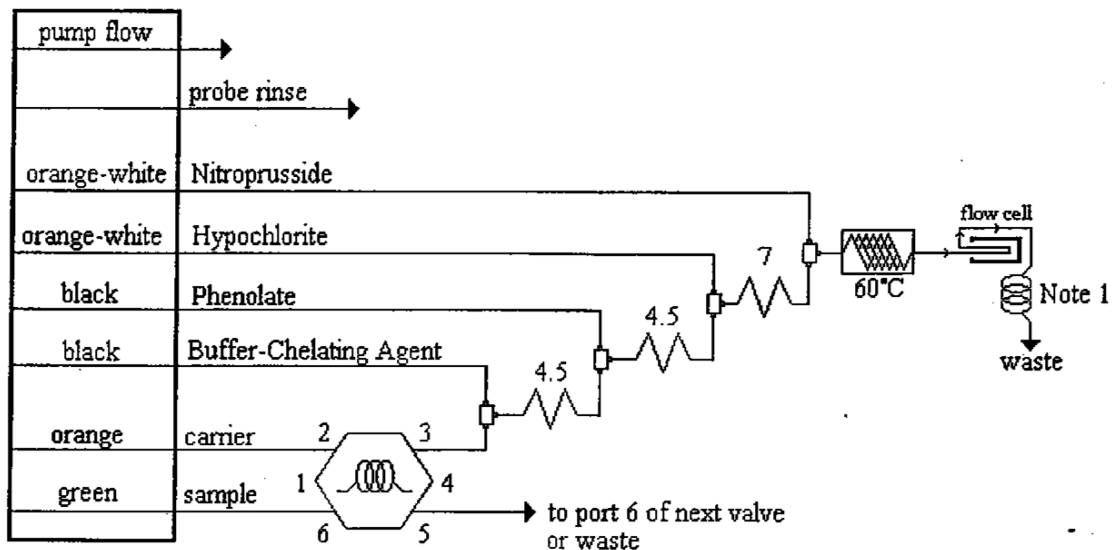
2. Analysis waste is collected under the rules of Satellite Accumulation at the site of generation and under the control of the operator of the process generating the waste. When the waste container is full it is transferred to the Central Accumulation Area.

20. Method References

1. Standard Method for the Examination of Water and Wastewater. 1997. 20th ED. Method 4500–NH₃ H.
2. Methods for Chemical Analysis of water and wastes. EPA-600/4-79-020 (Rev 2, August 1993). Method 350.1.
3. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Table II, Required Containers, Preservation Techniques, and Holding Times.
4. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix B. Definition and Procedures for Determining the Method Detection Limit
5. Keeney and Nelson. 1987. Nitrogen, Inorganic Forms. 33-3. Extraction of Exchangeable Ammonium, Nitrate, and Nitrite. Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties - Agronomy Monograph no. 9 (2nd edition)

21. Appendices

1. Ammonia Manifold Diagram




Carrier: DI water

Manifold Tubing: 0.5 mm (0.022 in) i.d. This is 2.5 µL/cm.

AE Sample Loop: 125 cm x 0.022 in. i.d.

QC8000 Sample Loop: 125 cm x 0.022 in. i.d.

Interference Filter: 630 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows 650 cm of tubing wrapped around the heater block at the specified temperature.

- 4.5: 70 cm of tubing on a 4.5 cm coil support
- 7: 135 cm of tubing on a 7 cm coil support
- 8: 168 cm of tubing on a 8 cm coil support
- 12: 255 cm of tubing on a 12 cm coil support
- 22: 550 cm of tubing on a 22 cm coil support

Note 1: 200 cm backpressure loop (0.022 in. i.d.)

Note 2: PVC PUMP TUBES MUST BE USED FOR THIS METHOD



2. Data System Parameters

21.2.1. Analyte Data:

21.2.1.1. Pump Speed:	35
21.2.1.2. Cycle Period:	65
21.2.1.3. Concentration units:	mg NH ₃ -N/L
21.2.1.4. Sample Period:	30 s
21.2.1.5. Inject to Peak Start:	80 s
21.2.1.6. Chemistry:	Direct

21.2.2. Calibration Data:

21.2.2.1. Calibration Rep Handling:	N/A
21.2.2.2. Calibration Fit Type:	1st Order Polynomial
21.2.2.3. Weighting Method:	None
21.2.2.4. Force through zero:	No

21.2.3. Sampler Timing:

21.2.3.1. Min. Probe in Wash Period:	12 s
21.2.3.2. Probe in Sample Period:	32 s

21.2.4. Valve Timing:

21.2.4.1. Time to Valve:	24 s
21.2.4.2. Load Period:	28 s
21.2.4.3. Inject Period:	37 s



Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Dioxin/Furan Organic Analysis H.R. Gas Chromatography/H.R. Mass Spectrometry EPA Method 1613B EPA Method 8290 HRSM01.2

**SOP 806S
Version 008**

**Revision Date: 10/22/18
Effective Date: 10/22/18**

Prepared by:

Peter Kepler

Approvals:

A handwritten signature in blue ink, appearing to read "Brian N. Bebee".

Brian N. Bebee, Laboratory Section Manager

A handwritten signature in blue ink, appearing to read "Bob Congleton".

Bob Congleton, Quality Assurance, Manager



1. Scope and Application

- 1.1. Method 1613B describes the detection and quantitation of tetra through octa Chlorinated Dibenzo-p-Dioxins (PCDDs) and Dibenzofurans (PCDFs) from various environmental sample matrices including sediments, soils, solid waste, ash, tissues, and waters.
- 1.2. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including EPA SW-846 Method 1613B, EPA CLP, NELAP and the Department of Defense Quality Systems Manual 5.0 (DoD-QSM). Appendix 20.1 outlines ARI's routine analytical procedure and additional requirements of in the DoD-QSM. **Analysts are responsible for determining which QA program is applicable to a set of samples prior to beginning analyzes and complying with all project specific analytical requirements.**
- 1.3. Specific quality control requirements shown use the control limits listed in Method 1613B since that has been the analysis of choice (instead of 8290A) for our clients. State of California work will be reported with Method 8290.
- 1.4. Some text has been taken directly from the four methods referenced in Section 19.
- 1.5. The analytes and routine reporting limits for this procedure are listed below:

ANALYTE	CAS NUMBER	WATER RL	SOIL RL.
2,3,7,8-TCDD	1746-01-6	10 pg/L	1 pg/g
2,3,7,8-TCDF	51207-31-9	10	1
1,2,3,7,8-PeCDD	40321-76-4	10	1
1,2,3,7,8-PeCDF	57117-41-6	10	1
2,3,4,7,8-PeCDF	57117-31-4	10	1
1,2,3,4,7,8-HxCDD	39227-28-6	10	1
1,2,3,6,7,8-HxCDD	57653-85-7	10	1
1,2,3,7,8,9-HxCDD	19408-74-3	10	1
1,2,3,4,7,8-HxCDF	70648-26-9	10	1
1,2,3,6,7,8-HxCDF	57117-44-9	10	1
1,2,3,7,8,9-HxCDF	72918-21-9	10	1
2,3,4,6,7,8-HxCDF	60851-34-5	10	1
1,2,3,4,6,7,8-HpCDD	35822-46-9	10	1
1,2,3,4,6,7,8-HpCDF	67562-39-4	10	1
1,2,3,4,7,8,9-HpCDF	55673-89-7	10	1
OCDD	3268-87-9	20	2
OCDF	39001-02-2	20	2
Total TCDD	41903-57-5	NA	NA
Total TCDF	55722-27-5	NA	NA
Total PeCDD	36088-22-9	NA	NA
Total PeCDF	30402-15-4	NA	NA
Total HxCDD	34465-46-8	NA	NA
Total HxCDF	55684-94-1	NA	NA
Total HpCDD	37871-00-4	NA	NA



Total HpCDF	38998-75-3	NA	NA
-------------	------------	----	----

- 1.6. Identification and quantitation of the non 2378-substituted (unnamed) PCDDs and PCDFs as totals are also described in this procedure to provide for total isomer quantitations.
- 1.7. This method is restricted to use by or under the supervision of analysts experienced in the use of high resolution gas chromatograph/high resolution mass spectrometry and skilled in the interpretation of high resolution spectrometry. Each analyst must demonstrate the ability to generate acceptable results with this method.
- 1.8. ARI routinely performs quantitation limit studies (QLS) for each extraction and analytical method performed using this SOP. The results of these studies are used to generate LOD and LOQ values to verify that the reporting limits are being met. The results are kept by the QA department, and are distributed to the bench chemists and the LIMS administrator. For current LOD and LOQ limits refer to Element LIMS.

2. Summary of Procedure

- 2.1. An aliquot of sample is extracted by a matrix appropriate technique. Typically, this will be a separatory funnel extraction for aqueous samples and a Soxhlet extraction for solid samples. Soxhlet extraction is used for tissue samples. Extraction standards are added at the time of initial extraction providing for isotope dilution quantification.
- 2.2. After extraction and prior to extract cleanup with multi-bed silica gel a cleanup standard (³⁷CL-2378-TCDD) is added to every extract to measure the efficiency of the cleanup process.
- 2.3. Next the extracts are subjected to the appropriate cleanups and concentrated to 10µL. The extract is now delivered to the instrument lab for analysis. 10µL of Injection standard is added just prior to the analysis of the sample extract achieving a final effective volume of 20µL.
- 2.4. Next, 1µL of the 20µL sample extract is injected into the column of a properly calibrated HRGC/HRMS system for chromatographic determination. Analyte identification of 2378-substituted (named) Dioxins and Furans is performed using the relative time of elution (RRT, relative to the appropriate internal standard) and comparison of mass spectra ion ratios. Quantitation is performed by comparing the detector responses of each analytes' two characteristic mass ions and internal standard two characteristic mass ions to the responses of these ions in a calibration curve containing those analytes at known concentrations.
- 2.5. Identification and quantitation of the non 2378-substituted (unnamed) isomers is also performed by comparing the relative retention times and ion ratios against predefined acceptance limits discussed in section 10.



3. Definitions

- 3.1. PCDDs-Polychlorinated tetra through octa dibenzo-p-dioxin homologues
- 3.2. PCDFs-Polychlorinated tetra through octa dibenzofuran homologues
- 3.3. Named-Named Furan and Dioxins are native 2378-substituted isomers
- 3.4. Unnamed-Unnamed Furan and Dioxins are native non 2378-substituted isomers.
- 3.5. HRMS-A High resolution mass spectrometer capable of performing selected ion monitoring at resolving power of at least 10,000 (at 10 percent valley definition).
- 3.6. HRGC-A high resolution gas chromatography system
- 3.7. Continuing Calibration Verification (CCV): A process used to verify that the current instrument calibration is acceptable every 12 hours and at the end of each analytical sequence.
- 3.8. Continuing Calibration Verification and Window defining Standard (CCVS): a standard prepared near the mid-point concentration of the initial calibration, and prepared from the same source as the initial calibration. This standard also contains the WDM isomers used to define the homologue windows and additional TCDDs to verify the 2378-TCDD peak resolution.
- 3.9. EICP- Extracted Ion Current Profile- A plot of the abundance of a specific ion as a function of time
- 3.10. Initial Calibration- A process used to generate a correlation between analyte response and analyte concentration by analyzing standards containing the analytes at known concentrations.
- 3.11. Initial Calibration Verification (ICV): A process used to verify that the current instrument calibration is accurate at the beginning of an analytical sequence.
- 3.12. Second source calibration verification Standard (SCV): A mid-point concentration standard from a source different than that used for the initial calibration used to demonstrate the accuracy of the initial calibration. The second source standard must be purchased from a different manufacturer than the calibration standard whenever possible.
- 3.13. Window defining mixture (WDM) Additional furans are used as retention time markers to define the beginning retention times for the dioxin and furan isomers and evaluate descriptor switching times.
- 3.14. Isomer specificity check standard (ICS): A check standard containing 2378 TCDF peak resolution testing isomers and 2378-TCDD peak resolution testing isomers.
- 3.15. Extraction standards (ES): Extraction standards are added to every sample and its associated qc at the time of initial extraction.
- 3.16. Cleanup standard (CS): The cleanup standard is added to every sample and its associated QC samples just prior to silica gel cleaning
- 3.17. Injection Standard (IS): Injection standards are added to every sample and its associated QC samples such that their concentration is the same in each of these sample types. Target analyte



- response is normalized to the response of these internal standards which are all at the same concentration in all the calibration standards.
- 3.18. Laboratory Control Sample (LCS) – A sample matrix, free from the analytes of interest, is spiked with verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system. Same as Blank Spike (BS) as used in Element
- 3.19. Laboratory Control Sample Duplicate (LCSD) – A sample matrix, free from the analytes of interest, is spiked with verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system. Same as Blank Spike Duplicate (BSD) as used in Element
- 3.20. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method. (DOD only)
- 3.21. Matrix Spike Duplicate (MSD): A sample prepared by adding a known mass of target analyte to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method.
- 3.22. Initial precision standard (IPR) – Same as the LCS, except used for an initial demonstration of precision and recovery to assess the analytical method. The IPR is to assure that the results produced by the laboratory remain within the method specified limits for precision and recovery.
- 3.23. Limit of detection (LOD) – An estimate of the minimum amount of a substance that an analytical process can reliably detect.
- 3.24. Limit of quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target analyte that can be reported with a specified degree of confidence.
- 3.25. Quantitation limit standard (QLS) – A sample matrix, free from analytes of interest, is spiked at the reporting limit with all the target analytes to generate LOD and LOQ statistics. The QLS spike assures that the reporting limits are being met for each matrix.
- 3.26. Estimated detection limit (EDL) – The concentration of an analyte required to produce a signal with peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8-substituted isomer for which the response is less than 2.5 times the background level.
- 3.27. LIMS (Laboratory Information Management System): Software used to compile and report final chromatographic data.
- 3.28. Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and interferences. It is processed



- simultaneously with and under the same conditions as samples through all steps of the analytical procedures.
- 3.29. Static Resolution Checks-Resolution checks to demonstrate the minimum HRMS resolving power of 10,000 at 10% valley for selected PFK peaks.
- 3.30. RRT-Relative Retention Time- The elution time of an analyte relative to the elution time of its associated extraction or injection standard.
- 3.31. Instrument Blank – Clean solvent analyzed using the same conditions as a regular sample. An Instrument blank may be used to monitor and/or remove sample carryover from one injection to another.
- 3.32. Toxicity Factors-Used to determine an overall toxicity of a sample by assigning a toxicity equivalency factor to all the 2378 substituted PCDDs and PCDFs and used to calculate a total toxicity equivalent.
- 3.33. EMPC-An Estimated maximum possible concentration is calculated for the 2378-substituted isomers that meet retention time and signal/noise criteria, but fail ion ratio limits shown in Appendix 20.4.
- 3.34. PFK-Perfluorokerosene-Technical mixture used to calibrate the exact m/z scale in the HRMS.

4. Interferences

- 4.1. Extraction Interferences: Raw HRGC/HRMS data from all instrument blanks, method blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.
- 4.2. Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, DI water, methanol, or ethanol followed by air drying only.
- 4.3. High purity reagents must be used to minimize interference problems. The use of nitrile gloves is recommended for all procedures.
- 4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, or the detector shows saturation due to analytes present in a sample, subsequent sample extract injections should be scrutinized for cross contamination.
- 4.5. Matrix interferants co-extracted with the sample include Polychlorinated Biphenyls, Polychlorinated Diphenyl ethers, Polychlorinated Naphthalenes and Polychlorinated Alkyldibenzofurans. Matrix interferences may be present at concentrations several orders of



magnitude greater than the analytes of interest and special cleanup steps may be necessary to assure the sensitivity and selectivity required by this method.

5. Safety

5.1. This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of safety data sheets (SDSs) should be available to all personnel involved in the chemical analysis of samples suspected to contain PCDDs/PCDFs. Additional information is also available at msdshazcom.com.

5.2. Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed.

5.2.1. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.2.2. Each laboratory must develop a strict safety program for the handling of PCDDs and PCDFs. The laboratory practices listed below are recommended.

5.2.3. Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood, or in a separate containment facility away from the main laboratory.

5.2.4. The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high boiling alcohols. Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength less than 290 nm for several days (use F 40 BL lamps, or equivalent). Using this analytical method, analyze the irradiated liquid wastes and dispose of the solutions when 2378-TCDD and 2378-TCDF congeners can no longer be detected.

5.2.5. The following precautions for safe handling of 2378-TCDD in the laboratory were issued by Dow Chemical U.S.A. (revised 11/78) and were amended for use in conjunction with this method. The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting



laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2378-TCDD isomer is extremely toxic to certain kinds of laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Many techniques used in handling radioactive and infectious materials are applicable to 2378-TCDD.

- 5.2.6. Protective equipment – Analysts must use disposable nitrile gloves, apron or lab coat, safety glasses and laboratory hood adequate for radioactive work.
- 5.2.7. Training -- Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.
- 5.2.8. Personal hygiene -- Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).
- 5.2.9. Confinement -- Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on bench tops.
- 5.2.10. Waste -- Good technique includes minimizing contaminated waste. Plastic bag liners will be used in waste cans.
- 5.2.11. Disposal of hazardous wastes -- Refer to the November 7, 1986 issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin containing materials.
- 5.2.12. Storage – All sample extracts and calibration standards will remain separate from the rest of the GC laboratory and be only stored in freezer# 6

6. Equipment and Supplies

6.1. Gas chromatograph/mass spectrometer system

- 6.1.1. Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, autosampler, and gases. The capillary column is directly coupled to the source of the mass spectrometer.
- 6.1.2. Fused-silica capillary column – Restek RTX-Dioxin2 -60 m x 0.25 mm ID 0.25 µm film thickness treated with a Restek proprietary cross-bonded phase.
- 6.1.3. High Resolution Mass spectrometer –An instrument capable of achieving a static resolving power of 10,000 (10 percent valley).
- 6.1.4. GC/MS interface – The GC interface must be able to withstand 350 degrees. The GC column is directly fitted into the ion source without being exposed to the ionizing electron beam.



- 6.2. Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on electronic media of all mass spectra obtained throughout the duration of the chromatographic program.
 - 6.2.1. The data system must be capable of acquiring data at a minimum of 10 ions in a single scan.
 - 6.2.2. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic intervals. It should also be able to provide hard copies of peak profiles to demonstrate the required resolving power.
 - 6.2.3. The data must be securely stored for at least seven years from date of acquisition.
- 6.3. Ancillary supplies specific to the analytical laboratory.
 - 6.3.1. Syringes 10, 25, and 100 μ l
 - 6.3.2. Fume hood with work bench
 - 6.3.3. 2 ml amber solution vials with Teflon faced screw cap
 - 6.3.4. Threaded Teflon faced screw caps and amber .3 ml autosampler vials
 - 6.3.5. Nonane in Teflon squirt bottle

7. Reagents and Standards

- 7.1. Stock solutions- Stock solution standards are used to prepare working solutions. Neats are not used for any standard preparations.
 - 7.1.1. Stock solutions expire either on the manufacturer's certified expiration date, or one year after they have been opened whichever occurs sooner. They must be replaced at this time.
 - 7.1.2. Ampulized Stock solutions must be stored at ambient temperature and protected from light.
 - 7.1.3. De-ampulized Stock solutions must be stored at $<0-6$ °C and protected from light.
 - 7.1.4. Stock solutions should be checked frequently for signs of concentration or degradation.
- 7.2. LCS stock solution-A solution containing all the native PCDDs and PCDFs diluted into the working LCS solution used to prepare IPR, LCS and QLS extracts. This solution is purchased in Nonane with concentrations ranging from 400-4000 ng/ml.
- 7.3. Extraction standard stock solution-This solution is diluted 50x to produce the working extraction standard solution. This solution contains the carbon ^{13}C -2378-substituted PCDDs and PCDFs used for isotope dilution quantitation and to measure extraction efficiency. This solution is purchased in Nonane with concentrations ranging from 100-200ng/ml.
- 7.4. Cleanup standard stock solution-This stock solution is diluted 50x to produce the cleanup standard working solution added prior to extract cleanup. This solution contains ^{37}CL -2378-TCDD used to monitor the cleanup process. This solution is purchased in Nonane at 40ng/ml



7.5. Working solutions- working solutions are prepared from stock solutions or purchased as commercially certified working solutions.

7.5.1. Working standards expire either on the date of expiration of the stock solutions they are made from, or on the manufacturer's certified expiration date, or one year after opening whichever occurs first. They must be replaced at this time.

7.5.2. Working standards in un-opened ampoules should be stored at ambient temperature

7.5.3. When working standard ampoules are opened, the standard must be transferred to a screw-top vial and stored at <0-6 °C and protected from light. The volume level of the standard should be marked on the vial.

7.5.4. Working standards should be checked frequently for signs of concentration or degradation.

7.5.5. Working solutions are made in Ethanol, Acetone or Nonane.

7.6. Injection standard working solution- A solution purchased at working solution level and added to the final extract prior to analysis. The IS contains ¹³C-1234-TCDD and ¹³C-123789-HCDD at 200ng/ml in Nonane. It is purchased as a certified solution. 10ul is added to the 10ul extract, resulting in a final volume of 20 ul.

7.7. Calibration working solutions- All calibration standards used to generate initial and continuing calibrations are purchased as certified solutions. None are diluted from a stock standard. Calibration working solutions are purchased in Nonane and range in concentration from 0.1ng/ml to 2000ng/ml. These mixes are commonly referred to as CSL, CS1, CS2, CS3, CS4, and CS5. All certified solutions should have an associated Certificate of Analysis and have a chemical purity > 98%.

7.7.1. Window Defining Working Solution- The CS3 verification mix also includes the window defining compounds for determining homologue RT ranges. It is called the CS3WT, and is also purchased as a certified solution.

7.7.2. Isomer Specificity Working solution- The ISC contains 2378-TCDD, 2378-TCDF, and the closest eluting isomers on the RTX-Dioxin2 column. The isomers are 1278-TCDD, 2348-TCDF, and 3467-TCDF. The ISC is prepared in Nonane at 10 ng/mL from individual isomer solutions.

7.7.3. LCS/IPR working solution-A solution containing all the native PCDDs and PCDFs diluted from the LCS/IPR stock solution used to prepare IPR and LCS extracts. This solution is made in Acetone.

7.8. QLS working solution-A solution containing all the native PCDDs and PCDFs diluted from the LCS stock solution used to prepare QLS extracts. This solution is made in Acetone.

7.9. Extraction standard working solution-This solution is diluted from the extraction standard stock solution. The solution contains the ¹³C-2378-substituted PCDDs and PCDFs used for isotope dilution



quantitation and to measure extraction efficiency. This solution is made in Ethanol for extraction purposes.

7.10. Cleanup Standard Working Solution-This working solution is diluted from the cleanup standard stock solution and added prior to extract cleanup. This solution contains ³⁷CL-2378-TCDD used to measure cleanup efficiency. This solution is made in Hexane at .8ng/ml.

7.11. ICVS solution-A Calibration solution at or near the curve mid-point used to verify the calibration curve. It should be purchased from a different supplier than the curve mixes, or from the same supplier with a different lot number.

7.12. Isomer Specificity Check Standard-Contains 2378-TCDD, 1278-TCDD, 2348-TCDF, 2378-TCDF, and 3467-TCDF. This solution is used to monitor the 2378-TCDD and 2378-TCDF peak resolution.

8. Sample and Extract Storage

8.1. Aqueous samples are to be maintained at 0-6 ° C in the dark from time of collection to receipt at the laboratory. Aqueous samples are stored at the same conditions in the lab.

8.2. Solid, mixed phase, and tissue samples are to be maintained at < 4 °C from time of collection to receipt at the laboratory. Store these matrices in the dark at < -10 °C at the lab.

8.3. There are no maximum holding times for CDDs/CDFs in any matrices if stored as above. Samples may be stored up to one year prior to extraction. Following extraction, extracts may be stored as above up to one year prior to analysis.

8.4. Extracts are delivered to freezer #6 in the instrument laboratory and recorded into the Dioxin extract freezer Log (7005f).

8.5. Analysts in the instrument lab assume custody of the sample extracts by signing the freezer log prior to analysis

8.5.1. Extracts analyzed on the same day of completed extraction may be stored at ambient temperature.

8.5.2. Extracts not analyzed on the same day of completed extraction must be stored at -10 to -20 °C in the dark until analysis.

8.6. All Extracts must be analyzed within one year from the initial date of extraction.

9. Quality Control

9.1. Quality control requirements are tabulated in Appendix 20.1.

9.1.1. Acceptance criteria for ARI's routine 1613B analyses are listed in this table in Appendix 20.1.



- 9.2. Method defined (1613B) default quality control limits for Extraction standards recovery, cleanup standard recovery, LCS and IPR recoveries and relative percent difference for sample duplicates will be used.
- 9.3. Statistical Control- Internal quality control limits for Extraction standards, cleanup standard, LCS and IPR recoveries and relative percent difference for sample duplicates are not statistically generated at this time.
- 9.3.1. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation.
- 9.3.2. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. Current control limits may be found on the ARI website
- 9.3.3. All analysts using this SOP must use it in conjunction with Control Limit documentation in order to assess data quality and any possible need for corrective actions.
- 9.3.4. Client specific or quality systems specific control limits (DoD-QSM) are used when specified by the client.

10. Calibration and Standardization

- 10.1.1. Calibration standards – Calibration curves will consist of 6 standards, CSL – CS5. The exception is for the CLP/HRSM01.2 contract, which specifies 5 levels, CS1 – CS5.
- 10.1.2. One of the calibration standards will be at (or below) the reporting limit, while the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the HRGC/HRMS system. The lowest (or second lowest) calibration point of each individual target analyte becomes the reporting limit for that analyte. The actual detection limit for target analytes will be determined by the EDL calculation for each undetected target.
- 10.1.3. All target analytes quantitated below the reporting limit must be qualified with a “J” flag to show the quantitation is below the associated reporting limit. The reporting limit for each project is determined by the specific level requested (i.e. PSDDA, normal water, etc.)
- 10.1.4. All Calibration standards are purchased as working solutions at concentrations of 0.1-2000ng/ml (CSL-CS5). See Section 7.7. The working solutions contain all standards and target analytes necessary for the calibration.
- 10.1.5. Each standard must contain all analytes requested for a specific project, and no target analyte may be quantitated without first being calibrated.
- 10.1.6. All standards should be stored at 0-6 °C after opening and should be discarded after one year, or sooner if check standards indicate a problem. The volume level of the solution should



be marked on the vial after opening. If volume loss becomes evident, or degradation is suspected, the standard should be replaced.

10.1.7. The CSL point is included in the initial calibration in order to meet PSSDA reporting limit requirements, and provide the lowest reporting limits for all projects and clients, except CLP/HRSM. The CSL is 5 times lower than the CS1 mix.

10.1.8. The six calibration standards CSL-CS5 are analyzed and used to calibrate all analytes except TCDD and TCDF. CS1 is the low curve point for these analytes, which meets all requested reporting limits.

Concentrations of calibration points used for initial concentration in ng/ml

Analyte	CSL	CS1	CS2	CS3	CS4	CS5
2378-TCDD	0.1	0.5	2	10	40	200
2378-TCDF	0.1	0.5	2	10	40	200
12378-PeCDD	0.5	2.5	10	50	200	1000
12378-PeCDF	0.5	2.5	10	50	200	1000
23478-PeCDF	0.5	2.5	10	50	200	1000
123478-HxCDD	0.5	2.5	10	50	200	1000
123678-HxCDD	0.5	2.5	10	50	200	1000
123789-HxCDD	0.5	2.5	10	50	200	1000
123478-HxCDF	0.5	2.5	10	50	200	1000
123678-HxCDF	0.5	2.5	10	50	200	1000
123789-HxCDF	0.5	2.5	10	50	200	1000
234678-HxCDF	0.5	2.5	10	50	200	1000
1234678-HpCDD	0.5	2.5	10	50	200	1000
1234678-HpCDF	0.5	2.5	10	50	200	1000
1234789-HpCDF	0.5	2.5	10	50	200	1000
OCDD	1.0	5	20	100	400	2000
OCDF	1.0	5	20	100	400	2000
¹³ C-2378-TCDD (ES)	100	100	100	100	100	100
¹³ C-2378-TCDF (ES)	100	100	100	100	100	100
¹³ C-12378-PeCDD (ES)	100	100	100	100	100	100
¹³ C-12378-PeCDF (ES)	100	100	100	100	100	100
¹³ C-23478-PeCDF (ES)	100	100	100	100	100	100
¹³ C-123478-HxCDD (ES)	100	100	100	100	100	100
¹³ C-123678-HxCDD (ES)	100	100	100	100	100	100
¹³ C-123478-HxCDF (ES)	100	100	100	100	100	100
¹³ C-123678-HxCDF (ES)	100	100	100	100	100	100
¹³ C-123789-HxCDF (ES)	100	100	100	100	100	100
¹³ C-234678-HxCDF (ES)	100	100	100	100	100	100
¹³ C-1234678-HpCDD (ES)	100	100	100	100	100	100
¹³ C-1234678-HpCDF (ES)	100	100	100	100	100	100
¹³ C-1234789-HpCDF (ES)	100	100	100	100	100	100
¹³ C-OCDD (ES)	200	200	200	200	200	200
³⁷ CL-2378-TCDD (CS)	0.1	0.5	2	10	40	200
¹³ C-1234-TCDD (IS)	100	100	100	100	100	100
¹³ C-123789-HxCDD (IS)	100	100	100	100	100	100

ES = Extraction Standard, CS = Clean-up Standard, IS = Injection Standard



10.2. MS tuning- prior to initial calibration, the HRGC/HRMS system must be hardware-tuned to meet the minimum resolving power of 10,000 for a minimum of three PFK masses in each scan function. Tuning is done using the 331 PFK mass or similar, although each function may have its own tune file based on an appropriate PFK mass in that function. Analysis cannot begin until 10,000 resolving power has been demonstrated throughout all functions.

10.2.1. Static resolution must be verified at the beginning and ending of each 12 hour analytical sequence bracket.

10.2.2. The total cycle scan time for each of the individual ion functions must be less than one second.

10.2.3. All analyses performed in the twelve-hour QC period following the static resolution check must use the same instrument parameters (GC program, MS parameters, etc.)

10.2.4. Column Performance must also be verified with the isomer specificity check standard (ISC) containing 2378-TCDF resolution testing isomers and 2378-TCDD resolution testing isomers before proceeding with the calibration.

10.2.5. Separation between 2378-TCDD and 1278-TCDD must show a maximum valley of 25%. Separation between 2378-TCDF, 2348-TCDF, and 3467-TCDF must show a maximum valley of 25% between all peaks. If these criteria are met, all analytes may reported from a single column run.

10.2.6. Verify the identification of all first and last eluters for each PCDF homologue group and assure retention times are greater than 10 seconds between ion function changes and any target analytes.

10.3. Signal to noise ratio-The signal to noise ratio must be verified to be greater than 10 for all calibration points used.

10.4. Ion Abundance ratios-All Analytes in all calibration points should meet the limits shown in table 3 (Appendix 20.3) for their respective ion abundance ratios.

10.5. Calculate Relative Response Factors (RRFs)

10.5.1. Evaluation of the initial calibration begins by calculating relative response factors (RRFs) for each analyte in each calibration standard. Areas from both the primary and secondary quantitation ions are added together to give the total ion area for all standards and targets. The formula for calculating each response factor involves the combined areas of both quantitation ions for the analyte and its associated internal standard as well as the concentration of the analyte and internal standard in the calibration standard according to the formula:

$$RRF = (A_s * C_{is}) / (A_{is} * C_s)$$

Where



As = The combined ion area of both ions from the analyte or surrogate
Cis = The concentration of the internal standard in ug/L
Ais = The combined ion area of both ions from the internal standard
Cs = The concentration of the analyte or surrogate in ug/L

10.5.2. The RRF for each analyte should consistent for each of the calibration levels. Special care should be taken to monitoring the RRF in the lowest calibration standard (CSL) to ensure adequate sensitivity at the reporting limit.

10.6. Analyte Linearity

10.6.1. After measuring the relative response factors for each analyte in each of the calibration standards, the linearity of the analyte must be measured.

10.6.2. The average RRF should be calculated for each compound using the formula

$RRF_{av} = \frac{\sum RRF_i}{n}$
Where
RRFi = the RRF of the analyte in each calibration level
n = the number of calibration levels (usually six or five)

10.6.3. The percent relative standard deviation (% RSD) should also be calculated for each compound using the formula

$RSD = \frac{100 * SD}{n} = 100 * \left(\frac{\sum (RRF_i - RRF_{av})^2}{(n-1)} \right)^{1/2} / RRF_{av}$
Where
RRFi = the RRF of the analyte in each calibration level
RRFav = the average RRF of the analyte over the entire calibration range
n = the number of calibration levels (usually six or five)

10.6.4. The % RSD should be less than 20% for each compound, in which case the average response factor will be used for quantitation as it is considered constant over the calibration range. Target analytes that exceed 20% RSD will attempt to utilize an alternative calibration option. **CLP HRSM01.2: Target analytes require 20% RSD. Labels require 35% RSD.**

10.6.4.1. Before attempting an alternative calibration model the analyst should ensure that the RSD failure is not due to detector or chromatographic system saturation and that the chromatographic system is functioning properly. Should saturation or chromatographic activity be evident, the analyst should correct the problem and reanalyze the affected calibration standards. In reality, if the system is operating well, all targets and labels should have % RSDs well within limits. If any compound fails to meet the RSD limits, maintenance is likely required.



10.6.5. Although alternative calibration methods are optional, ARI does not use alternative calibration methods for PCDF analysis. If % RSD values are > 20% for any analytes, corrective action should be taken and the calibration rerun.

Evaluation of retention times - The relative retention time (RRT) of each target analyte in the calibration standard should agree within 0.05 RRT units for each calibration point. Late-eluting target analytes usually have much better agreement. The RRT is calculated by dividing the retention time of the target analyte/surrogate by the retention time of its assigned internal standard. All relative retention times should be within the ranges previously established for the RTX-Dioxin2 column used by ARI.

10.6.6. All named isomers with labeled extraction standards must show an absolute retention time -1 to +3 seconds of that for the corresponding labeled standard.

10.7. Initial Calibration verification - Prior to use for sample processing, the acceptability of a calibration curve should be verified through analysis of a second source calibration verification solution (SCV). The SCV ideally should be purchased from a different supplier than the working standards used in the calibration curve. The SCV may be from the same supplier as the calibration standards, but the SCV must be from a different lot number than the calibration solutions. Target analytes should have % D < 20% when compared to the curve, and labels should have % D < 30%. Any targets or labels exceeding these limits should be noted.

10.8. Calibration Acceptance.

10.8.1. An initial calibration for an analyte is deemed valid when it meets all criteria discussed in sections 10.1 through 10.9

Quantitated values for any analyte which fail calibration acceptance criteria must be at a minimum approved by the organics manager, project manager, and client and will be discussed in the case narrative.

10.8.2. Daily GC/MS calibration verification - Performed at the beginning and ending of each 12-hour analytical sequence. NOTE: The ending continuing calibration verification is technically not a 1613B method requirement (as it is for 8290 and CLP), but it will always be analyzed and included in the data package.

10.8.3. MS tuning- prior to calibration verification, each GC/MS system must be hardware-tuned to meet the minimum resolving power of 10,000 for a minimum of three PFK masses in each scan function. Sample analyses may not begin until all these criteria are met. Static resolution must be verified at the beginning and ending of all analytical sequences.

10.8.4. .All analyses performed in the twelve-hour QC period following the static resolution check must use the same instrument parameters (GC program, MS parameters, etc.)



10.8.5. Column Performance (ISC check) must also be verified before proceeding with sample analysis. CLP HRSM01.2 requires a passing ISC check at the end of each 12-hour sequence as well. Resolution measurement on the RTX-Dioxin2 column includes the following isomers in the ISC Mix: Separation between 2378-TCDF, 2348-TCDF, and 3467-TCDF must show a maximum valley of 25% between all peaks. Separation between the 2378-TCDD and the 1278-TCDD isomers must show a maximum valley of 25% between peaks.

10.8.6. Ion Abundance ratios-All analytes must meet the limits shown in table 3 (Appendix 20.3) for their respective ion abundance ratios.

10.8.7. The relative response factors calculated in Section 10.6 are used to measure the validity of the initial calibration by using them to calculate the percent difference (for average RRF calibrations) or percent drift (for linear fit or quadratic fit calibrations.)

10.8.7.1.1. Calculate the percent difference using:

$\% \text{ Difference} = \frac{\text{RRF}_i - \text{RRF}_c}{\text{RRF}_i} * (100)$
Where:
RRFi = Average relative response factor from initial calibration.
RRFc = Relative response factor from current verification standard.

10.8.7.1.2. Percent difference for each native analyte must meet the limits shown in Table 20.9. **CLP HRSM01.2 has standardized CCV limits: Target analytes require %D within 25%. Labeled surrogates require %D within 35%. Also, DOD has limits of 20% for targets and 30% for labels.** Problems similar to those listed under the minimum response factors could affect this criterion. See Section 16.3 for procedures for dealing with linearity failure.

10.8.7.1.3. Reporting data for analytes failing any acceptance criteria must be discussed in the analysts notes and be approved by the Organics manager, project manager, client and discussed in the case narrative.

10.8.7.1.4. Evaluation of retention times - The relative retention time (RRT) of each target analyte in the calibration standard should agree within 0.005 RRT units for each calibration point. Late-eluting target analytes usually have much better agreement. The RRT is calculated by dividing the retention time of the target analyte/surrogate by the retention time of its assigned internal standard. The relative retention times must meet those limits established by ARI.

10.8.8. All 2378-substituted isomers with labeled extraction standards must show an absolute retention time -1 to +3 seconds (-.02 to +.05 minutes) of that for the corresponding labeled standard



10.8.9. The results from the continuing calibration verification analysis must meet the acceptance criteria detailed above in Sections 10.11 and 10.12.

11. Procedure

11.1. Prior to the determinative analysis, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods.

11.2. Sample Preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	Separatory funnel, SPE
Soil/sediment	Soxhlet, Microwave
Tissue	Soxhlet

11.3. Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Matrix	Methods
Waters	Multibed Silica/ florisil/ acid washing
Soil/Sediment	Multibed Silica/ florisil/ acid washing
Tissues	Multibed Silica/ florisil/ acid washing

11.4. The recommended HRGC/HRMS operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration).

Mass range:	Discrete 5 function descriptor
Scan time:	<1 sec/scan
Initial temperature:	160°C, hold for 1 minute
1st Temperature program:	160-200°C at 40C°/min
2nd Temperature program:	200-300°C at 3C°/min
3rd Temperature program:	300-320 at 15C°/min
Final temperature:	320°C, hold for 9.3 minutes
Injector temperature:	280°C
Transfer line temperature:	280°C
Source temperature:	290°C
Injector:	Grob-type, splitless/split
Sample volume:	1 µL
Carrier gas:	Helium at 40 cm/sec.



- 11.5. Prior to sample analysis the GC/MS system must be tuned as described in Section 10.2, and must have an acceptable initial calibration curve (the requirements for the calibration curve are found in Sections 10.3 and 10.9).
- 11.6. Prior to sample analysis the continuing calibration verification is analyzed (CS3) and this ICV must meet the criteria found in Sections 10.11 -10.12. If time remains in the 12 hour QC period begun with the initial calibration, the midpoint calibration standard from the initial calibration may be used as the ICV provided it meets the requirements.
- 11.7. HRGC/HRMS analysis
- 11.7.1. Difficult sample matrices may require that the sample extract be screened on a GC/ECD or GC/MS using a similar type of capillary column. This will minimize contamination of the HRGC/HRMS system from unexpectedly high concentrations of organic compounds. Samples showing a high background or lipid content may require a modified extraction using less sample material.
- 11.7.2. Inject 1 μ L of the 20 μ L sample extract (10 μ L extract plus 10 μ L Injection Standard) into the HRGC/HRMS system. The volume injected (1 μ L) should contain 100 pg/ μ L of the injection standards. The injection volume must be the same volume used for the calibration standards. The recommended GC/MS operating conditions to be used are specified in Section 11.4.
- 11.7.3. When the response for any target analyte except OCDD/OCDF exceeds the high point of the initial calibration curve) corrective action will be required. Dilution may be performed on the extract as described in section 16.10 or Sample re-extraction may take place using less sample material. See section 16.10 for guidance on over range values. Dilution for OCDD/OCDF is required only if the peak is saturated.
- 11.8. Perform all qualitative and quantitative measurements as described in Section 11. Store the remaining extract at -10 to -20°C protected from light in screw-cap vials equipped with un-pierced Teflon lined septa.

12. Data Analysis and Calculations

12.1. Qualitative identification-

12.2. An analyte is identified by comparison of the sample EICP characteristic ion ratios to the reference EICP ion ratios generated in the initial calibration. The referenced method ion ratios must be met by the laboratory using the conditions of this SOP. Method specific reference ion ratios are shown in table 3 (appendix 20.3). Alternatively, ion ratios within $\pm 10\%$ of the last CS3 calibration point or continuing verification whichever is most recent may be used. The following retention time criteria must be also satisfied to verify identification for any target Analyte.



- 12.2.1. 2378-substituted isomers with corresponding labeled standards will require an absolute retention time at maximum height within -.02 to +.05 minutes of that for corresponding labeled standards. In addition, the two quantitation ion RTs must be within ± .03 minutes of each other. The RRT must be within .005 RRT units of that in calibration verification standard.
- 12.2.2. 2378-substituted isomers without corresponding labeled standards must show the RRT must to be within .005 RRT units of that in calibration verification standard.
- 12.2.3. Non 2378-substituted isomers require that the retention time window be established by the window defining mixture included in the CS3 standard for each homologue group. In addition, RTs for both quantitation ions must be within ± .03 minutes of each other in the peak profile.
- 12.3. Ion abundance ratios must meet for any PCDD or PCDF to be reported as a non-EMPC. See the ion abundance ratios shown in table 3. Alternatively, ion ratios within ±10% of the last CS3 calibration point or continuing verification whichever is most recent may be used. PCDDs and PCDFs with failing ion ratios are reported as EMCP's on the final data reports. Ion abundance ratios apply to all analytes reported by this method, except for the cleanup standard which only uses one quantitation ion. EMPC values are not to be corrected for ion ratio.
- 12.4. Signal to noise ratio of all calibration standards compounds must be > 10.
- 12.5. Signal to noise ratio for all reported sample/QC peaks must be > 3.
- 12.6. Polychlorinated diphenyl ether (PCDE) interferences must be evaluated for all 2378-substituted PCDF isomers. PCDE interferences will not be evaluated for the non 2378-substituted isomers. PCDE's at the same retention time (± .03 minutes) as any detected 2378-sustituted furan isomer, that also have a height > 1% of either furan isomer, will require the furan value to be flagged as potentially false positive due to an interference. Corrective action may also be warranted. See section 16.12 for further guidance. See Appendix 20.10 for the theory of PCDE interference.
- 12.7. Quantitative analysis
- 12.7.1. When a compound has been identified, the quantitation of that compound will be based on the summated integrated abundance from the EICP of the primary and secondary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used are shown in Table 3 (Appendix 20.3)
- 12.7.2. Calculate the concentration of each identified analyte in the sample as follows:
- 12.7.3. Water

Concentration (pg/L) =	$\frac{(Ax)(Is)(Vt)}{(Ais)(RRF)(Vo)(Vi)}$
Where:	



A_x = Area of characteristic ions for compound being measured
I_s = Amount of internal standard injected (pg)
V_t = Total volume of the extract (μ L)
A_{IS} = Area of characteristic ions for the internal standard
RRF = Relative response factor for compound being measured
V_o = Volume of water extracted (L)
V_i = Volume of extract injected (μ L)

12.7.4. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)

$\text{Concentration (pg/g)} = \frac{(A_x)(I_s)(V_t)}{(A_{IS})(RRF)(V_i)(W_s)}$ <p>where:</p> <p>A_x = Area of characteristic ions for compound being measured I_s = Amount of internal standard injected (pg). V_t = Total volume of the extract (μL) A_{IS} = Area of characteristic ions for the internal standard RRF = Relative response factor for compound being measured V_i = Volume of extract injected (μL) W_s = Dry weight of the sample extracted (g)</p>

12.7.5. Concentrations for unnamed PCDDs and PCDFs isomers in the sample are also quantitated using an average of the response factors from the named 2378-substituted isomers at the same level of chlorination.

12.7.6. An EDL is calculated for all non-detects in the method blank and samples. The EDL becomes the limit of detection reported for that individual analyte.

12.7.6.1. The EDL calculation for a water sample is calculated as follows:

$\text{Aqueous EDL (pg/L)} = \frac{(3)(H_x)(I_s)(D)}{(H_{IS})(RRF)(V_o)}$
Where:
H_x = Combined height of ions for compound being measured
I_s = Total pg of internal standard added (e.g. 2000pg)
D =Dilution factor
H_{IS} = Combined height of ions for the internal standard
RRF = Relative response factor for compound being measured
V_o = Volume of water extracted (L)

12.7.6.2. The EDL calculation for a solid sample is calculated as follows:



Solid EDL (pg/g) =	$\frac{(3)(H_x)(I_s)(D)}{(H_{IS})(RRF)(W)}$
Where:	
H _x = Combined height of ions for compound being measured	
I _s = Total pg of internal standard added (e.g. 2000pg)	
D = Dilution factor	
H _{IS} = Combined height of ions for the internal standard	
RRF = Relative response factor for compound being measured	
W = Weight of solid extracted (g)	

12.8. Data Processing and LIMS entry

12.8.1. All the calculations above are done by the TargetLynx data processing software and/or the Element LIMS system. A working knowledge of Targetlynx and Element is required.

12.8.2. When evaluating data for a sequence, first determine if all calibrations, mass resolution checks, and ISC checks met their respective QC criteria. **Note that 8290 and CLP/HRSM01.2 require a closing CCV, and CLP requires a closing ISC as well.** Closing res checks are required by all methods. If any required standards fail to meet QC criteria, take corrective action and rerun any affected samples.

12.8.3. For sample data, check IS response for each run. Although there are no method limits for IS recovery, recoveries should generally be within a range of -50% to +100% from the ICV. Anomalies (especially on the low side) should be investigated and possibly require rerun.

12.8.4. Evaluate labeled surrogate recoveries. Surrogate recovery limits vary by compound, but are in the range of 25-150%. Any recoveries that are near the edge of that range should be checked against the relevant limit. Once the data is imported into Element, recoveries outside of acceptable range will be listed in red.

12.8.5. Evaluate the peaks for all detected Dioxins/Furans (DFs). All reported peaks must have S/N >3 for both quant ions, and the quant ions must have RT's within .03 min of each other. Additionally, the RT for each quant ion must be within -.02 to +.05 min of the associated surrogate. Peaks that do not satisfy these criteria should be deleted.

12.8.6. Evaluate the RRT's for all 2378-DFs. All 2378-DFs should have RRT's with the ranges established for the RTX-Dioxin2 column. All non-2378-DF RT's must fall within the associated homologue range established by the marker peaks in the CS3WT. All peaks outside of the range markers should be deleted.



12.8.7. Evaluate the integrations for all DFs. Baselines that are unreasonable in the opinion of the analyst should be manually adjusted, unless the adjustment would have insignificant impact on the peak concentration. Manual integrations are shown on the chromatograms and listed on both the raw data report and the audit report produced by TargetLynx. This audit report must be included in the final data package, and for HRSM01.2 and DOD the report must be signed by the analyst. For CLP and DOD, the data reviewer must also indicate this report was reviewed.

12.8.8. Once the analyst is satisfied with the data for the sequence, the processed data set is saved to the instrument folder on the target server, so that it may be accessed by others. The list of manual integrations (Audit Report) should be printed to PDF and included in the data package with the sequence. See 12.8.24.

12.8.9. All calibration runs, ISC checks, and resolution checks for the sequence should be printed to PDF in the ServerFolders\Data_PDF\Autospec folder. Using PDFCreator, merge each CS3 and its associated res check and ISC into a single pdf with the CS3 filename.

12.8.10. All sample and QC files are also printed directly to PDF in the ServerFolders\Data_PDF\Autospec folder. The file name must be edited to match the run file name, with the pdf file extension. e.g. 18061002.pdf. Element will automatically associate the pdf with the data file of the same name.

12.8.11. The data set is exported to Element from TargetLynx through the File menu, Export, XML. Name the export file the same as the data batch.

12.8.12. In Element, create a sequence that matches the run log, if not already done. Choose the extraction batch and add samples and QC. Also add ICV, CCVs, and ISCs (Res). Enter the IS ID and standards ID's. Check that Analysis method, instrument, calibration, and sequence date are correct. Fill in the requested info under User Fields. Also, in the Benchsheet for the batch, edit the status to "Processing." Then under Extracts, edit the location of the extracts to "Dioxin lab." This should be done when the extracts are put on the instrument for analysis, to update the chain of custody.

12.8.13. Import the data through the DET table and Data Tool, using the "Waters Masslynx Dioxin .xml" file type. Choose the target\share drive folder in which the Targetlynx xml file was saved, then select the files to be imported. Check that the cross table file listed on the bottom of the Data Tool window is the correct Dioxin cross table, before merging the files.

12.8.14. After merge, check that all files are listed in the Merged Upload tab. For those that are not listed, replace the instrument name with the correct Element name under the Instrument Data tab, then Refresh. All files should now appear under the Merged Upload tab. Save the xls (Excel) file in the appropriate folder on the data server.



12.8.15. In the DET table, first Save, then Query the data. The data fields should be populated for all files that were imported. Lock the data, then update the status to “Processing” if not done previously.

12.8.16. If any files are dilutions, enter the appropriate dilution factor in the Diln column **for the surrogates only**. Recoveries will be corrected and should no longer be red. Target compound values are already corrected for dilution, based on the diluted surrogate recoveries. For special cases where a split was taken from the extract during extraction, the split factor is entered in the DILN column for target analytes and totals, but not surrogates (because surrogates are added post-split and should be at normal levels).

12.8.17. After dilution factors have been entered and saved, run the “rev_DioxinEMPC.exe” program using the Print button. This program will add EMPC flags and adjust MDLs/MRLs based on the surrogate dilution factor. “Z” flags will be added to indicate adjusted reporting limits. This program should always be run to get EMPC flags, even if there are no dilutions in the sequence.

12.8.18. Because the quantitation of 123789-HxCDD is based on the average of two HxCDD surrogates, the average response of the 2 surrogates must be manually calculated and entered in Element. 13C12-123478/123678-HxCDD is listed as a virtual, non-reported surrogate in Element, and is used only for Form 7 percent D calculation. A spread sheet is used to average the areas of the 4 quant ions. This value is entered in the Response field for the virtual surrogate for all calibration files (Cal, ICV, CCV). This field is left blank (and will be red) for all non-calibration files.

12.8.19. The percent valley between ISC isomers must also be manually entered. Print to PDF a close up view of the TCDD/TCDF peaks in the ISC chromatogram. With a ruler, measure the valley height and the height of the smaller adjacent peak for both TCDD and TCDF. Calculate the percent of valley height to adjacent peak height and label the chro with this calculation. The percent valley for both compounds must be < 25% to be in control. Enter the calculated percentage in the RES column for TCDD and TCDF in all ISC files. All other compounds in the ISC files are irrelevant and may be deleted.

12.8.20. “E” flags are indicated in the DET table in the FResult column, but must be manually entered in the Qualifier column. Add the “E” qualifier to all target compounds where indicated. A dilution is required for “E” values on any target compounds other than OCDD/OCDF. Per EPA, only saturated OCDD/OCDF peaks require dilution. **Special note:** For diluted files, target compound values are already corrected for dilution based on the diluted surrogates. Actual on column values must be back calculated by dividing the IResult by the dilution factor. e.g. For a 10x dilution of a sample where OCDD has an IResult of 5000 and a FResult of 10000 E, the



true on column value for OCDD is 500 (5000/10). This is below the upper calibration limit of 2000, and therefore no "E" qualifier is warranted. All potential "E" flags for diluted files must be similarly evaluated. "E" flags indicated for surrogates in Element can be disregarded.

12.8.21. Homologue peak counts are required for CLP/HRSM01.2. The values are automatically imported into the DET AnalyteInfo 7 field through the "rev_DioxinEMPC.exe" program. Because PeCDF's occur in 2 functions, however, the two PeCDF values must be summed and manually entered for the PeCDF total. Peak counts should be included in the DET table for all HRSM01.2 samples and blanks.

12.8.22. Sample chromatograms should be evaluated for potential chlorinated diphenyl ether (CDPE) interference, which may inflate the response of the target Furans. CDPE's are very similar compounds to Furans and can fragment into the same quant ions. The data reports include a chromatogram for potential CDPE masses with each Furan homologue group. If there is an integrated CDPE peak within .03 min of a target Furan peak, and the CDPE peak has a height > 1% of the Furan height, the Furan value should get an "X" flag, indicating potential CDPE interference. The "X" qualifier text must be filled in each time, but can be copied/pasted from a saved text file to avoid typing. See Appendix 20.10 for detailed CDPE theory.

12.8.23. The HRMS Reviewer Checklist should be filled in once all the data has been imported and evaluated. Items in red should either be fixed or addressed with comments in the lower box. General comments should be listed in the Additional Notes at the bottom.

12.8.24. A PDF of the Sequence should be created once the raw data has been evaluated and all manual integrations have been applied. This can be done before or after the data is imported to Element. The Sequence PDF should include the Element Sequence, including relevant user data, a run log showing data acquisition times, and the Targetlynx Audit report. The latter two reports are printed to PDF from TargetLynx, and can then be edited with sequence comments and analyst initials as needed. Merge the 3 files into a single PDF in PDFCreator, name as the Sequence number, and place in the Data_PDF\Sequence folder.

12.8.25. Once the Sequence data is ready for review and all associated PDFs have been attached, the status should be changed to Analyzed.

13. Method Performance

13.1. The QA department measures method performance using a combination of initial performance and recovery (IPR) studies, ongoing performance and recovery (LCS) studies, quantitation limit studies (QLS) and the monitoring of extraction and cleanup standard recoveries.



- 13.1.1. Limits of Detection (LOD)- detection limits for all analytes quantitated using this SOP are determined by an estimated detection limit (EDL) calculation for each individual sample and named congener reported.
- 13.1.2. IPR studies are performed each year for each analyte by each preparatory and analytical method (for example, analytes quantitated for in sediment samples will have IPR studies performed for both the microwave and soxhlet extraction).
- 13.1.3. LCS spikes are prepared with every extraction batch and result values may be found for each analyte on the ARI website.
- 13.1.4. QLS spikes are used to statistically derive LOD and LOQ results which are used to verify the LOQ.
- 13.1.5. Laboratory precision and bias measurements are performed by monitoring extraction and cleanup standard recoveries in samples and quality control samples.
- 13.1.6. Control limits may be calculated by monitoring these recoveries. These control limits are disseminated to the bench chemists and LIMS administrator for use in monitoring method performance in real time. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found on the ARI website.
- 13.1.7. Method default control limits from method 1613B for extraction and cleanup standard recoveries will be used until a sufficient number of data points have been collected to generate meaningful statistics. ARI may use these in-house limits to monitor method performance, but they will not supersede those limits listed in the method 1613B.

14. Pollution Prevention

- 14.1. All syringe rinsing must be performed over charcoal to minimize the exposure of the environment to solvent or extract. The charcoal container must remain covered when not in use to prevent fugitive emissions.
- 14.2. All GC split vents will be connected to a charcoal filter and an exhaust vent.
- 14.3. All MS vacuum pumps will be connected to an exhaust vent.
- 14.4. All spent vials and pipettes are placed into the blue waste vial receptacle in the Dioxin extraction lab for proper disposal.
- 14.5. Wherever possible the final sample extract volume should be as small as possible to minimize the generation of waste.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

- 15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 above.
- 15.2. Method Blanks- For non CLP contract work, the method blank should contain less than the reporting limit of all analytes except OCDD/OCDF, which can be up to 5 times the RL. Corrective



action should be performed for any detected target analyte in a sample that is also found in the method blank at a concentration greater than the RL. **For CLP HRSM01.2, all target analytes other than OCDD/OCDF should be less than 1/2 the CRQL in the method blank. OCDD/OCDF should be less than 3 times the CRQL to be in compliance.**

15.3. Extraction and cleanup standard Recoveries

15.3.1.1. All method blanks, IPR, LCS, duplicates, SRMs and samples must have acceptable extraction and cleanup standard recoveries. Standard recoveries are listed in table 5 (Appendix 20.5) and are not to exceed the method default limits as shown.

15.3.2. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet project specific standard acceptance criteria that supersede those limits listed in Table 5.

15.3.3. Extraction and cleanup standard recovery acceptance windows are ideally determined statistically from method and matrix specific laboratory data updated on a periodic basis. Certain methods or clients may specify project specific surrogate recovery acceptance windows. ARI will use 1613B method default limits until appropriate in-house limits are generated.

15.3.4. Extraction and cleanup standard acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.

15.4. Performance and recovery Control Samples (IPR and LCS)

15.4.1. The IPR/LCS/LCSD recovery values should fall within the method specified recovery acceptance limits shown in table 6 (Appendix 21.6). IPR/LCS/LCSD recovery acceptance windows are ideally determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Project or method specific limits may supersede laboratory acceptance criteria.

15.5. Matrix Spike/Matrix Spike Duplicates (MS/MSD)- DOD ONLY- (NOTE: Must be reported with Element)

15.5.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified LCS recovery acceptance limits. If a MSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.

15.5.2. MS/MSD recovery and RPD acceptance windows are ideally determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Certain methods or clients may require project specific MS/MSD recovery and RPD acceptance windows. MS/MSD recoveries are advisory and should not be used to reject batch data.



15.6. Holding Times

15.6.1. Samples should be extracted within holding times (one year for all samples).

15.6.1.1. Extracts must be analyzed within the extract holding time (one year from the initial date of extraction).

15.6.1.2. In the event that re-extraction due to an out of control event requires that samples be re-extracted after their one year holding time has elapsed, the analyst should analyze and report both extraction sets, whenever practical, distinguishing between the initial extraction and re-extraction on all deliverables. This will document that the samples were originally extracted within holding times and may allow for comparisons that will determine whether the sample was compromised in the interval between extractions.

15.6.1.3. If any extracts are analyzed after the one-year extract holding time has elapsed, the analyst must document this in the analytical notes accompanying the data so that it may be included in the case narrative.

16. Corrective Actions for Out of Control Events

16.1. Mass Spectrometer Tuning

16.1.1. MS tuning- prior to initial calibration, each GC/MS system must be hardware-tuned to meet the minimum resolving power of 10,000 (at 10% valley) for 3-5 PFK masses representing each scan function utilized. Analyses must not begin until all these criteria are met with no exceptions. Evaluate the static resolution check not only for resolution but to insure that the level of PFK ion bleed is less than one volt for each mass.

16.1.2. If the re-tuned mass spectrometer still fails to meet the criteria found in 16.1.1 the MS may require maintenance. Maintenance may include, but is not limited to: replacing the filaments, exchanging the MS inner source, exchanging the MS outer source, cleaning the MS inner or outer source lenses, and adjusting the slit settings.

16.2. Ion ratio factors- If the ion ratio factors exceed the limits found in table 3 (Appendix 20.3), the mass spectrometer or chromatographic system may need maintenance. Inspect the MS system for leaks or other tuning issues. Should none be found, perform maintenance on the chromatographic system. This maintenance includes, but is not limited to: replacing the inlet liner, cleaning the inlet liner, cleaning or replacing the inlet seal, cleaning or replacing the inlet body, replacing the split line, cleaning the split arm, clipping a length from the front of the column, or replacing the column. Any maintenance is to be documented in the maintenance logbook for that instrument.

16.3. Signal/Noise Failure-Initial calibration is not acceptable until all calibration points have S/N > 10. Corrective action is required if this limit is not met.



16.4. Initial calibration linearity failure- should any of the analytes in the initial calibration show RSDs greater than 20% corrective action is required and sample analysis should not begin until the problem is corrected.

16.5. Continuing verification linearity failure- should any of the named analytes, extraction standards, or cleanup standard in the continuing calibration verification show % D greater than the limits shown in Appendix 20.9 corrective action is required and sample analysis should not begin until the problem is corrected. The closing continuing calibration verification will also be evaluated to these same tolerances and any failures clearly documented in the analysts notes for inclusion in the case narrative.

16.5.1. DoD-QSM requires that %D for all analytes in the ICV or CCV be $\leq 20\%$ (50% for end of batch CCV). For DoD analyses, if no samples have been analyzed and less than 1 hour elapsed since the failed CCV, two additional consecutive ICVs or CCVs may be analyzed. This is not required; the analyst may default to Section 16.5

16.5.1.1. When both of these CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.5.1.2. If either of the two CCVs fail or their analysis cannot be started within one hour, associated samples may not be reported and the instrument must be re-calibrated.

16.6. Extraction and cleanup standards

16.6.1. When the extraction standards or cleanup standard fail to meet their recovery acceptance criteria, reanalyze the extract.

16.6.2. If the extraction and cleanup standard recoveries do not meet their recovery acceptance criteria after reanalysis, check calculations, sample preparation logs, the extraction and cleanup standard spiking and calibration solutions and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the extraction or cleanup standards meet their acceptance criteria. If the sample preparation logs indicate that the incorrect amount of extraction or cleanup spiking solution was added either recalculate standard recoveries based on the actual amount of standard spiking solution added, or re-extract/reanalyze the sample, adding the correct amount of standard spiking solution. If the standard compound spiking solution and/or instrument calibration solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze samples.

16.6.3. If the analytical instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. This correction will mostly involve maintenance similar to the maintenance discussed in Section 16.2. Verify that the standard recoveries meet their acceptance criteria. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.



16.6.4. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps.

16.6.4.1. Re-extract and reanalyze the sample. The laboratory may decide to extract a smaller sample volume or amount in order to reduce the interfering aspect of the sample matrix.

16.6.4.2. If the extraction and (or) cleanup standard recoveries meet acceptance criteria in the re-extracted/reanalyzed sample, then the problem with the initial analysis is deemed to be within the laboratory's control. Therefore, submit data only from the re-extraction/reanalysis if the re-extraction was performed within holding time, otherwise report both sets of data.

16.6.4.3. If the extraction and (or) cleanup standard recoveries fail to meet the acceptance criteria in the re-extracted/reanalyzed sample, then submit data from both analyses, distinguishing between the initial analysis and the re-extraction/reanalysis on all deliverables.

16.7. Method Blanks- Corrective action for a method blank may involve re-extraction and reanalysis of all associated samples in the case where blank concentrations are greater than $\frac{1}{2}$ of the reporting limit, except for OCDD/OCDF, which can be up to 5 times the RL. Sample hits less than 10 times the MB concentration will be "B" flagged.

16.8. LCS/IPR control Samples

16.8.1. If the LCS compounds fail to meet recovery acceptance criteria, reanalyze the extract.

16.8.2. If the LCS recoveries do not meet their recovery acceptance criteria after reanalysis, check calculations, sample preparation logs, the LCS compound spiking and calibration solutions and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the LCS compound recoveries meet their acceptance criteria. If the sample preparation logs indicate that the incorrect amount of LCS compound spiking solution was added either recalculate LCS recoveries based on the actual amount of LCS compound spiking solution added or re-extract/reanalyze the samples, adding the correct amount of LCS spiking solution. If the LCS compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze samples.

16.8.3. If the analytical instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the LCS recoveries meet their acceptance criteria. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.8.4. If the LCS compounds still fail to meet their acceptance criteria, re-extract and reanalyze the LCS and all associated samples and QC samples if deemed appropriate (i.e. after consideration of all batch QC data) or mandated by contract-specific requirements. Any



decision to forgo re-extraction/reanalysis based on failure to meet LCS acceptance criteria will require approval of the Project Manager and the Lab Manager, at a minimum.

16.9. Matrix Spike/Matrix Spike Duplicates-DoD only-(reportable in Element only)

16.9.1. All MS/MSD control limits are advisory and should not be used to reject batch data.

16.10. Over range values- Should the quantitated value of any analyte except OCDD/OCDF exceed the working range of the curve, a dilution of the original extract may be performed. Over range values will be qualified with an "E" flag. Sample extracts may be diluted a maximum of 50x, so that the labeled surrogates are not diluted below approximately 1 pg on column. The concentration of the injection standard must remain at 100pg/ul in all dilutions, as in undiluted extracts. An aliquot of the diluted extract is analyzed and only the over range analytes are reported for the dilution run. Samples requiring greater than a 50x dilution to bring all analytes within curve range will require a re-extraction with a smaller sample volume (weight). OCDD/OCDF may be reported as "E" values. See 16.10.1. See Appendix 20.11 for dilution procedure.

16.10.1. When ions from a target compound in the sample saturate the detector or when the chromatographic system is overloaded the analyst must;

16.10.1.1. Analyze a Solvent Blank consisting of clean solvent until the system has been decontaminated.

16.10.1.2. Evaluate subsequent samples and QC for any possible carryover or contamination.

16.10.1.3. The chromatographic system should be decontaminated before the analytical sequence may be resumed.

16.11. EMPC - When named target analytes do not meet ion abundance ratio criteria they must be calculated as an EMPC and flagged as an EMPC on the final report. See Appendix 20.2 for EMPC area correction calculations.

16.12. PCDE interference - Named target analytes showing PCDE interference will be evaluated as follows. In cases where the area of the interference is less than 1% area of either Furan quantitation ion, no corrective action is required. In cases where the area of interference is greater than 1% of either Furan quantitation ion, the furan value will be "X" flagged. In cases where the interference exceeds 10%, ARI may perform additional cleanups on the original extract and/or may re-extract the sample at a smaller volume. Such corrective actions are discretionary and must be approved by the Organics supervisor and project manager. See appendix 20.10 for further discussion of PCDE interferences.

16.13. PFK traces must not exceed 20% variation for the lock mass in each function. Negative peaks in the PFK trace caused by interferences are acceptable, as long as the general trend of the trace is still within the 20% limit, and the chromatography of IS, labeled surrogates, and target



analytes are unaffected, and the labeled surrogate values are within method recovery limits (See Appendix 20.5). Corrective action is required if all of the above conditions are not met.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

- 17.1. See Section 16.1 for guidance on dealing with out-of-control tuning events.
- 17.2. See section 16.2 for guidance on ion ratio limit failures for initial and continuing calibrations.
- 17.3. See Section 16.3 for guidance on dealing with signal/noise limit failures.
- 17.4. See Section 16.6 for guidance on dealing with initial calibration linearity failures (%RSD).
- 17.5. See Section 16.7 for guidance on dealing with continuing verification linearity failures (%D).
- 17.6. See Section 16.8 for guidance on dealing with extraction and cleanup standard control limit failures.
- 17.7. See Section 16.9 for guidance on dealing with method blank related out-of-control events.
- 17.8. See Section 16.8 for guidance on dealing with IPR/LCS recovery limit failures.
- 17.9. See Section 16.9 for guidance on dealing with MS/MSD control limit failures. -DoD only
- 17.10. See Section 16.10 for guidance on over range value events.
- 17.11. See Section 16.11 for guidance on reporting values as an EMPC.
- 17.12. See Section 16.12 for guidance on reporting values with PCDE interference.
- 17.13. See Section 16.13 for guidance on reporting data with PFK interference

18. Routine Instrument Maintenance

- 18.1 GC Maintenance. If chromatography shows excess tailing, or TCDD/TCDF resolution is poor, change the injector liner and clip one or two loops from the front of the column. Remember to adjust the RT windows for the five functions in the acquisition method. One loop corresponds to approximately 0.3 min of RT shift.
- 18.2 Source Maintenance. If tuning is abnormal and/or sensitivity declines significantly, check the inner source. If it looks dirty or has been in use more than a couple months, replace the inner source with a clean one. Also look at the outer source. If it looks particularly dirty, or if the clean inner source does not improve performance sufficiently, replace the outer source as well. Always have a clean inner source (including new filament) and outer source available to use if needed.
- 18.3 Preventative Maintenance. ARI will always have a service contract, which includes a yearly preventative maintenance visit. This visit normally includes changing pump oil, cleaning all lenses in the source, and possibly in the analyzer, as well as checking the source and collector slits. For other non-routine performance issues, especially electronic or computer related, call Waters for service.

19. Waste Management



- 19.1. All extract vials must be disposed of by placing them in the blue hazardous waste drum in the instrument part storage area set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.
- 19.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner. The charcoal waste container must be covered when not in use.
- 19.3. All spent charcoal must be disposed of by placing it in the dioxin charcoal disposal bin located in the dioxin extractions lab.
- 19.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

20. Method References

- 20.1. Method 1613B - "Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS", Revision B, October 1994.
- 20.2. Method 8290A - Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), Revision 1, February 2007.
- 20.3. "Determinative Chromatographic Separations": Method 8000C, Test Methods for Evaluating Solid Waste (SW-846), Revision 3, March 2003.
- 20.4. "Department of Defense Quality Systems Manual for Environmental Laboratories", Version 5.0, July 2013.
- 20.5. Method 8290 - Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), Revision 0, September, 1994.
- 20.6. Multi-Media, Multi-Concentration Dioxin and Furan Analysis (DLM 02.2) SOW. EPA CLP. December 2009.

21. Appendices

- 21.1. Appendix 20.1: Quality Control Requirements
- 21.2. Appendix 20.2: Example EMPC calculations
- 21.3. Appendix 20.3: Method 1613B Retention Time References
- 21.4. Appendix 20.4: Method 1613B Ion Abundance Ratios and QC Criteria
- 21.5. Appendix 20.5: Method 1613B Labeled Compound Recovery When All CDDs/CDFs Are Tested
- 21.6. Appendix 20.6: Method 1613B IPR/LCS Recovery Acceptance Criteria
- 21.7. Appendix 20.7: Retention Time Window Defining Isomers



21.8. Appendix 20.8: ARI five Function Scan Descriptor

21.9. Appendix 20.9: Method 1613B Initial and continuing calibration verification %RSD and %D requirements.

21.10. Appendix 20.10: Theory of CDPE interference.

21.11. Appendix 20.11: Extract dilution procedure

21.12. Appendix 20.12: Example of ISC peak resolution calculation



Appendix 20.1. Quality Control Requirements for Dioxin/Furan Analysis by HRGC/HRMS (Method 1613B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analytical capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, test method, or sample matrix.	QC acceptance criteria published by ARI, if available; otherwise, method-specified criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA.	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure. No analysis shall be allowed by analyst until successful demonstration of capability is complete.
LOD determination and verification (See Box D-13)					
establishment and verification (See Box D-14)					
Tuning	At the beginning and the end of each 12-hour period of analysis.	Static resolving power $\geq 10,000$ (10% valley) for identified masses per method, and lock-mass ion between lowest and highest masses for each descriptor and level of reference compound $\leq 10\%$ full-scale deflection, per method.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be accepted without a valid tune.
GC column performance check	Prior to ICAL or calibration verification. Use GC performance check solution per method.	Peak separation between 2378-TCDD and other TCDD isomers result in a valley of $\leq 25\%$, per method; and Identification of all first and last eluters of the eight homologue retention time windows; and Absolute retention times for switching from one homologous series to the next ≥ 10 sec. for all components of the mixture.	Correct problem then repeat column performance check.	Flagging criteria are not appropriate.	



Appendix 20.1. Quality Control Requirements for Dioxin/Furan Analysis by HRGC/HRMS (Method 1613B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial calibration (ICAL) for all analytes identified in method	ICAL prior to sample analysis, as needed by the failure of calibration verification standard, and when a new lot is used as standard source for HRCC-3, sample fortification (IS), or recovery solutions.	Ion abundance ratios in accordance with criteria in Table 8 of the method; and S/N ratio ≥ 10 for all target analyte ions; and RSD $\leq 20\%$ for the response factors (RF) for all 17 unlabeled standards and RSD $\leq 20\%$ for the RFs for the 9 labeled IS.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed. Calibration may not be forced through origin.
Calibration verification	At the beginning of each 12-hour period.	Ion abundance ratios in accordance with criteria in Table 8 of the method; and meets method 1613B %D requirements listed in Appendix 20.9	Correct problem, repeat calibration verification standard. If that fails, repeat ICAL and reanalyze all samples analyzed since the last successful CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last successful calibration verification.	Problem must be corrected. Results may not be reported without a valid calibration verification. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Method blank	One per preparatory batch, run after calibration standards and before samples.	No analytes detected $\geq \frac{1}{2}$ LOQ. or $\geq 5\%$ of the associated regulatory limit for the analyte or $\geq 10\%$ of the sample result for the analyte, whichever is greater, per method.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS	One per preparatory batch.	QC acceptance criteria specified by method, 1613B. Appendix 20.6	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Sample duplicate	(OPTIONAL)	RPD $\leq 25\%$ (between sample and sample duplicate), per method.	Contact the client as to additional measures to be taken.		
Extraction and cleanup standards	Every field sample, standard, and QC sample.	% recovery for each IS in the original sample (prior to dilutions) must be within 1613B method requirements.	Correct problem, then reprep and reanalyze the samples with failed recoveries.	Apply Q-flag to results of all affected samples.	



Appendix 20.3: Retention Time References, Quantitation References, Relative Retention Times, and Minimum Levels for CDDS & CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum Level		
			Water pg/L;ppq	Solid ng/kg;ppt	Extract pg/μL; ppb
COMPOUNDS USING ¹³ C ₁₂ -1,2,3,4-TCDD AS THE INJECTION STANDARD					
2,3,7,8-TCDF	¹³ C ₁₂ -1,3,7,8-TCDF	0.999-1.003	10	1	0.5
2,3,7,8-TCDD	¹³ C ₁₂ -2,3,7,8-TCDD	0.999-1.002	10	1	0.5
1,2,3,7,8-PeCDF ³	¹³ C ₁₂ -1,2,3,7,8-PeCDF	0.999-1.002	50	5	2.5
2,3,4,7,8-PeCDF	¹³ C ₁₂ -2,3,4,7,8-PeCDF	0.999-1.002	50	5	2.5
1,2,3,7,8-PeCDD	¹³ C ₁₂ -1,2,3,7,8-PeCDD	0.999-1.002	50	5	2.5
¹³ C ₁₂ -2,3,7,8-TCDF	¹³ C ₁₂ -1,2,3,4-TCDD	0.923-1.103			
¹³ C ₁₂ -2,3,7,8-TCDD	¹³ C ₁₂ -1,2,3,4-TCDD	0.976-1.043			
¹³ C ₁₂ -2,3,7,8-TCDD	¹³ C ₁₂ -1,2,3,4-TCDD	0.989-1.052			
¹³ C ₁₂ -1,2,3,7,8-PeCDF	¹³ C ₁₂ -1,2,3,4-TCDD	1.000-1.425			
¹³ C ₁₂ -2,3,4,7,8-PeCDF	¹³ C ₁₂ -1,2,3,4-TCDD	1.011-1.526			
¹³ C ₁₂ -1,2,3,7,8-PeCDD	¹³ C ₁₂ -1,2,3,4-TCDD	1.000-1.567			
COMPOUNDS USING ¹³ C ₁₂ -1,2,3,7,8,9-HxCDD AS THE INJECTION INTERNAL STANDARD					
1,2,3,4,7,8-HxCDF	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	0.999-1.001	50	5	2.5
1,2,3,6,7,8-HxCDF	¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	0.997-1.005	50	5	2.5
1,2,3,7,8,9-HxCDF	¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	0.999-1.001	50	5	2.5
2,3,4,6,7,8-HxCDF	¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	0.999-1.001	50	5	2.5
1,2,3,4,7,8-HxCDD	¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	0.999-1.001	50	5	2.5
1,2,3,6,7,8-HxCDD	¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	0.998-1.004	50	5	2.5
1,2,3,7,8,9-HxCDD	²	1.000-1.019	50	5	2.5
1,2,3,4,6,7,8-HpCDF	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	0.999-1.001	50	5	2.5
1,2,3,4,7,8,9-HpCDF	¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	0.999-1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDD	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	0.999-1.001	50	5	2.5
OCDF	¹³ C ₁₂ -OCDD	0.999-1.008	100	10	5
OCDD	¹³ C ₁₂ -OCDD	0.999-1.001	100	10	5
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	0.944-0.970			
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	0.949-0.975			
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	0.977-1.047			
¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	0.959-1.021			
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	0.977-1.000			
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	0.981-1.003			
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	1.043-1.085			
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	1.057-1.151			
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	1.086-1.110			
¹³ C ₁₂ -OCDD	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	1.032-1.311			

² The retention time reference for 1,2,3,7,8,9-HxCDD is ¹³C₁₂-1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for ¹³C₁₂-1,2,3,4,7,8-HxCDD and ¹³C₁₂-1,2,3,6,7,8-HxCDD.

³ The last eluting TCDF (1289) elutes after the first PeCDF (13468) congener on the RTX-DIOXIN2 column. The window is set from the last eluting TCDF (1289) marker. Additional PeCDFs (12468 and 13678) are also used to ensure the windows have been set correctly.



Appendix 20.4: Theoretical Ion Abundance Ratios and QC Limits

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	QC Limits ¹	
			Lower	Upper
4 ²	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
6 ³	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.04	0.88	1.20
7 ⁴	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

¹ QC limits represent $\pm 15\%$ windows around the theoretical ion abundance ratios.

² Does not apply to ³⁷Cl₄-2,3,7,8-TCDD (cleanup standard).

³ Used for ¹³C₁₂-HxCDF only.

⁴ Used for ¹³C₁₂-HpCDF only.

Appendix 20.5: Labeled Compound Recovery When All CDDs/CDFs Are Tested

Compound	Test Conc. (ng/mL)	Labeled Compound Recovery	
		(ng/mL) ¹	(%)
¹³ C ₁₂ -2,3,7,8-TCDD	100	25 – 164	25 – 164
¹³ C ₁₂ -2,3,7,8-TCDF	100	24 – 169	24 – 169
¹³ C ₁₂ -1,2,3,7,8-PeCDD	100	25 – 181	25 – 181
¹³ C ₁₂ -1,2,3,7,8-PeCDF	100	24 – 185	24 – 185
¹³ C ₁₂ -2,3,4,7,8-PeCDF	100	21 – 178	21 – 178
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	100	32 – 141	32 – 141
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100	28 – 130	28 – 130
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	100	26 – 152	26 – 152
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	100	26 – 123	26 – 123
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	100	29 – 147	29 – 147
¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	100	28 – 136	28 – 136
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	100	23 – 140	23 – 140
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	100	28 – 143	28 – 143
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100	26 – 138	26 – 138
¹³ C ₁₂ -OCDD	200	34 – 313	17 – 157
¹³ C ₄ -2,3,7,8-TCDD	10	3.5 – 19.7	35 – 197

¹ Specifications given as concentrations in the final extract, assuming a 20 μ L volume.

Appendix 20.6: Acceptance Criteria for IPR/LCS Results When All CDDs/CDFs Are Tested¹



CDD/CDF	Test Conc. (ng/mL)	IPR ^{2,3}		LCS (ng/mL)	VER (ng/mL)
		S (ng/mL)	X (ng/mL)		
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	2	8.7-13.7	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71	39-65
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67	41-60
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80	41-61
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82	39-64
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67	39-64
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81	41-61
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67	45-56
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65	44-57
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65	45-56
2,3,4,6,7,8-HxCDF	50	7.4	37-74	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69	43-58
OCDD	100	19	89-127	78-144	79-126
OCDF	100	27	74-146	63-170	63-159
¹³ C ₁₂ -2,3,7,8-TCDD	100	37	28-134	20-175	82-121
¹³ C ₁₂ -2,3,7,8-TCDF	100	35	31-113	22-152	71-140
¹³ C ₁₂ -1,2,3,7,8-PeCDD	100	39	27-184	21-227	62-160
¹³ C ₁₂ -1,2,3,7,8-PeCDF	100	34	27-156	21-192	76-130
¹³ C ₁₂ -2,3,4,7,8-PeCDF	100	38	16-279	13-328	77-130
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	100	41	29-147	21-193	85-117
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100	38	34-122	25-163	85-118
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	100	43	27-152	19-202	76-131
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	100	35	30-122	21-159	70-143
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	100	40	24-157	17-205	74-135
¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	100	37	29-136	22-176	73-137
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	100	35	34-129	26-166	72-138
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	100	41	32-110	21-158	78-129
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100	40	28-141	20-186	77-129
¹³ C ₁₂ -OCDD	200	95	41-276	26-397	96-415
¹³ C ₄ -2,3,7,8-TCDD	10	3.6	3.9-15.4	3.1-19.1	7.9-12.7
2,3,7,8-TCDD	10	2.7	8.7-12.4	7.3-14.6	8.2-12.3
2,3,7,8-TCDF	10	2	9.1-13.1	8.0-14.7	8.6-11.6
¹³ C ₁₂ -2,3,7,8-TCDD	100	35	32-115	25-141	85-117
¹³ C ₁₂ -2,3,7,8-TCDF	100	34	35-99	26-126	76-131
¹³ C ₄ -2,3,7,8-TCDD	10	3.4	4.5-13.4	3.7-15.8	8.3-12.1

¹ All specifications are given as concentrations in the final extract, assuming a 20 µL volume.

² s = standard deviation of the concentration.

³ X = average concentration.



Appendix 20.7: Retention Time Window Defining Isomers		
PCDD / PCDF	First Eluted	Last Eluted
TCDF	1368	1289
TCDD	1368	1289
PeCDF	13468	12389
PeCDD	12479	12389
HxCDF	123468	123789
HxCDD	124679	123789
HpCDF	1234678	1234789
HpCDD	1234679	1234678

RTX-DIOXIN2 TCDD SPECIFICITY TEST STANDARD

2378-TCDD
1278-TCDD

RTX-DIOXIN2 TCDF SPECIFICITY TEST STANDARD

2348-TCDF
2378-TCDF
3467-TCDF



Appendix 20.8: Five Function Scan Descriptor				
DESCRIPTOR	EXACT MASS	MASS TYPE	SUBSTANCE	
1	303.9016	M	TCDF	
	305.8987	M+2	TCDF	
	315.9419	M	¹³ C-TCDF	
	317.9389	M+2	¹³ C-TCDF	
	319.8965	M	TCDD	
	321.8936	M+2	TCDD	
	327.8847	M	³⁷ CL-TCDD	
	330.9792	LOCK	PFK	
	331.9368	M	¹³ C-TCDD	
	333.9339	M+2	¹³ C-TCDD	
	339.8597	M	PeCDF	
	341.8567	M+2	PeCDF	
	375.8364	M+2	HxCDF	
	409.7974	M+2	HpCDF	
	2	339.8597	M	PeCDF
		341.8567	M+2	PeCDF
		342.9792	LOCK	PFK
351.9000		M	¹³ C-PeCDF	
353.8970		M+2	¹³ C-PeCDF	
355.8546		M+2	PeCDD	
357.8516		M+4	PeCDD	
367.8949		M+2	¹³ C-PeCDD	
369.8919		M+4	¹³ C-PeCDD	
409.7974		M+2	HpCDF	
3		373.8208	M+2	HxCDF
	375.8178	M+4	HxCDF	
	380.9760	LOCK	PFK	
	383.8639	M	¹³ C-HxCDF	
	385.8610	M+2	¹³ C-HxCDF	
	389.8157	M+2	HxCDD	
	391.8127	M+4	HxCDD	
	401.8559	M+2	¹³ C-HxCDD	
	403.8529	M+4	¹³ C-HxCDD	
	445.7555	M+4	OCDPE	
	4	407.7818	M+2	HpCDF
		409.7788	M+4	HpCDF
		417.8253	M	¹³ C-HpCDF
419.8220		M+2	¹³ C-HpCDF	
423.7766		M+2	HpCDD	
425.7737		M+4	HpCDD	
430.9728		LOCK	PFK	
435.8169		M+2	¹³ C-HpCDD	
437.8140		M+4	¹³ C-HpCDD	
479.7165		M+4	NCDPE	
5		441.7428	M+2	OCDF
	443.7399	M+4	OCDF	
	457.7377	M+2	OCDD	
	459.7348	M+4	OCDD	
	469.7779	M+2	¹³ C-OCDD	
	471.7750	M+4	¹³ C-OCDD	
	480.9696	LOCK	PFK	
	513.6775	M+4	DCDFE	



Appendix 20.9: Calibration requirements for initial and continuing verifications

Compound	Soln. Conc. (ng/mL)	Labeled Compounds	
		ICAL	CCAL (%D)
¹³ C ₁₂ -2,3,7,8-TCDD	100	20% RSD	82-121
¹³ C ₁₂ -2,3,7,8-TCDF	100	20% RSD	71-140
¹³ C ₁₂ -1,2,3,7,8-PeCDD	100	20% RSD	62-160
¹³ C ₁₂ -1,2,3,7,8-PeCDF	100	20% RSD	24 – 185
¹³ C ₁₂ -2,3,4,7,8-PeCDF	100	20% RSD	21 – 178
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	100	20% RSD	32 – 141
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100	20% RSD	28 – 130
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	100	20% RSD	26 – 152
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	100	20% RSD	26 – 123
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	100	20% RSD	29 – 147
¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	100	20% RSD	28 – 136
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	100	20% RSD	23 – 140
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	100	20% RSD	28 – 143
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100	20% RSD	26 – 138
¹³ C ₁₂ -OCDD	200	20% RSD	17 – 157
¹³ C ₄ -2,3,7,8-TCDD	10	20% RSD	35 – 197

Appendix 20.9: Calibration requirements for initial and continuing verifications

Compound	Soln. Conc. (ng/mL)	Native Compounds	
		ICAL	CCAL (%D)
2,3,7,8-TCDD	10	20% RSD	78-129
2,3,7,8-TCDF	10	20% RSD	84-120
1,2,3,7,8-PeCDD	50	20% RSD	78-130
1,2,3,7,8-PeCDF	50	20% RSD	82-120
2,3,4,7,8-PeCDF	50	20% RSD	82-122
1,2,3,4,7,8-HxCDD	50	20% RSD	78-128
1,2,3,6,7,8-HxCDD	50	20% RSD	78-128
1,2,3,7,8,9-HxCDD	50	20% RSD	82-122
1,2,3,4,7,8-HxCDF	50	20% RSD	90-112
1,2,3,6,7,8-HxCDF	50	20% RSD	88-114
1,2,3,7,8,9-HxCDF	50	20% RSD	90-112
2,3,4,6,7,8-HxCDF	50	20% RSD	88-114
1,2,3,4,6,7,8-HpCDD	50	20% RSD	86-116
1,2,3,4,6,7,8-HpCDF	50	20% RSD	90-110
1,2,3,4,7,8,9-HpCDF	50	20% RSD	86-116
OCDD	100	20% RSD	79-126
OCDF	100	20% RSD	63-159



Appendix 20.10: Theory of CDPE Interferences

20.10 The theory of Chlorinated Diphenyl Ether (CDPE) interference is that because they are such similar compounds to Chlorinated Furans (CDFs), during ionization they will fragment into the exact CDF quant masses. This creates a potential for false positive CDF values.

For example, for potential PCDF interference, the HPCDPE mass 409.7974 is monitored. As evidenced by the spectra of HPCDPE, it can be shown that it will fragment into the PCDF quant masses 339.8597 and 341.8567, and it is impossible to measure exactly how much of the peak areas at those masses came from the CDPE fragment. The TCDF value must therefore be flagged as a false positive because there was a CDPE detected at the same retention time which will add to the PCDF quant mass peaks.

From the spectra of CDPEs it can also be determined that the area of the masses contributing to the CDF quant ions are generally 2-4 times the area of the respective CDPE molecular mass being monitored. The potential interference amount can then be estimated by multiplying the CDPE area by the factor of 2-4. Therefore, if the CDPE area is 2% of the CDF area, approximately 4-8% of the CDF area is likely from the CDPE contribution.

Appendix 20.11: Extract Dilution Procedure

20.11. Because of the unique nature of dioxin extracts, and the need to add injection standard at a specific ratio to the extract volume, they should be diluted as follows:

5X Dilution: 10 μ L nonane, 10 μ L IS, 5 μ L sample

10X Dilution: 9 μ L nonane, 9 μ L IS, 2 μ L sample

This procedure assumes the original extract had a final volume of 20 μ L, including 10 μ L of internal standard. Multiple dilutions can be made to get higher dilution factors such as 25X or 50X. Also note that on- column values for target analytes in dilutions already have the dilution factor included, since they are calculated from the labels which have been diluted. Dilution values are normally very close to the values in the original extract, unless the original value was from a saturated peak.



Standard Operating Procedure

Sulfide by Iodometric Titration

SOP 650S
Version 001

Revision Date: 11/30/16
Effective Date: 11/30/16

Prepared by:

Mike Perkins

Approvals:

A handwritten signature in blue ink, appearing to read "Casey English".

Casey English, Laboratory Supervisor

A handwritten signature in blue ink, appearing to read "Eric Larson".

Eric Larson, Inorganics Division Manager



Annual Review

SOP Number:

Title:

Revision:

Revision Date:

Effective date:

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>



Standard Operating Procedure

Sulfide by Iodometric Titration

1. Scope and Application

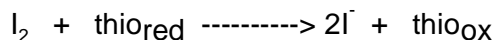
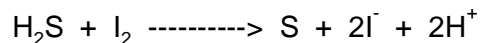
- 1.1. Sulfide in a water or soil sample exists in a variety of states dependent upon pH and redox potential of the sample matrix. Primary forms include H_2S , HS^- , S^{2-} , and various metal sulfide complexes which vary widely in their degree of solubility. Preserved aqueous samples or distillates will have sulfide present in the form of a metal complex (zinc sulfide).
- 1.2. Sulfide can be analyzed by either direct iodometric titration or by the spectrophotometric methylene-blue procedure. The difference is one of sensitivity and detection limit. Titration can be used for higher levels of sulfide (>1.0 mg/L) while the spectrophotometric procedure must be used for concentrations <1 mg/L. If samples are known to contain high levels of sulfide, it is more efficient and accurate to analyze them using the titrimetric procedure.
- 1.3. The iodometric titration procedure is applicable to the determination of total and dissolved acid soluble sulfide at concentrations in excess of 1 mg/L in drinking, surface, saline waters, domestic and industrial wastes, and in sample distillates. This procedure (along with potentiometric determination) is specified for distillates from the SW-846 9030 distillation for acid soluble and acid insoluble sulfides. The procedure is also specified for the standardization of stock sulfide solutions when used for the preparation of standards in the colorimetric analysis.
- 1.4. This SOP follows protocol as given in EPA 376.1, SW-846 9034 and Standard Methods 4500-S²-F.

2. Summary of the Procedure

- 2.1. The iodometric method for the determination of sulfide is based upon the stoichiometric oxidation-reduction reactions that occur between sulfide and iodine in acid solution. Sulfide becomes oxidized to sulfur while iodine (I_2) becomes reduced to colorless iodide (I^-). A known amount of iodine is added to the test solution and allowed to react with sulfide under acidic conditions. Excess iodine remaining in solution is then titrated with sodium thiosulfate



reducing agent using starch or Thyodine indicator for the end point detection. Relevant reactions are:



Knowing the equivalents of iodine originally added to the solution (mL iodine X normality of iodine) and the equivalents of reducing agent (mL thio X normality thio) required to reduce the remaining iodine after reaction with sulfide allows for the calculation of sulfide by difference according to the following equation.

$$\text{mg S}^-/\text{L} = [(\text{mL I}_2 \times \text{N I}_2) - (\text{mL thio} \times \text{N thio})] \times 16,000 / \text{mL sample}$$

3. Detection Limit

- 3.1. The detection limit for the method is specified at 1 mg/L using the designated normality of the iodine and thiosulfate reagents. A concentration of 1 mg/L is coded into LIM's for the titrimetric procedure.
- 3.2. The actual detection limit is based upon the volume and concentration of reagents used and upon the resolution of the burette employed for the titration. The Class A burettes used are graduated in units of 0.05 mL with a resolution of 0.02 mL. Coupled with a 50 mL sample volume, 0.025 N iodine and 0.025 N sodium thiosulfate, the titration would yield a theoretical detection limit of 0.4 mg/L.

4. Definitions

- 4.1. Sulfide in a water or soil sample exists in a variety of states dependent upon pH and redox potential of the sample matrix. Primary forms include hydrogen sulfide (H₂S), bisulfide (HS⁻), and various metal sulfide complexes which vary widely in their degree of solubility. Sulfide itself (S²⁻) is generally negligible due to the high dissociation constant of hydrogen sulfide. Preserved aqueous samples or distillates will have sulfide present in the form of a metal complex (zinc sulfide).
- 4.2. Total Sulfide includes soluble hydrogen sulfide (H₂S), dissociated HS⁻ and sulfides present as complexes within the suspended phase of the sample (generally metal complexes).
- 4.3. Dissolved sulfide is that sulfide remaining in solution after suspended solids have been removed. Dissolved sulfide can only be determined on samples that have not been preserved with zinc acetate.
- 4.4. Unionized hydrogen H₂S may be calculated from the concentration of dissolved sulfide, the sample pH and the ionization constant for H₂S.



- 4.5. Stoichiometry is the study and calculation of the quantitative relationships of the reactants and products in a chemical reaction. In general chemical reactions will combine in definite ratios of chemical elements. Stoichiometric relationships are those in which the reactants and products exist in direct proportion thus allowing calculation of one component from knowledge of the other.
- 4.6. Redox potential. The term redox comes from oxidation reduction potential (ORP) and is a measure of the electronegativity (Eh) of a system expressed in units of volts or millivolts. Redox potential is a measure of the tendency for a system to either gain or lose electrons when it is subject to change by introduction of a new species. A system with a higher redox potential (positive mv, oxidizing conditions) will have a tendency to gain electrons from new species (i.e. oxidize them and becoming reduced) and a system with a lower redox potential (negative mv, reducing conditions) will have a tendency to lose electrons to new species (i.e. reduce them and become oxidized).
- 4.7. 4.5. Preparation and Analytical batches. Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** (i.e. a sulfide distillation is involved) is composed of one to 20 environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. The twenty environmental samples do not include method blanks, LCS, matrix spikes or matrix duplicates. At a minimum, each batch must include a Method Blank, a Laboratory Control Standard mid-range on the standard curve, and a Detection and Quantitation Limit (DQL) standard prepared at a concentration equal to the low curve point (0.05 mg/L). An analytical batch (i.e. just the colorimetric analysis) is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An **analytical batch** can include prepared samples originating from various quality system matrices and can exceed 20 samples (NELAC 2007. Quality Systems: General Requirements. The NELAC Institute, V1M2 CLN_IS_122807, December, 2007).

5. Interferences

- 5.1. Sulfides are highly volatile and subject to rapid oxidation to elemental sulfur and sulfate. Exercise care in the handling of samples to minimize atmospheric contact
- 5.2. Reduced compounds that react with iodine (e.g. sulfite, thiosulfate) will yield false positive results.



- 5.3. Turbid and/or intensely colored samples can interfere with the detection of the end-point for the titration.
- 5.4. Interferences can be removed by precipitation of sulfide using zinc acetate and then re-suspending the zinc acetate precipitate in clean de-oxygenated water.

6. Safety

- 6.1. Hydrogen sulfide gas is toxic. The gas can inhibit olfactory senses such that exposure to toxic levels may not be apparent to the exposed person(s). The gas can form sulfuric acid in solution leading to corrosive properties. The gas is toxic to fish and other aquatic organisms. There is a local (King County Metro) 10 mg/L sink disposal limit on solutions containing hydrogen sulfide.
- 6.2. Stock and Intermediate sulfide standards and samples with sulfide in excess of 10 mg/L should be oxidized prior to sink disposal. For oxidation, carry out the following operations:
 - 6.2.1. Place spend standards and samples into a suitable 1 liter plastic beaker. Stir and test with lead acetate paper to confirm the presence of sulfide.
 - 6.2.2. Treat with small additions of calcium hypochlorite (bleach) to oxidize the sulfide. Test with lead acetate paper to confirm absence of sulfide.
 - 6.2.3. Dispose of the treated solution to the sink and flush with cold water.
- 6.3. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available.
- 6.4. Eye protection, gloves and lab coats should be worn when handling all samples, spike solutions, acids, caustics and other reagents. Safety glasses must be worn all the time in the Laboratory.
- 6.5. Use CAUTION with strong irritants such as acids, bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals.
- 6.6. Review the Laboratory Safety Manual and the Contingency Plans and Emergency Procedures for a Hazardous Waste Generator.



- 6.7. Use CAUTION with strong irritants such as acids, bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals.
- 6.8. There is a local (King County) 10 mg/L sink disposal limit on solutions containing hydrogen sulfide. Stock and intermediate sulfide standards should be oxidized prior to sink disposal.
- 6.8.1. Carry out the following operations in fume hood.
 - 6.8.2. Place spent standards into a suitable 1 liter plastic beaker. Stir and test with lead acetate paper to confirm presence of sulfide (blackening of the paper).
 - 6.8.3. Treat with small additions of calcium hypochlorite to oxidize sulfide. Test with lead acetate paper to confirm absence of sulfide (a negative test).
 - 6.8.4. Dispose of the treated standards to the sink and flush with cold tap water.
- 6.9. All the non-hazardous wastewater can be dumped into sink if its pH range is 10 to 5. If it is not, the wastewater has to be neutralized before dumping. Review the Laboratory Safety Manual and the Contingency Plans and Emergency Procedures for a Hazardous Waste Generator.
- 6.10. Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.
- 6.11. A reference file of material data handling sheets is kept in the office area, across from the entrance to the tech room (room A316J). Refer to this file for any material you handle. Update this file upon receiving new chemicals or reagents. The MSDS for many chemicals can also be viewed online, at <http://hazard.com/MSDS/>.

7. Equipment and Supplies

- 7.1. Routine laboratory glassware for titration.
- 7.2. Magnetic stirrer with Teflon stir bars
- 7.3. Volumetric flasks
- 7.4. Digital Buret (calibrated)
- 7.5. Glass Buret (Kimax, Class A, 10 / 0.05 mL)
- 7.6. Automatic Pipettors (calibrated)

8. Reagents and Standards



- 8.1. Oxygen-free deionized water. Prepare approximately 2 liters de-oxygenated deionized water (DDIW) by purging with an inert gas (nitrogen or helium) for 15 to 20 minutes. Use this de-oxygenated water to prepare stock, intermediate, and curve sulfide standards. Store in a tightly covered container (i.e. a 2 liter flask with Parafilm seal). The DDIW should be prepared daily. Some reagents and all sample dilutions should be made with DDIW. Open only when needed.
- 8.2. Hydrochloric Acid (6N). Carefully, and with mixing, add 500 mL conc. HCl to 400 mL deionized water. Allow to cool and bring to final volume of 1000 mL.
- 8.3. Sodium Thiosulfate (0.025N). Dissolve 6.205 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 500 mL deionized water. Add 1.5 mL 6N sodium hydroxide and dilute to 1000 mL. Standardize daily against standard potassium bi-iodate solution
- 8.4. Potassium bi-iodate primary standard (0.025 N). Dissolve 0.8124 g $\text{KH}(\text{IO}_3)_2$ in deionized water and dilute to 1000 mL. Record the exact weight of salt used and the prepared volume (mL). Equivalents of bi-iodate = grams $\text{KH}(\text{IO}_3)_2 / 32.495$.
- 8.5. Potassium iodide (KI): Iodine standard (0.025 N). Dissolve 20-25 grams potassium iodide (KI) in 500 mL DI and then add 3.2 g iodine (FW I = 126.9045), when the iodine has dissolved, dilute to 1000 mL. Store in amber glass bottle at room temperature, avoid direct sunlight. Standardize against the standardized sodium thiosulfate solution.
- 8.6. Thyodene Indicator (Fisher T138-100).
- 8.7. Sulfide Standard. Dissolve approximate 0.5 grams crystalline $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (FW = 240.18, 13.35% S) in 100 mL DDIW. Standardize daily against standardized iodine/thiosulfate solutions. Record the exact weight of crystals used as a check on standardization. *NOTE: due to the deliquescent nature of sodium sulfide and the possibility of oxidized coatings on the surfaces of the crystals, you cannot accurately weigh the salt to obtain a value for the sulfide content of the standard solution. The sulfide stock solution must be titrated to determine its actual concentration. The value derived from the weight of salt used is an approximation only and should be around 0.6 mg/mL when prepared as directed.*
- 8.8. DQL Standard. This standard will be used to evaluate detection and quantitation limits according to protocol described in "DQFAC Single Laboratory DL-QL Procedure (Version 2.4)". The initial QL standard will be set at a concentration of 1 mg/L. The benchsheet will calculate the volume of standardized sulfide to be added to 50 mL of de-oxygenated water for the preparation of the standard.

9. Sample Collection, Preservation, Shipment and Storage

- 9.1. See the Sulfide Distillation / Preservation SOP 640S.



- 9.2. Samples for “Total Sulfide” must be preserved at the time of collection. Unless the requested analysis is for soluble or dissolved sulfide, preservation of aqueous samples is accomplished in the field by the addition of zinc acetate resulting in the formation of slightly soluble zinc sulfide (a white colored precipitate). The pH of the sample must also be adjusted to greater than 9 with sodium hydroxide.
- 9.3. Sample bottles sent out to clients will contain the required volume of 2N zinc acetate (0.5 mL or 0.2 mL 2N /100 mL sample volume). To avoid the transport and usage of caustic chemicals by field personnel, sodium hydroxide is added once the samples are returned to the laboratory.
- 9.4. Upon receipt in the laboratory, the samples are adjusted to pH >9 using 6N sodium hydroxide. The lab must verify that the sample bottle is labeled “zinc acetate” and that the pH is >9. Laboratory personnel will add zinc acetate and sodium hydroxide as necessary.

10. Quality Control

- 10.1. Demonstration of Capability. Each analyst using this procedure must perform an initial “Demonstration of Capability” by preparing and analyzing 4 replicates of a QC Check Solution. The recovery (Accuracy) must be within $\pm 10\%$ with a relative standard deviation (Precision) less than 1%.
- 10.2. Method Detection Limit (MDL): MDL are determined as described in ARI SOP 1018S
- 10.3. Reagent Blank (Method Blank). The Method Blank for the Titration is provided by the analysis of DI water blanks during the course of sample analysis. If a distillation procedure is used for a given batch analysis, the method blank will also include a DI water blank run through all steps of the distillation. One method blank will be extracted for each batch of 20 or fewer samples.
- 10.4. Laboratory Fortified Blank (Blank Spike or laboratory Control Sample). The Blank Spike for the Titration is provided by the analysis of DI water spiked with known amounts of sulfide (approximately 15 mg/L). This standard is un-distilled and provides both Initial and continuing verification during the course of the analysis. If a distillation procedure is used for a given batch analysis, a 15 mg/L distillation standard will also be included. This standard is used to verify recovery through all steps of the batch analysis. An additional blank spike for DQL analysis will be prepared at a level of 1 mg/L for on-going analysis of Detection and Quantitation Limits. One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.
- 10.5. Matrix Spike (MS) and Matrix Spike Duplicate (MSD). Matrix spikes will be run for each of 1 in 20 client samples (5% spiking) or as requested by the client. These spikes will be used



to evaluate the accuracy (% Recovery) of the analysis relative to the sample matrix. Spiking will be at a level in the range of 1 to 10 times the sample background or at a minimum of 10 mg/L (10 times the detection limit at 1 mg/L). MSD's for the evaluation of the precision of the analysis (Relative Standard Deviation, RSD) will be run upon request of the client. Otherwise, precision of the analysis will be evaluated by the duplicate analysis of at least one client sample in twenty (5% duplication). Upon client's request one MS/MSD will be extracted for each batch of 20 or fewer samples, providing sufficient sample is available for the analysis.

10.6. Standards, Surrogate Standards. Not Applicable to Iodometric sulfide analysis..

10.7. For every set of samples (not to exceed twenty samples), a reagent blank, two lab fortified blanks and duplicate matrix spikes must be prepared. If there is insufficient sample available to prepare duplicate sample matrix spikes, prepare one reagent blank, two laboratory fortified blanks, and one matrix spike. If there is insufficient sample available to prepare a single sample matrix spike, prepare one reagent blank, two laboratory fortified blanks, and no matrix spike.

11. Calibration and Standardization

11.1. All determinations are documented on the Excel spreadsheet used for daily analysis.

11.2. Standardization of sodium thiosulfate against potassium bi-iodate. This titration would not be necessary if using commercially prepared, certified, 0.025N thiosulfate solution. However, if the normality of the thiosulfate solution came into question, it could be verified using this procedure.

11.2.1. Dissolve approximately 1 g potassium iodide (KI) in 50-100 mL DI contained in a 100 mL beaker.

11.2.2. Add 1 mL 6N HCl and 2 mL 0.025 N bi-iodate solution.

11.2.3. Dilute to 200 mL and titrate with the sodium thiosulfate solution. Calculate Normality of the thiosulfate as

$$11.2.4. \text{ mL bi-iodate} \times \text{Normality bi-iodate} / \text{mL thiosulfate}$$

11.2.5. Calculations are done on the bench sheet automatically. The value should fall within 10% of the prepared normality. If it does not, the bench sheet will flag the occurrence "Chk for Error" and the analyst should evaluate their procedure and/or prepare a fresh thiosulfate solution.

11.2.6. Conduct three replicate titrations and record data on bench sheet.

11.3. Standardization of iodine solution



11.3.1. Add 3 mL of the iodine solution and 0.5 mL of 6N HCl to a 125 mL Erlenmeyer flask

11.3.2. Titrate with standardized thio to light straw yellow color.

11.3.3. Add 1 scoop of thyodene indicator and continue titration to just remove the blue color. Record the mL of thiosulfate used and then repeat the titration 2 more times.

11.3.4. Normality is calculated from the mean of the three replicate determinations as:

$$\text{Normality iodine} = (\text{mL thio} \times \text{Normality thio}) / \text{mL iodine}$$

11.4. Standardization of sulfide stock solution.

11.4.1. The standardization of the stock is based upon iodometric titration in which hydrogen sulfide (H₂S) becomes oxidized to sulfur (S) while iodine (I₂) becomes reduced to iodide (I⁻) according to the following reaction:



11.4.2. When the solution is titrated with standardized thiosulfate reducing agent, any iodine remaining in solution will be reduced to iodide while thiosulfate is oxidized to tetrathionate as follows:



11.4.3. Knowing the equivalents of iodine originally added to the solution (mL iodine X normality iodine) and the equivalents of reducing agent (mL thiosulfate X normality thiosulfate) required to reduce any iodine remaining after reaction with sulfide allows for the calculation of sulfide (16 mg/meq) by difference, as follows:

$$\text{mg S}^-/\text{mL} = \{[(\text{mL I}_2 \times \text{N I}_2) - (\text{mL S}_2\text{O}_3^{2-} \times \text{N S}_2\text{O}_3^{2-})] \times 16\} / \text{mL sample}$$

11.4.4. Proceed as follows:

11.4.4.1. Add 3 mL of standardized iodine solution and 0.5 mL of 6N HCl to a 125 mL Erlenmeyer titration flask. Add 50 mL deoxygenated DI water and mix.

11.4.4.2. Add 1 mL of the sulfide stock solution, mix gently and titrate with standardized thiosulfate to a light straw yellow color.



11.4.4.3. Add one scoop of thyodene indicator and continue titration to just remove the blue color. Record the volume of iodine and the mL of thiosulfate in the appropriate cells of the benchsheet.

11.4.4.4. Repeat the titration 2 more times. Sulfide concentration in the stock solution (mg S/mL) is calculated as the average of the three replicate determinations. This solution will be used for the preparation of the verification standard and for conducting matrix spikes.

12. Procedure

12.1. Obtain a copy of the Sulfide Titration Benchsheet. Manually record all data as you proceed through the analysis.

12.2. Fill the burette with sodium thiosulfate solution. Conduct the standardization routines as described above.

12.3. Prepare Calibration Verification and Distillation Check standards, as necessary, by entering the mL of stock standard added to a specified mL of DDIW water. Use the appropriate cells of the benchsheet to enter these data. Calculations are done automatically.

12.4. Analyze an initial undistilled, calibration verification standard and blank as prepared above. If distillation is used, run the distillation blank and standard as prepared above.

Titrate as follows:

12.4.1. Add 3 mL of iodine and 0.5 mL of HCl to the titration flask.

12.4.2. Next add 50 mL of the blank or standard solution.

12.4.3. If the iodine color disappears, you must add additional iodine and record the total volume of iodine added.

12.4.4. Proceed with the titration by rapidly adding sodium thiosulfate to a light yellow color.

12.4.5. Add 1 or 2 scoops of thyodene and note the dark blue/Black color.

12.4.6. Gradually add thiosulfate to a light blue color. Continue dropwise addition to just discharge the blue.

12.4.7. Record all data and notes on the benchsheet. The sulfide concentration will be calculated upon entry of the data into the computer.



- 12.4.8. Confirm recovery of the verification standard within 10 percent of its prepared concentration.
- 12.5. Proceed with sample analysis only after successful analysis of the verification standard.
- 12.5.1. Add 3 mL of iodine and 0.5 mL of HCl to a clean titration flask.
- 12.5.2. Gently mix the sample to achieve a uniform distribution of any precipitate and add 50 mL to the flask. If a sample aliquot is diluted to 50 mL, you will enter the actual mL of sample used.
- 12.5.3. If the iodine color disappears, you must add additional iodine and record the total volume of iodine added.
- 12.5.4. Proceed with the titration as previously run.
- 12.5.5. Record all data and notes on the benchsheet: The sulfide concentration will be calculated upon entry of the data into the computer. If a sample returns a value < 1mg/L, the colorimetric procedure should be used and the benchsheet will flag it as "Use colorimetric analysis".
- 12.6. If distillation has been used to remove interference and/or concentrate the sulfide, enter the sample and distillation volumes (mL) in the appropriate boxes on the benchsheet, Sample concentration will appear in the column headed "Concentration if distilled" and is calculated as:
- $(\text{mg/L distillate} \times \text{mL distillate}) / \text{mL sample distilled}$**
- 12.7. Matrix QC samples (duplicates and spikes) should have been prepared at the time the sample was distilled.
- 12.8. If distillation is not used, enter a zero in the "Distill Volume" column or leave it blank.
- 12.9. For each batch of samples or job number, process at least 1 duplicate and 1 spiked sample. The format sections of the benchsheet may be copied and pasted into the desired location on the benchsheet. Proceed as follows:
- 12.9.1. enter the sample ID, the "dup" and "ms" will be added automatically.
- 12.9.2. enter the mL of sample titrated and, if distillation was used, the mL of sample distilled.
- 12.9.3. Spiking will be conducted using the Stock Sulfide standard. Enter the mL of stock standard added, sample volume will be automatically assigned based



upon your entries above. Suggested spike levels are 0.2 mL of stock to 50 mL sample. In any event, the spike concentration should be in the range of 1 to 10 times the ambient background concentration.

12.9.4. RPD and % Recovery values will be calculated automatically. If any value is less than 1 mg/L, an "na" flag will appear.

12.10. After every 10 samples, process a blank and check standard. Finish every run with a final blank and check standard.

12.11. Enter data into computer. Place a copy of the computed data reduction into every Job File run. The original is placed in chronological sequence in the Methods file.

13. Review

13.1. The analyst verifies Service Request, reviews the SOP, obtains the appropriate benchsheets and proceeds with the analysis. A handwritten benchsheet is generated and the data are then entered into the computer for data reduction.

13.2. The final computer generated benchsheet, the handwritten copy and the distillation log (if run), are all placed into the job folder. A copy of the handwritten benchsheet and a copy of the final benchsheet are placed into the method folder in chronological sequence.

13.3. The analyst enters the data into LIMs to create the initial analyte worklist.

13.4. The supervisor reviews the job folder for completeness of analysis (all requested parameters have been run) and sufficiency of Quality Control.

13.5. The analysis package and LIMs worklist files are then reviewed by the Conventional QA reviewer. Worklists are distributed and final LIMs report printed.

13.6. The final report is reviewed for accuracy and completeness and then signed by the Conventional QA reviewer. The report is then delivered to the Project Manager

14. Data Analysis and Calculations

14.1. See "Calibration and Standardization".

15. Method Performance

15.1. A detection and quantitation study will be conducted with undistilled Method Blanks and the DQL standard at 1 mg/L. These will be used to calculate the detection and quantitation limits for the analysis of sulfide using the titrimetric procedure. Calculated limits will be evaluated relative to the method specified limit of 1 mg/L.

16. Pollution Prevention



16.1. These procedures may result in the generation and identification of aqueous wastes having sulfide concentrations in excess of 10 mg/L. These will be collected and treated to oxidize contained sulfide prior to sink discharge.

17. Data Assessment and Acceptance Criteria for QC Measure

17.1. If the initial verification standard (ICV) and blank (ICB) are not within control limits ($\pm 10\%$ for the standard and <1.0 mg/L for the blank), the analysis will stop. The analyst will immediately re-analyze the out-of-control sample to confirm the original observation. If re-analysis returns an acceptable result, analysis will proceed. If re-analysis confirms the out-of-control condition the analyst must evaluate the source of the problem. New solutions (verification standard and/or blank) will be prepared and the verification repeated. Do not proceed with sample analysis until the titration has been verified.

17.2. If either the distilled standard or blank returns a value outside the respective control limits an error message will appear. Otherwise, the % recovery will appear. If the distilled standards are not within control limits, the analyst will first re-analyze the LCS sample distillate to confirm the out lying value. If confirmed, the error is most likely due to recovery from the distillation process (you should have just confirmed that the titration was OK!). In this case, all samples associated with that distillation batch are suspect. The analyst should notify the supervisor of the recovery error and allow the supervisor to determine whether the entire batch should be re-distilled. If insufficient sample remains, all samples associated with that distillation should be flagged with a warning regarding possible recovery error.

17.3. If any of the continuing verification standards or blanks returns an out-of-control value the analysis will be immediately stopped and the problem identified. The analyst should first re-analyze the standard or blank to confirm its outlying value. If confirmed, the analyst must re-standardize the reagents, verify the titration and re-analyze all samples preceding the out-of-control condition and after the last in-control condition. Samples must be bracketed by in-control verification standards and blanks.

17.4. For replicate analysis, if the RPD for duplicate determinations is greater than 20%, the analyst should re-analyze both samples to confirm the initial values. If either



concentration is less than 5X the detection limit, then the absolute difference between the two should be less than or equal to the detection limit.

17.4.1. If the out-of-control values are confirmed, consult the supervisor and process one additional replicate, as necessary. Report the results for triplicates along with the relative standard deviation (RSD) and note on the analyst's comment sheet triplicates were run due to the out-lying RPD.

17.5. If the matrix spike returns a value less than the titrated sample concentration, a new matrix spike should be prepared and distilled (as necessary) at a level of 1 to 10 times the sample concentration. If the matrix spike returns an out-of-control value, the analyst should first re-analyze the distillates to confirm the values. If the out-of-control values are confirmed, consult the supervisor and process an additional spike, as necessary. Report the results for both spikes along with the percent recovery and note on the analyst's comments sheet that additional spikes were run due to an initial outlying recovery.

18. Corrective Actions for Out of Control Events

18.1. As defined above

19. Contingencies for Handling Out-of-Control or Unacceptable Data

19.1. In the event of significant batch QC failure, analysis will stop and the analyst will perform corrective action as discussed above.

19.2. In general, sample data associated with out-of-control batch QC sample results (Method blanks, calibration verification and Laboratory Control Samples) will not be reported. Re-runs will be conducted based upon availability of sample volume. If insufficient sample remains or the remaining sample has been compromised by other withdrawals from the sample bottle or by holding time, the client will be notified to determine an appropriate course of action.

19.3. Batch analysis is not controlled by Matrix Specific QC and failing matrix QC does not reflect a failure in the analytical protocol. Failing matrix QC will be reported to the client along with supporting information as may be available to qualify the result.

19.4. All QC failures and associated corrective actions will be documented on the Yellow Corrective Action Sheets.

20. Waste Management



20.1. These procedures may result in the generation and identification of aqueous wastes having sulfide concentrations in excess of 10 mg/L. These will be collected and treated to oxidize contained sulfide prior to sink discharge.

21. Method References

21.1. EPA 376.1. Sulfide, Method 376.1 (Titrimetric, Iodine). Methods for the Chemical Analysis of Water and Wastes. EPA /600/4-79020

21.2. SW-846. Titrimetric Procedure for Acid Soluble and Acid Insoluble Sulfides, Method 9034, USEPA. Test Methods for Evaluating Solid Waste.

21.3. Standard Methods, 4500-S₂⁻ F-00. Iodometric Method. Standard Methods for the Examination of Water and Wastewater.

22. Appendices

22.1. Titrimetric Sulfide Excel Benchsheet



Appendix 22.1:

SULFIDE BENCHSHEET (TITRATION)		Date	Analyst						
SM 4500-S2- F-00 Iodometric Method		Distillation							
If distilled, specify Procedure:		Finish							
Buret used for titrations:									
CalibrationData		ZnOAc:							
1. Standardization of sodium thiosulfate titrant									
Thiosulfate ID: _____									
Bi-iodate ID: _____									
<i>Titration of bi-iodate with thiosulfate</i>									
Stock bi-iodate = 0.8116 grams to 1000 mL	mL bi-iodate =	3.00	3.00	3.00					
Normality = 0.025	mL thiosulfate =	3.15	3.12	3.13					
<i>Normality thiosulfate = (mL bi-iodate*normbio) / mL thiosulfate =</i>									
		0.024	0.024	0.024					
0.024									
2. Normality of Iodine Soln									
Iodine ID: _____									
<i>Titration of Iodine with thiosulfate</i>									
	mL iodine =	3.00	3.00	3.00					
	mL thiosulfate =	3.080	3.060	3.050					
<i>Normality iodine = (mL thiosulfate*nthio) / mL iodine =</i>									
		0.025	0.024	0.024					
0.024									
3. Standardization (Sulfide Stock Solution)									
Stock ID = 0066-9									
Approx conc in 100ml									
g Na2S = 0.7626 mg /mL = 1.018	mL Standard =	1.00	1.00	1.00					
	mL iodine =	3.00	3.00	3.00					
	mL thiosulfate =	1.16	1.20	1.16					
<i>Sulfide (mg/mL) = ((mL iodine*ni)-(mL thio *nthio))*16 / mL standard =</i>									
		0.728	0.713	0.728					
0.723									
4. Verification Standard									
Add 1.0 mL Stock to 50 mL DI water	CV = 14.5	mg/L sulfide							
5. DQL Standard									
Add 0.1 mL Stock to 50 mL DI water	DQL = 1.0	mg/L sulfide confirm 1.0							
6. Distillation Standard									
Add 1.0 mL Stock to 50 mL DI water	Dist Chk = 14.5	mg/L sulfide							
SAMPLE DATA									
<i>Calculation: mg/L = (((mL I X N I) - (mL thio X N thio)) X 16,000) / mL sample</i>									
	DISTILL DATA		TITRATION DATA						
SAMPLE ID	Sample Volume (mL)	Trap Volume (mL)	Sample Volume (mL)	IODINE ADDED (mL)	Thiosulfate TITRANT (mL)	CONC (mg S/L)	Concentration If distilled (mg S/L)		
ICB	50.0	50	50.0	3.0	3.05	0.1	0.1		
ICV	50.0	50	50.0	3.0	1.10	15.0	15.0		103.88%
DQL	50.0	50	50.0	3.0	2.93	1.0	1.0		102.03%
Dist Blank	50.0	50	25.0	3.0	3.05	0.2	0.2		
Dist Check	50.0	50	25.0	3.0	2.10	14.7	14.7	102%	101.94%
CCB									
CCV									



Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

GC-MS Analysis of PAH/PCP Method 8270E – Selective Ion Monitoring (SIM)

**SOP 801S
Revision 012**

**Revision Date: 6/25/19
Effective Date: 6/25/19**

Prepared by:

Peter Kepler, Van Spohn

Approvals:

A handwritten signature in blue ink that reads "Brian N. Bebee".

Brian N. Bebee, Laboratory Section Manager

A handwritten signature in blue ink that reads "Bob Congleton".

Bob Congleton, Quality Assurance Manager



GC-MS Analysis of PAH/PCP Method 8270 – Selective Ion Monitoring (SIM)

1. Scope and Application

1.1. This procedure utilizes Method 8270E acquiring in the selected ion mode (8270E sim) to determine the concentration of selected semi volatile organic compounds in extracts prepared from various types of sediments, soils, solid waste matrices, tissues, and waters. See Appendix 20.2 for the compounds that may be determined using this method. EPA Method 8270E will be reported for State of California work.

1.2. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including the EPA SW-846 methods and the Department of Defense Quality Systems Manual (DoD-QSM). Some text is directly from the referenced documents. The table in Appendix 20.1 outlines ARI’s routine in-house acceptance criteria. DOD-QSM acceptance criteria are shown in Appendix B of DOD-QSM 5.3. Acceptance criteria for projects requiring modified DOD-QSM criteria are provided by the project manager and are project specific. Analysts are responsible for determining which QA program is applicable to a set of samples prior to beginning analyzes and complying with all project specific analytical requirements.

1.3. The reference methods for this procedure are listed in Section 19.

1.4. Method 8270E sim is used primarily in the analysis of polynuclear aromatic hydrocarbons (PAH), and Pentachlorophenol (PCP). Appendix 20.2 includes a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system. Detailed lists of project-specific compounds may be found in the LQAP for a given project. Other compounds may be analyzed if specifically requested.

1.5. Pentachlorophenol is an active analytes and subject to erratic chromatographic behavior, especially if the GC system is contaminated. Derivatization of PCP with Diazomethane is utilized by this method to reduce activity.

1.6. Estimated Method Reporting Limits (MRL)

Analysis code	Water MRL	Soil MRL
8270D-sim PAH	0.1µg/L	5.0µg/kg
8270D-sim PAH/PCP	0.1µg/L 0.5µg/L for PCP	5.0µg/kg 25µg/kg for PCP
8270D-sim PAH low	0.01µg/L	0.5µg/kg
8270D-sim Alkyl PAH	0.1-1.0µg/L	5.0-50µg/kg



1.7. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.8. ARI routinely performs Method Detection Limit (MDL) studies for each extraction and analytical method performed using this SOP. The results of these studies help define the reporting limits of data generated. The results are kept by the QA department, and are distributed to the bench chemists and the ELEMENT administrator. For current MRLs and MDLs, see Element

2. Summary of Procedure

2.1. An aliquot of sample for matrices suitable for analysis by GC/MS SIM) is extracted by a matrix appropriate sample technique. Usually this aliquot will be 500 mL for aqueous samples and 10 grams for solid samples. Sample extraction will typically be by either continuous liquid-liquid extraction or separatory funnel extraction for aqueous samples and microwave for solid samples. The extracted sample is subjected to any appropriate cleanup and then concentrated. Final extract volume will normally be 0.5 mL for aqueous samples and either 0.5 or 1mL for solid samples. The extract is then delivered to Refrigerator 15.

2.2. After the instrument lab has assumed custody of the sample, it is injected onto the column of a properly calibrated GC/MS system for chromatographic determination. If the analyte PCP is to be determined, the extract is derivatized using diazomethane before chromatographic determination. Analyte identification is performed using the relative time of elution (RRT, relative to the appropriate internal standard) and comparison of mass spectra to a spectral library. Quantitation is performed by comparing the detector responses of each analytes' characteristic mass ion and internal standard characteristic mass ion to the responses of these ions in a calibration curve containing those analytes at known concentrations.

3. Definitions

3.1. SIM - Selected Ion Monitoring- a mode of data acquisition wherein the mass spectrometer is programmed to scan for a limited number of specific masses, increasing the amount of time spent searching for each of these masses.

3.2. Initial Calibration Verification (ICV): A process used to verify that the current instrument calibration is acceptable at the beginning of an analytical sequence

3.3. Continuing Calibration Verification (CCV): A process used to verify that the current instrument calibration is acceptable during or at the end of an analytical sequence.

3.4. Decafluorotriphenylphosphine, (DFTTP): used to demonstrate acceptable tuning parameters.



- 3.5. Method detection Limit (MDL): The lowest result that can reliably be distinguished in a matrix from a blank.
- 3.6. Extracted Ion Current Profile (EICP): A plot of the abundance of a specific ion as a function of time
- 3.7. Second Source Verification (SCV): A process used to verify that the current instrument verification is acceptable.
- 3.8. Internal Standard (IS): Internal standards are compounds added to each standard, sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of these internal standards.
- 3.9. Blank Spike (BS): A sample matrix, free from the analytes of interest, spiked with verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system.
- 3.10. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, a BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS.
- 3.11. Laboratory Information Management System (LIMS): Software used to compile and report final chromatographic data. The use of the term "Element" refers to the LIMS system.
- 3.12. Limit of Detection (LOD): The lowest result that can be reported while meeting method precision and accuracy requirements.
- 3.13. Method Reporting Limit (MRL): The lowest result that may be reported unqualified based upon the lowest curve point.
- 3.14. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method.
- 3.15. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision.
- 3.16. Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and interferences. It is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures.
- 3.17. Organic-free reagent water (OFW): Organic-free reagent water, all references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.
- 3.18. Method Detection Limit (MDL) spike: A matrix spike prepared at the reporting limit and used to calculate the MDL.



- 3.19. Reconstructed Ion Current (RIC): A plot of the total instrument response versus time
- 3.20. Relative Retention Time (RRT): The elution time of an analyte relative to the elution time of its associated internal standard
- 3.21. Instrument Blank (IB): Clean solvent containing internal standards at the appropriate level for the analysis is analyzed using the same conditions as a regular sample. An instrument blank is analyzed to detect and/or remove sample carryover from one analysis to another.
- 3.22. Surrogate (SURR): A substance with properties that mimic analytes of interest. It is unlikely to be found in environment samples and is added to them to monitor extraction efficiency.
- 3.23. Low level calibration verification (LCV): Lowest calibration standard used for an initial calibration.
- 3.24. Target software (TARGET): Chromatographic analysis software from Thermo Thru-Put version 4.14.

4. Interferences

- 4.1. Extraction Interferences: Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem. Most commonly this will involve contamination with the phthalate esters.
- 4.2. Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride followed by baking the glassware at 500 degrees centigrade overnight.
- 4.3. High purity reagents must be used to minimize interference problems.
- 4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, or the detector shows saturation due to analytes present in a sample, subsequent samples should be scrutinized for cross contamination.
- 4.5. Matrix interferences may be removed using sample clean-ups depending on the list of target analytes, these may include (but are not limited to) the use of solid phase extraction clean-up, silica gel, absorption chromatography or gel permeation chromatography. See the appropriate extractions SOPs for clean-up applicability to matrices or target analytes.
- 4.6. Deactivated glassware must be used when extracting samples for the lower level PAH analysis due the activity of these Targets at trace levels.

5. Safety



- 5.1. The toxicity and carcinogenicity of each reagent used in this method is not precisely defined. However, all compounds and solutions should be treated as health hazards, and exposure of these chemicals to skin and clothing should be minimized to the lowest possible level by whatever means available.
- 5.2. Contact with all chemicals should be minimized by the used of nitrile gloves, safety glasses, and laboratory coats.
- 5.3. All materials should be handled in the fume hoods to avoid exposure to fumes.
- 5.4. All GC split vents and vacuum exhaust are connected to an exhaust vent or charcoal filter.
- 5.5. Special care should be taken when derivitizing samples for PAH/PCP analysis. The Diazomethane gas produced by the reaction of Diazald, sodium hydroxide, and methanol is both toxic and explosive. The derivatization **MUST** take place within a fume hood, and the analyst should work with the sash down and full protective wear.
- 5.6. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult with SDS sheets for all chemicals handled. SDS are available on-line at www.msds hazcon.com.

6. Equipment and Supplies

6.1. Gas chromatograph/mass spectrometer system

- 6.1.1. Gas chromatograph - An analytical system with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, autosampler, and gases. The capillary column should be directly coupled to the source of the mass spectrometer.
- 6.1.2. Fused-silica capillary column - 30 m x 0.25 mm ID (or 0.32 mm ID) 0.25 -0.5 μ m film thickness. (Restek Rxi-17SIL MS or equivalent).
- 6.1.3. Mass spectrometer - Capable of scanning from 35 to 500 AMU every 1 second or less. The mass spectrometer must can produce a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all the criteria in Appendix 20.3 when 1-2 μ L of the GC/MS tuning standard is injected through the GC (50 ng or less of DFTPP).
- 6.1.4. GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration for each compound of interest and achieves acceptable tuning performance criteria. For a capillary column, the interface is usually capillary-direct into the mass spectrometer source.

6.2. Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on electronic media of all mass spectra obtained throughout the duration of the chromatographic program.



- 6.2.1. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits.
- 6.2.2. The data system should be equipped with the most recent version of the EPA/NIST Mass Spectral Library.
- 6.2.3. The data must be securely stored for at least seven years from date of acquisition in Target.

7. Reagents and Standards

- 7.1. Stock standard solutions (1000 - 10,000 µg/L) - Standard solutions can be prepared from neat standards or purchased as certified solutions. Certificates of analysis for all purchased neats and solutions are kept electronically in Element.
- 7.2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 7.2.1. All Components and reagents used for any standard preparation are entered in Element
- 7.2.2. The laboratory should have high purity acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, methanol and other appropriate solvents for preparing standards.
- 7.2.3. Organic-free reagent water - All references to water in this method refer to ASTM Type 1 18 megaohm organic-free reagent water.
- 7.2.4. Neat standards are not assigned an expiration day and are considered never expired regardless of what is shown on the standard certificate.
- 7.2.5. Stock Standard Preparation
- 7.2.6. Prepare stock standard solutions by accurately weighing about 0.2500 g of pure material. Dissolve the material in pesticide quality methylene chloride or other suitable solvent and dilute to volume in a 25 mL volumetric flask. Larger or smaller volumes can be used at the convenience of the analyst. When compound purity is assayed to be 97% or greater, the weight may be used without correction to calculate the concentration of the stock standard.
- 7.2.7. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.
- 7.2.8. Transfer the stock standard solutions into amber bottles with Teflon lined screw-caps. Store at >0 to 6°C and protect from light.



- 7.2.9. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.
- 7.2.10. Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.
- 7.2.11. Stock standard solutions must be replaced 1 year after being de-ampullated.
- 7.2.12. A PDF record of analysis must be attached to the standard in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.
- 7.3. Internal Standard Stock Solution - The internal standards employed are naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12. Other compounds may be used as internal standards if the method requirements are met. Dissolve 0.250 g of each compound with a small volume of methylene chloride or appropriate solvent. Transfer to a 250mL volumetric flask and dilute to volume with methylene chloride. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d12. The resulting solution will contain each standard at a concentration of 1,000µg/ml.
- 7.3.1. Each 0.1 mL aliquot of the sample extract undergoing analysis should be spiked with 2µL of the internal standard solution, resulting in a concentration of 2ng/µL of each internal standard (for example, when preparing a sample aliquot of 0.3ml, spike the extract with 6µl of the internal standard stock). Low PAH internal standard is at 0.2µg/mL final concentration
- 7.4. Surrogate Stock Standards - The surrogate standards employed are 2,4,6-tribromophenol, 2-Methylnaphthalene-d10, Fluoranthene-d10, and Dibenzo(a,h)anthracene-d14.
- 7.5. Prepare a stock solution containing all the PAH base surrogates 2-Methylnaphthalene-d10, Fluoranthene-d10, and Dibenzo(a,h)anthracene-d14 by dissolving 250mg of each into a 50 mL volumetric flask. Bring the solution up to volume with methylene chloride. The resulting solution will contain the surrogates at 5000µg/ml.
- 7.6. Prepare a stock solution containing 2,4,6-tribromophenol by dissolving 250mg of each into a 50mL volumetric flask. Bring the solution up to volume with methylene chloride. The resulting solution will contain the surrogate at 5000µg/ml.
- 7.7. Working solutions- working standards are prepared from stock standards or purchased as commercially certified mixtures.
- 7.7.1. Working standards expire on the date of expiration of the stock solutions they are made from, on the manufacturer's certified expiration date or within one year from date of preparation, whichever comes first. They must be replaced now.
- 7.7.2. Working standard solutions must be replaced 1 year after being de-ampullated.
- 7.7.3. Working standards must be stored at >0 to 6°C and protected from light.



7.7.4. Working standards should be checked frequently for signs of concentration or degradation.

7.7.5. A PDF record of analysis must be attached to the standard (non-virtual only) in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.

7.8. Surrogate working standards

7.8.1. Surrogate calibration standard- the surrogate calibration standard is prepared by diluting the surrogate stock in methylene chloride such that the concentration of each analyte is 50µg/ml (5µg/mL for low PAH) This solution is used to calibrate the instrument to quantitate surrogate concentrations.

7.8.2. Surrogate spiking standard- the surrogate spiking standard is prepared by diluting the surrogate stock such the concentrations of the surrogates are 15-75µg/mL (1.5-7.5 for low PAH) prepared in acetone. This solution is used to spike all extracted samples and QC samples with surrogates.

7.9. Matrix spike working standards- the matrix spiking standards are used to prepare MS/MSD sets as well as BS/BSDs.

7.9.1. The matrix spiking solution is purchased commercially and contains all the analytes in acetone. The concentration of each analyte is 15µg/mL (1.5µg/ml for low PAH)

7.9.2. If alternative matrix spiking solutions are required (for example, a matrix spike containing an extra analyte not contained in the full spike) an appropriate concentration should be determined, and the solution prepared in a water-soluble solvent (usually methanol or acetone) at that concentration.

7.9.3. Calibration working standards- the standards used to prepare calibration curves are usually purchased as commercially certified mixtures. Working calibration solutions are prepared by diluting these standards in methylene chloride such that the concentration of each analyte is 50

7.9.4. Calibration working standards for PCP/PAH analysis are prepared in Hexane saturated with Diazomethane gas to derivatize the PCP to a methyl ester.

7.9.5. GC/MS working tuning standard- a tuning standard should be prepared containing 500µg/mL each of DFTPP (Decafluorotriphenylphosphine); p,p'-DDT, Pentachlorophenol, and Benzidine. This should be used to prepare the 25µg/mL or less standard used to tune the instrument in cases where the mid-level calibration standard is acquired in selected ion mode.

7.9.6. Derivatization apparatus and reagents for Diazomethane gas (PCP analyses only)

7.9.6.1. A 60 mL VOA vial, with cap and Teflon lined septum.

7.9.6.2. A Teflon tube pushed through the septum of the 60ml vial



7.9.6.3. Diazald

7.9.6.4. 3M NaOH in Methanol

8. Sample Collection, Preservation, Shipment, Storage, Holding Times and Disposal.

8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 °C.

8.2. Samples must be stored at ARI, at >0 to 6 °C until final disposal.

8.3. Samples must be extracted within holding times determined from the day of sampling. The standard holding time for water samples is seven days. The standard holding time for solid samples is 14 days.

8.4. Solid and sediment samples may be stored at -10 to -20 °C to extend the holding time to one year.

8.5. Extracts are delivered to Refrigerator 15 in the instrument laboratory by extractions technicians.

8.5.1. Analysts in the instrument lab assume custody of the sample extracts and then move them into Refrigerator 18 in a bin assigned in Element

8.5.2. Extracts must be stored at >0 to 6 °C and protected from light.

8.5.3. Extracts must be analyzed within 40 days of extraction.

8.5.4. Extracts must be stored in their assigned Element bin.

8.5.5. Extracts may be deposited 40 days after the analysis has been completed and the Element bin will be recycled for future use.

8.5.6. Extract will be disposed in the large blue barrel in the satellite accumulation area designated for extract vials. Disposed extracts are now marked in Element as disposed.

9. Quality Control

9.1. Quality control requirements related to tuning, initial and continuing calibration are detailed in Section 10 of this document.

9.2. Surrogates

9.2.1. Surrogate standards are added to every sample and associated QA (MB, BS, MS etc.) prior to extraction to monitor extraction efficiency.

9.3. Method Blanks and Instrument Blanks

9.3.1. A method blank is a volume of a clean reference matrix (OFW or sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

9.3.2. Method blank extraction and analysis are performed as follows:



9.3.2.1. MBs must be processed with every batch of 20 or fewer samples of similar matrix

9.3.2.2. Method blanks should be analyzed on each GC/MS system used to analyze associated samples. When a method blank shows contamination the blank should be re-vialled and reanalyzed to confirm the contamination.

9.3.2.3. A method blank for water samples consists of 0.5-1L volume of reagent water. For medium and low-level soil/sediment samples, a method blank consists of 1g to 10g of sodium sulfate. Extract, concentrate, cleanup and analyze the method blank according to procedures used for water; tissue; or solid (soil or sediment) samples.

9.3.2.4. An instrument blank consisting of internal standard and clean solvent is analyzed prior to sample analysis after the ICV when a method blank is not analyzed.

9.4. Blank Spikes (BS)

9.4.1. To evaluate the accuracy of the analytical method independent of matrix-related effects, a matrix-specific blank spike (BS) must be included in each preparation batch. The BS must contain all surrogates and target analytes required by the method.

9.4.2. In instances where insufficient sample volumes exist to perform an MS/MSD analysis, an BS/BSD may be performed upon client request to assess the precision of the analytical method. A BSD, when required, is prepared and analyzed identically to the BS.

9.4.2.1. The recovery of each blank spike target must be evaluated and reported

9.4.2.2. The RPDs between the BS/BSD samples must be measured and reported.

9.4.2.3. Evaluate the BS/BSD RPD and note any deviation >30% in the reviewer checklist.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. To evaluate the effects of the sample matrix on the methods used for ABN analyses, a mixture of all target compounds is spiked into two aliquots of a sample and analyzed using the same method as all other samples.

9.5.2. A matrix spike and matrix spike duplicate should be extracted and analyzed for every 20 field samples of a similar matrix or whenever samples are extracted by the same procedure.

9.5.2.1. The recovery of each matrix spike must be evaluated and reported.

9.5.2.2. The RPDs between the MS/MSD samples must be measured and reported.

9.5.2.3. Evaluate the MS/MSD RPD and note any deviation >30% in the reviewer checklist.

9.5.3. As part of a client's QA/QC program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to the laboratory for analysis. The laboratory will not perform MS/MSD analysis on any of the field QC samples.

9.5.4. If a client designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the laboratory shall choose



another sample on which to perform an MS/MSD analysis. At the time the selection is made, the laboratory shall notify the client that insufficient sample was received and identify the sample selected for the MS/MSD analysis. The rationale for the choice of another sample other than the one designated by the client shall be documented in the narrative.

9.5.5. If there is insufficient sample to perform a requested MS/MSD, the laboratory should contact the client to inform them of the situation. The client will either approve that no MS/MSD is required, require that a reduced sample aliquot be used for the MS/MSD analysis or request that a BS/BSD (See Section 9.4.2) analysis be performed. The laboratory shall document the client's decision in the narrative.

9.5.6. Dilution of MS/MSD extracts to get either spiked compounds or native analytes on scale is not necessary.

9.5.7. Duplicate Analysis

9.5.8. When mandated by project-specific requirements, a duplicate analysis of a given sample may be performed as an independent assessment of method precision. A duplicate consists of an independently prepared second aliquot of a given sample carried through the entire analytical process.

9.5.9. The RPDs between the Sample and Sample duplicate must be measured and reported.

9.5.10. Evaluate the Sample and Sample duplicate RPD and note any deviation >30% in the reviewer checklist.

9.5.11. When mandated by project-specific requirements, an SRM (Standard Reference Material) sample will be analyzed as an independent assessment of method performance.

9.5.12. The recovery of each target in the SRM must be compared to the true value provided by the SRM provider to be evaluated and reported. Any targets not meeting the recovery limits will require corrective action.

9.6. Internal Standard Response (EICP) area and retention time data must be evaluated during and/or immediately after the analysis. The response for the ICV internal standards must be within the inclusive range of -50.0 to +100.0 percent of the response of the internal standards in the most recent mid-point of the initial calibration analysis. The response for each sample, associated batch QC, and the CCV internal standards must be within the inclusive range of -50.0 to +100.0 percent of the response of the internal standards in the most recent ICV. The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the ICV and the last CCV run or from the middle point of the initial calibration. The retention time shift for each of the internal standards must be within ± 0.166 minutes (10 seconds) between samples/associated batch QC and the ICV.



9.7. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for BS/BSD are statistically generated on a periodic basis. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. All analysts using this SOP must use it in conjunction with Control Limit documentation to assess data quality and any possible need for corrective actions. Current control limits may be found in the Element.

9.8. Initial Demonstration of Proficiency- Each analyst must demonstrate initial proficiency with each sample preparation and determinative method combination performed, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat these procedures whenever new staff is trained or significant changes in instrumentation or procedure are made. See EPA Methods 8000 and 3500 for information on how to accomplish this demonstration.

10. Calibration and Standardization

10.1. Calibration standards

10.1.1. A minimum of six calibration standards should be prepared.

10.1.2. One of the calibration standards must be at the reporting limit, while the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. The lowest calibration point of each individual target analyte becomes the reporting limit for that target. All target analytes quantitated below the lowest calibration point for any target analyte must be qualified with a "J" flag to show the quantitation is below the working range of the curve and therefore is an estimate.

10.1.3. Calibration standards are prepared from the working calibration solutions at concentrations of 0.1, 0.5, 1.0, 2.5, 5.0 and 10µg/ml.

10.1.4. Low PAH calibration standards are prepared from the working calibration solutions at concentrations of 0.01, 0.05, 0.1, 0.25, 0.5 and 1.0µg/ml.

10.1.5. PAH/PCP standard Concentrations standards are prepared from the working calibration solutions at concentrations of 0.1, 0.5, 1.0, 2.5, 5.0 and 10µg/mL with PCP and Tribromophenol at 0.5, 2.5, 5.0, 12.5, 25.0 and 50µg/ml.

10.1.6. The calibration curve standards are made as needed and the internal standard solution is added prior to analysis.

10.1.7. Each standard must contain all analytes requested for a specific project, and no target analyte may be quantitated without first being calibrated.



10.1.8. All standards should be stored at >0 to 6°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The ICV/CCV standard should be prepared weekly with the preparatory date on the label and stored at >0 to 6°C. If the analyst suspects degradation the standard should be replaced.

10.1.9. The calibration standards are analyzed, and a minimum of six curve points are used to calibrate each analyte as follows:

Compounds that are routinely calibrated at 10, 5, 2.5, 1.0, 0.5, and 0.1 µg/ml		
Naphthalene	Benzo(b)thiophene	2-methylnaphthalene
1-methylnaphthalene	2-Chloronaphthalene	Biphenyl
2,6-Dimethylnaphthalene	Acenaphthylene	Acenaphthene
Dibenzofuran	2,3,5-Trimethylnaphthalene	Fluorene
Dibenzothiophene	Phenanthrene	Anthracene
Carbazole	1-methylphenanthrene	Fluoranthene
Pyrene	Benzo(a)anthracene	Chrysene
Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(j)fluoranthene
Benzo(e)pyrene	Benzo(a)pyrene	Perylene
Dibenzo(a,h)anthracene	Indeno(1,2,3-cd) pyrene	Benzo(g,h,i)perylene
2-methylnaphthalene-d10 (SS)	Fluorene-d10 (SS)	Dibenzo(a,h)anthracene-d14 (SS)

Compounds that are routinely calibrated (Low PAH) at 1.0, 0.5, 0.25, 0.10, .05, and .01 µg/ml		
Naphthalene	Benzo(b)thiophene	2-methylnaphthalene
1-methylnaphthalene	2-Chloronaphthalene	Biphenyl
2,6-Dimethylnaphthalene	Acenaphthylene	Acenaphthene
Dibenzofuran	2,3,5-Trimethylnaphthalene	Fluorene
Dibenzothiophene	Phenanthrene	Anthracene
Carbazole	1-methylphenanthrene	Fluoranthene
Pyrene	Benzo(a)anthracene	Chrysene
Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(j)fluoranthene
Benzo(e)pyrene	Benzo(a)pyrene	Perylene
Dibenzo(a,h)anthracene	Indeno(1,2,3-cd) pyrene	Benzo(g,h,i)perylene
2-methylnaphthalene-d10 (SS)	Fluorene-d10 (SS)	Dibenzo(a,h)anthracene-D14 (SS)

Compounds that are routinely calibrated (PCP/PAH) at 50, 25, 12.5, 5.0, 2.5, and 0.5 µg/ml		
---	--	--



Pentachlorophenol	Tribromophenol (SS)	
-------------------	---------------------	--

10.2. MS tuning- prior to initial calibration, each GC/MS system must be hardware-tuned to meet the criteria in Appendix 20.3 for a 50ng total or less injection of DFTPP. Analyses must not begin until all these criteria are met. Evaluate the ion abundance by using any of the following three scenarios: Use a single spectrum at the apex of the DFTPP peak, use the mean of the apex and the preceding and following scans (the mean of a symmetric pattern of scans about the apex), or use the average across the entire peak. The tune must satisfy the ion abundance acceptance criteria listed in Appendix 20.3. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. Do not subtract part of the DFTPP peak.

10.2.1. The GC/MS tuning standard is also used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD must not exceed 20%. DDT percent breakdown is calculated by dividing the sum of the DDD and DDE areas by the sum of the areas of DDT, DDE and DDD and then multiplying this result by 100. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. Peak tailing factors will be calculated using the procedure detailed in Appendix 20.6 using a Target macro to calculate the tailing factor.

10.2.2. Tailing factors must be <2.0 for benzidine and pentachlorophenol. See Section 16.3 for procedures on how to bring the instrument into compliance for tuning, DDT breakdown, or peak tailing factors.

10.2.3. The tune standard is run in the full scan mode separate from the calibration standards and must meet all ion abundance criteria shown in Appendix 20.3 before the initial calibration may continue.

10.2.4. All analyses performed in the sequence following the tune standard must use the same instrument parameters (GC program, MS parameters, etc.)

10.3. Calculate Relative Response Factors (RFs)

10.3.1. Evaluation of the initial calibration begins by calculating response factors (RRFs) for each analyte in each calibration standard. The formula for calculating each response factor involves the areas of the quantitation ion of the analyte and its associated internal standard as well as the concentration of the analyte and internal standard in the calibration standard according to the formula:

$RRF = (As * Cis)/(Ais * Cis)$
Where
As = The peak area of the analyte or surrogate



Cis = The concentration of the internal standard in µg/L
Ais = The peak area of the internal standard
Cs = The concentration of the analyte or surrogate in µg/L

10.3.2. The RRF for each analyte should meet the advisory RRF listed for the analyte in Appendix 20.2 for each of the calibration levels. Special care should be taken to monitoring the RRF in the lowest calibration standard to ensure adequate sensitivity at the reporting limit. The minimum RRF for any target for all calibration levels is 0.01

10.3.3. Analytes which fail the minimum RRF guidance listed in Section 10.3.2 should be noted in the reviewer checklist.

10.4. Analyte Linearity.

10.4.1. After measuring the relative response factors for each analyte in each of the calibration standards, the linearity of the analyte must be measured.

10.4.2. The average RRF should be calculated for each compound using the formula

$RRF_{av} = \frac{\sum RRF_i}{n}$
Where
RRFi = the RRF of the analyte in each calibration level
n = the number of calibration levels (usually six or five)

10.4.3. The percent relative standard deviation (% RSD) should also be calculated for each compound using the formula

$RSD = \frac{100 * SD}{RF_{av}} = 100 * ((\sum (RRF_i - RRF_{av})^2) / (n-1))^{1/2} / RRF_{av}$
Where
RRFi = the RRF of the analyte in each calibration level
RRFav = the average RRF of the analyte over the entire calibration range
n = the number of calibration levels (usually six or five)

10.4.4. The % RSD should be less than 15% for each compound, in which case the average response factor will be used for quantitation as it is considered constant over the calibration range. Target analytes that exceed 15% RSD will attempt to utilize an alternative calibration option.

10.4.4.1. Before attempting an alternative calibration model, the analyst should ensure that the RSD failure is not due to detector or chromatographic system saturation and that the chromatographic system is functioning properly. Should saturation or chromatographic activity



be evident, the analyst should correct the problem and reanalyze the affected calibration standards.

10.4.4.2. A linear fit calibration that does not include the origin and generates a coefficient of determination (R^2) that is greater than or equal to 0.99 is acceptable. ARI will primarily attempt to force calibration curve through zero. Forcing the curve through zero is not the same as including the origin as a point in the calibration. When the curve is forced through zero, the intercept is set to 0 before the regression is calculated, thereby setting the bias to favor the low end of the calibration range by “pivoting” the function around the origin to find the best fit and resulting in one less degree of freedom.

10.4.4.3. Next the analyst may attempt a quadratic non-linear calibration which may be used with target analytes that have six or more calibration points only. An additional initial calibration point may be considered for target analytes that require non-linear calibration if only five calibration points are available.

10.4.4.4. An analyte is determined to meet the calibration criteria found in Section 10.4.4, even if its RSD exceeds 15% if the analyte has an acceptable linear or quadratic fit curve with a coefficient of determination (R^2) greater than 0.99.

10.4.4.5. See EPA Method 8000C Section 11 for reference to linear fit and non-linear (quadratic) calibration.

10.4.5. Targets requiring either a linear or quadratic fit will be documented in the reviewer checklist.

10.4.6. Individual targets that are unable to meet the above requirements in Section 10.4.4.4 must be documented in the reviewer checklist

10.4.7. Special care should be taken to monitor the RRF in the lowest calibration standard to ensure adequate sensitivity at the method reporting limit. In addition, the lowest calibration point should be recalculated (not reanalyzed) using the final calibration curve in which the standard is used. The recalculated concentration, especially where linear and quadratic fits are used, should be within $\pm 50\%$ of the standard's true concentration. The recalculated concentration of the standards above the low point should be $\pm 30\%$. If a failure occurs in the lowest calibration point and it is equivalent to the method reporting limit (MRL), the analyte should be reported as estimated near that concentration or the MRL should be reestablished at a higher concentration. Following examination of the ICAL and any corrective action, all compounds not meeting the calibration acceptance criteria must be documented on the reviewer's checklist.

10.5. Calibration Acceptance

10.5.1. A calibration for an analyte is deemed valid when it meets the RSD criteria found in 10.4.4 and 10.4.4.4



10.5.2. Due to the large number of analytes that may be assayed using this SOP, some analytes may fail to meet the calibration acceptance criteria. The method allows some flexibility in dealing with such cases.

10.5.2.1. A calibration curve may be considered valid even with some analytes failing the criteria so long as the number of analytes failing the acceptance criteria found in Section 10.5.1 is equal to or less than 10% of the total number of analytes calibrated including surrogates (e.g. a calibration with sixty analytes may have up to six analytes exceed the acceptance criteria.)

10.5.2.2. Quantitated values for analytes which fail calibration acceptance criteria must be flagged with a "Q" qualifier for all detected analytes and noted on the Reviewer checklist.

10.6. Evaluation of retention times - The relative retention time (RRT) of each target analyte in the calibration standard should agree within 0.05 RRT units. Late-eluting target analytes usually have much better agreement. The RRT is calculated by dividing the retention time of the target analyte/surrogate by the retention time of its assigned internal standard.

10.6.1. The internal standards selected should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards.

10.7. Calibration curve verification - Prior to use for sample analysis, the acceptability of a calibration curve must be verified through analysis of a second source calibration verification (SCV) obtained from a second source. The SCV must be derived from a different manufacturer than the stock standard used to prepare the calibration curve when available. The SCV should show 70 - 130% (80 – 120% for DOD-QSM analyses) recovery for all compounds when compared to the initial calibration curve. Due to the large number of analytes that may be assayed using this SOP, some analytes may fail to meet the calibration acceptance criteria. Up to 10% of analytes may exceed the SCV criteria if they show a recovery within 50-150% of the true value for in-house analyses. No exceptions for DOD-QSM are allowed.

10.8. The reference mass spectrum used to verify the identity of analytes should be updated from the mid-point of the initial calibration.

10.9. Daily GC/MS calibration verification - Performed at the beginning of each 12-hour analytical shift.

10.9.1. The GC/MS tuning standard is not required for GC/MS calibration verification.

10.9.2. Analysis of an initial calibration verification (ICV) at mid-concentration (2.5 or 0.25µg/mL), containing each compound of interest, including all required surrogates, must be performed daily before analysis. Next, a continuing calibration verification (CCV) must be run after every 12 hours of analysis time and at the end of the analytical sequence, using the introduction technique used for the initial calibration. The results from the ICV analysis must meet the acceptance criteria detailed below. See section 10.9.2.7 and 10.9.2.8 for CCV acceptance criteria.



10.9.2.1. Calculate Relative Response Factors- A system performance check must be made at the start of every 12-hour shift. This is the same check that is applied during the initial calibration. Calculate the RRF for each analyte. Each compound should meet the advisory minimum relative response factor found in Appendix 20.2 If the minimum relative response factors are not met, the system should be evaluated, and corrective action may be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the guard column/analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins. See Section 16.5 for procedures for dealing with RRF failures.

10.9.2.2. Analyte linearity- The response factors calculated in Section 10.9.2.1 are used to measure the validity of the initial calibration by using them to calculate the percent difference (for average RRF calibrations) or percent drift (for linear fit or quadratic fit calibrations.)

10.9.2.2.1. Calculate the percent difference using:

$\% \text{ Difference} = \frac{\text{RRF}_i - \text{RRF}_c}{\text{RRF}_i} * (100)$
Where:
RRFi = Average relative response factor from initial calibration.
RRFc = Relative response factor from current verification check standard.

10.9.2.3. If the percent difference for each analyte is less than or equal to 20% the initial calibration verification (ICV) is valid. Problems like those listed under the minimum response factors could affect this criterion. See Section 16.6 for procedures for dealing with %D failure.

10.9.2.4. The responses and retention times in the calibration check standard must be evaluated immediately after data acquisition. Chromatography system maintenance (shortening the column, etc.) may change retention times. Corrective action is required when:

10.9.2.5. Relative retention times change.

10.9.2.6. The response (EICP) of any internal standard (IS) is in the acceptable range of -50% to +200% using the IS in the mid-point standard level (25ng/ul) from the most recent initial calibration as the reference.

10.9.2.7. Much in the manner that a certain number of analytes may fail the initial calibration criteria, the method allows a certain number of analytes to fail the criteria set above for initial calibration verification. In the case of the initial calibration verification (ICV), many analytes less than or equal to 20% of the total number of calibrated analytes (including surrogates) may exceed the criteria set in Sections 10.9.2.1 and 10.9.2.2.



10.9.2.8. Reported values for the analytes failing the acceptance criteria must be flagged with a “Q” qualifier and noted in the Reviewer checklist.

10.9.2.9. A continuing calibration verification may be used as an initial calibration verification to extend the analytical sequence if the CCV meets all requirements as required for the ICV

10.9.2.10. (CCV criteria) If the percent difference for each analyte is less than or equal to 50% the continuing calibration verification (CCV) is valid. Problems like those listed under the minimum response factors could affect this criterion. See Section 16.6 for procedures for dealing with %D failure.

10.9.2.11. (CCV criteria) The response (EICP) of any internal standard (IS) is in the acceptable range of -50% to +200% using the IS reference from the ICV.

10.10. Additional guidance for selected ion monitoring (SIM) analysis.

10.10.1. The exact mass acquired (i.e. mass 188.1 not 188) should include the mass defect.

10.10.2. The dwell time must be adjusted for each ion descriptor such that a minimum of five scans per chromatographic peak are acquired.

10.10.3. Two ions should be monitored for each target and their spectra should be updated from the calibration mid-point

11. Procedure

11.1. Prior to using this method, the samples must be extracted using the appropriate sample preparation and cleanup methods.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561, 3565
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

11.2. Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Polynuclear aromatic hydrocarbons	3630, 3660, 3640

11.3. Derivatization- When Pentachlorophenol (PCP) is a requested analyte, the extracts must be derivatized with diazomethane prior to GC/MS analysis. All derivatization MUST take place within the fume hood.



11.3.1. Add one pipette of Hexane saturated with Diazomethane gas to the extract reduced to a volume of 2-3ml. The solution should turn light yellow indicating the diazomethane is saturated in the solution. This procedure is done in the extraction lab prior to final blowdown.

11.3.2. Do not perform any cleanups on the extracts for the PCP/PAH analysis.

11.4. The recommended GC/MS operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration).

Quantitation Mass range:	Discrete ion
Tuning Mass Range	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	60°C, hold for 2 minutes
Temperature program:	60-130°C at 30C°/min 130-330°C at 20C°/min
Final temperature:	330°C, hold for 5 minutes
Injector temperature:	270°C
Transfer line temperature:	300°C
Source temperature:	According to manufacturer's specifications (230°C for Agilent 5973 MSD)
Injector:	Grob-type, splitless/split
Sample volume:	1-2 µL
Carrier gas:	Helium at 30 cm/sec.

11.5. Prior to sample analysis the GC/MS system must be tuned as described in Section 10.2 and must have an acceptable initial calibration curve (the requirements for the calibration curve are found in Section 10.3 and 10.4).

11.6. Prior to sample analysis an initial calibration verification (ICV) standard must be analyzed, and this ICV must meet the criteria found in Section 10.9. If time remains in the 12-hour QC period begun with the initial calibration, the midpoint calibration standard from the initial calibration may be used as the CCV provided it meets the requirements found in Section 10.9.

11.7. Next, a method blank or an instrument blank must be analyzed after the ICV and prior to sample analysis to ensure the system is free of contaminants. If the method blank shows contamination, then it may be appropriate to analyze an instrument blank to demonstrate the source of contamination is not the result of carryover from standards or samples.

11.8. GC/MS analysis

11.8.1. It is highly recommended that the extract be screened on a GC/FID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high



concentrations of organic compounds and may show high background samples that should be analyzed using a medium/high level extraction.

- 11.8.2. Spike a 0.3ml aliquot of the 0.5-1ml extract obtained from sample preparation with 6 μ L of the internal standard solution just prior to analysis. This is the equivalent internal standard concentration of 2 μ g/mL (low 0.2 μ g/mL) of each standard in the sample. This aliquot should be prepared in an amber glass autosampler vial and sealed with a PTFE crimp cap.
- 11.8.3. Analyze the 0.3 ml aliquot by GC/MS. The injection volume must be the same volume used for the calibration standards. The recommended GC/MS operating conditions to be used are specified in Section 11.4.
- 11.8.4. If the response for any target analyte exceeds 10/50 μ g/mL (high point of the initial calibration curve for PAHs or PCP respectively), the extract must be diluted and re-analyzed. See Section 16.12 for guidance on dilutions. In the case of low sim PAH if the response for any target analyte exceeds 1 μ g/mL, then extract dilution must take place. See section 16.12 for guidance on dilutions.
- 11.8.5. Perform all qualitative and quantitative measurements as described in Section 11. Store the extracts at >0 to 6°C, protected from light in screw-cap vials equipped with un-pierced PTFE lined septa.

12. Data Analysis and Calculations

12.1. An analyte is identified by comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this SOP. These standard reference spectra may be obtained through analysis of the calibration standards and should be updated with every initial calibration. The characteristic ions are defined as the three ions of greatest intensity, or any ions over 30% intensity relative to the base ion, if less than three such ions occur in the reference spectrum. Two criteria must be satisfied to verify identification: (1) elution of sample component at or near the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component mass spectrum/ion abundances and the standard component mass spectrum/ion abundances.

12.2. The intensities of the characteristic ions must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

12.3. The sample component RRT must compare within 0.05 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12-hour QC period as the sample.

If co-elution of interfering components prohibits accurate assignment of the sample component RRT



from the total ion chromatogram, the RRT should be assigned by using extracted ion-current profiles for ions unique to the component of interest.

12.4. All ions present in the standard mass spectra at a relative intensity greater than 10% (the most abundant ion in the spectrum is equal to 100% intensity) should be present in the sample spectrum. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Spectral enhancement can sometimes create these discrepancies.

12.4.1. The relative intensities of ions specified in Section 12.1 must agree within plus or minus 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample abundance must be between 20 and 80 percent.) If not, the compound may be flagged with an "M" if the analyst determines that the identification is valid (favors false positive).

12.4.2. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs and reported as the average of both compounds by the analyst.

12.4.3. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes co-elute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

12.5. Quantitative analysis

12.5.1. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of a given analyte. If secondary ion quantitation is necessary due to interference, then a short quantitation report list is generated. This quantitation contains the integrated areas of the affected compounds, based on the secondary ion(s) for that compound, and of the relevant internal standards. Identical reports must be generated for the sample with



interference and for the relevant initial calibration. The report for the initial calibration is used to generate a relative response factor for the affected compound based on its secondary ion. This relative response factor is then used in the calculations for that compound in the affected sample. Note that the source of the relative response factor for the aforementioned situation differs from the quantitation using the primary characteristic ion (when free of interference). All quantitation using the primary characteristic ion use the average relative response factor from the initial calibration. The short quantitation report may be hand calculated by the analyst if it is signed and dated by the analyst. The report must be included with the data file PDF in Element.

12.5.2. Calculate the concentration of each identified analyte in the sample as follows:

Concentration ($\mu\text{g/L}$) = $\frac{(A_x)(I_s)(V_t)}{(A_{IS})(RRF)(V_o)(V_i)}$
where:
A_x = Area of characteristic ion for compound being measured
I_s = Amount of internal standard injected (ng).
V_t = Volume of total extract
A_{IS} = Area of characteristic ion for the internal standard
RRF = Relative response factor for compound being measured
V_o = Volume of water extracted (ml)
V_i = Volume of extract injected (μL)

12.5.3. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)

Concentration ($\mu\text{g/kg}$) = $\frac{(A_x)(I_s)(V_t)}{(A_{IS})(RRF)(V_i)(W_s)(D)}$
where:
A_x = Area of characteristic ion for compound being measured
I_s = Amount of internal standard injected (ng).
V_t = Volume of total extract
A_{IS} = Area of characteristic ion for the internal standard
RRF = Relative response factor for compound being measured
V_i = Volume of extract injected (μL)
W_s = Weight of sample extracted or diluted in grams
D = % Dry weight of sample = 1.0 on an as received basis



13. Method Performance

13.1. The QA department measures method performance using a combination of continuing MDL studies, quarterly LOD verifications, performance evaluation samples, standard reference materials, and the monitoring of surrogate and spike recoveries.

13.1.1. Detection limits- the LOD for all analytes quantitated using this SOP are set using the MDL studies. The detection limit indicates the lowest result that can reliably be distinguished in a matrix from a blank.

13.1.2. LOD verifications are performed each quarter for each analyte by each preparatory and analytical method.

13.1.3. MDL, LOD and MRL values may be found for each analyte in Element

13.2. Laboratory precision and bias measurements are performed by monitoring surrogate and spike recoveries in samples and quality control samples.

13.2.1. Control limits are calculated from these recoveries.

13.2.2. These control limits are disseminated to the bench chemists and ELEMENT administrator for use in monitoring method performance in real time.

13.2.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found in Element

13.3. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in Section 12.3 and Appendix 2.2 of ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC is kept on record in SharePoint

13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.

13.5. The experience of the analyst must weigh heavily in the interpretation of the chromatogram.

14. Pollution Prevention

14.1. All syringe rinsing must be performed over charcoal to minimize the exposure of the environment to solvent or extract.

14.2. Charcoal containers must be covered when not in use to prevent fugitive vapors from escaping.

14.3. All GC split vents will be connected to an exhaust vent or charcoal filter.

14.4. All MS vacuum pumps will have a charcoal exhaust filter.

14.5. All spent vials are placed into the blue waste drum for proper disposal after analysis is finished.

14.6. Open solvent containers should only be present when actively preparing samples.



14.7. Wherever possible the final sample extract volume should be as small as possible to minimize the generation of waste.

15. Data Assessment and Acceptance Criteria for QC Measure

15.1. Requirements relating to initial and continuing calibration are detailed in Section 10 of this document.

15.2. Method Blanks and Instrument Blanks- The method blank must contain less than 1/2 the reporting limit (MRL) of the targeted analytes or corrective action is required.

15.3. Internal Standards- All samples and associated QC internal standard EICP areas following the ICV must meet the technical acceptance criteria listed in Section 9.6.

15.4. Surrogate Recoveries

15.4.1. All method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates, SRMs or other samples must have acceptable surrogate recoveries. See Element for the most recent control limits.

15.4.2. Recoveries outside of the in-house QC limits should not necessarily be used to reject batch data, but will require corrective action.

15.4.3. Any surrogate recovery less than 10% will require corrective action.

15.4.4. These requirements do not apply to subsequent dilutions of samples where a prior analysis of the diluted sample extract shows acceptable surrogate recovery.

15.4.5. Certain methods or clients may specify project specific surrogate recovery acceptance windows.

15.4.6. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet project specific surrogate acceptance criteria, even when the criteria are labeled as advisory in the reference method.

15.4.7. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.

15.5. Blank Spikes (BS)/Blank Spike Duplicates (BSD)

15.5.1. The BS recovery values should fall within the specified recovery acceptance limits. If an BSD is performed then relative percent difference (RPD) acceptance limits may also apply, if available.



15.5.2. BS recovery acceptance windows are determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Project or method specific limits may supersede laboratory acceptance criteria.

15.5.2.1. The RPDs between the BS/BSD samples must be measured and reported

15.5.2.2. Evaluate the BS/BSD RPD and note any deviation >30% in the reviewer checklist.

15.5.3. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.

15.6. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.6.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified recovery acceptance limits.

15.6.2. MS/MSD recovery and RPD acceptance windows are ideally determined statistically from method and matrix-specific laboratory data updated on a periodic basis. Certain methods or clients may require project specific MS/MSD recovery and RPD acceptance windows.

15.6.2.1. The RPDs between the MS/MSD samples must be measured and reported.

15.6.2.2. Evaluate the MS/MSD RPD and note any deviation >30% in the reviewer checklist.

15.6.3. Method default limits of 30-160% are also applied for any combination of sample matrix, preparation, clean-up, method or instrument without statistical limits.

15.7. Holding Times

15.7.1. Samples must be extracted within holding times (7 days for water samples and 14 days for solid samples).

15.7.2. Extracts must be analyzed within the extract holding time (40 days from the initial date of extraction).

15.7.3. In the event that re-extraction due to an out of control event requires that samples be re-extracted after their extraction holding time has elapsed (7 days for water and 14 days for tissues/solids) the analyst should analyze and report both extraction sets, whenever practical, distinguishing between the initial extraction and re-extraction on all deliverables. This will document that the samples were originally extracted within holding times and may allow for comparisons that will determine whether any of the more volatile analytes were lost in the interval between extractions.

15.7.4. If any extracts are analyzed after the 40-day extract holding time has elapsed, the analyst must document this in the reviewer checklist.

16. Corrective Actions for Out of Control of Unacceptable Data

16.1. Corrective actions may include any, but are not limited to, the following:



- 16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the reviewer checklist.
 - 16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.
 - 16.1.3. Repreparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.
 - 16.1.4. Reanalysis – the extract aliquot that was originally prepared is reinjected and run on the gas chromatograph again.
 - 16.1.5. Re-extraction – a re-extraction request is filled out (Form 0030F). Copies of the form are provided to the extractions department, the project manager, the QA manager and the lab manager. The remaining sample is extracted.
 - 16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in ELEMENT.
 - 16.1.7. Recalibration – a new initial calibration is evaluated, and the associated samples reanalyzed.
 - 16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.
 - 16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.
- 16.2. Mass Spectrometer Tuning
- 16.2.1. When the MS does not produce an acceptable mass spectrum when injected with 25 µg/mL of DFTPP, re-inject the DFTPP. If the spectrum again fails to meet the criteria found in Appendix 20.3, the MS may need to be re-tuned.
 - 16.2.2. If the re-tuned mass spectrum still fails to meet the criteria found in Appendix 20.3, the MS may require maintenance. The MS should be vented, and maintenance may include replacing the filaments, cleaning the MS source, cleaning the MS lenses, cleaning the MS mass selective filter, or replacing the electron multiplier. All maintenance must be documented in Element.
- 16.3. If Peak tailing factors and or DDT breakdown exceed the limits found in Section 10, the chromatographic system may need maintenance. Inspect and perform maintenance on the chromatographic system. This maintenance may include, but is not limited to: replacing the inlet liner and liner packing, cleaning the inlet liner, cleaning or replacing the inlet seal, cleaning or replacing the inlet body, replacing the split line, cleaning the split arm, clipping a length from the front of the column, or replacing the column. All maintenance must be documented in Element.



16.4. When an Initial Calibration RSD for an analyte exceeds 15%

16.4.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.4.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

16.5. RRF failure- If the minimum RRF of 0.01 is not met for all analytes and calibration points perform any appropriate corrective action found in section 16.1

16.6. When an Initial Verification (ICV) fails:

16.6.1. At the discretion of the analysts, a second ICV may be immediately run after the failing ICV. If the second ICV meets all ICV criteria, then the sequence may begin.

16.6.2. If the second injection of the ICV fails, perform the appropriate corrective action(s) from Section 16.1 and re-calibrate the instrument.

16.6.3. DoD-QSM requires that %D for all analytes in the ICV is $\leq 20\%$. For DoD analyses, immediately analyze two additional consecutive ICVs.

16.6.3.1. When both ICVs meet acceptance criteria the analytical sequence may be continued.

16.6.3.2. If either fails or if two consecutive ICVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.6.4. If a CCV is used both as an ICV and CCV (in the middle of an analytical sequence) then the ICV requirements must be applied.

16.7. When a Continuing Calibration Verification (CCV) fails:

16.7.1. Perform any appropriate corrective action(s) from Section 16.1 if not a DoD-QSM project.

16.7.2. DoD-QSM requires that %D for all analytes in the CCV be $\leq 50\%$. For DoD analyses, immediately analyze two additional consecutive CCVs.



16.7.2.1. When both CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.7.2.2. If either fails or if two consecutive CCVs cannot be run, perform corrective actions and repeat the analytical sequence.

16.8. Internal Standards

16.8.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.8.1.1. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.

16.8.1.2. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.

16.8.1.3. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

16.8.1.4. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".

16.9. Surrogates

16.9.1. Examine the bench sheet to verify spiking levels are correct.

16.9.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.9.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.

16.10. Method Blanks and Instrument Blanks-

16.10.1. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.10.2. Corrective action for a method blank which fails acceptance criteria may involve re-extraction and reanalysis of all associated samples and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager.

16.10.3. Corrective action for an instrument blank which fails acceptance criteria may involve re-preparation of the instrument blank and re-analyzing the instrument sequence.

16.11. Blank Spikes (BS)/Blank Spike Duplicates (BSD)

16.11.1. Examine the bench sheet to verify spiking levels are correct.

16.11.2. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.

16.12. Matrix Spike (MS)/Matrix Spike Duplicates (MSD)

16.12.1. Examine the bench sheet to verify spiking levels are correct.

16.12.2. Recoveries are advisory and should not necessarily result in re-extraction.



- 16.12.3. Proceed with any appropriate corrective action from 16.1, based on analyst discretion.
- 16.13. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve; a dilution must be performed such that the analyte's quantitated value is within the curve range.
- 16.13.1. Additional internal standard must be added to the diluted extract to maintain the required 2µg/mL (0.2µg/mL for low sim) of each internal standard in the extracted volume.
- 16.13.2. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.
- 16.13.3. When peaks from an analyte saturate the detector
- 16.13.3.1. The analyst must note the saturation in the reviewer checklist.
- 16.13.3.2. The analyst should analyze an Instrument Blank consisting of clean solvent until the system has been decontaminated
- 16.14. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.
- 16.14.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)
- 16.14.1.1. All QC limit issues (including continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

- 17.1. See Section 16.2 for guidance on dealing with out-of-control tuning events.
- 17.2. See section 16.3, 16.4 and 16.5 for guidance on dealing with out-of-control events related to initial calibrations (RRF or RSD), peak tailing factors, or DDT breakdown.
- 17.3. See section 16.6 for guidance on dealing with ICV out-of-control events.
- 17.4. See section 16.7 for guidance on dealing with CCV out-of-control events.
- 17.5. See Section 16.8 for guidance on dealing with internal standard out-of-control events.
- 17.6. See Section 16.9 for guidance on dealing with surrogate out-of-control events.
- 17.7. See Section 16.10 for guidance on dealing with method blank and instrument blank related out-of-control events.
- 17.8. See Section 16.11 for guidance on dealing with BS/BSD related out-of-control events.



- 17.9. See Section 16.12 for guidance on dealing with MS/MSD related out-of-control events.
- 17.10. See Section 16.13 for guidance on dealing with over range value related out-of-control events.
- 17.11. See Section 16.14 for guidance on dealing with particular circumstances out-of-control events.

18. Waste Management

- 18.1. All extract vials and standard vials must be disposed of by placing them in the blue hazardous waste drum in the station set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.
- 18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.
- 18.3. All spent charcoal must be disposed of by placing it in the charcoal disposal bin located in the hazardous waste storage area.
- 18.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

- 19.1. "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Method 8270E, Test Methods for Evaluating Solid Waste (SW-846), Revision 6, June 2018.
- 19.2. "EPA Method 625.1-Base/neutrals and acids", Appendix A to CFR Part 136, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. December 2016.
- 19.3. "Determinative Chromatographic Separations": Method 8000D, (SW-846), Revision 5, March 2018.
- 19.4. "Department of Defense (DOD) Department of Energy (DOE) Consolidated Quality Systems Manual for Environmental Laboratories", Final Version 5.3 2019.

20. Appendices

- 20.1. Appendix 20,1: ARI Acceptance Criteria
- 20.2. Appendix 20. 2: PAH Target analyte List
- 20.3. Appendix 20.3: DFTPP key ions and ion abundance criteria.
- 20.4. Appendix 20.4: Example Chromatogram of Calibration standard
- 20.5. Appendix 20.5: Example pages from GC/MS PAH organics virtual logbook
- 20.6. Appendix 20.6: Peak Tailing Factor Calculation
- 20.7. Appendix 20.7: Selected PCB congeners by GC/MS
- 20.8. Appendix 20.8: Method 625.1 requirements



Analytical Resources, Incorporated
Analytical Chemists and Consultants



Appendix 20.1

ARI ACCEPTANCE CRITERIA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method (see ARI SOP 1017S)	QC acceptance criteria published by DoD, if available; otherwise method specified criteria.	1) Recalculate results 2) Locate and correct the source of the problem and repeat the test for all parameters of interest.	Not applicable (NA)	This is a demonstration of ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., LCS or PT sample) as described in ARI SOP 1017S. Analysis is not allowed by analyst until she/he has completed a successful demonstration of capability.
Method detection limit (MDL) study	At initial set-up and subsequently once per 12-month period; otherwise quarterly MDL verification checks shall be performed (see box D-18)	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or reconduct MDL study	NA	Samples should not be analyzed without a valid MDL.
Tuning	Prior to the initial calibration	Refer to method for specific ion criteria.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
DDT breakdown check	Prior to the initial calibration	Degradation < 20% for DDT. Benzidine and PCP peak tailing must be <2.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.
Retention time (RT) window calculated for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	RT width is ± 3 times standard deviation for each analyte RT from 72-hour study.	NA	NA	
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.	



QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	1)Analytes' RRFs must meet 0.01 across calibration range. 2) Analytes' RSDs must be less than or equal to 15%, or the analyte must employ a linear or non-linear calibration model with a coefficient of determination (R ²) greater than 0.99. 3)Up to 10% of the total analytes may fail 1 and 2 above.	Correct problem then repeat initial calibration.	Analytes which fail the RRF or RSD/R ² limits must have their values flagged with Q qualifiers to mark the values as estimates.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification	Once after each initial calibration	Value of second source for all analytes within ± 30% of expected value (initial source) Up to 10% of analytes may exceed SCV criteria if they show a recovery within 50-150% of the true value	Correct problem, verify second source standard. Rerun verification. If that fails, correct problem and repeat ICAL	Flagging criteria are not appropriate.	Historic data shows that some analytes will very seldom meet ±20% when purchased from different vendors. Second sources may not be available for all analytes.
Retention time established for all analytes and surrogates	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	NA	NA	
Initial and Continuing Calibration verification (ICV/CCV)	Daily, before sample analysis (ICV); after every 12 hours of analysis time; and at the end of the analytical batch run (CCV).	1. Analytes RRF must meet 0.01 2. ICV %Difference/Drift for analytes ≤ 20%D Up to 20% of the target analytes may fail the criteria in 1 and 2 so long as the sample analyses associated with the ICVS are Q flagged. 3: CCV %Difference/Drift for analytes ≤ 50%.	ICV FAILURE: Correct problem, then rerun ICV. If that fails, repeat initial calibration. CCV FAILURE: Perform corrective action from section 16.1	Apply Q-flag to reported target analytes exceeding criteria.	.
Internal standards verification	All ICV	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL or most recent ICV. EICP area within - 50% to + 100% of ICAL midpoint standard	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	Flagging criteria are not appropriate.	Sample results are not acceptable without a valid IS verification.
Internal standards verification for samples, batch QC, and CCV	All samples, batch QC, and the CCV	Retention time ± 10 seconds from retention time of the ICV. EICP area within -50% to +100% of ICV	Rerun affected samples	If corrective action fails in field samples, associated batch QC, or the CCV apply *-flag to the non-compliant IS.	



QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank and instrument blank	One per preparatory batch	No analytes detected > ½ MRL. For common laboratory contaminants, no analytes detected ≥ MRL.	Correct problem, if required, re-prepare then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) reported above the MRL to all samples in the associated preparatory batch for method blanks exceeding criteria. Flagging criteria are not appropriate for instrument blanks.	
Blank spike control sample (BS) containing all reported analytes & surrogates	One BS per preparatory batch	QC acceptance criteria specified by ARI LQAP.	Correct problem, then re-prepare and reanalyze the BS. Perform corrective action from section 16.1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to BS results.	
Blank Spike Duplicate (BSD)	Project specific	RPD ≤30% between BS and BSD	Perform corrective action from section 16,1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to BSD results.	The data shall be evaluated to determine the source of difference.
Matrix spike (MS)	One MS per preparatory batch per matrix	For matrix evaluation, use QC acceptance criteria specified by ARI LQAP for MS. MS recoveries are advisory.	Perform corrective action from section 16.1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to MS results.	For matrix evaluation only. If MS results are out of control, data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	RPD ≤ 30% (between MS and MSD or sample and sample duplicate) Limits are advisory.	Perform corrective action from section 16.1	Apply * flag to the specific analyte(s) if acceptance criteria are not met to MSD results.	The data shall be evaluated to determine the source of difference.
Surrogate spike	All field and QC samples	Method-specified criteria or laboratory's own in-house criteria; all surrogate recoveries must be > 10%.)	For QC and field samples, correct problem then re-prepare and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Apply * flag to the specific analyte(s) if acceptance criteria are not met to surrogate results.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Results reported between LOD and LOQ	When requested	Peak integration should meet signal to noise ratio of 3:1	NA	Apply J-flag to all results between MDL and MRL.	



Appendix 20.2 PAH Target Analytes, Quantitation Ions, Calibration Criteria and Associated Internal Standards

Internal Standard Associated Analyte	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD ¹	Max %D ¹
D8-Naphthalene (IS) ²		136	--			
Naphthalene	91-20-3	128	--	0.70	15.0	20.0
D10-2-Methylnaphthalene (SS) ³	7297-45-2	152	150, 153	0.70	15.0	20.0
2-Methylnaphthalene	91-57-6	142	141, 143	0.70	15.0	20.0
1-Methylnaphthalene	90-12-0	142	141, 143	0.70	15.0	20.0
Benzo(b)Thiophene	95-15-8	134	89	0.01	15.0	20.0
D10-Acenaphthene (IS)		164	--			
2-Chloronaphthalene	00091-58-7	162	162	0.01	15.0	20.0
Biphenyl	92-52-4	154	153	0.01	15.0	20.0
2,6-Dimethylnaphthalene	581-42-0	156	155	0.01	15.0	20.0
Acenaphthylene	208-96-8	152	150, 151	0.90	15.0	20.0
Acenaphthene	83-32-9	153	152, 154	0.90	15.0	20.0
Dibenzofuran	132-64-9	168	139, 169	0.80	15.0	20.0
2,3,5-Trimethylnaphthalene	2245-38-7	170	155	0.01	15.0	20.0
Fluorene	86-73-7	166	165, 167	0.90	15.0	20.0
D10-Phenanthrene (IS)		188	--			
Dibenzothiophene	132-65-0	184	185	0.01	15.0	20.0
Pentachlorophenol ⁴	87-86-5	280	278	0.05	15.0	20.0
2,4,6-Tribromophenol (SS) ⁵	118-79-6	141	143	0.05	15.0	20.0
Phenanthrene	85-01-8	178	176, 179	0.70	15.0	20.0
Anthracene	120-12-7	178	176, 179	0.70	15.0	20.0
Carbazole	86-74-8	167	166	0.01	15.0	20.0
1-methylphenanthrene	832-69-9	192	191	0.01	15.0	20.0
Fluoranthene-d10 (SS)	93951-69-0	212	208	0.60	15.0	20.0
Fluoranthene	206-44-0	202	200, 201	0.60	15.0	20.0
Pyrene	129-00-0	202	200, 201	0.60	15.0	20.0
D12-Chrysene (IS)		240	--			
Benzo(a)anthracene	56-55-3	228	226, 229	0.80	15.0	20.0
Chrysene	218-01-9	228	226, 229	0.70	15.0	20.0
D12-Perylene (IS)		264	--		15.0	
Benzo(b)fluoranthene	205-99-2	252	250, 253	0.70	15.0	20.0
Benzo(k)fluoranthene	207-08-9	252	250, 253	0.70	15.0	20.0
Benzo(j)fluoranthene	205-82-3	252	250, 253	0.70	15.0	20.0
Benzo(e)pyrene	192-97-2	252	250, 253	0.70	15.0	20.0
Benzo(a)pyrene	50-32-8	252	250, 253	0.70	15.0	20.0



Perylene	198-55-0	252	250, 253	0.01	15.0	20.0
Indeno(1,2,3-cd) pyrene	193-39-5	276	274, 277	0.50	15.0	20.0
D14-Dibenz(a,h)anthracene (SS)	D-53-70-3	292	291	0.40	15.0	20.0
Dibenz(a,h)anthracene	53-70-3	278	139, 279	0.40	15.0	20.0
Benzo(g,h,i)perylene	191-24-2	276	274, 277	0.50	15.0	20.0

- 1 – A maximum of 2 compounds are allowed > 20%RSD .
- 2 – Compounds followed by (IS) are internal standards
- 3 – Compounds followed by (SS) are surrogate standards
- 4 – Optional Analyte
- 5 – This surrogate added only when Pentachlorophenol is a targeted analyte



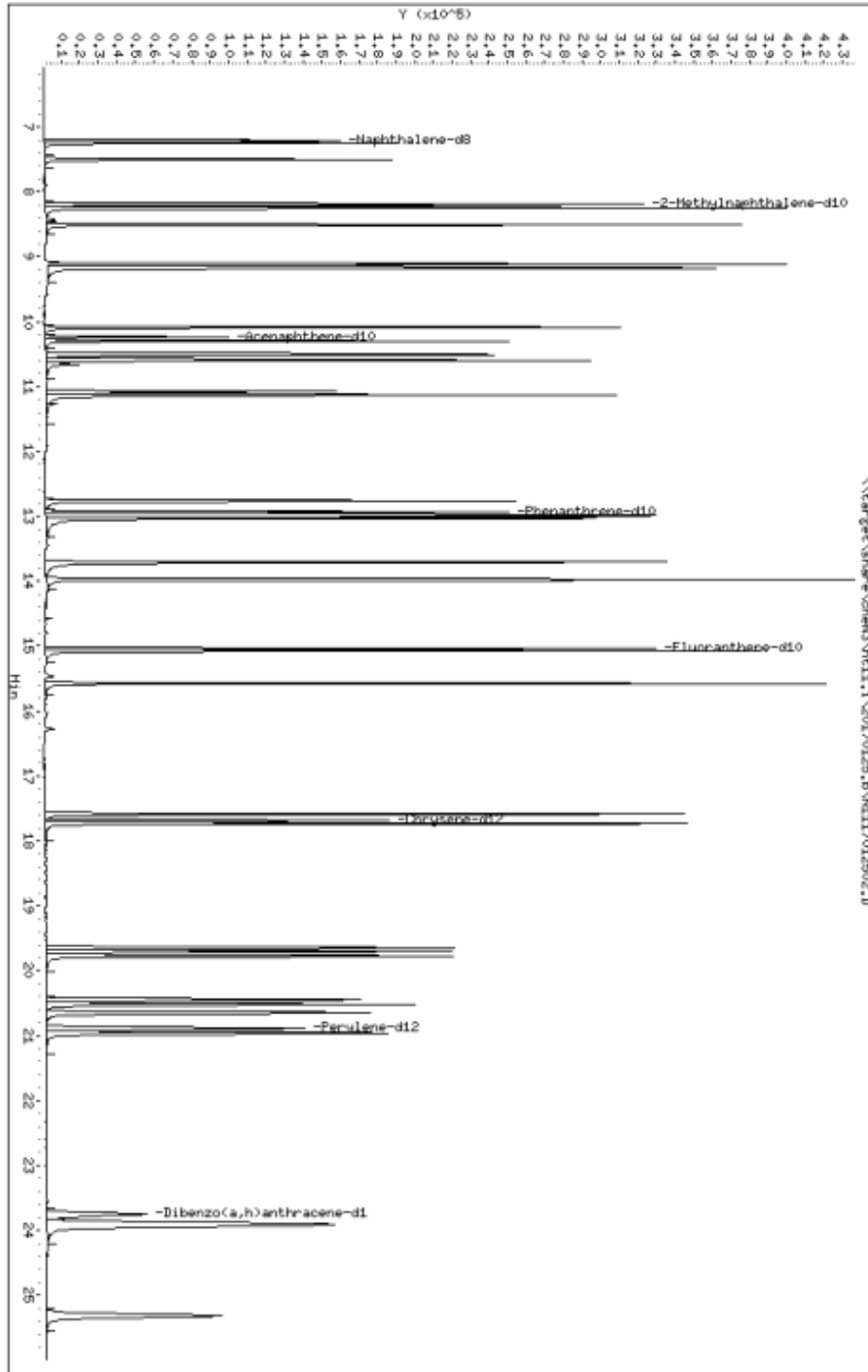
Appendix: 20.3 DFTPP KEY IONS AND ION ABUNDANCE CRITERIA¹

Mass	Ion Abundance Criteria
68	< 2% of mass 69
69	Present
70	< 2% of mass 69
197	< 2% of mass 198
198	Base peak or Present
199	5-9% of mass 198
365	> 1% of base peak
441	< 150% of mass 443
442	Base peak or Present
443	15-24% of mass 442

1. Raw data is rounded to three significant figures and one or less decimal point before comparison to the abundance criteria.



Appendix: 20.4 EXAMPLE CHROMATOGRAM OF CALIBRATION STANDARD



Data File: \\target\share\chem3\nt11.1\20170125_B\N117012502.D
Date: 25-Jan-2017 09:42
Client ID:
Sample Info: SFA0256-1014
Column phase: Kx1-17511 HS

Instrument: nt11.1
Operator: VTS
Column diameter: 0.25



Appendix: 20.5 EXAMPLE PAGES OF VIRTUAL LOGBOOK



ANALYSIS SEQUENCE
SFA0255

Printed: 1/26/2017 8:12:55AM

Instrument: NT11 Element Column ID: E006480
Calibration ID: ZL00083 Tune File: 161216.U
EM Voltage: 2353

Lab Number	Sample Name	Analysis	Container	Order	STD ID	ISTD ID	Comments
SFA0255-TUN1	DFTPP	QC		1	E007446		
SFA0255-ICV1	Initial Cal Check	QC		2	E006577	E002870	
BFA0320-BLK1	Blank	QC		3		E002870	
BFA0320-BS1	LCS	QC		4		E002870	
17A0190-02	DA2 (Basin 3) 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		5		E002870	
17A0190-03	DA3 (Basin 4) 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		6		E002870	
17A0190-04	DA4 (Basin 5) 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		7		E002870	
17A0195-01	KSC - MH-20.237 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		8		E002870	
17A0195-02	KSC - MH-20.235 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		9		E002870	
17A0195-03	KSC - MH-16.12 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		10		E002870	
17A0195-04	KSC - MH-15.10 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		11		E002870	
BFA0320-MS1	Matrix Spike	QC		12		E002870	
BFA0320-MSD1	Matrix Spike Dup	QC		13		E002870	
17A0195-05	KSC - OF-16 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		14		E002870	
17A0195-06	KSC - OF-NDP 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		15		E002870	
17A0190-01	DA1 (Rx System) 8270D	SIM PAH Low (0.01 ug/L - 0.5 ug/L)		16		E002870	
SFA0255-CCV1	SIM PAH 250	QC		17	E006577	E002870	



INTERNAL STANDARD SUMMARY FOR DATABATCH - \\target\share\chem3\nt11.i\20170125.b

Time	Filename	LabID	ClientID	DF																	
1	0926	N1117012501.D	SFA0255-TUN1		1																
																					1 (NO LSTDS FOUND)
2	0942	N1117012502.D	SFA0255-ICV1		1	7.21	221638	10.23	145546	12.92	286458	17.69	270379	20.89	263628						
3	1013	N1117012503.D	SFA0255-LCV1		1	7.21	236521	10.23	149706	12.94	296790	17.69	297882	20.89	286171						
4	1046	N1117012504.D	BFA0320-BLK1		1	7.21	209823	10.24	127178	12.92	240475	17.69	261459	20.89	268502						
5	1118	N1117012505.D	BFA0320-BB1		1	7.21	224643	10.23	146324	12.92	287697	17.68	288037	20.89	287256						
6	1149	N1117012506.D	17A0190-D1		5	7.21	297737	10.23	144735	12.92	252088	17.69	245938	20.89	282243						
7	1220	N1117012507.D	17A0190-B2		1	7.21	220793	10.23	142050	12.92	276263	17.69	236499	20.89	259121						
8	1252	N1117012508.D	17A0190-B3		1	7.21	234838	10.23	150579	12.92	290487	17.68	261735	20.89	269272						
9	1324	N1117012509.D	17A0190-B4		1	7.22	211399	10.24	127812	12.92	218356	17.69	218439	20.90	260632						
10	1356	N1117012510.D	17A0195-D1		1	7.21	224142	10.23	148934	12.92	285573	17.69	239906	20.89	263386						
11	1427	N1117012511.D	17A0195-B2		1	7.21	230494	10.23	152661	12.92	293341	17.69	251162	20.89	271337						
12	1458	N1117012512.D	17A0195-B3		1	7.21	223053	10.23	147219	12.92	290845	17.69	248371	20.89	270876						
13	1530	N1117012513.D	17A0195-B4		1	7.21	238864	10.23	154039	12.92	297532	17.69	244430	20.89	275138						
14	1601	N1117012514.D	BFA0320-BB1		1	7.21	253560	10.23	168800	12.92	322809	17.69	291355	20.89	307409						
15	1632	N1117012515.D	BFA0320-BBD1		1	7.21	244945	10.23	162638	12.92	307675	17.69	263454	20.89	287731						
16	1704	N1117012516.D	17A0195-B5		1	7.21	224053	10.23	130718	12.92	235703	17.69	229616	20.89	262068						
17	1735	N1117012517.D	17A0195-B6		1	7.21	228375	10.23	150175	12.92	297429	17.69	264403	20.89	292951						
18	1806	N1117012518.D	17A0190-D1		1	7.21	225836	10.23	129678	12.93	230786	17.69	290847	20.91	316538						
19	1838	N1117012519.D	SFA0255-OCV1		1	7.21	213637	10.24	152986	12.94	294773	17.69	251512	20.89	304195						



MANUAL INTEGRATION SUMMARY FOR DATABATCH - \\target\share\chem3\nt11.i\20170125.b
ARI Job No.: SFAO Method: DFTPP.m Instrument: nt11.i Date: 25-JAN-2017

Time	Filename	LabID	ClientId	DF	Manually Integrated Compounds
0926	N1117012501.D	SFA0255-TUN1		1	NO MANUAL INTEGRATION
0942	N1117012502.D	SFA0255-ICV1		1	NO MANUAL INTEGRATION
1013	N1117012503.D	SFA0255-LCV1		1	NO MANUAL INTEGRATION
1046	N1117012504.D	SFA0320-BLK1		1	NO MANUAL INTEGRATION
1118	N1117012505.D	SFA0320-BB1		1	NO MANUAL INTEGRATION
1149	N1117012506.D	17A0190-01		5	NO MANUAL INTEGRATION
1220	N1117012507.D	17A0190-02		1	Acenaphthene,
1252	N1117012508.D	17A0190-03		1	NO MANUAL INTEGRATION
1324	N1117012509.D	17A0190-04		1	NO MANUAL INTEGRATION
1356	N1117012510.D	17A0195-01		1	1-Methylnaphthalene,
1427	N1117012511.D	17A0195-02		1	1-Methylnaphthalene,
1458	N1117012512.D	17A0195-03		1	NO MANUAL INTEGRATION
1530	N1117012513.D	17A0195-04		1	NO MANUAL INTEGRATION
1601	N1117012514.D	SFA0320-MB1		1	NO MANUAL INTEGRATION
1632	N1117012515.D	SFA0320-MSD1		1	NO MANUAL INTEGRATION
1704	N1117012516.D	17A0195-05		1	1-Methylnaphthalene,
1735	N1117012517.D	17A0195-06		1	1-Methylnaphthalene,

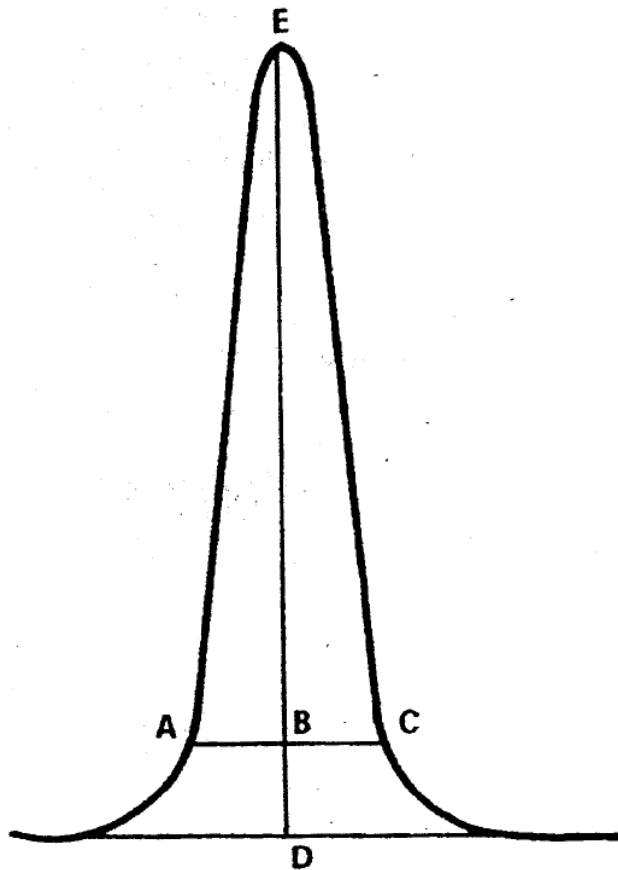


Analytical Resources, Incorporated
Analytical Chemists and Consultants



Appendix 20.6: Peak Tailing Factor Calculations

$$RF = \frac{(A_p)(C_p)}{(A_b)(C_p)}$$



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$



Appendix 20.7: Selected PCB congeners by GC/MS

Selected PCB congeners may also be analyzed under the guidance of this SOP. The selected PCB method utilizes a unique scan descriptor tailored for the characteristic PCB ions. The SOP pertains to all aspects of the selected PCB congener analysis with modifications made to the scan descriptor and a specific PCB congener calibration. The target congeners for this procedure are PCB-8, PCB-18, PCB-28, PCB-44, PCB-52, PCB-66, PCB-101, PCB-105, PCB-118, PCB-126, PCB-128, PCB-138, PCB-153, PCB-169, PCB-170, PCB-180, PCB-187, PCB-195, PCB-206, PCB-209. Two internal standards used for quantitation are d10-Phenanthrene and d12-Chrysene. The target analytes and associated internal standards are shown below in table 1. The calibration is a six-point calibration from 5ng/ml to 1000ng/ml. The six calibration points used are 5, 10, 25, 50, 75, and 100ng/ml. The second source calibration verification is not run with the calibration as one is not readily available. Eight discrete sim scan descriptors are employed: one for each native/c13 congener pair and one for each internal standard. The internal standard concentration is static at 200ng/ml for all calibration levels.

See table 1 below which outlines the ions acquired during acquisition and the calibration requirements.

Table 1
PCB Target Analytes, Quantitation Ions,
Calibration Criteria and Associated Internal Standards

Internal Standard Associated Analyte	CAS Number	Primary Ion	Secondary Ion(s)	Min RRF	Max %RSD	Max %D
D10-Phenanthrene (IS)	1517-22-2	188	184			
PCB-8	34883-43-7	222	152, 186	0.2	15.0	20.0
PCB-18	37680-65-2	186	256, 221	0.2	15.0	20.0
PCB-28	7012-37-5	258	186, 150	0.2	15.0	20.0
PCB-44	41464-39-5	222	292, 257	0.2	15.0	20.0
PCB-52	35693-99-3	292	222, 184	0.2	15.0	20.0
PCB-66	32598-10-0	292	220, 184	0.2	15.0	20.0



PCB-101	37680-73-2	326	254, 291	0.2	15.0	20.0
PCB-105	32598-14-4	326	256, 292	0.2	15.0	20.0
PCB-118	31508-00-6	326	256, 207	0.2	15.0	20.0
PCB-153	35065-27-1	360	290, 207	0.2	15.0	20.0
c13-PCB-37	208263-79-0	270	268, 198	0.2	15.0	20.0
c13-PCB-47	NA	304	302, 232	0.2	15.0	20.0
c13-PCB-54	234432-88-3	304	302, 232	0.2	15.0	20.0
c13-PCB-111	235416-29-2	338	336, 266	0.2	15.0	20.0
D12-Chrysene (IS)	1719-03-5	240	241			
PCB-126	57465-28-8	326	254, 207	0.2	15.0	20
PCB-128	38380-07-3	362	290, 325	0.2	15.0	20
PCB-138	35065-28-2	360	325, 290	0.2	15.0	20
PCB-169	32774-16-6	207	362, 290	0.2	15.0	20
PCB-170	35065-30-6	396	324, 281	0.2	15.0	20
PCB-180	35065-29-3	207	394, 324	0.2	15.0	20
PCB-187	52663-68-0	394	324, 361	0.2	15.0	20
PCB-195	52663-78-2	281	358, 430	0.2	15.0	20
PCB-206	40186-72-9	207	281, 464	0.2	15.0	20
PCB-209	2051-24-3	498	428, 356	0.2	15.0	20
c13-PCB-138	208263-66-5	372	370, 302	0.2	15.0	20.0
c13-PCB-178	232919-67-4	406	408, 336	0.2	15.0	20.0

This procedure is being developed to access the validity of polymeric sampling procedures in aquatic environments and must meet all method requirements for DFTPP tuning, peak tailing, and DDT breakdown as detailed in the main section of this SOP.



Appendix 20.8: Modifications Required for EPA Method 625.1 (These modifications are only implemented when specifically requested by a client, otherwise method 625.1 is analyzed as 8270E described previously in this SOP)

Please refer to SOP 804S section 20.7 for guidance.

Standard Operating Procedure

Carbon Analysis of Soil and Sediment

**SOP 671S
Version 002**

**Revision Date: 5/24/2019
Effective Date: 5/24/2019**

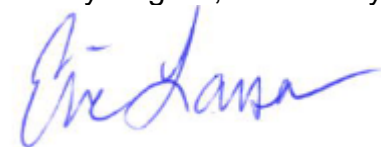
Prepared By:

Casey English

Approvals:



Casey English, Laboratory Supervisor



Eric Larson, Inorganics Division Manager



1. Scope and Application

- 1.1. This SOP covers the determination of Total Carbon (TC), Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) in soils and sediments.
- 1.2. There are a number of procedures available for the analysis of Carbon in soils and sediments. Most of these have been reviewed by Schumacher (2002). The procedure used by ARI is Temperature-dependent and gas switching differentiation with IR detection of evolved carbon dioxide (CO₂) using components of procedures specified by Plumb (1981), PSEP (1986, 1993), Pitt et al, (2003), EPA, LG601 (2005), DIN EN 15936, DIN 19539, DIN EN 13137, ISO 10694, (LECO, 1996, soot quantification method of Gustafsson et al. (1997), (Nelson and Sommers, (1996), Zimmerman et al, (1997) and Abstracts, (2003 Meeting of ASA, Denver, CO)
- 1.3. In Temperature-dependent and gas switching differentiation, the analysis is for TOC, TIC, TC and ROC (Elemental Carbon), separated by temperature and time coupled with gas switching techniques to separate TIC from ROC. Carbon will be converted to CO₂ as a result of oxidative combustion. Complete combustion of inorganic carbonates requires temperatures in excess of 950 °C while organic materials will generally combust at temperatures in excess of 500 °C (Plumb, 1981).
- 1.4. The above reference methods for the analysis of carbon in soil or sediment samples are all similar. Each method addresses temperature dependent separation of TOC and TIC. Measurement of evolved organic carbon is dependent upon the capabilities of the analytical instrumentation and methods generally defer to the specific instrument manufacturer's instructions for detailed operating procedures and protocol. Methods vary with respect to the temperature used for organic and inorganic separation and the quantification procedures used. Our procedure follows the Elementar specified procedures. (Note: SW-846 Method 9060A is a procedure for the combustion analysis of TOC in aqueous solutions. It provides neither discussion of nor procedures for the analysis of organic carbon in soils or sediments).
- 1.5. We use an Elementar Soli TOC Cube Elemental analyzer with IR detection.

2. Summary of the Procedure

- 2.1. A soil or sediment sample received for Carbon analysis is evaluated, homogenized, and a representative aliquot (0.005 to 2.000 g) is taken and weighed into a clean crucible.
- 1.6. The sample is then dried at 70 °C to remove excess moisture before analysis.
- 1.7. The sample is combusted with a temperature ramp of 90° K/min from ambient to 400°C in a nitrogen+oxygen gas flow producing a TOC peak. After a wait time of 240sec. The furnace then ramps up to 900°C and switches gas flow to pure nitrogen producing a TIC peak. After an additional wait time of 150sec, the gas is then switched back to Nitrogen+Oxygen to produce the



elemental carbon as ROC peak. At each of these hold points, the evolved gas from combustion is passed through a platinum catalyst to insure conversion of combustion products to CO₂.

- 1.8. The gas then travels through a series of water traps and halide scrubbers to remove interfering components and into the CO₂ sensitive infrared detector of the Soli TOC Cube where it is quantified as % carbon.
- 1.9. Samples which exceed the range of the standard curve are diluted with pre-combusted silica gel or Ottawa sand and then re-combusted for carbon determination.
- 1.10. Samples are processed independently for the determination of dry weight (percent solids at 104°C) then corrected for the standard dry weight at 104 °C for reporting as percent carbon.

3. Definitions

- 3.1. The total carbon (TC) content of solids may be divided into inorganic and organic forms. Inorganic carbon (IC) consists primarily of carbonates or mineral complexes thereof, predominantly calcite (CaCO₃), aragonite (denser, more packed CaCO₃, the main component of mollusk shells), and dolomite (CaMg(CO₃)₂), among others. Total organic carbon (TOC) includes organics derived from the decomposition of plants and animals (naturally occurring organic matter or NOM) and organics derived from spills or releases of synthetic or natural contaminants to the environment. These may include both volatile and non-volatile species.
- 3.2. Preparation and Analytical Batches. NELAC (2011) defines Preparation and Analytical batches as follows: “*Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.*” For TOC analysis, the preparation batch will be those samples which are processed together in an Element Batch. This will be limited to 20 samples which have gone through weighing and the drying steps of the preparation, as necessary. The analytical batch will be the actual combustion of the prepared samples for the determination of carbon which may include more than one preparation batch.
- 3.3. Analytical Blanks. Several types of blanks can be run during the analytical process.
 - 3.3.1. Method Blanks (BLK). The Method Blanks consist of approximately 200mg of pre-combusted Ottawa sand which is processed along with each batch of samples. Method blanks



are used for verifying the absence of contamination through the preparation process and the calculation of Detection and Quantitation limits.

- 3.3.2. Crucible Blanks (Blank), Crucible blanks have no added solid material and can be processed as samples throughout the run to clean the crucibles or verify absence of contamination or carry-over. There is no need to document boat cleaning procedures.
- 3.4. Detection Limit (DL). The detection limit is that concentration of analyte that produces a response that can be considered significantly different from that of a “zero standard” or blank with a false positive rate (reporting the presence of analyte when it is absent) less than or equal to 1% (DQFAC, 2007). The DL must be based upon the Method Blank.
- 3.5. Method Detection Limit (MDL). The MDL is, “...the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero...”, as defined in 40 CFR part 136 Appendix B. The MDL is conceptually equivalent to the DQFAC detection limit when determined using a low level standard.
- 3.6. Level of Quantitation (QL). That concentration of analyte that can be considered significantly different from the DL based upon statistical considerations and components of the calibration (DQFAC, 2007). The QL targets a false negative rate (reporting the absence of analyte when it is present) of 5%. The QL must be greater than the DL and at least equivalent to the lowest point on the standard curve. The QL serves as the reporting limit. Observed concentrations less than the QL will be reported as non-detects at the level of the QL. The QL must be based upon the complete analysis of a standard prepared at a concentration of at least 2 times the DL. The QL standard is prepared in pre-combusted, ground Ottawa Sand.
- 3.7. Calibration Verification Standard (CVS). A standard made from another source at a concentration within the calibration range. An independent source is defined as a source different than that used to make the calibration standards. This standard is run at the beginning of every sequence (Initial Calibration Verification) and then again after every ten samples processed (Continuing Calibration Verification). The CVS verifies the calibration, not the method.
- 3.8. Standard Reference Materials (SRM). These are sediment standards from the National Institute of Standards and Technology (NIST) that have “Reference Values”, for the analyte being tested. Reference Values are non-certified values that NIST considers to be the best estimate of the true value of the analyte. These “Reference Materials” are used to verify recovery of a known concentration of carbon when run through the appropriate steps of the analysis.



3.8.1. NIST 8704 “Buffalo River Sediment” has an assigned reference value for Total Carbon (TC = 3.351 ± 0.017 %C).

3.8.2. NIST 1941B, “Organics in Marine Sediments” has an assigned reference value for Total Organic Carbon (TOC = 2.99 ± 0.24 %C).

4. Interferences

4.1. Sample homogeneity. Distribution of organic matter within a sample is critical for Carbon analysis (Schumacher 2002). This especially applies to solid phase samples. Samples must be thoroughly mixed and/or blended (homogenized) prior to withdrawing the sub-sample for analysis so that it accurately represents both the sample and the data needs of the client. Many sediment and some soil samples are fairly fine-grained and homogeneous such that sub-sampling is not a significant issue. However, many samples can be extremely heterogeneous, ranging from fine silts and sand to coarse rocks, shell fragments, and organic debris (roots, leaves, wood chips, etc.). Large inorganic particles (greater than 2mm) are generally inert and do not contribute significantly to the Carbon content (Schumacher, 2002). From a practical point of view, large organic debris, rocks, gravel, and shell fragments would be difficult to accurately sub-sample and process. Organics of significance are generally associated with the finer grained materials so that inclusion of coarse organic elements may bias the observed result and data objectives of the client (Schumacher, 2002). However, such particles may also be covered by significant organic surface films of detritus and periphyton which may or may not be of interest to the client. Removal of coarse elements from the sample may or may not be in line with the objectives of the client. The Project Manager should be consulted prior to commencing analysis on heterogeneous samples so that they may discuss acceptable protocol with the client and other labs that may be processing the same sample (e.g. if Carbon data is being used for carbon normalization then the sample base for all affected analytes should be equivalent). Exclusion or inclusion of coarse elements from any sample should only be conducted upon the direction of the project manager and, preferably, the client. *Note: When conducting an environmental investigation, the investigator generally has some specific purpose in mind. He/she then designs and executes a sampling program oriented toward providing information relative to that specific purpose. One goal of environmental sampling is that the sample be representative of either the environment from which it was taken or some specific characteristic of interest. Any unbiased environmental sample has the potential to contain materials (rocks, biological material, multiple phases etc.) that are non-representative of either the matrix or the characteristic. Such materials will often be excluded or separated from the sample when they are judged to be irrelevant to the specific purpose of the investigation or the characteristic of interest. A fundamental principle of*



environmental sampling is that only the designer of the sampling program makes decisions concerning the representativeness of materials contained within a sample. That person makes the decision to exclude materials from the sample. When a sample arrives at the laboratory, ARI can only assume that it represents the specific purpose and desires of the investigator. Decisions as to the exclusion of materials or separation of phases have already been made by the investigator and sampling personnel. It is not the role of ARI personnel to exclude materials or phases from a sample for analysis unless it is done with the knowledge and under the specific direction of ARI's client.

- 4.2. Volatiles - Volatile organic carbon will be lost from the sample matrix as a result of oven drying. We are unaware of any readily available procedure for including the volatile content in the TOC analysis of soils or sediments without adding significant time and expense to the analysis. Additionally, Carbon is generally expressed on the basis of sample dry weight at 104 °C. To reduce the temperature related loss of volatile organics, solid samples are dried at 70 °C with the analysis conducted on the dried sample. A separate aliquot of sample is taken for the analysis of percent solids at 104 °C which is used for conversion to the 104 °C dry weight basis.
- 4.3. Oily Samples. Oily samples and/or those containing petroleum residues present significant problems for Carbon analysis in that they may not dry properly at 70 °C and may be subject to significant loss of volatiles. Additionally, they will likely require significant dilution to fit within the range of the standard curve. Such samples should be analyzed on an "as received" basis (i.e. no correction for dry weight) with a known weight of sample being diluted directly to pre-combusted silica gel or Ottawa sand. The PM should be contacted prior to beginning the analysis of these kinds of samples.

5. Safety

5.1. The procedure for Carbon involves high temperature combustion of sample aliquots. Use caution and common sense when working around or replacing components of Soli TOC Cube. The toxicity or carcinogenicity of each reagent used in this SOP is not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available. Environmental Samples may contain hazardous materials; always treat them as potential health hazards. Use CAUTION with strong irritants such as acids, bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals. Avoid contact of these irritants with skin and clothing by appropriate use of gloves, apron, face-mask, hood shield, etc. Safety glasses must be worn all the time in the Lab.



Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

- 1.11. All safety procedures outlined in the laboratory Chemical Hygiene Plan must be following.
- 1.12. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult the SDS for all chemicals handled. SDS are also available online at www.msds hazcon.com, as linked on the ARI intranet.

6. Equipment and Supplies

1. General supplies and glassware

- 6.1. Carbon analyzer, Elementar Soli TOC Cube
- 6.2. Combustion catalyst. Platinum (Elementar S05 001 380)
- 6.3. Stainless Steel crucibles (Elementar S03 002 278)
- 6.4. Cotton wadding (Lohmann & Rauscher REF 10 111)
- 6.5. Brass Wool (Elementar S38.00-0124)
- 6.6. Quartz wool (Elementar S03 679 908)
- 6.7. Corundum balls (Elementar S50 008 467)
- 6.8. Sicapent (Elementar S03 960 352)
- 6.9. Drying oven. Maintained at 70 ± 2 °C.
- 6.10. Analytical balance (accurate to 0.0001g)
- 6.11. Nitrogen (99.995% pure)
- 6.12. Ultra pure oxygen (99.995% pure)

7. Reagents and Standards

- 7.1. All stock chemicals, reagents, standards, and standard solutions must be entered into the Element database at the time they are received and/or prepared. Element will assign a unique identifier to each chemical and prepared solution.
- 7.2. Organic Carbon Standard. Cellulose (44.44% Carbon by weight). (MP Biomedicals P/N:0219149980 or similar (Assay >95% pure))
- 7.3. Inorganic Carbon Standard. Calcium Carbonate (12.01% Carbon by Weight). (Elementar P/N: B35.00-0155 or similar (Assay >95% pure))



- 7.4. Elemental Carbon Standard. Carbon (99.95% pure Carbon by weight). (Aldrich P/N: 484164-10g or similar (Assay >95% pure))
- 7.5. Calibration Verification Standard (Elementar S05 005 345 TOC/TIC/TC standard or similar)
- 7.6. Standard Reference Material (SRM). Due to the high cost of these SRM's, they will be processed only upon client request.
- 7.7. The TOC SRM is, NIST 1941B, "Organics in Marine Sediment" with a reference TOC content of 2.99 ± 0.24 %C (range of 27,500 to 32,300 mg/kg).
- 7.8. The TC SRM is NIST 8704, "Buffalo River Sediment" with "Reference Value" for TC in the range of 3.351 ± 0.017 %C. NIST 8704 is used only when Total Carbon is the requested analyte.
- 7.9. Ottawa Sand (or equivalent), washed, ground, and ignited (EMD SX0075-1, Fisher MSX0075-1).
- 7.10. While Ottawa Sand is stated to be "washed and ignited", it will be washed and pre-combusted at 950 °C for at least 2 hours before being used to prepare the method blank and for standard and sample dilution.
 - 7.10.1. Place 400g of Attowa sand into the ball mill and grind to a fine powder over the course of a few days. The mill must be checked to be sure grinding is sufficient to continue to the combustion step.
 - 7.10.2. Transfer the ground sand to a container (stainless steel or porcelain evaporating dish) suitable for combustion.
 - 7.10.3. Combust in the muffle furnace at 950 °C for at least 2 hours to remove any residual carbon.
 - 7.10.4. Allow the furnace to cool to a reasonable temperature to be safely removed from the furnace and then finish cooling to room temperature under desiccation.
 - 7.10.5. After completely cooled to room temperature, transfer to a tightly closed glass container and store in a desiccator. The container should be labeled and dated.
- 7.11. DQL Standard. This is a low-level standard prepared by spiking pre-combusted and ground Ottawa Sand with the standard of the analyte to be analyzed to a concentration of approximately 200 ppm (0.02%C). Actual concentration will vary relative to gravimetric parameters at the time of preparation.
 - 7.11.1. The sand and standard mixture must be thoroughly homogenized in order to achieve a uniform, homogeneous, mixture of the sand and standard. Very important! Grind the sand to a very fine powder and mix thoroughly before use. Then transfer to a tightly closed glass container and store in a desiccator. The container should be labeled and dated.
- 7.12. The DQL standard and the Ottawa Sand blank should be run with each analytical batch.



8. Sample Collection, Preservation, Shipment and Storage

- 8.1. The carbon concentration of collected samples can be altered due to microbial degradation, chemical oxidation and volatilization due to physical processing (drying and selective removal of materials) prior to analysis (Schumacher, 2002). All of these factors should be taken into consideration when handling samples for analysis and interpreting results from that analysis.
- 8.2. Samples can be collected in clean, either glass or plastic, jars with Teflon[®] lined caps
- 8.3. Analytical holding times vary relative to author and the treatment of the sample. In general, samples should be processed within 14 days (Lloyd Kahn, 1988; Fox, 1991) but some extend this to 28 days (Schumacher, 2002) or, if frozen, 6 months (PSEP, 1986). ARI uses a holding time of 14 days for prepping un-frozen samples, extending this to 6 months if samples are frozen.
- 8.4. Sub-sampling to achieve a representative aliquot can have a significant impact upon the resulting concentration (**Read Section 4.2 for a discussion of the influence of sample heterogeneity**). Sample processing should be discussed with the PM prior to commencing analysis for non-routine matrices. Ideally, the client will have removed, at the time of collection, coarse elements and artifacts they do not want included in the analysis. Occasionally, ARI will receive multiphase heterogeneous samples. Do not process multiphase samples without specific, documented instructions from ARI's Project Manager and/or Client.

9. Quality Control (*Essential QC components following 40 CFR Part 136.7, May 18, 2012, EPA 2012 Method Update Rule.*)

- 9.1. Demonstration of Capability. *Each analyst using this procedure must run an initial "Demonstration of Capability" by preparing and analyzing 4 replicates of a NIST standard reference material (SRM). The recovery (Accuracy) must be within the expected range of the standard with a relative standard deviation (Precision) less than 20%. An on-going DOC will be provided by the analysis and recording of the SRM for each batch of carbon analyses conducted..*
- 9.2. Method Detection Limit. *The detection limit for this procedure has been determined by on-going analysis of Ottawa Sand Method Blanks following the protocol of the Federal Advisory Committee on Detection and Quantitation Procedures (FACDQ10-13, August 2007).*
- 9.3. Method Blank (BLK). *As documented in this SOP.*
- 9.4. Laboratory Blank Spike (BS). *A matrix blank spiked with a known concentration of the analyte to be tested.*
- 9.5. Matrix Spike (MS) and Matrix Spike Duplicate (MSD as required). *As documented in this SOP.*
- 9.6. Calibration. *As documented in this SOP.*
- 9.7. Control charts for trend analysis. *As documented within Element LIMS system.*
- 9.8. Corrective action (root cause analysis). *As documented in this SOP*



- 9.9. QC acceptance criteria. *As documented in this SOP.*
- 9.10. Definition of preparation and analytical batches. *See section 3.2.*
- 9.11. Frequency for conducting QC elements. *QC samples will be run with each batch of samples as defined above.*
- 9.12. Quality control is provided by the analysis of blanks and standards at the level of instrumental calibration and sample preparation. Standard Reference Materials will be inclusive of all preparation steps as appropriate to the analyte being measured.
- 9.13. Negative control, the absence of carbon background or contamination, is provided by the analysis of crucible blanks and the calibration verification blanks. Method Blanks, prepared with pre-combusted Ottawa Sand, will be run to verify absence of contamination through the procedure.
- 9.14. Positive control within the level of calibration is provided by the recovery of carbon from a second source carbon standard. The source of this carbon standard is different from that used for instrument calibration and hence it serves as a calibration verification standard.
- 9.15. Two Standard Reference Materials (SRMs) are available. One, NIST 8704, (Buffalo River Sediment) has a reference value for Total Carbon and the other, NIST 1941B, (Organics in Marine Sediment), has a reference value for Total Organic carbon. NIST 8704 is used only when Total Carbon is the requested analyte. NIST 1941B (Organics in Marine Sediments) is the routine SRM for TOC.
- 9.16. Quality control with respect to the sample matrix is provided by the analysis of replicate and matrix spike samples. Review the service request to identify any client specific QC requests (*e.g. specific samples to be used, number of replicates, number of spikes*). Normally, duplicate analysis (duplicate withdrawals from the original sample jar) on a single sample from within each client batch of 20 or less samples will be run. If more than 20 samples or if matrices differ significantly, additional sample replicates may be required.
- 9.17. Replicate aliquots are taken from the original sample jar (*after removal of any non-representative material*). The replicates are used to evaluate both the precision of the analysis and heterogeneity in the distribution of carbon in the original matrix. Batch analysis will not be controlled by measures of dispersion (*relative percent difference or relative standard deviation*) due to the potentially inherent variability of soil or sediment samples. Rather, measures of dispersion will be reported to the client so that they may evaluate how closely the reported values represent the actual concentration of carbon in the sample submitted for analysis.
- 9.18. Matrix spikes. One additional aliquot from the same sample (*after removal of any non-representative material*) used for replication will be taken for matrix spike analysis. Batch analysis will again not be controlled by the result of the matrix spike. The matrix spike will be used to



evaluate the accuracy of the analysis and the influence of the matrix and sample processing upon the observed carbon content. Spiking will be conducted by adding a known weight of standard to a known wet weight of sample (prior to drying). Clients may sometimes request Matrix Spike duplicates (MSD) in order to provide estimates for both accuracy and precision on a single sample matrix.

10. Calibration and Standardization

- 10.1. Carbon standards are prepared at known concentrations as indicated by the equipment manufacturers guidelines.
- 10.2. A standard curve is derived from least squares linear regression of the output peak area as a function of the known carbon injected.
- 10.3. The carbon for dry sample combustion is calculated from the regression slope and intercept statistics.
- 10.4. Calibration procedure. Calibration consists of two steps, defining the standards on the curve and then analyzing them. Calibration should be conducted if major maintenance is performed and/or upon confirmed failure of calibration verification standards.
- 10.5. Consult the Software User manual for Defining the Standards.
- 10.6. Cleaning the crucibles. Crucibles should be pre-combusted to remove all traces of organic residue that might be present after cleaning. Crucibles will be placed into a stainless steel pan and combusted at 900°C for at least 30 minutes to remove all carbon residuals. Store the crucibles in a covered container while they are not being actively used.
- 10.7. Running the Standards. Consult the Software User manual.
- 10.8. The Correlation Coefficient (r) for the curve (or for each curve if using the split curve function) should be greater than 0.995. The instrument returns the Coefficient of Determination (r^2) and this must be greater than 0.995 to satisfy the requirement for r ($r^2 = 0.990$ equals $r = 0.995$). If it is not, evaluate the curve to determine if any of the injections depart significantly from the line of best fit. Uncheck the questionable standard and recalculate the curve. If the r value is greater than 0.995 the curve is acceptable.

11. Procedure

- 11.1. The Ottawa Sand BLK and the MRL Standard should be prepared along with each batch of samples being processed. The sand has been pre-combusted and stored in a desiccator (see Section 7.7). The DQL standard has been prepared and stored in a desiccator. Take



- approximately 0.2 gram of the blank sand and the DQL standard and process them along with the samples.
- 11.2. The SRM (NIST 1941 B for TOC, and NIST 8704 for TC, see Section 7.6) only needs to be run when requested by the client.
 - 11.3. Initial Sample processing: The analyst should carefully evaluate the sample prior to preparation and identify its color, predominant grain size (percent gravel, sand, silt, clay or combinations of these) and the presence of any artifacts or inclusions. These characteristics should be used to determine the likely appropriate amount of sub sample required for the analysis and should be documented on the analysts Green Sheet, as appropriate for anomalies.
 - 11.4. In general, coarse elements (large rocks or shell fragments) which are either too large to fit in the crucible, or are not representative of the bulk of the sample might be excluded. Contact the PM if there is any ambiguity as to what should or should not be included in the sample aliquot taken for analysis. Do not exclude or remove any coarse elements unless there is documented authorization from the PM and/or client.
 - 11.5. Obtain clean crucibles for the sequence QC, Batch QC, and for each sample. Enter the sequence, batch, and sample ID's into the instrument sequence screen then place a clean crucible in the balance and tare the balance. Transfer 0.005 to 3.000 grams (*depending on expected concentration*) of the well homogenized sample (*after exclusion of any coarse elements*) to the crucible, and weigh (x.xxxx grams) by pressing the print button on the balance. This will record the result as the sample wt.(g) for analysis into the instrument sequence.
 - 11.6. Take at least one sample, from each batch of client's samples, for batch QC analysis. Spike by adding a known weight of standard at the desired concentration for the sample (~0.0300 for unknown samples) to the wet weight of sample in the crucible. Record the weight of the standard used to "memo" column of the sequence.
 - 11.6.1. $(\text{Spike weight(g)} \times \%C \text{ of spiked standard}) / (\text{weight of sample(g)}) = \%C \text{ spiked}$.
 - 11.7. Transfer the crucibles to a drying oven set at 70 ± 2 °C. Samples must be dry enough not to introduce a significant moisture content to the instrument. Residual moisture will be removed during analysis by the Sicapent dryer tube.
 - 11.8. Remove crucibles from the oven and transfer to the autosampler. Store dried samples in a desiccator if they will not be analyzed immediately.
 - 11.9. To set-Up, Elementar Soli TOC Cube. Follow the instructions in the Short manual for packing, installation and conditioning of the combustion tube, catalyst, filter, absorber, drying tubes, and for proper initialization of the instrument.
 - 11.10. Sample Analysis. Refer to the User manual for operation instructions.



- 11.11. Begin each sequence with at least 1 crucible burn, and 2 daily factor samples for the analyte(s) to be analyzed.
- 11.12. Samples may not be entirely homogenous. If a particular burn looks out of line with other samples within the batch, it would be advisable to re-run the sample to confirm. Process a third replicate for any suspect sample.

12. Review

- 12.1. The supervisor reviews the Service Request, enters information into the Conventionals database and assigns samples to the analyst.
- 12.2. The analyst verifies Service Request, reviews the SOP, and any special workorder/project special requests, and proceeds with the analysis.
- 12.3. The Analyst enters data into the Element LIMS system and checks the entered data for errors and completeness before setting the status to Analyzed.
- 12.4. Peer review is then performed on the final data and it is again checked for errors and status will continue to Peer Reviewed.
- 12.5. The supervisor or lead analysts then review the final generated results. Upon satisfactory review Status is then changed to Reviewed and data is ready for release by the project manager.



13. Data Analysis and Calculations

13.1. The Soli TOC Cube results are exported as %C Wet. No further calculations are required before entry to the Element LIMS system. Final results will be calculated on a dry weight basis at 104°C within the Element LIMS system.

13.2. Calculations performed by the instrument:

Absolute element content
 a = absolute element content in [mg] $a = \frac{w \cdot c}{100}$
 w = sample weight in [mg]
 c = element concentration in [%]

Calibration coefficient
 y = absolute element content in [mg] $y = a + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4$
 a...e = calibration coefficients
 x = peak area

Daily factor
 f = daily factor $f = \frac{C_{theo}}{C_{act}}$
 c_{theo} = theoretical element concentration
 c_{act} = element concentration computed actually

Element concentration of analysis samples
 c = element concentration in [%] $c = \frac{a \cdot 100 \cdot f}{w}$
 a = absolute element content in [mg]
 f = daily factor
 w = sample weight in [mg]

factor for polynomials of the 1st degree
 r² = correlation coefficient $r^2 = \frac{\left[\sum(x_i y_i) - \frac{(\sum x_i)(\sum y_i)}{n} \right]^2}{\left[\sum x_i^2 - \frac{(\sum x_i)^2}{n} \right] \left[\sum y_i^2 - \frac{(\sum y_i)^2}{n} \right]}$
 x_i = peak area of the corresponding sample
 y_i = absolute content of the corresponding sample
 n = number of samples
 i = index from 1 to n

Blank value determination
 /b = blank value $\bar{b} = \frac{\sum b_i}{n}$
 b_i = peak areas of the individual blank samples
 n = number of blank samples
 i = index from 1 to n

Blank value compensation
 a_{comp} = compensated peak area $a_{comp} = a - \bar{b}$
 a = measured peak area of the sample
 /b = blank value

14. Method Performance

14.1. Detection and quantitation studies are conducted following protocol as outlined by the Federal Advisory Committee on Detection and Quantitation Procedures (DQFAC DQ10-13, 8/31/2007).



Analysis for Method Blanks and spikes at the Quantitation Limit are conducted with each analytical run. Data are evaluated after each run and summarized on an annual basis.

15. Pollution Prevention

15.1. Not Applicable.

16. Data Assessment and Acceptance Criteria

16.1. For each burn, the % carbon value will be compared to the high and low values for the standard curve. If the value is greater than the high curve the burn will be flagged by the software as C1=TOC400, C2=ROC900, C3=TIC900.

16.1.1. If the value is below the low curve the burn will be flagged "C#u" (# being the analyte defined by the instrument).

16.1.2. If the value is above the high curve, the burn will be flagged "C#o". the analyst must either use a smaller sample weight for combustion or use a dilution. If the burn result is below the low curve point, the analyst should increase the burn weight.

16.1.3. The weight of the sample analyzed can bias sample results by decreasing precision of lower concentration samples if not analyzed at an appropriate volume. If the result for a sample is <5x the RL, and the weight burnt was <0.5g, the sample should be re-analyzed at a higher burn weight to produce a more accurate result.

16.2. Initial Calibration Verification (ICV) and Calibration Blank (ICB) must be run at the beginning of each sequence. Continuing Calibration Verification standards and blanks (CCV, CCB) must be run after every ten analytical samples in the sequence and at the end of each run. The calibration verification standards must agree within $\pm 10\%$ of the "true" value and the concentration of the blanks should be less than the Reporting limit ($\frac{1}{2}$ the RL for DoD).

16.3. Blank (BLK) must be run with each batch. Result should be less than the Reporting limit ($\frac{1}{2}$ the RL for DoD).

16.4. Blank Spike (BS) must be run with each batch. Control limits for the BS are $\pm 20\%$.

16.5. SRM samples are processed along an analytical batch when requested by the client. The TOC SRM is, NIST 1941B, "Organics in Marine Sediment" with a reference TOC content of 2.99%. The TC SRM is NIST 8704, "Buffalo River Sediment" with "Reference Value" for TC of 3.351%C. Control limits for either SRM are $\pm 20\%$.

16.6. Triplicate analysis. One sample per batch of 20 samples or job is prepped and analyzed in triplicate. The RSD is calculated within LIMS. Ideally, the value for the RSD should be less than



20%. Due to the inherent variability of Carbon in solids, we do not control on the RSD and no corrective action will be taken other than to advise the PM and client of the variability.

16.7. Matrix Spikes. One sample per batch of 20 samples or job is prepped and analyzed as a matrix spike. The appropriate spike is added to the wet sample and is processed through all steps of the analysis. Ideally, the spike recovery should be 75 -125% of the added concentration. Again, due to the inherent variability of TOC in solids, we do not control on the matrix spike recovery and no corrective action will be taken other than to advise the PM and client of the recovery and probable causes for excessively low or high values.

17. Corrective Actions for Out of Control Events

17.1. If Initial Calibration Verification (ICV) or Initial Calibration Blank (ICB) are out of QC limits, new calibration standards or new ICV solution should be made and the instrument re calibrated. If the Continuing Calibration Verification (CCV) or Continuing Calibration Blank (CCB) are out of QC limits, all samples not bracketed between in control condition must be re-run.

17.2. If results are outside the limits, the supervisor will review the entire procedure with the analyst to verify that correct procedures are being followed or check the instrument to make sure it is working properly.

17.3. If the SRM is not within 75-125% of its "true" value, it will be re-run to confirm the outlying condition. If confirmed, the analyst should verify operating conditions with respect to cleanliness of the crucibles, accuracy of the weight of sample combusted and dry status of the SRM. Re-run the SRM after verifying proper operating conditions and note the condition on the Corrective Action form. The SRM is prepared with the batch and therefore the batch samples will be controlled based upon the recovery value and the batch will be re-prepped.

17.4. If any of the following situations arises, the supervisor will be immediately notified, and the project manager be informed for resolution with the client:

17.4.1. The original sample contains excessive large coarse elements.

17.4.2. Samples have exceeded holding times.

17.4.3. There is insufficient sample to run the analysis.

18. Contingencies for Handling Out of Control or Unacceptable Data

18.1. In the event of significant QC failure, analysis will stop and the analyst will perform corrective action as discussed above. In general, out-of-control sample results will not be entered into the LIMs system but set to non-reportable. Re-runs will be conducted based upon availability of sample volume. If insufficient sample remains or the remaining sample has been compromised



by modification of the remaining sample volume or by holding time, the client will be notified to determine an appropriate course of action.

19. Waste Management

19.1. There are no known hazardous chemicals associated with this procedure.

20. Method References

- 20.1. Schumacher, B. A. 2002. Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments. USEPA. Ecological Risk Assessment Support Center. NCEA-C-1282. EMASC-001.
- 20.2. Geology.com. "The acid test for carbonate minerals and carbonate rocks".
- 20.3. Lloyd Kahn. 1988. "Determination of Total Organic Carbon in Sediment". USEPA, Region II, Edison, NJ.
- 20.4. Plumb, R.H., 1981. "Procedures for Handling and Chemical Analysis of Sediment and Water Samples". USEPA, USACOE. Environmental Laboratory, USAE, Waterways Experiment Station.
- 20.5. PSEP 1986. Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound. March 1986. (Minor Corrections April 2003). Total Organic Carbon (TOC).
- 20.6. PSDDA Clarification Paper. K. Bragdon-Cook. 1993. Recommended Methods for Measuring TOC in Sediments
- 20.7. David Fox. 1991. Revised Modifications to Holding Times for PSDDA Chemical Analysis.
- 20.8. WSDOE. 2009. Quality Assurance Project Plan. The Puget Sound Assessment and Monitoring Program: Sediment Monitoring Component. Washington State Department of Ecology. Publication No. 09-03-121.
- 20.9. NELAC (2011). TNI Standard. Volume 1. Management and Technical Requirements for Laboratories Performing Environmental Analysis. The NELAC Institute. Publication EL-V1-2011.
- 20.10. EPA LG601 2005. Standard Operating Procedure for Analysis of Total Organic Carbon in Sediments (Dry Combustion, IR Detection). EPA, Great Lakes National Program Office. Revision 04, March 2005.
- 20.11. Test Methods for Evaluating Solid Wastes. EPA, SW-846. Volume 1C. Method 9060A. Rev. Nov. 1990.
- 20.12. DQFAC, 2007. DQFAC Single Laboratory DL-QL Procedure (Version 2.4). Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs.



- 20.13. DIN EN 15936 - Sludge, treated biowaste, soil and waste – Determination of total organic carbon (TOC) by dry combustion.
- 20.14. DIN 19539 - Investigation of solids — Temperature-dependent differentiation of total carbon.
- 20.15. DIN EN 13137 - Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments.
- 20.16. ISO 10694 - Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis).
- 20.17. Pitt, J.L., T.L. Provin, F.M. Hons, F. Dou, and J.S. Waskom.
- 20.18. Abstracts, 2003 Meeting of ASA, Denver, CO.
- 20.19. Elementar 2018 Soli TOC Cube Operation Manual.

21. Appendices



Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Chlorinated Pesticides EPA Method 8081B

**SOP 423S
Revision 019**

**Revision Date: 2/11/2020
Effective Date: 2/11/2020**

Prepared by:
Van Spohn

Approvals:

A handwritten signature in blue ink that reads "Brian N. Bebee".

Brian N. Bebee, Laboratory Section Manager

A handwritten signature in blue ink that reads "David R. Mitchell".

David R. Mitchell, Quality Assurance Manager



Annual Review

SOP Number: 423S

Title: Chlorinated Pesticides EPA Method 8081B

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____



1. Scope and Application

1.1. This document describes the procedures used by Analytical Resources Inc. (ARI) to implement EPA Method 8081B for qualitative and quantitative analysis of sample extracts for organo-chlorine pesticides. This SOP is written to meet the requirements of EPA Method 8081B Revision 2, November 2000 and EPA Method 608. Specific requirements for Method 608 are listed in Appendix 20.4 when required.

1.1.1. Routine analytes for this procedure are listed in Table 01:

Table 01	
Compound / Analyte Name	CAS Number
Aldrin	309-00-2
<i>alpha</i> -BHC	319-84-6
<i>beta</i> -BHC	319-85-7
<i>delta</i> -BHC	319-86-8
<i>gamma</i> -BHC (Lindane)	58-89-9
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
<i>cis</i> -Chlordane	5103-71-9
<i>trans</i> -Chlordane	5103-74-2
Dieldrin	60-57-1
Endosulfan-I	959-98-8
Endosulfan-II	33213-65-9
Endosulfan Sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Methoxychlor	72-43-5
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3

1.1.2. Additional single component analytes may include those listed in Table 02:

Table 02	
Compound / Analyte Name	CAS Number
2,4'-DDD	3424-82-6
2,4'-DDE	53-19-0
2,4'-DDT	789-02-6
Oxychlordane	27304-13-8
<i>trans</i> -Nonachlor	39765-80-5
<i>cis</i> -Nonachlor	5103-73-1
Mirex	2385-85-5



1.1.3. Additional multi-components analytes may include those listed in Table 03:

Table 03	
Compound / Analyte Name	CAS Number
Chlordane (N.O.S.)	57-74-9
Chlordane (Technical)	12789-03-6
Toxaphene	8001-35-2

1.2. Trans-Chlordane (CAS#5103-74-2) is named as such in EPA Method 8081B (Feb 2007). It has also been named *gamma*-Chlordane and beta-Chlordane previously. *Cis*-Chlordane (CAS#5103-71-9) is also named in EPA Method 8081B (Feb 2007). It has also been named *alpha*-Chlordane previously.

1.3. Total Chlordane's are calibrated and reported as not otherwise specified (N.O.S) chlordane (CAS#57-74-9). Technical Chlordane (CAS#12789-03-06) may also be requested on a project specific basis. N.O.S. chlordane is used for calibration and pattern matching when technical chlordane is requested.

1.4. This method is restricted to use by analysts experienced in the use of a gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5. The additional multi-component analytes are mixtures that may interfere with identification and quantification of other target analytes. These mixtures are also prone to environmental degradation (weathering) that may alter their composition compared to non-weathered standards. In samples containing these multi-component mixtures a higher level of analyst expertise is required to assure proper qualitative and quantitative analysis.

1.6. This method employs a single injection, dual column system. Injected sample extract flows from the GC injection port onto a guard column and then is split onto two analytical columns using a glass "Y" connector. Each column elutes into a separate ECD detector resulting in two chromatograms for each sample injection.

1.7. Procedures described in this document allow the flexibility to meet the requirements of various analytical programs, including the EPA SW-846 methods, the NELAC Institute Program and the Department of Defense Quality Systems Manual (DoD-QSM). The table in Appendix 20.2 outlines ARI's routine procedure. The table in appendix 20.3 shows acceptance criteria for EPA method 608 when requested. DOD-QSM acceptance criteria are shown in Appendix B of DOD-QSM 5.3. Acceptance criteria for projects requiring modified DOD-QSM criteria are provided by the project manager and are project specific. **Analysts are responsible for determining which QA program is applicable to a set of samples prior to beginning analyzes and complying with all project specific analytical requirements.**



1.8. The reference methods for this procedure are listed in Section 20.

1.9. Detection Limits

1.9.1. Detection limits depend on the volume of sample extracted, the final extract volume and the lowest calibration point of the instrument calibration. The MRL values found in Table 4 are for those analytes curved to the lowest values. For those analytes shown in Table 5 to have higher values for the low point of the initial calibration the MRL will be raised proportionately.

Sample Matrix	Extraction Solvent	Sample Volume or Weight	Final Volume (mL)	Reporting Limit (ppb)
Water	CH ₂ Cl ₂	500 mL	5.0	.025-0.05
Water (low)	C ₆ H ₁₄	1000 mL	0.5	.000625-.00125
TCLP Extract	CH ₂ Cl ₂	100 mL	10.0	.250-.500
Soil/ Sediment (low)	CH ₂ Cl ₂	12.5 g	2.5	0.5-1.0
Soil/ Sediment	CH ₂ Cl ₂	12 g	4.0	1.7-3.3
Soil/ Sediment (med)	CH ₂ Cl ₂	5 g	40.0	20
Tissue	CH ₂ Cl ₂	5 g (wet)	10	5

1.9.2. Batch MRL standards are prepared and analyzed with sample batches and are used to statistically determine method detection limits (MDL) and method reporting limits (MRL). MRL spikes are prepared and analyzed quarterly or more frequently, as necessary to establish LOD and MRL.

2. Summary of the Procedure

2.1. Surrogate standards are added to a measured volume or weight of sample which is extracted using an appropriate organic solvent and extraction technique. The resulting extract is concentrated to a specified final volume. Project or Protocol required Quality Assurance Samples are prepared and analyzed using identical techniques.

2.2. A variety of cleanup steps may be applied to the extracts, depending on the nature of any co-extracted matrix interferences and the requested target analytes. All cleanup techniques must be applied to all sample extracts including QC samples (MB, BS, MS, MRL, etc.).

2.2.1. Acid cleanups are sometimes used for non-acid labile analytes, a list of analytes appropriate for acid cleanups is found in Appendix 20.4.



- 2.3. Following any cleanup, the extract is concentrated to a designated final effective volume and delivered to ARI's Gas Chromatography Laboratory for identification and quantification of organochlorine pesticides.
- 2.4. Following addition of internal standards 1 μ L of the extract is injected onto a GC using an auto-sampler and split-less injection technique.
- 2.5. The injected sample is split onto two columns by passing through a glass Y connector. Analytes are detected and quantified using ECD detectors.
- 2.6. Identified Target analytes are quantified using an internal standard procedure as described in Section 12.2

3. Definitions

- 3.1. BNB (1-Bromo-2-Nitrobenzene): Internal standard.
- 3.2. Initial Calibration Verification (ICV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable.
- 3.3. Continuing Calibration Verification (CCV): An instrument calibration standard is used to verify that the current instrument calibration is acceptable.
- 3.4. Continuing Calibration Verification Standard (CCVS): The standard prepared at the mid-point concentration of the initial calibration, and prepared from the same source as the initial calibration used to perform the ICV and CCV.
- 3.5. DCBP (Decachlorobiphenyl): Surrogate standard.
- 3.6. ECD (Electron Capture Detector): A detector with a high specificity and sensitivity to organic molecules with highly electronegative functional groups. An ECD is especially suitable for identifying and quantifying organochlorine compounds including Aroclors and selected pesticides and herbicides.
- 3.7. HBBP (2,2',4,4',5,5'-Hexabromobiphenyl): Internal standard.
- 3.8. Second source Calibration Verification (SCV): An instrument calibration standard purchased from a secondary vendor is used to verify that the current instrument calibration is acceptable.
- 3.9. Second Source Calibration Verification Standard (SCVS): A midpoint concentration standard from a source different than that used for the initial calibration used to demonstrate the validity of the initial calibration. The second source standard must be purchased from a different vendor than the calibration standard whenever possible.
- 3.10. Instrument Blank (IB): A QC sample made by adding surrogates to clean solvent used to measure instrument background.
- 3.11. Internal Standard (IS): internal standards are compounds added to each standard,



sample, and QC sample such that their concentration is the same in each of these sample types. Target analyte response is normalized to the response of these internal standards.

- 3.12. Blank Spike (BS) – A sample matrix, free from the analytes of interest, spiked with verified amounts of analytes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system. Pesticides (Section 7.1) are the routine BS analytes. All Pesticides must be included in an BS at least once every two years.
- 3.13. Blank Spike Duplicate (BSD): A replicate BS often used to assess the precision of an analytical method. When insufficient sample volumes exist to perform a required MS/MSD analysis, an BS/BSD may be performed to assess the precision of the analytical method. The BSD is prepared and analyzed identically to the BS. Pesticides (Section 7.1) are the routine BSD analytes. All Pesticides must be included in a BS at least once every two years.
- 3.14. ELEMENT (Laboratory Information Management System): Software used to compile and report final chromatographic data.
- 3.15. MDL (Method detection Limit): The lowest result that can reliably be distinguished in a matrix from a blank. Also referred to as the limit of Detection (LOD)
- 3.16. MRL (Method Reporting Limit)–The lowest result that may be reported unqualified based on the lowest curve point. Also referred to as the Minimum Reporting Limit.
- 3.17. Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the sample matrix on the recovery efficiency of an analytical method.
- 3.18. Matrix Spike Duplicate (MSD): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure analytical precision.
- 3.19. Method Blank (MB): A sample of a matrix like the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
- 3.20. MRL Spike (Method Reporting Limit Spike): A matrix spike prepared at reporting limit, used to determine the MDL and MRL.
- 3.21. Solvent Blank (SB) – Clean solvent is analyzed using the same conditions as a regular sample. A solvent blank is analyzed to detect and/or remove sample carryover from one analysis to another.
- 3.22. Surrogate – A substance with properties that mimic the analyte of interest. It is unlikely to



be found in environment samples and is added to them for quality control purposes.

3.23. Target Software: Software used to integrate and reduce raw chromatographic data.

3.24. TCMX (Tetrachloro-m-Xylene): Surrogate standard

4. Interferences - Sources of interference in this method can be grouped into three broad categories:

4.1. Contaminated solvents, reagents and/or sample processing hardware.

4.1.1. Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

4.1.1.1. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and by checking all solvents and reagents for phthalate contamination.

4.1.1.2. Method interferences may be reduced by washing all glassware with hot, soapy water and then rinsing them with warm tap water, acetone, and methylene chloride.

4.1.1.3. Glassware should be baked at 450°C for a minimum of 4 hours after washing to further reduce interference problems.

4.1.1.4. High purity reagents must be used to minimize interference problems.

4.2. Contaminated GC carrier gas, parts, column surfaces and/or detector surfaces

4.2.1. Chromatographic interference

4.2.1.1. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination (if needed).

4.2.1.2. Multi-component mixtures such as Toxaphene may interfere with the identification and quantitation of individual chemical compounds.

4.2.1.3. Other organic compounds may be extracted along with the target analytes and interfere with the analysis of pesticides.

4.3. Matrix Interferences

4.3.1.1. High molecular weight materials (waxes, lipids, etc.) and certain co-eluting Organophosphorus pesticides may be eliminated by the Gel Permeation Chromatography cleanup pesticide option (EPA Method 3640).



- 4.3.1.2. Co-eluting Chlorophenols may be eliminated by Silica Gel (EPA Method 3630), Florisil (EPA Method 3620), or Alumina (EPA Method 3610) cleanup.
- 4.3.1.3. Co-eluting PCBs, although they are generally not removed by cleanup, may cause interferences that result in raised reporting limits.
- 4.3.1.4. Phthalate esters may be removed using alumina clean-up (EPA Method 3610.)
- 4.3.1.5. The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur may be removed using the TBAS method (EPA Method 3660.) as described in ARI SOP 334S. Sulfur contamination should be expected with sediment samples; therefore, all sediment extracts must be treated with TBAS. Sample extracts still requiring additional cleanup for Sulfur interferences can be treated with an additional TBAS clean-up.
- 4.3.1.6. Interferences co-extracted from the samples will vary considerably from sample to sample. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

5. Safety

- 5.1. The toxicity and carcinogenicity of each reagent used in this method is not precisely defined. However, all compounds and solutions should be treated as health hazards, and exposure of these chemicals to skin and clothing should be minimized to the lowest possible level by whatever means available.
- 5.2. Wear nitrile gloves, safety glasses, and laboratory coats when working with reagents, standards and sample extracts to minimize exposure to chemicals.
- 5.3. All GC split vents are connected to an exhaust vent.
- 5.4. Open containers of solvents, reagents or sample extracts must be handled in the fume hoods to avoid exposure to potentially toxic fumes.
- 5.5. ARI maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (SDS) is available to all personnel involved in the chemical analysis. Consult with SDS sheets or available online at www.msds hazcon.com for all chemicals handled.

6. Equipment and Supplies

- 6.1. Gas chromatograph: Analytical systems complete with a temperature-programmable gas chromatograph equipped with a split-less injection system and all required accessories including:



6.1.1. Autosampler

6.1.2. Analytical columns Fused-silica capillary columns - One of the two following column pairs are commonly used. Columns used may vary depending on currently available technology (other column pairs that generate equivalent data may be used):

6.1.2.1. Column 1: Stx-CLP1, 30 m, 0.32 mm ID, 0.50 μ m film. Column 2: Stx-CLP2, 30 m, 0.32 mm ID, 0.50 μ m film.

6.1.3. Siltek® glass press tight angled y-connectors.

6.1.4. Siltek® coated 5m 0.53 mm ID pre-columns.

6.1.5. ECD detectors

6.2. Data system - A computer system must be interfaced to the GC. The system must allow the recording of instrument response as a function of time

6.2.1. The data must be securely stored for at least seven years from date of acquisition in Target.

6.3. Syringes - 10 μ L, 25 μ L, 50 μ L, 100 μ L, 500 μ L, 1000 μ L

6.4. Volumetric flasks, Class A - 10 mL to 1000 mL.

6.5. Bottles – amber glass with Teflon-lined screw caps or crimp tops.

6.6. Autosampler vials- amber 2 ml autosampler vials with Teflon-lined crimp caps

7. Reagents and Standards

7.1. Stock standard solutions (1,000-10,000 μ g/L) – Standard solutions can be prepared from neat standards or purchased as certified solutions. Certificates of analysis for all purchased neat's and solutions are kept electronically in Element.

7.2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2.1. All Components and reagents used for any standard preparation are entered in Element.

7.2.2. The laboratory should have high purity acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, methanol and other appropriate solvents for preparing standards.

7.2.3. Organic free water (OFW) – All references to water in this method refer to ASTM Type 1 18 megaohm organic free reagent water.

7.2.4. Neat standards are not assigned an expiration day and are considered never expired regardless of what is shown on the standard certificate (COA).



7.3. Stock Solutions

7.3.1. Prepare stock standard solutions by accurately weighing about 0.2500g of pure material. Dissolve the material in pesticide free grade methylene chloride or other suitable solvent and dilute to volume in a 25ml volumetric flask. When neat compounds are assayed to be 97% or greater purity, their weight may be used without correction to calculate the concentration of a stock standard.

7.3.2. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source. Certificate of Analysis for certified compounds and solutions are stored electronically in Element as a .pdf.

7.3.3. Transfer the stock standard solutions into amber bottles with Teflon lined screw-caps. Store at 0 to 6°C and protect from light.

7.3.4. Stock standard solutions must be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.3.5. Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates they have degraded, or they expire.

7.3.6. Stock standard solutions must be replaced one year after being de-ampullated.

7.3.7. A PDF record of analysis for stock solutions prepared in-house must be attached to the standard registry in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.

7.3.8. Internal Standard Stock Solution - The internal standards employed are 1-Bromo-2-Nitrobenzene and 2,2',4,4',5,5'-Hexabromobiphenyl. Other compounds that meet the method IS requirements may be used.

7.3.8.1. Prepare a stock solution with each IS at a concentration of 1000 µg/ml by dissolving 0.1g of each in a 100 mL volumetric flask and dilute to volume with hexane.

7.3.9. Surrogate Stock Standards- The surrogate standards employed are tetrachloro-m-xylene (TCMX) and decachlorobiphenyl.

7.3.9.1. Prepare a stock solution with each surrogate at a concentration of 1000 ug/mL by dissolving 0.1g of material in a 100 mL volumetric flask and dilute to volume with a hexane.

7.4. Working solutions- working standards are prepared from stock standards or purchased as commercially certified mixtures.

7.4.1. Working standards expire either on the date of expiration of the stock solutions they are made from, or on the manufacturer's certified expiration date or within six months from date of preparation, whichever comes first. They must be replaced at this time.

7.4.2. Working standard solutions must be replaced six months after being de-ampullated.



- 7.4.3. Working standards must be stored at 0 to 6°C and protected from light.
- 7.4.4. Working standards must be checked frequently for signs of concentration or degradation.
- 7.4.5. A PDF record of analysis must be attached to the standard registry (non-virtual only) in Element and a notation entered in the comments indicating which instrument and the date the verification was performed.
- 7.4.6. Internal Standard Working Solution-
- 7.4.6.1. Prepare an Internal Standard Working Solution by diluting the Internal Standard Stock Solution such that the concentration of each internal standard is 8µg/mL.
- 7.4.6.2. Each 0.1mL aliquot of the sample extract undergoing analysis must be spiked with 1µL of the internal standard solution, resulting in a concentration of 80ng/mL of each internal standard (for example, when preparing a sample aliquot of 0.3ml, spike the extract with 3µl of the internal standard working solution).
- 7.4.7. Working Standards
- 7.4.7.1. A surrogate spiking standard is prepared by diluting the TCMX and DCBP surrogate stock such that the concentration of each analyte is 2µg/mL. This solution is prepared in Acetone. This solution is used to spike all extracted samples and QC samples with surrogates.
- 7.4.7.2. Blank Spike Working Standard is used to prepare the BS, and when applicable the BSD.
- 7.4.7.3. The BS working spike is prepared from commercially certified mixtures.
- 7.4.7.4. The BS working solution contains those analytes that per Table 05 are curved down to 1.25ng/mL on column at a concentration of 2µg/mL. Those analytes that per Table 5 are curved down to 2.5ng/mL are present in the BS working solution at a concentration of 4µg/mL. Toxaphene is present in the BS working solution at a concentration of 20µg/mL. Methoxychlor, per Table 5 is curved to 12.5ng/mL and is present in the BS working solution at a concentration of 200ug/mL.
- 7.4.7.4.1. Blank spikes containing nearly all the target analytes that are used.
- 7.4.7.5. Matrix Spike Working Standards are used to prepare MS/MSD sets.
- 7.4.7.5.1. Commercially certified solutions are used to prepare the matrix spiking working standards.
- 7.4.7.5.2. MS/MSD spikes containing nearly all the target analytes that are used.
- 7.4.7.5.3. MRL spike working standards made from certified solutions are used to prepare MRL spikes.
- 7.4.8. Calibration working standards- the standards used to prepare calibration curves are purchased as commercially certified mixtures.



7.4.8.1. Prepare calibration working standards by diluting these commercially certified standards such that the concentration of each analyte in each calibration standard corresponds to the concentration found in Table 05.

Table 05								
Compound / Analyte Name	CAS Number	Calibration Standard Concentrations ng/mL						
		1	2	3	4	5	6	7
Routine Analytes								
Aldrin	309-00-2	1.25	2.50	5.0	10.0	20.0	40.0	80.0
<i>Alpha</i> -BHC	319-84-6	1.25	2.50	5.0	10.0	20.0	40.0	80.0
<i>beta</i> -BHC	319-85-7	1.25	2.50	5.0	10.0	20.0	40.0	80.0
<i>delta</i> -BHC	319-86-8	1.25	2.50	5.0	10.0	20.0	40.0	80.0
<i>gamma</i> -BHC (Lindane)	58-89-9	1.25	2.50	5.0	10.0	20.0	40.0	80.0
<i>cis</i> -Chlordane	5103-71-9	1.25	2.50	5.0	10.0	20.0	40.0	80.0
<i>trans</i> -Chlordane	5103-74-2	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Endosulfan-I	959-98-8	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Heptachlor	76-44-8	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Heptachlor epoxide	1024-57-3	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Hexachlorobenzene	118-74-1	1.25	2.50	5.0	10.0	20.0	40.0	80.0
Hexachlorobutadiene	87-68-3	1.25	2.50	5.0	10.0	20.0	40.0	80.0
4,4'-DDD	72-54-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
4,4'-DDE	72-55-9	2.50	5.0	10.0	20.0	40.0	80.0	160.0
4,4'-DDT	50-29-3	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Dieldrin	60-57-1	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endosulfan-II	33213-65-9	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endosulfan Sulfate	1031-07-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endrin	72-20-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endrin aldehyde	7421-93-4	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Endrin ketone	53494-70-5	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Methoxychlor	72-43-5	12.5	25.0	50.0	100.0	200.0	400.0	800.0
Additional Analytes								
2,4'-DDD	3424-82-6	2.50	5.0	10.0	20.0	40.0	80.0	160.0
2,4'-DDE	53-19-0	2.50	5.0	10.0	20.0	40.0	80.0	160.0
2,4'-DDT	789-02-6	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Oxychlordane	27304-13-8	2.50	5.0	10.0	20.0	40.0	80.0	160.0
<i>trans</i> -Nonachlor	39765-80-5	2.50	5.0	10.0	20.0	40.0	80.0	160.0
<i>cis</i> -Nonachlor	5103-73-1	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Mirex	2385-85-5	2.50	5.0	10.0	20.0	40.0	80.0	160.0
Multicomponent Analytes								
Chlordane (technical)	57-74-9	200						
Toxaphene	8001-35-2	500	1000	2500	5000	10000		



8. Sample Collection, Preservation, Shipment, Storage and Disposal.

- 8.1. Samples must be collected in an appropriate container, transported to ARI and stored under custody at >0 to 6 °C.
- 8.2. Samples must be stored at ARI, at >0 to 6 °C until final disposal.
- 8.3. Extracts
 - 8.3.1. Extracts are delivered to Refrigerator 15 in the instrument laboratory by extractions technicians.
 - 8.3.2. Analysts in the instrument lab assume custody of the sample extracts and then move them into Refrigerator 17 in a bin assigned in Element
 - 8.3.3. Extracts must be stored at >0 to 6 °C and protected from light.
 - 8.3.4. Extracts must be analyzed within 40 days of extraction initiation.
 - 8.3.5. Extracts must be stored in their assigned Element bin.
 - 8.3.6. Extracts may be disposed 40 days after the analysis has been completed and the Element bin will be recycled for future use.
 - 8.3.7. Extracts will be disposed in the large blue barrel in the satellite accumulation area designated for extract vials. Disposed extracts are now marked in Element as disposed.

9. Quality Control

- 9.1. ARI in-house Quality control requirements are tabulated in Appendix 20.2.
 - 9.1.1. Acceptance criteria for ARI's routine analyzes listed in the column title "ARI Acceptance Criteria".
 - 9.1.2. When DoD-QSM acceptance criteria differ, they are provided in the "DoD-QSM Acceptance" column.
- 9.2. ARI routinely checks the effect of the matrix on both method precision and bias. At a minimum, this check should include the analysis of at least one matrix spike and one duplicate unspiked sample, or one MS/MSD pair with each preparation batch of up to 20 samples of the same matrix.
 - 9.2.1. Endrin and DDT Degradation
 - 9.2.1.1. Endrin and DDT are especially susceptible to chemical degradation (breakdown) during the gas chromatographic analysis. The degradation generally occurs in the injection port. Endrin may be converted into endrin ketone and endrin aldehyde while 4,4'-DDT may degrade forming 4, 4'-DDE and/or 4, 4'-DDD. The degradation of Endrin and 4, 4'-DDT must be assessed for a given chromatographic system prior to analyses.
 - 9.2.1.2. A Degradation Standard (DS) is analyzed along with all initial calibrations and with each ICV/CCV. The DS contains Endrin and DDT at concentrations of 0.1 µg/mL.



9.2.1.3. DDT breakdown is calculated as follows:

DDT % Breakdown = $((DDE + DDD) / (DDT + DDE + DDD)) 100$
where:
DDE = chromatographic response for 4,4'-DDE
DDD = chromatographic response for 4,4'-DDD
DDT = chromatographic response for 4,4'-DDT

9.2.1.4. Endrin breakdown is calculated as follows:

Endrin % Breakdown = $((EA + EK) / (E + EA + EK)) 100$
where:
E = chromatographic response for Endrin
EA = chromatographic response for Endrin Aldehyde
EK = chromatographic response for Endrin Ketone

9.2.1.5. The breakdown of Endrin and 4, 4'-DDT must each be $\leq 15\%$ or corrective action is required. Corrective actions are provided in Section 16.

9.2.2. Internal Standard Response

9.2.2.1. For each IS, area and retention time data are evaluated during and/or immediately after the analysis.

9.2.2.2. The response for each of the internal standards must be within the inclusive range of -50.0% to $+100.0\%$ of the response of the internal standards in the most recent initial calibration at the CCV level.

9.2.2.3. The retention time shift for each of the internal standards must be within ± 0.02 minutes (1.2 seconds) between the sample and the most recent continuing calibration verification.

9.2.2.4. When the IS criteria are out of control for one column but are acceptable on the other column, the in-control column may be used to quantify analytes without corrective action.

9.2.2.5. Corrective action is required when IS criteria are out of control on both columns and/or any analyte may not be quantified on an in-control column.

9.3. Method Control

9.3.1. Surrogate Standards

9.3.1.1. Surrogate Standards, tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCBP) are added to every sample analyzed including all QA samples.



9.3.1.2. The recovery of spiked surrogate standards is calculated and compared to established control limits.

9.3.1.3. Corrective action is required when a surrogate standard recovery is outside of established control limits.

9.3.2. Method Blanks

9.3.2.1. A method blank (MB) analysis is required for each sample extraction batch. A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified solid matrix for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination resulting from the processing and analysis of samples.

9.3.2.2. Method blank extraction and analysis are performed as follows:

9.3.2.2.1. Whenever samples from different SDGs are extracted by the same procedure up to 20 samples may be batched together with the same method blank.

9.3.2.2.2. Each 20 samples in an SDG, excluding matrix spike/matrix spike duplicates, that are of a similar matrix (water, soil/sediment) or similar concentration (soil/sediment only) would constitute a separate extraction batch.

9.3.2.2.3. Each MB must contain all method specific surrogate standards.

9.3.2.2.4. Method blanks must be analyzed on each analytical instrument used to analyze associated samples.

9.3.2.2.5. Target analytes are identified and quantified in the MB.

9.3.2.2.6. Corrective action is required when the concentration of any target analyte in the method blank is greater than half the analyte reporting limit.

9.3.2.2.7. The Method blank may be re-analyzed when the GC instrument is the suspected source of contamination.

9.3.3. Blank Spikes (BS)

9.3.3.1. BS analyses evaluate the accuracy of the analytical method independent of matrix-related effects, a matrix-specific BS must be included in each preparation batch.

9.3.3.2. Spiked target analytes are identified and quantified in the BS.

9.3.3.3. Corrective action is required when the recovery of spiked analytes is outside of established control limits.

9.3.3.4. An associated blank spike duplicate (BSD) may be required to assess method precision.

9.3.3.5. BS and BSD samples must contain all surrogates required for sample analysis.



9.3.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.3.4.1. A matrix spike and matrix spike duplicate are extracted and analyzed for every batch of 20 field samples of a similar matrix or whenever samples are extracted by the same procedure at the same time.

9.3.4.2. A client's QA/QC samples (equipment rinses, field/trip blanks etc.) must not be used for MS/MSD analyzes

9.3.4.3. When ARI's client designates a sample to be used as an MS/MSD, that sample must be used. When there is insufficient sample to perform an MS/MSD, then the laboratory may upon consulting with the client, choose another sample for the MS/MSD, reduce the MS/MSD or utilize BS/BSD analysis to assess method precision. The rationale for the choice a sample other than the one designated by the client must be documented in the narrative.

9.3.4.4. Dilution of MS/MSD extracts to get either spiked compounds or target analytes on scale is not required.

9.3.5. Method Reporting Limit Spike (MRL)

9.3.5.1. MRL analyses evaluate the LOD and the MRL of the analytical method independent of matrix-related effects, a matrix-specific MRL may be included in each preparation batch.

9.3.5.2. Spiked target analytes are identified and quantified in the MRL.

9.3.5.3. Corrective action is not required for MRL recoveries.

9.3.5.4. MRL extracts must contain all surrogates required for sample analysis.

9.3.6. Statistical Control- Internal quality control limits for analyte spike and surrogate recoveries and relative percent difference for matrix spike and matrix spike duplicates are statistically generated on a periodic basis.

9.3.6.1. These quality control limits are provided to bench chemists, managers, and QA staff as tools for assessing data quality in real-time at the point of data generation.

9.3.6.2. Practical considerations relating to their dynamic nature require their presentation in a document separate from this SOP. Current control limits may be found in Element.

9.3.6.3. All analysts using this SOP must use it in conjunction with Control Limit documentation to assess data acceptability and/or the need for corrective actions.

9.4. Method performance must be re-evaluated every time there is a change in instrument type, personnel or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in Appendix 2.2 of ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive in



SharePoint. Each DOC must be documented and stored in the SharePoint/ARIQA/Employee lists directories.

10. Calibration and Standardization

- 10.1. Prepare calibration standards at the concentrations listed in Table 05. Spike all calibration solutions with Internal Standard as described in Section 11.6.
- 10.2. Toxaphene is calibrated using a single standard at 2.5 ppm. When Toxaphene is identified in a sample, the sample must be re-analyzed along with a six-point Toxaphene calibration.
- 10.3. Technical Chlordane is calibrated using a single standard at 0.2 ppm. When Chlordane is identified in a sample above 0.02 ppm, the sample must be re-analyzed along with a six-point Chlordane calibration.
 - 10.3.1. An MRL level Chlordane standard will be run in conjunction to the single standard and evaluated with the main list of pesticide analytes, to Chlordane for the component Chlordane in an MRL level of Chlordane. This MRL level will be compared manually against the method blank and samples and if all analyte hits fall below these MRL levels then a zero will be entered for Chlordane when reporting. If on the other hand there is a hit above the component chlordane MRL levels for any of the identified compounds, then the sample and associated method blank will be quantitated for Chlordane against the single standard to determine if the response is above the MRL for the multi-component analyte.
- 10.4. Begin the initial calibration sequence by injecting the priming standard. After the priming standard, inject the DS and evaluate it per the criteria found in Section 9.2.1. When the DS meets the acceptance criteria, inject the IB.
- 10.5. After evaluating the IB for background instrument contamination, analyze 1 μ L of each of the initial calibration standards described in Section 10 containing the Internal Standard and tabulate the peak area against the peak area of the internal standard. The injection volume and instrument operating conditions used for the initial calibration must be used for all subsequent sample analysis.
- 10.6. Calculate a relative response factor (RRF) for each target analyte and surrogate using the formula:

$RRF = (A_X C_{IS}) / (A_{IS} C_X)$
where:
A_X = Peak area for the peak being measured
A_{IS} = Peak area of the internal standard
C_{IS} = Concentration of the IS associated with the peak



$C_x = \text{Concentration of the analyte}$

10.7. Calculate the average RRF for each peak. The formula is:

Average RRF = $\Sigma \text{RRF}_i / n$
where:
RRF _i = the peak response factor for each quantitation peak in the calibration standard
N = the total number of standards (usually 7)

10.8. The relative standard deviation (RSD) for each analyte RRF is determined by dividing the standard deviation of the peak RRFs by the peak's average RRF. The formula is:

$\text{RSD} = \text{SD} / (\text{Ave RRF}) = \frac{((\Sigma (\text{RRF}_i - \text{Ave RRF})^2) / (n-1))^{1/2}}{\text{Ave RRF}}$

10.9. Determine the percent relative standard deviation:

$\% \text{RSD} = \text{RSD} * 100$
--

10.9.1. When the %RSD calculated in Section 10.9 is less than 20 for each analyte the Average RRF is used to quantify target analytes. When quantitating toxaphene or other multi-component analytes, choose three to five of the major peaks (the peak height of each of these peaks should be greater than 25% of the peak height of the most intense peak.) Calculate the %RSD for each of these peaks. Each should meet the 20% RSD criteria.

10.9.2. When the %RSD for any analyte is > 20 corrective action is required. Corrective actions are described in Section 16.

10.9.3. When other corrective actions are not effective a linear calibration model may not be appropriate or achievable and alternative calibration models may be employed: Alternate calibration models must not be used in lieu of proper instrument maintenance.

10.9.3.1. Linear calibration using a least squares regression.

10.9.3.1.1. A minimum of 5 calibration concentrations are required.

10.9.3.1.2. The curve must not include the origin, but should be forced through the origin.

10.9.3.1.3. The coefficient of determination, (r^2) must be ≥ 0.990 .

10.9.3.1.4. The low point of the curve must be evaluated against the linear regression equation to ensure that the calculated concentrations are not negative.



- 10.9.3.2. A quadratic regression model may be used to generate a calibration curve when linear calibration models will not yield acceptable results.
- 10.9.3.2.1. This model requires a minimum of 6 calibration points.
- 10.9.3.2.2. The curve must not include the origin, but should be forced through the origin.
- 10.9.3.2.3. The coefficient of determination, (r^2) must be ≥ 0.990 .
- 10.9.3.2.4. The calibration curve should be visually inspected to ensure that there are no parabolas or repeating functions in the calibration range.
- 10.9.4. All corrective actions and or deviations from use of %RSD to evaluate an initial calibration must be fully documented on the reviewer checklist.
- 10.10. Retention time windows
- 10.10.1. ARI uses a default retention time window of ± 0.02 minutes. Gas chromatographs equipped with Electronic Pressure Control (EPC) maintains exceptionally constant retention times.
- 10.10.2. Several years of experience working with difficult matrices have shown that narrower retention time windows often lead to false negatives in samples with high background contamination or with very complex sample matrices. When narrower retention time windows (i.e. 0.03 min.) are required the analyst should still use a window of ± 0.02 minutes to evaluate the chromatogram for interferences.
- 10.10.3. Retention time windows are established for each initial calibration. The retention times of all analytes in all calibration verifications (ICV & CCV) must fall within the retention time windows set by the initial calibration standards.
- 10.10.3.1. In some instances, it may be appropriate to update the retention times with an opening continuing calibration and documented in the run log and reviewer checklist.
- 10.10.4. The experience of the analyst must weigh heavily in the interpretation of the chromatogram. In the case of multi-component analytes Toxaphene and Technical Chlordane the analyst must rely primarily on pattern recognition to identify target analytes.
- 10.11. Initial Calibration Verification – Initial calibrations are verified at the time they are generated by the analysis of an SCV. This is a standard prepared at a similar concentration as the midpoint standard of the curve, but prepared from a source different than the one used to prepare the initial calibration.
- 10.11.1. Calculate the concentration of each analyte in the SCV.
- 10.11.2. Calculate the recovery of each target analyte in the SCV using the following formula:

$$\% \text{Recovery} = ((\text{ICV} / \text{IC}) 100$$



Where:
IC = Analyte concentration in the initial calibration
ICV = Calculated analyte concentration in the initial calibration verification

10.11.3. The recovery of each analyte in the SCV must be within 80-120% of the true value.

10.11.3.1. When the % recovery is unacceptable corrective action is required. Corrective action may include any of the following:

10.11.3.1.1. Prepare and analyze a second SCV to determine if the first SCV was properly prepared.

10.11.3.1.2. Continue with the analysis following supervisory approval and documentation of the results included with the calibration.

10.11.3.1.3. Recalibration

10.12. An initial calibration must be verified during all sample analytical sequences through the process of continuing calibration verification. This involves analyzing an initial calibration verification (ICV) at the beginning of an analytical sequence and subsequent continuing calibration verification standard (CCV) prepared at the calibration midlevel from the same source as the initial calibration.

10.12.1. ICV/CCVS must be analyzed

10.12.1.1. Prior to sample analysis (ICV) and after every 10 field samples or 12 hours, and at the end of the analysis sequence (CCV).

10.12.1.2. CCVs may be analyzed more often as determined by the analyst.

10.12.1.3. When samples are to be run immediately following an initial calibration, a ICV is not required when the midpoint calibration standard meets the ICV requirements.

10.12.2. To be valid, an ICV/CCV must meet the following criteria.

10.12.2.1. For each analyte, calculate the per cent difference or percent drift (%D) between CCVS concentration and the known concentration using the following formula:

% D = ((CCV – IC) / IC) 100
where:
IC = Analyte concentration in the initial calibration
CCV = Analyte concentration in the continuing calibration

10.12.2.2. The limit on the %D for each compound is ±20%. For multi-component analytes (Chlordane and Toxaphene), calculate the %D for each quantified peak. So long as the average %D of all the quantitation peaks is less than 20%, the multi-component calibration is acceptable.



- 10.12.2.2.1. When %D is acceptable, proceed with analyzes.
- 10.12.2.2.2. When the %D is unacceptable corrective action is required. Possible corrective actions are described in Section 16.
- 10.12.2.3. When any of the CCV criteria are not met, all affected samples must be re-analyzed, except as follows.
 - 10.12.2.3.1. When the concentration of a CCV analyte is > 120% of the expected value, and the analyte was undetected in the samples affected by the CCV, the samples do not need to be re-analyzed. A high CCV indicates that had the analyte been present it would have been detected.
 - 10.12.2.3.2. When the concentration of an analyte with an unacceptable CCV is present in the extract above the linear calibration range, the sample does not need to be re-analyzed. In this case, the extract must be diluted and reanalyzed with an acceptable CCV.
 - 10.12.2.3.3. Any CCV standard that does not meet the $\pm 20\%$ criteria may be re-analyzed if not more than 12 hours has elapsed or 10 field samples run since the injection of the opening CCV for that bracket. If the re-analysis also fails to meet the acceptance criteria corrective action must be performed. No samples may be analyzed without an acceptable opening CCV.
 - 10.12.2.3.4. CCVs with calculated concentrations < 80% of the expected value may be acceptable with written approval by supervisory, management or data review personnel preferably after consultation with the client.
 - 10.12.2.3.5. All CCV exceptions must be clearly documented in the Reviewer Checklist.
- 10.12.2.4. The retention times for all ICV and CCV compounds must fall within the windows established by the initial calibration or the last updated continuing calibration verification. Retention times may be updated at the beginning of an analytical bracket from the continuing calibration verification that begins that bracket.

11. Procedure

11.1. Essential steps in the analytical procedure are listed in Table 6. Details for each step are provided in the subsequent sections. It is not necessary to perform the procedures in the order given in Table 06.

Table 06	
Analytical Procedure	
Section:	Procedure
12.2	Examine project and extraction documentation



12.3	Establish appropriate instrument operating conditions
12.4	Prepare or obtain all required standards
12.5	Obtain sample extracts
12.6	Add internal standard
12.7	Load autosampler
12.8	Enter sample sequence into GC data system
12.9	Start analytical instrument run
12.10	Evaluate ICal and ICV or CCV
12.11	Evaluate CCVs during sequence
12.12	Evaluate DS
12.13	Evaluate the Chromatogram for the presence
12.14	Dilute extracts and re-analyze as necessary
12.15	Verify integration and manually integrate as necessary
12.16	Quantify Analytes
12.17	Archive extract vials
12.18	Export Data to ELEMENT
12.19	Prepare & submit analytical documentation

11.2. Examine Project Documentation

- 11.2.1. Sample receiving documents and Special Analytical Requirements form may contain information affecting the analysis such as unusual analytes, project required data quality objectives, etc.
- 11.2.2. Organic extraction documents may contain useful sample or extract specific information and includes screening to which may be used to adjust extract concentration prior to analysis.
- 11.2.3. It is highly recommended that the extract be screened on a GC/ECD using the same type of capillary column. This will minimize contamination of the GC system from unexpectedly high concentrations of organic compounds and may show high background samples that should be analyzed using a medium/high level extraction. If the screening chromatograms indicate the presence of elemental sulfur, remove the sulfur using elemental Mercury as described in Appendix 20.3. All associated QA sample (MB, BS, MS etc.) extracts must be included in the cleanup batch.



11.3. The recommended GC operating conditions are as follows (samples must be run using the same instrument conditions as the initial calibration). Conditions are instrument dependent and may vary. See Table 07 for typical instrument conditions.

Table 07	
Typical GC Operating Conditions	
Initial temperature:	100°C, hold for 1 minute
Temperature program:	100-230°C at 30C°/min hold 5 mins. 230-315°C at 30°C /min
Final temperature:	315°C, hold for 4 minutes
Injector temperature:	220°C
Detector temperatures:	325°C
Detector make-up gas flows	60 mL/min (front) and 50 mL/min (back)
Column initial flow	4.2 mL/min
Injector:	Grob-type, split-less/split
Injector Pressure	20 psi
Split flow	20 mL/min at 0.5 minutes
Sample volume:	1-2 µL

11.3.1. Make sure the correct GC method is in use

11.4. The following standards or solution must be prepared for the analytical process

11.4.1. Priming Standard

11.4.2. Degradation Standard

11.4.3. Instrument Blank

11.4.4. Calibration standards

11.4.5. Calibration verification standards

11.5. Obtain sample extracts and accept custody by signing the Extract Custody Log Book

11.6. Add internal standard

11.6.1. Measure a 0.3-0.5 ml aliquot of the sample extract obtained from sample preparation. Use a 10 µL syringe to add 1 µL of Internal Standard spiking solution for each 0.1 mL of extract. This results in a concentration of 80 ng/µL of each internal standard in the extract. This aliquot should be prepared in a clear glass autosampler vial and sealed with a crimp cap. Store the un-spiked volume of extracts at >0 to 6°C, protected from light in screw-cap vials equipped with un-pierced Teflon lined septa.

11.7. Load autosampler with the aliquots prepared in Section 12.6.1.

11.8. Enter the analytical sequence into the Chemstation software.



- 11.9. Begin the analytical sequence.
 - 11.9.1. The injection volume must be the same volume used for the calibration standards.
 - 11.9.2. Recommended GC operating conditions are specified in Section 11.3.
 - 11.9.3. The Chemstation system is used for data acquisition only.
 - 11.9.4. The raw data files are transferred to the Target server for processing.
 - 11.9.5. The “Target” software assigns the chromatographic baseline and integrates the electronic signal producing a chromatogram.
- 11.10. Evaluate ICal and ICV or CCV
 - 11.10.1. Prior to sample analysis the GC system must have an acceptable initial calibration curve (the requirements for the calibration curve are in Section 10.) The initial calibration must include the analysis of the IB and the DS.
 - 11.10.2. Prior to sample analysis a CCV must be analyzed, and this CCV must meet the criteria found in Section 10. If time remains in the 12-hour QC period begun with the initial calibration, the midpoint calibration standard from the initial calibration may be used as the CCV provided it meets the requirements found in Section 10.
 - 11.10.3. CCVS must be analyzed every 10 field samples, or every 12 hours whichever occurs first.
 - 11.10.4. Sample analysis may continue if the CCVs meet the criteria in Section 10
- 11.11. Evaluate CCVs during sequence
- 11.12. Evaluate DS
 - 11.12.1. Sample analysis may continue as long as the breakdown of both 4, 4'-DDT and Endrin are $\leq 15\%$ each.
- 11.13. Examine the chromatogram for the presence of elemental sulfur.
 - 11.13.1. If the presence of sulfur interferes with the analysis an extra Sulfur cleanup may be performed on the affected extract and all associated QA sample extracts. The clean-up procedure is outlined in Appendix 20.3. Following clean-up, the sample extracts must be re-analyzed starting at Section 12.7.
 - 11.13.2. When there is no evidence of Sulfur in the processed chromatogram proceed to Section 11.8.10
- 11.14. Dilute extracts and re-analyze as necessary
 - 11.14.1. If the response for any target analyte exceeds the high point of the initial calibration curve, extract dilution must take place. Dilution should occur such that the analytes exceeding the curve range are kept within the upper half of the curve when the dilution is analyzed.



- 11.15. Verify that the computer has and correctly identified the chromatographic baseline and integrated all peaks correctly.
 - 11.15.1. If corrections are required, manually re-integrate the data file following guidelines in SOP 1021S “Manual Integration of Chromatographic Peaks”.
 - 11.15.2. Manual integrations must be identified on the raw data and explained in the reviewer checklist in the final data package.
 - 11.15.3. Note the manually integrated peaks on a hardcopy of the final chromatogram.
 - 11.15.4. Print before and after chromatograms of the manually integrated sample and when appropriate print magnified chromatograms to demonstrate and justify manual integrations (raw data printouts will include the chromatogram and will show baseline corrections).
- 11.16. Perform all qualitative and quantitative measurements as described in Section 13.
- 11.17. Archive the sample extracts at >0 to 6°C and protected from light in Refrigerator 17.
- 11.18. Following the data analysis, export the final concentration data to the laboratory information management system (ELEMENT) so that final reports may be generated.
- 11.19. Prepare and submit analytical documentation.
 - 11.19.1. Place copies of all bracketing CCVs, raw data for all the samples and associated QC, the ELEMENT report, manual integration summary report, run log and an analyst’s note form in the project folder.
 - 11.19.2. Make sure the Reviewer checklist include all deviations from standard procedure and any other noteworthy information concerning the project analyzes.
 - 11.19.3. Submit the project file to data review.

12. Data Analysis and Calculations

- 12.1. Analyte Identification
 - 12.1.1. A sample is tentatively determined to contain a specific analyte when the analyte’s peak falls within the retention time window for the peak determined during the initial calibration on one column.
 - 12.1.2. Positive identification occurs:
 - 12.1.2.1. When a peak is detected in the appropriate retention window on both columns.
 - 12.1.2.2. And the relative percent difference (RPD) between the two responses is $< 40\%$.
 - 12.1.2.2.1. If the RPD is $>40\%$ between the responses the analyte may still be reported with a P qualifier at the analysts’ discretion.
 - 12.1.2.3. Calculate the concentration of the analyte for each column using the procedure in Section 12.2.
 - 12.1.2.4. Report the higher of the two calculated concentrations.



- 12.1.2.5. ARI will report the higher concentration following Method 8000C. This approach is conservative relative to protection of the environment. In certain instances or for project specific requirements, it may be appropriate to report the lower concentration as allowed in Method 8000C. This approach is only valid at the discretion of an experienced analyst and must be noted in the analyst's notes and in the project narrative.
- 12.1.3. When overlapping or co-eluting peaks preclude identification of an analyte on one or both columns:
- 12.1.3.1. Report the higher of the two column values and qualify the value with a "Y" flag indicating a raised reporting limit.
- 12.1.3.2. This flag indicates the analyte is not detected at or above the reported concentration. The Y flag is equivalent to the U flag with a raised reporting limit.
- 12.1.4. When an analyte is identified by the data system in the sample on either column, but the retention time is outside the retention time windows.
- 12.1.4.1. Report the higher of the two column values qualified with the "Y" flag. Note: the retention time windows in the data system should be intentionally set wide to screen for this type of interference.
- 12.1.5. When the analyte is present on both columns, within the established retention time windows and the RPD between the two values is $\geq 40\%$
- 12.1.5.1. Report the higher value qualified with a "P" flag.
- 12.2. Analyte Quantitation:
- 12.2.1. Calculate the concentration of each identified analyte in the sample extract as follows:
- 12.2.1.1. Water:

Concentration ($\mu\text{g/L}$) =	$\frac{(A_x)(I_s)(V_t)(DF)}{(A_{IS})(RRF)(V_o)(V_i)}$
Where:	A_x = Peak area of the compound
	I_s = Amount of internal standard injected (ng).
	V_t = Final Volume of extract
	A_{IS} = Peak area of the internal standard
	RRF = Relative response factor the compound
	C_x = Concentration of the analyte
	V_o = Volume of water extracted (ml)
	V_i = Volume of extract injected (μL)
	DF = Sample Dilution Factor (1 for undiluted samples)

- 12.2.1.2. Sediment/Soil/Sludge (on a dry weight basis) and Waste (normally on a wet weight basis)



Concentration ($\mu\text{g}/\text{kg}$) =	$\frac{(A_x)(I_s)(V_t)(DF)}{(A_{IS})(RRF)(V_i)(W_s)(D)}$
where:	
A_x = Peak area of the compound	
I_s = Amount of internal standard injected (ng).	
V_t = Final Volume of extract	
DF = Sample Dilution Factor (1 for undiluted samples)	
A_{IS} = Peak area of the internal standard	
RRF = Relative response factor for the compound	
V_i = Volume of extract injected (μL)	
W_s = Weight of sample extracted or diluted in grams	
D = % Dry weight of sample = 1.0 on an as received basis	

12.2.2. Quantitation of Multiple Component Analytes: Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handling Toxaphene and Technical Chlordane.

12.2.2.1. Toxaphene, when identified should be quantitated against a five-point curve using 3-5 major peaks. Note Section 10.2 regarding toxaphene calibration.

12.2.2.2. Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-chlordane (gamma and alpha), respectively, are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

12.2.2.3. The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

12.2.2.4. Unless otherwise requested, chlordane should always be quantitated as alpha-chlordane and gamma-chlordane, not a technical chlordane mixture.

12.2.2.5. When required, the analyst may quantitate technical chlordane residues using 3 to 5 major peaks from a technical chlordane calibration standard.



13. Method Performance

- 13.1. The QA department measures method performance using a combination of annual method detection limit (MDL) studies, quantitation limit spikes (MRL) studies, performance evaluation samples, and the monitoring of surrogate and spike recoveries.
- 13.2. Detection limits- detection limits for all analytes quantitated using this SOP are set using the lowest effective point of the initial calibration curve and validated by quantitation limit spike studies.
 - 13.2.1. MDL studies are performed only for major instrument or procedure changes.
 - 13.2.2. LOD and MRL values determined from MRL studies may be found for each analyte in Element.
- 13.3. Laboratory precision and bias measurements are performed by monitoring surrogate and spike recoveries in samples and quality control samples.
 - 13.3.1. Control limits are calculated from these recoveries.
 - 13.3.2. These control limits are disseminated to the bench chemists and ELEMENT administrator for use in monitoring method performance in real time.
 - 13.3.3. As these limits are updated regularly, their dynamic nature prevents their inclusion in this SOP. However, they may be found in Element.
- 13.4. This method should be performed only by experienced GC analysts, or under the close supervision of such analysts.
- 13.5. **The experience of the analyst must weigh heavily in the interpretation of the chromatogram.** In the case of multi-component analytes such as Toxaphene or Technical Chlordane an analyst must rely primarily on pattern recognition to identify target analytes.
- 13.6. Method performance must be re-evaluated every time there is a change in instrument type, personnel, or method. Method performance will be demonstrated using the Demonstration of Capability (DOC) procedure described in Section 12.3 and Appendix 2.2 of ARI SOP 1017S. A certification statement and all raw data from the DOC will be forwarded to QA for approval and archive. Each DOC must be documented in the instrument maintenance logbook.

14. Pollution Prevention

- 14.1. All GC split vents will be connected to an exhaust vent.
- 14.2. All syringe rinses are discharged into activated charcoal. Spent charcoal is properly disposed of as "Solvent Contaminated Solids" by ARI's designated Treatment, Storage and Disposal Facility.
- 14.3. Disposed expired standards into the designated barrel in the hazardous waste room.



14.4. Mercury contaminated autosampler vials are placed in the designated container in Fume Hood 34 (satellite accumulation) then transferred to the “Mercury Debris” in the Hazardous Waste Storage Area for pick by.

14.5. Autosampler vials containing sample extracts are placed in the satellite accumulation station in the GC store room for eventual removal by an EPA approved Treatment, Storage and Disposal Facility.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Concentrations of target analytes are calculated for both GC columns and compared for consistency.

15.2. When a confirmed analyte’s concentration is less than 1/2 the reporting limit, the analyte is not reported. A confirmed analyte at a concentration greater than 1/2 the reporting limit but less than the reporting limit may be reported with a "J" qualifier at the analyst’s discretion. Project specific requirements may dictate that all confirmed hits above 1/2 the reporting limit in the method blank will be reported.

15.3. If the response of any target analyte exceeds the calibration range of the system, dilute the extract so the analyte concentration falls within the range of the calibration curve and re-analyze. Flag reported concentrations which exceed the curve with an “E” flag on final data reports.

15.4. Requirements relating to initial and continuing calibration are detailed in Section 10 of this document.

15.5. Method Blanks must contain less than 1/2 the reporting limit of the targeted analytes or corrective action is required as described in Section 16.6.

15.6. Internal Standard peak areas must meet the technical acceptance criteria listed in Section 9.2.2 of this SOP.

15.7. Surrogate Recoveries

15.7.1. All samples, method blanks, blank spikes, matrix spikes, matrix spike duplicates, duplicates, RMs or other samples must have acceptable surrogate recoveries. Surrogate recoveries are considered unacceptable when they fall outside statistically generated control limits found in the ARI’s LQAP.

15.7.2. Surrogate recovery acceptance windows are determined statistically from method and matrix specific laboratory data and are updated on a periodic basis. Certain methods or client projects may specify project specific surrogate recovery acceptance windows.

15.7.3. These requirements do not apply to subsequent dilutions of samples where a prior analysis of the diluted sample extract shows acceptable surrogate recovery.



15.7.4. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet project specific surrogate acceptance criteria, even when the criteria are labeled as advisory in the reference method.

15.7.5. Surrogate acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.

15.8. Blank Spikes (BS)

15.8.1. Blank spike recovery values must fall within the specified recovery acceptance limits or corrective action is required. If a BSD is performed then relative percent difference (RPD) acceptance limits also apply when available.

15.8.2. BS recovery acceptance windows are determined statistically from method and matrix-specific laboratory data and are updated on a periodic basis. Project or method specific limits may supersede laboratory acceptance criteria.

15.8.3. When mandated by contract-specific requirements, corrective actions must be performed in response to failure to meet spike acceptance criteria, even when the criteria are labeled as advisory in the reference method.

15.8.4. Spike acceptance criteria are both matrix and concentration level specific (e.g. low level vs. medium level soils). When analyzing matrices or concentration levels for which no acceptance criteria are available, the closest approximation of available acceptance criteria may be provided as estimates for advisory purposes only.

15.9. Matrix Spike/Matrix Spike Duplicates (MS/MSD)

15.9.1. Matrix Spike/Matrix Spike Duplicate recovery values should fall within the specified recovery acceptance limits. When a MSD is performed then relative percent difference (RPD) acceptance limits also apply when available.

15.9.2. MS/MSD recovery and RPD acceptance windows are determined statistically from method and matrix-specific laboratory data and are updated on a periodic basis. Certain methods or clients may require project specific MS/MSD recovery and RPD acceptance limits.

15.10. Holding Times

15.10.1. Extracts must be analyzed within 40 days from the date of extraction.

15.10.2. In the event that re-extraction due to an out of control event requires that samples be re-extracted after their extraction holding time has elapsed (seven days for water and fourteen days for unpreserved tissues/solids/soils/sediments) the analyst will analyze and report both extraction sets and distinguish between the initial extraction and re-extraction on



all deliverables. This will document that the samples were originally extracted within holding times and may allow for comparisons that will determine whether data quality was affected by the samples being analyzed out of holding.

15.10.3. If any extracts are analyzed after the 40 day extract holding time has elapsed, the analyst must document this in the reviewer checklist accompanying the data so that it may be included in the narrative.

16.11 Analytical Sequences

16.11.1 For GC and GCMS analysis; Analysts should not intersperse instrument blanks between samples and closing calibrations or method blanks. If instrument blanks are run between samples and QC samples or standards then every sample in the job or the bracket must be preceded by an instrument blank. Also, QC samples should be run with their associated samples and; specifically, running all method and spike blanks at the beginning of an analytical queue prior to samples is strongly discouraged.

16. Corrective Actions for Out of Control Events

16.1. Corrective actions may include any, but are not limited to, the following:

16.1.1. Narration – the failure and the extent of the failure (i.e. the percent deviation from the expected value) will be described in the reviewer checklist.

16.1.2. Reevaluation – the data will be reconsidered by the analyst and then the analyst will corroborate with a peer analyst or supervisor to confirm or revise the initial evaluation.

16.1.3. Re-preparation – the remaining unanalyzed aliquot of the extract is transferred to a new vial and analyzed.

16.1.4. Reanalysis – the extract aliquot that was originally prepared is reinjected and run on the gas chromatograph again.

16.1.5. Re-extraction – a re-extraction request is filled out (Form 0030F). Copies of the form are provided to the extractions department, the project manager, the QA manager and the lab manager. The remaining sample is extracted.

16.1.6. Instrument Maintenance – this will vary with the problem experienced and the analyst's experience and a description of the maintenance performed will be documented in ELEMENT.

16.1.7. Recalibration – a new initial calibration is evaluated and the associated samples reanalyzed.

16.1.8. Revised data submission – if it is determined through reevaluation or reanalysis that an error was made and subsequently corrected then the data will be resubmitted with the



appropriate corrections and explanation for data review. Both the original and finalized data will be provided for data review.

16.1.9. Formal corrective action entry – formal corrective actions are entered into the ARI database, when an out of control event cannot be remedied through the above corrective action process.

16.2. When an Initial Calibration Verification (ICV) RSD for an analyte exceeds 20%

16.2.1. Examine the initial calibration analyses. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.

16.2.1.1. When the failure appears to be the result of an improperly prepared calibration standard, re-prepare the standard and reanalyze it. Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option, and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed, or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

16.3. When an Initial or Continuing Calibration Verification (ICV or CCV) fails:

16.3.1. Perform the appropriate corrective action(s) from Section 16.1 and re-calibrate the instrument.

16.3.2. DoD-QSM requires that %D for all analytes in the ICV or CCV be $\leq 20\%$ (50% for end of batch CCV). For DoD analyses, if no samples have been analyzed and less than 1 hour elapsed since the failed CCV, two additional consecutive ICVs or CCVs may be analyzed. This is not required; the analyst may default to Section 16.3.1.

16.3.2.1. When both of these CCVs meet acceptance criteria, samples analyzed since the last acceptable CCV may be reported and the analytical sequence continued.

16.3.2.2. If either of the two CCVs fail or their analysis cannot be started within one hour, associated samples may not be reported and the instrument must be re-calibrated.

16.4. Internal Standards

16.4.1. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.

16.4.1.1. If the calculations were incorrect, correct the calculations and verify that the internal standard response met their acceptance criteria.



- 16.4.1.2. If the internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare solutions and re-extract/reanalyze the samples.
 - 16.4.1.3. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.
 - 16.4.1.4. If the above actions do not correct the problem, then the problem may be due to a sample "matrix effect".
- 16.5. Surrogates
- 16.5.1. Examine the bench sheet to verify spiking levels are correct.
 - 16.5.2. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.
 - 16.5.2.1. If the above actions do not correct the problem, then the problem may be due to a sample matrix effect.
- 16.6. Method Blanks- Corrective action for a method blank which fails acceptance criteria may involve re-extraction and reanalysis of all associated samples and/or "B" flagging of the associated sample data. Each occurrence will be evaluated on an individual basis upon consultation with the Project Manager, the client, the Laboratory Supervisor, and the Laboratory Manager. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.
- 16.7. Blank Spikes (BS)
- 16.7.1. Control limits for this method are published in Element. If the problem is limited to only a few analytes outside of the allowable control limits the data may be reportable after consultation with the project manager and (or) organics manager.
 - 16.7.2. Examine the bench sheet to verify spiking levels are correct.
 - 16.7.3. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.
- 16.8. Matrix Spike/Matrix Spike Duplicates
- 16.8.1. Examine the bench sheet to verify spiking levels are correct.
 - 16.8.2. Recoveries are advisory and should not necessarily result in re-extraction.
 - 16.8.3. Proceed with any appropriate corrective action from 17.1, based on analyst discretion.
- 16.9. Sample Dilution- Should the quantitated value of any analyte exceed the working range of the curve, a dilution must be performed such that the analyte's quantitated value is within the curve range.
- 16.9.1. Additional internal standard must be added to the diluted extract to maintain the required 80 ng/mL of each internal standard in the extracted volume.
 - 16.9.2. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.
 - 16.9.3. When peaks from an analyte saturate the detector:



- 16.9.3.1. The analyst must flag all affected analytes with an S flag.
- 16.9.3.2. The analyst should analyze an Instrument Blank consisting of clean solvent until the system has been decontaminated.
- 16.10. In particular circumstances, the Project Manager (PM) may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as data usability and turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples (detection limits will not be compromised since response has improved). QC criteria specified in the work plan will be considered by the Project Manager.
 - 16.10.1. The samples need not be re-analyzed if the PM so instructs the analyst. The analyst should have the PM initial all such decisions. It is preferable that the Client be consulted, but that decision is made by the PM. (See ARI Project Management SOP #005S)
 - 16.10.2. All QC limit issues (including continuing calibration limits and all QC recovery limits) may be decided by the PM, the data reviewer, and/or GC Supervisor, preferably after consultation with the Client.
- 16.11. If contaminants (including target and non-target compounds) continue to cause significant interference, even after all relevant cleanups have been performed; the sample should be re-extracted at a level appropriate to the amount of contamination. The particular re-extraction level should be based on the initial analysis or pre-analysis GC-ECD screen. The experience and discretion of the analyst and section supervisor will be relied upon for re-extraction decisions. The PM will be notified if re-extraction at a different level is required.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

- 17.1. See Sections 16.2 and 16.3 for guidance on dealing with initial and continuing calibration out-of-control events.
- 17.2. See Section 16.4 for guidance on dealing with internal standard out-of-control events.
- 17.3. See Section 16.5 for guidance on dealing with surrogate out-of-control events.
- 17.4. See Section 16.6 for guidance on dealing with method blank related out-of-control events.
- 17.5. See Section 16.7 for guidance on dealing with blank spike related out-of-control events.
- 17.6. See Section 16.8 for guidance on dealing with MS/MSD related out-of-control events.
- 17.7. See Section 16.9 for guidance on dealing with over range related out-of-control events.

18. Waste Management

- 18.1. All extract vials must be disposed of by placing them in the blue hazardous waste drum in the lab set aside for this purpose. No vials may be thrown in the trash or receptacles not expressly designated for this purpose.



- 18.2. All solvents must be disposed of by pouring them out over charcoal. No solvent may be poured down the drain or disposed of in any other non-hygienic manner.
- 18.3. All spent charcoal must be disposed of by placing it in the charcoal disposal bin located in the extractions lab.
- 18.4. Waste must not be accumulated in the fume hoods and must be disposed of at the appropriate waste disposal location.

19. Method References

- 19.1. U.S. EPA, Test Methods for Evaluating Solid Waste (SW-846), Method 8081B, Organochlorine Pesticides By Gas Chromatography, Revision 2, November 2000
- 19.2. Department of Defense, Quality Systems Manual for Environmental Laboratories, Final Version 4.2, June, 2003
- 19.3. "Determinative Chromatographic Separations": Method 8000C, Test Methods For Evaluating Solid Waste (SW-846), Revision 3, March, 2003.

20. Appendices

- 20.1. Acid Lability of Chlorinated Pesticides and PCBs
- 20.2. Pesticide Quality Control Requirements
- 20.3. Modifications Required for EPA Method 608



Table 20.1 Acid Lability of Chlorinated Pesticides and PCBs

Acid Lability of Chlorinated Pesticides & PCBs			
Compound	Labile	Partially Stable	Stable
Aldrin			X
Chlordane			X
Dieldrin	X		
4,4'-DDT			X
4,4'-DDE			X
4,4'-DDD			X
α -Endosulfan	X	X	
β -Endosulfan		X	
Endosulfan sulfate			X
Endrin	X		
Endrin Aldehyde	X		
Endrin Ketone	X		
Heptachlor			X
α -BHC			X
β -BHC			X
γ -BHC (Lindane)			X
δ -BHC			X
Toxaphene			X
Archlor - 1016			X
Archlor - 1221			X
Archlor - 1232			X
Archlor - 1242			X
Archlor - 1248			X
Archlor - 1254			X
Methoxychlor	X	X	
Hexachlorobenzene			
Hexachlorobutadiene			
DCBP (surr.)			X
TCMX (surr.)			X



Appendix 20.2: Pesticide Quality Control Requirements

QC Requirement	Minimum Frequency	ARI Acceptance Criteria	DoD-QSM Acceptance	Corrective Action (see Section 17)	Flagging Criteria
Demonstration of capability (DOC). DOC requirements are outlined in ARI SOP 1017S.	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method.	ARI spike recovery QA limits	QC acceptance criteria published by DoD, if available; otherwise method specified criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria.	Not applicable (NA)
Method detection limit (MDL) study	At initial set-up and subsequently once per 12 month period; otherwise quarterly MDL verification checks shall be performed.	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Same	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study.	NA
Retention time (RT) window width for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	ARI uses a default retention time window of 0.5 minutes	RT width is ± 3 times standard deviation for each analyte RT from 72-hour study.	NA	NA
Breakdown check (Endrin and DDT)	Daily prior to analysis of samples	Degradation < 15% for both Endrin and DDT.	Same	Correct problem and then repeat breakdown check.	Flagging criteria are not appropriate.
Minimum five-point Initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	One of the options below: Option 1: RSD for each analyte $\leq 20\%$ Option 2: non-linear regression: coefficient of determination (COD) $r^2 \geq 0.99$ (6 points required)	Same	Correct problem then repeat initial calibration.	Flagging criteria are not appropriate.
Second source initial calibration verification (SCV)	Once after each initial calibration	Value of second source for all analytes within $\pm 20\%$ of expected value (initial source)	Same	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat initial calibration.	Flagging criteria are not appropriate.
Retention time window position established for each analyte and surrogate	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	Same	NA	NA
Retention time Window verification for each analyte and surrogate	Each calibration verification standard	Analyte within established window	Same	Correct problem, then reanalyze all samples analyzed since the last acceptable retention time check. If they fail, redo ICAL and reset retention time window.	Flagging criteria are not appropriate for initial verification.



QC Requirement	Minimum Frequency	ARI Acceptance Criteria	DoD-QSM Acceptance	Corrective Action (see Section 17)	Flagging Criteria
Calibration verification (initial [ICV] and continuing [CCV])	ICV: Daily, before sample analysis CCV: After every 10 field samples and at the end of the analysis sequence	All analytes within $\pm 20\%$ of expected value from the ICAL	Same	ICV: Correct problem, rerun ICV. If that fails, repeat initial calibration. See section 5.5.10 and box 55. CCV: Correct problem then repeat CCV and reanalyze all samples since last successful calibration verification.	ICV: Flagging criteria are not appropriate. CCV: Flagging criteria are not appropriate.
Method blank	One per preparatory batch	No analytes detected	No analytes detected $> \frac{1}{2}$ MRL. For common laboratory contaminants, no analytes detected \geq MRL.	Correct problem, then see criteria in box D-5; if required, reprep then reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch
Blank Spike (BS) containing all analytes and surrogates to be reported	One BS per preparatory batch	ARI BS control limits	QC acceptance criteria specified by DoD	Correct problem, then reprep and reanalyze the BS and all samples in the associated preparatory batch, if sufficient sample material is available.	If corrective action fails and there is insufficient sample material; report and discuss in the reviewer checklist.
Matrix spike (MS)	One MS per preparatory batch per matrix.	ARI MS control limits	For matrix evaluation, use QC acceptance criteria specified by DoD for BS.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix	ARI BS control limits	RPD $\leq 30\%$ (between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.
Surrogate spike	All field and QC samples	ARI control limits	Analytes identified in DoD-QSM Appendix DoD-D. QC acceptance criteria for BS specified by DoD, if available; otherwise method-specified criteria or laboratory's own in-house criteria	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	For the specific analyte(s) in all field samples collected from the same site matrix as the parent, apply J-flag if acceptance criteria are not met.
Confirmation of positive results (second column or second detector)	All positive results must be confirmed.		Calibration and QC criteria same as for initial or primary column analysis. Results between primary and second column RPD $\leq 40\%$.	NA	Apply J-flag if RPD $> 40\%$. Discuss in the reviewer checklist.
Results reported between LOD and MRL	NA		NA	NA	Apply J-flag to all results between LOD and MRL.



Appendix: 20.3 Modifications Required for EPA Method 608

20.3 Modification Required for EPA Method 608 (These modifications are only implemented when specifically requested by a client, otherwise Method 608 is analyzed as described in previously in this SOP)

20.4.1 The Initial Calibration for Method 608 is a minimum of 3 points instead of the 5 required in Method 8081B.

20.4.2 Initial calibration RSD for Method 608 must be < 10% with no exceptions.

20.4.3 Continuing calibration RSD for Method 608 must be < 15% with no exceptions.

Standard Operating Procedure

Total Solids

**SOP 1023S
Revision 002**

**Revision Date: 8/22/19
Effective Date: 8/22/19**

Prepared by:

Van, Spohn, Dave Mitchell

Approvals:

Bob Congleton

Laboratory / Section Manager



Standard Operating Procedure: Total Solids

1. Scope and Application

- 1.1. Analyte concentrations in solid samples are reported on a dry weight basis unless project documentation indicates otherwise. A “Total Solids” (TS) percentage must be determined to correlate analyte concentration with dry weight.
 - 1.1.1. TS are determined by drying a portion of sample at elevated temperature for 12 to 24 hours and calculating percent total solids as outlined below.
 - 1.1.2. TS must be determined immediately before, or immediately after weighting samples for the preparation process.
 - 1.1.3. TS must be determined separately for each sample container and may be used for all analyzes from that container.
 - 1.1.4. When TS must be determined in less than 12 hours, a microwave procedure may be used. The procedure is posted on the microwave oven in the Organics Extraction Laboratory and included as Appendix A of this SOP. The microwave procedure is only for “rush” or emergency situations. Do not use the microwave procedure for routine samples.
- 1.2. The procedure in this document is used to determine Total Solids (TS) for reporting of data from solid samples (soil, sediment, etc.) on a “dry weight” basis. This SOP is used by the Organics Extraction, Volatile Organics and Metals Laboratories. When TS is specifically requested as a reportable analyte, the TS is determined in ARI’s Conventional Laboratory following SOP 639S “Solids”.

2. Summary of the Procedure

- 2.1. A weighed portion of sample is oven dried and the percent difference between the wet and dry sample calculated.

3. Definitions

- 3.1. Total Solids. (TS). The total weight of all solid materials (dissolved and particulate) contained per unit weight or volume of sample. For soils or sediments, it is the weight remaining after drying a known weight of sample, usually expressed as a percent.

4. Interferences



- 4.1. Heterogeneous samples: Samples must be appropriately mixed prior to withdrawing the aliquot for analysis. Anything, including non-representative artifacts, that will interfere with the ability to take a representative sub-sample must be documented on the analysts "Green sheet" and discussed with the Project Manager prior to beginning the analysis. Do not exclude any materials from the sample without discussion with the Project Manager.
- 4.2. Sample residues for weighing must be at room temperature to avoid convective interference in the balance chamber.
- 4.3. Constant dry weight is assumed to be reached after the sample has dried for a period of 12 to 24 hours. In the event that the sample has not been dried for the minimum 12 hours, or upon specific request from the client, attainment of constant dry weight must be documented.

5. Safety

- 5.1. Environmental Samples may contain hazardous materials; treat them as potential health hazards.
- 5.2. The drying oven must be contained in a hood or vented to prevent potentially toxic fumes from a heavily contaminated sample from entering the laboratory.
- 5.3. Always wear safety glasses and hand protection when working with hot samples.

6. Equipment and Supplies

- 6.1. ALUMINUM WEIGHING DISHES.
- 6.2. DRYING OVENS Gravity convected, adjustable to maintain 104 ± 2 °C. Gravity convection is preferred for the drying of samples since mechanically convected ovens can create drafts that could displace dried materials from their containers. Mechanically convected ovens should only be used for drying of equipment and materials used for the analysis.
- 6.3. Analytical balance. The balance used must be capable of measurement to 3 places. Balance verification is accomplished using ASTM E 617-97 traceable weights. The calibration weight must return a value within 1 mg or 10% of its known weight, whichever is less.
- 6.4. Weights for balance verification. Troemner Calibration weights, ASTM E 617-97 traceable (equivalent to old NBS Class S and S-1 standards). Each weight set is certified every 5 years by an outside metrology laboratory. A certificate documenting the "true" weight of each calibration weight accompanies each set.

7. Reagents and Standards

- 7.1. Not Applicable

8. Sample Collection, Preservation, Shipment and Storage



8.1. Sub-sampling is a critical component of solids analysis. In order to obtain accurate and reproducible results, be certain that the sample is well mixed and that the particulates are uniformly distributed throughout the sample prior to withdrawing the aliquot.

9. Quality Control

9.1. Balance Verification. Each analytical balance is verified against ASTM E 617-97 traceable (NIST equivalent to older NBS Class S and S-1 standards) weights at the beginning each weighing cycle.

9.2. Record which analytical balance and oven are used for the TS determination on the bench sheet

9.3. Verify that the oven used is at $104 \pm 2^\circ \text{C}$.

9.4. Record the Oven ID on the TS bench sheet.

10. Calibration and Standardization

10.1. The accuracy of each analytical balance is verified daily against ASTM E 617-97 traceable (NIST equivalent to old NBS Class S and S-1 standards) weights covering the range of determination.

10.2. The balance verification is documented in a balance specific logbook.

11. Procedure

11.1. Analyte concentrations in solid samples are reported on a dry weight basis unless project documentation indicates otherwise. A "Total Solids" (TS) percentage must be determined to correlate analyte concentration with dry weight.

11.1.1. TS are determined by drying a portion of sample at $104 \pm 2^\circ \text{C}$ for 12 to 24 hours and calculating percent total solids as outlined below.

11.1.2. TS must be determined immediately before, or immediately after weighting samples for the preparation process.

11.1.3. TS must be determined separately for each sample container and may be used for all analyzes from that container.

11.1.4. When TS must be determined in less than 12 hours, a microwave procedure may be used. The procedure is posted on the microwave oven in the Organics Extraction Laboratory. The microwave procedure is only for "rush" or emergency situations. Do not use the microwave procedure for routine samples.

11.1.5. TS determined using this procedure are used to calculate analytes values reported on a dry weight basis. Total Solids as a reported analyte is performed in ARI's Conventional Laboratory following SOP 639S "Solids".

11.2. Obtain a copy of Total Solids Bench Sheet (Form 5050F) and enter the header information, analyst name, date, oven ID, balance ID and ARI sample identification(s).



- 11.3. Verify that the balance calibration has been documented for the day using bracketing weights. If not, verify and document balance accuracy before proceeding using the procedure described in ARI SOP 1003S.
- 11.4. Zero the balance.
- 11.5. Obtain an empty aluminum weighing pan write the sample number on the pan with permanent marker.
- 11.6. Weigh the empty pan and record its weight to the nearest 0.01 gram in the "Tare Weight" column of the TS bench sheet. Record all digits displayed by that balance. Do not round the numbers.
- 11.7. Make sure the sample is homogenous by thorough mixing.
 - 11.7.1. Decant and discard any water layer from solid samples to be extracted for semi-volatile organics (SVOA) extractions prior to homogenization.
 - 11.7.1.1. Shared samples (multiple analyses from the same sample container) are not decanted.
 - 11.7.2. Samples for volatile organics analysis (VOA) must not be homogenized in this manner. Ideally a second container which may be homogenized will be collected for VOA TS determination. When the second container is not available the TS determined in another lab section may be used. In this case, the source of the TS data must be clearly identified on the TS bench sheet.
- 11.8. Weigh 10 ± 5 grams of wet sample into the weighing pan. Record the exact weight to the nearest 0.01 gram in the "Tare + Sample Wet" column of the log form. Using less sample is permissible only when less than 5 g of sample are available.
- 11.9. Verify and record oven temperature on the TS bench sheet.
- 11.10. Place the weighing pans in the oven, record the time, and dry at an oven temperature of 102-106°C overnight (12-24 hours) but no longer than 24 hours. If dried for less than 12 hours, it must be documented that constant weight was attained.
 - 11.10.1. To demonstrate that constant weight has been attained, data must be recorded for a minimum of two repetitive weigh/dry/weigh cycles with a minimum of 1-hour drying time in each cycle.
 - 11.10.2. Constant weight would be defined as a loss in weight of no greater than 0.01g between the initial and final weightings of the last cycle.
- 11.11. Remove pans from the oven and allow them to equilibrate to ambient temperature for no more than one hour.
- 11.12. Record analyst name, oven temperature, date, and the time of removal on the TS bench sheet.
- 11.13. Verify the balance accuracy and record the results in the balance specific logbook.



11.14. When cool, weigh and record the exact weight to the nearest 0.01 grams in the "Tare + Sample Dry" column of the log form.

11.14.1. When dry samples cannot be weighed within 60 minutes of removal from the oven, they must be placed in a desiccator to prevent adsorption of moisture from the atmosphere.

11.14.2. When wet samples less than 0.5 g are used, the dry sample must be cooled in a desiccator.

11.15. Data Entry Procedures:

11.15.1. Organics Extraction Laboratory: Enter in Element LIMS using worklist

11.15.2. Metals Preparation Lab: Data is entered into dBase

11.15.3. VOA laboratory: Enter in Element LIMS using worklist

11.16. Place the Total Solids Benchsheet in the appropriate project folder.

12. Review

12.1. Supervisor reviews Service Request and assigns analysis and communicates any special instructions to the analyst as appropriate.

12.2. Analyst reviews Service Request and any special instructions, obtains the appropriate bench sheet and proceeds with the analysis. A handwritten bench sheet is generated, and the data are then entered into the computer for data reduction.

12.3. Creation of Worklists. The final computer-generated result is placed into the method folder in chronological sequence and a copy is placed into the job folder. The data undergo supervisor review and the analysts then enters the data into Element LIMS to create the worklist.

12.4. Distribution of worklists. The supervisor reviews the Element LIMS input, distributes acceptable data and returns the analysis package to analyst for placement in the job folder.

12.5. The completed analysis package is then reviewed by a QA Reviewer and the final report printed.

12.6. The final report is then again reviewed for accuracy and completeness, signed by the QA reviewer and delivered to the Project Manager for final disposition to the client.

13. Data Analysis and Calculations

13.1. TS is a gravimetric determination in which the dry weight of solid residue is expressed relative to the volume or mass of sample used to obtain that residue. Specific calculations are as follows:

13.1.1. Percent solids for reporting chemistry data is calculated by the Element LIMS as follows:

$$\% \text{ Solids} = \left[\frac{(\text{Tare} + \text{Sample Dry}) - \text{Tare}}{(\text{Tare} + \text{Sample Wet}) - \text{Tare}} \right] * 100$$

14. Method Performance



14.1. Approximately 10 grams of sample are typically taken for analysis. While the balance reports to 0.001 g, a sensitivity of 0.01 g is routinely used to report data. This yields a method sensitivity of 0.1% for TS.

15. Pollution Prevention

15.1. Not Applicable

16. Data Assessment and Acceptance Criteria for Quality Control Measures

16.1. Samples dried less than 12 hours

16.1.1. Demonstrate constant weight as described in Sections 11.10.1 and 11.10.2.

16.2. When samples have dried more than 24 hours

16.2.1. Repeat the TS determination on an additional sample aliquot.

16.2.2. When sample is not available or a repeat determination is not practical, document the excessive weighing time on the TS bench sheet in the comments section.

16.3. When the balance is out of control

16.3.1. Use the corrective action procedures in ARI SOP 1003S to bring balance back in control.

16.3.2. When balance is out of calibration or non-functional use a similar balance from another lab section.

16.4. Oven temperature is out of control

16.4.1. Adjust oven temperature and allow the temperature to equilibrate to required range.

17. Corrective Actions for Out of Control Events

17.1. Not Applicable

18. Contingencies for Handling Out-of-Control or Unacceptable Data

18.1. Not Applicable

19. Waste Management

19.1. Samples may contain RCRA hazardous constituents and these are screened in ARI's Element LIMS system. Samples which Element LIMS identified as containing one or more hazardous constituents will be segregated into identified waste profiles and disposed of through our RCRA TSD (Treatment, Storage Disposal facility). Samples not having identified hazardous constituents are disposed as routine garbage.

20. Method References

20.1. USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis. ILM05.3 March 2004. Exhibit D.



20.2. USEPA Contract Laboratory Program, Statement of Work for Organic Superfund Methods
SOM02.4 October 2016. Exhibit D.

20.3. ASTM D 4643 – Microwave Method of Drying Soils

21. Appendices

21.1. Appendix 20.1 - Total Solids by Microwave Method



Appendix 20.1: Total Solids by Microwave Method

1. Weigh a 100 mL glass beaker to the nearest 0.01 grams
2. Record the weight on the Total Solids Bench Sheet as “Tare Weight”
3. Add approximately 20 grams of sample to the 100 mL beaker
4. Record the weight of the beaker and sample to the nearest 0.01 grams
5. Set the microwave oven in the defrost mode.
6. Place the sample beaker in the microwave oven and heat the sample for 4 minutes in the defrost mode
7. If the sample still appears wet microwave an additional 2 minute in the defrost mode.
8. Repeat the two-minute heating cycles until the sample appears to be dry or mostly dry.
9. When sample is dry or nearly dry remove it from the microwave and use a clean glass stir rod to break up any chunks making sure not to remove any sample from the beaker.
10. Record the sample beaker weight on a separate sheet of paper.
11. Microwave the sample for 2 minutes in the defrost mode and allow it to cool to ambient temperature.
12. Reweight the sample beaker.
13. If the weight is reduced 0.02 or more grams, repeat the Steps 11 and 12 until no weight loss is noted.
14. Record the final weight as “Dry Weight” on the bench sheet.
15. Enter data into ARI’s Element LIMS system.

Standard Operating Procedure

Particle Size Distribution – PSEP Method

Effective Date: 12/06/18

Prepared By:

Harold Benny

Approvals:

Laboratory / Section Manager

Quality Assurance

1.0 PURPOSE AND SCOPE

This procedure describes methods, materials, equipment, and special conditions required to determine the particle size distribution for sediment samples by the PSEP METHOD. Wet sieving separates sample into two size fractions; particle sizes $> \#230$ sieve and particle sizes $< \#230$ sieve. Fine fractions are further subdivided using a pipetted technique that depends on the differential settling rates of different particles.

Particle size determinations can either include or exclude organic material. If organic material is removed prior to analysis, the "true" (i.e., primarily inorganic) particle size distribution is determined. If the organic material is included in the analysis, the "apparent" (i.e., organic plus inorganic particle size distribution is determined).

2.0 EQUIPMENT

- 2.1 Balance (Capable of precision to 0.1mg)
- 2.2 Drying Oven – The oven is thermostatically controlled chamber capable of maintaining a uniform and consistent temperature of $90 \pm 2^\circ \text{C}$.
- 2.3 Mechanical Sieve Shaker – A mechanical device used to spin and vibrate a nest (stack) of sieves at a constant rate and energy level to separate a given sample into the individual particle sizes.
- 2.4 Sieves – A nest of sieves including #4 (4.75mm), #10 (2.0mm), #18 (1.0mm), #35 (0.500mm), #60 (0.250mm), #120 (0.125mm) and #230 (.063).
- 2.5 Clock – A suitable timing device capable of measurements to the nearest second
- 2.6 Sedimentation Cylinders and Rubber Stopper
- 2.7 Temperature logger for room ambient temperatures
- 2.8 Desiccator
- 2.9 25ml in 1/10 Pipette and Rubber Bulb
- 2.10 Funnel
- 2.11 Rubber Policeman
- 2.12 Tare Dishes
- 2.13 Wire or Bristle Brush and Wax Paper
- 2.14 Lab Stand with Clamps
- 2.15 Lab Tape
- 2.16 Spoons and Spatulas

3.0 REAGENTS

- 3.1 Solution of SODIUM HEXAMETAPHOSPHATE $\text{Na}(\text{PO}_2)_6$ – A solution is made by mixing 40 grams sodium hexametaphosphate $\text{Na}(\text{PO}_2)_6$ in 1000ml of distilled water (0.1 Molar). Mix the solution thoroughly and let stand overnight. Pipette 5, 10 ml aliquots into weighed tares and oven dry. Record the dry weight in the batch notebook. Average the five weights and record average in notebook. The solution expires in one month.

4.0 DEFINITIONS

- 4.1 Test Environment – A fairly constant temperature of approximately 20°C during analysis. Small fluctuations in temperature may introduce differences that are of practical significance. A data logger will be used to monitor test temperatures.
- 4.2 Sieve Time – Samples will be sieved for 15 minutes, unless client requests a different time for consistency with previous testing.

- 4.3 Sieves – Sieves are frames that hold wire cloth that has various size openings. The operator will visually examine the sieves for defects (i.e., tears, plugging, holes) prior to each use. Do not use damaged sieves.
- 4.4 Flocculation – The process where finely suspended particles agglomerate and settle out of solution

5.0 DOCUMENTATION

- 5.1 PIPETTE GRAIN SIZE ANALYSIS data sheet 1115F.

6.0 QUALITY CONTROL

- 6.1 A batch of samples shall not exceed 20 individual samples. If the job has more than 20 samples they may be broken down into batch sizes that are less than 20. One sample from each batch shall be run in triplicate, giving a maximum batch size of 22 samples. The triplicate shall be reported on a separate plot and summary table with all pertinent data that applies to that sample. The average value for each size fraction shall be presented, as well as the relative percent standard deviation for that data point. Usually, a sample is chosen that is representative of the batch. A minimum of 5 grams passing the #230 sieve is required for the pipette portion of the analysis. Sandy samples may not have this much material passing the #230 sieve, and thus are not normally used for the triplicate. If all samples are sandy, then one of these may be used.
- 6.2 The client usually defines the maximum standard deviation for the project, but if not, a maximum deviation of 5 shall be used. If the triplicate has standard deviations greater than the specified (or lab maximum) then the entire set of samples shall be re-analyzed, unless the samples are non-standard. Non-standard samples may include contaminated samples, i.e., samples contaminated with diesel, or other tarry materials that would cement particles together. Samples that have been frozen prior to receipt by the lab would also be considered non-standard.

7.0 PROCEDURE

7.1 Sample Preparation

- 7.1.1 Remove the samples from the cooler/refrigerator and allow them to warm to room temperature. This ensures that the samples are not frozen. Check the HLB sample numbers against the client numbers to verify that they are correct. Notify supervisor for ID discrepancies.
- 7.1.2 Label and pre-weigh two tare dishes, one for the total solids portion of the sample and one for the wet sieving portion.
- 7.1.3 Carefully homogenize the sample to incorporate any overlying water.
- 7.1.4 Remove the total solids portion of the sample (approximately 25 grams), weigh it in the labeled tare dish, and record weight on the data sheet to the nearest 0.1mg. Dry the sample in oven for a minimum of 16 hours (overnight) or until completely dry, cool it in a desiccator, weigh, and record the weight on the data sheet.
- 7.1.5 Remove wet the sieve portion of sample (approximately 40 to 150 grams), weigh it in a labeled tare dish, and record the weight on the data sheet to the nearest 0.1mg. The critical factor for the sample size determination is the weight of the fine-grained material that will be used for the pipette analysis. Ideally, the total dry weight of fine-grained material in the 1000 ml-graduated cylinder should equal approximately 15 grams. Estimate the fraction of material finer than the #230 sieve, along with the moisture content (i.e., if the moisture content is 100%, and the percent finer than the #230 is estimated at 50%, an acceptable sample size could be approximately 80 grams).
- 7.1.6 Clean workstation when sample preparation is finished. Initial and date data sheet.

7.2 Wet Sieving

- 7.2.1 Label cylinders with sample number by using lab tape.
- 7.2.2 Place a #230 sieve in the funnel over a 1,000 ml cylinder using lab stands with clamps. Moisten sieve using a light spray of distilled water.
- 7.2.3 Add 20-30mls of distilled water in sample tare dish and stir to suspend the fine-grained material.
- 7.2.4 Pour sample and water onto sieve and gently agitate sieve to separate fractions. Aggregated clumps of sediment can be gently broken down with a rubber policeman. For sample spillage, see 9.0 CORRECTIVE ACTION.
- 7.2.5 Continue washing sample with a fine spray of distilled water until only clear water passes through sieve. See 9.0 CORRECTIVE ACTION if liquid passes 1000ml mark.
- 7.2.6 Rinse all remaining material off the #230 sieve back into the tare dish. Place sample in oven, minimum of 16 hours (overnight) until a constant weight is obtained.
- 7.2.7 Clean workstation when wet sieving is finished. Initial and date data sheet.

7.3 Sieving the Sand-Gravel Fraction

- 7.3.1 Remove plus #230 material tare dish from the oven and cool in a desiccator to room temperature.
- 7.3.2 Set up a nest of sieves with the coarsest on the top and grading down to the finest on the bottom over a sieve pan. This set of sieves will include the #4, #10, #18, #35, #60, #120, and #230. Clean any dirty sieves with a wire or bristle brush and tap sieve on table with all edges evenly to remove debris.
- 7.3.3 Weigh the sample and tare dish and record the weight on the data sheet to the nearest 0.1mg.
- 7.3.4 Add the sample to the uppermost (#4) sieve in nest. Use a brush to clean the entire sample from the tare dish and gently break up any agglomerations of material that may have formed due to drying.
- 7.3.5 Place the nest of sieves in mechanical sieve shaker and place the metal lid on the top of the stack. Set timer for 15 minutes, and close the door to the shaker. Remove the nest of sieves when shaker is finished.
- 7.3.6 Empty the top sieve by inverting it over a glossy piece of paper or tag board. Run a bristle brush over bottom of sieve to remove all particles. Tap sieve evenly on table.
- 7.3.7 Carefully pour sample from the paper into the tare dish, weigh it to the nearest 0.1mg, and record the weight on the data sheet.
- 7.3.8 Repeat 6.3.6 and 6.3.7 with each remaining sieve. Tare out the weight of an empty foil pan on the balance and pour the contents of the sieve pan into it. Weigh and record the weight of the < #230 material and record this on the data sheet. Empty the contents of the foil pan into the silt-clay fraction in the cylinder. Compare the total weight retained with the original dry weight to ensure that no material was lost in the sieving process. If weights are significantly different, see section 9.0 CORRECTIVE ACTION. Note large amounts of organic material (e.g., wood debris, grass, shells) or unusual material in any size fraction on the data sheet.
- 7.3.9 Clean workstation when work is finished. Initial and date the data sheet.

7.4 Pipetting the Silt-Clay Fraction

- 7.4.1 Add 10ml of $\text{Na}(\text{PO}_2)_6$ dispersant to each silt-clay fraction cylinder and fill to the line with distilled water. Record the batch number of dispersant used on data sheet.
- 7.4.2 Using a #13 rubber stopper, mix suspensions by inverting cylinder end over end for 60 cycles.
- 7.4.3 Allow the mixed suspension to stand for 2-3 hours and check for signs of flocculation. See 9.0 CORRECTIVE ACTION if flocculation occurs.
- 7.4.4 Label and pre-weigh all fraction tares to the nearest 0.1mg and record on data sheet.

- 7.4.5 Print out a set of withdrawal time stickers on the computer. Attach stickers to the corresponding data sheets.
- 7.4.6 Verify that the temperature logger is functional, and record the initial temperature.
- 7.4.7 Use rubber stopper and mix suspensions by inverting cylinder end over end approximately 60 times per one minute. For sample spillage see 9.0 CORRECTIVE ACTION.
- 7.4.8 After 20 seconds, withdraw a 20ml aliquot from a depth of 20 cm below the surface of the suspension using a 25ml 1/10 pipette with rubber bulb. It is critical that the solution be disturbed as little as possible when the pipette aliquots are taken.
- 7.4.9 Transfer aliquot to pre-weighed tare and rinse pipette by drawing approximately 20ml distilled water into pipette and transferring rinse into the same tare.
- 7.4.10 Withdraw another 20ml aliquot at the depth of 10 cm below the surface of the suspension at the appropriate time as listed in TABLE 1 according to the average room temperature. For missed pipetting times see 9.0 CORRECTIVE ACTION.
- 7.4.11 Dry all aliquots in oven to a constant weight at 90°C.
- 7.4.12 Cool dried samples to room temperature in a desiccator, weigh to the nearest 0.1mg, and record on data sheet.
- 7.4.13 Keep workstation clean. Initial and date the data sheet.

TABLE 1. Withdrawal Times for Pipette Samples

Diameter Finer (phi)	Diameter Finer (um)	Withdrawal Depth (cm)	Elapsed Time for Withdrawal of Sample in						
			Hours (h) Minutes (m) and Seconds (s)						
			18°	19°	20°	21°	22°	23°	24°
4.0	62.5	20	20s	20s	20s	20s	20s	20s	20s
5.0	31.2	10	2m	1m 57s	1m 54s	1m 51s	1m 49s	1m 46s	1m 44s
6.0	15.6	10	8m	7m 48s	7m 36s	7m 25s	7m 15s	7m 5s	6m 55s
7.0	7.8	10	31m 9s	31m 11s	30m 26s	29m 41s	28m 59s	28 m 18s	27 m 39s
8.0	3.9	10	2h 8m	2h 5m	2h 2m	1h 59m	1h 56m	1h 53 m	1h 51 m
9.0	1.95	10	8h 32m	8h 18m	8h 6m	7h 56m	7h 44m	7h 32 m	7h 22 m
10.0	0.98	10	34h 6m	33h 16m	32h 28m	31h 40m	30h 56m	30h 12 m	29h 30 m

8.0 CALCULATIONS

8.1 MOISTURE CONTENT and TOTAL SOLIDS

Total solids content is determined as follows:

$$\text{Percent Solids} = \frac{(A - B) (100)}{(C - B)}$$

Where: A = weight of tare and dry sample residue
 B = weight of tare
 C = weight of tare and wet sample

8.2 SAND and GRAVEL FRACTION

The sand and gravel fractions of the sample are reduced as follows:

$$\text{Percent retained (for a given sieve)} = C/D * 100$$

Where: C = cumulative weight retained for a given sieve
D = total dry sample weight

8.3 SILT and CLAY FRACTION

The total weight of the phi-sized interval in the 1000ml graduated cylinder is determined as follows:

$$\text{Phi weight} = 50 ((E - G) - (F - G))$$

Where: E = weight of residue in a 20ml aliquot for a given phi size boundary
F = weight of residue in a 20ml aliquot for next larger phi size boundary
G = weight of dispersant and dissolved salt in a 20ml aliquot

9.0 SAFETY

- 9.1 Lab wear including a lab coat, safety glasses, and gloves should be worn at all time.
- 9.2 Care should be taken not to inhale fine dust while sieving. A dust mask should be worn when sieving.
- 9.3 The sieve shaker is loud, and the lid should be closed while in operation.
- 9.4 Keep workstation clean at all times. Wipe any spills to avoid safety hazards.

10.0 CORRECTIVE ACTION

- 10.1 Sample loss during wet sieving - If sample is spilled on table, use distilled water to wash spillage into tare dish. If sample is lost on the floor, see supervisor. A significant loss may result in a redo.
- 10.2 Excess wash volume – If wash volume exceeds 1000ml mark during wet sieving, let sample evaporate to obtain an acceptable volume.
- 10.3 Sample loss during sieving – Attempt to brush spilled sample into tare dish prior to weighing. It is extremely important to keep worktables and floor clean prior to sieving in case a spill occurs.
- 10.4 Sample Flocculation – Flocculation results in a curdling and rapid settling of lumps of particles or by the presence of a thick, soupy layer on the bottom of the cylinder passing abruptly into clear water above. When flocculation occurs, add dispersant in 10ml increments until no noticeable flocculation is observed. Record the total volume of dispersant added on the data sheet.
- 10.5 Sample spillage during cylinder mixing – If rubber stopper is not tight on cylinder and spillage occurs, continue pipetting procedure. Note approximate amount of spilled liquid on data sheet.
- 10.6 Missed pipetting aliquots – If withdrawal is missed the suspension may be re-mixed and the missed aliquot can be taken at the appropriate time. It is not necessary to take the initial 20ml aliquot for this corrective action.

11.0 REFERENCES

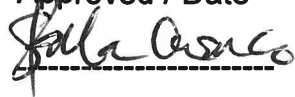
- 11.1 Folk, Robert L., 1978, The Petrology of Sedimentary Rocks, Hemophile Publishing Co., Austin TX
- 11.2 USACOE 1995, Puget Sound Estuary Protocols, U.S. Army Corps of Engineers, Seattle WA

Laboratory Data Consultants, Inc. (LDC)

SOP #14.0.0 REV 1.0
January 16, 2020

**STANDARD OPERATING PROCEDURE
FOR DATA REVIEW/
DATA VALIDATION PROCESS**

Approved / Date

 1/16/20

Stella Cuenco
Operations Manager/
Principal Chemist

1.0 PURPOSE

The data review and validation level of effort required for the Scope of Work outlined for any project will encompass several activities. The steps are categorized below. To perform the tasks, LDC will not use subcontractors since they would reduce the quality and control of the work product.

2.0 CUSTOMER Data Packages delivered via email or CD/DVD or LDCAdvantage.

Data deliverables are delivered to the Data Control Manager. The data is copied to \\LDCArchive and saved under the date received folder by Client Name and project on the LDC file server network. Data deliverables are printed for Login.

If the Data arrived via CD/DVD, the original media is placed with the hardcopy data package on the shelf after printing and saving data to the \\LDCArchive folder.

3.0 SAMPLE LOGIN

All samples submitted for data validation are entered into the LDC Log-in system. The system generates various spreadsheets for sample tracking, listings of laboratory and client identifications, sampling dates, analysis requested, matrix, and project due date. These tracking documents are distributed to all data validation, QA and project management staff.

Laboratory Data Consultants, Inc. (LDC)

SOP #14.0.0 REV 1.0
January 16, 2020

4.0 DEFINITIONS

The following definitions are provided for this SOP.

Definitions

- LDC Number - Project number given to a Group of SDG numbers to form a batch.
- SDG Number - Data package number given to a Group of samples by the analytical laboratory.

5.0 PRE SCREENING OF DATA PACAKGES

The pre-screening is performed concurrently with the sample log-in process. This task verifies sample chain-of-custody, data package completeness, and concurrence with the authorized delivery order.

6.0 DATA VALIDATION

The execution of the data review task requires the highest level of effort. The review process will be handled in a stepwise fashion including manual and automated data review. The validator will use manual review to document each finding on a Validation Findings form. Along with the finding, the reviewer will document the date of the occurrence, the lab reference identification, the validation criteria, the associated samples, and the qualification of the data. A Validation Checklist form is marked noting if validation criteria was met or exceeded. A Validation Checklist is enclosed for review (Exhibit A). These checklists are used as an inventory sheet to assure all samples were reviewed for each criteria. The findings documented on the Validation Findings form will be transcribed into the final summary report. Examples of recalculation and findings worksheets used for Level 4 validation are available for review upon request.

All initial validation performed by Laboratory Data Consultants, Inc. has a secondary peer review. All final reports will be reviewed by a Senior Chemist or Principal Chemist.

7.0 LDC Validation Data Packages

LDC Validation Data Packages are processed and stored in the archive room 2D. Once the LDC Validation report has been delivered to client, the ST (Attachment 1: Sample Table) is pulled from active job file.

Laboratory Data Consultants, Inc. (LDC)

SOP #14.0.0 REV 1.0
January 16, 2020

8.0 FIRST REPORT REVIEW

The first review of the data validation report verifies that all findings and data qualification has been accurately transferred from the data validation worksheets. All sample identifications, methods, formatting, and general text are reviewed.

9.0 SENIOR REPORT REVIEW

The senior review of the data validation report verifies that all findings, data qualification, and professional judgments previously integrated into the reports reflect the overall quality of the data. Any additional comments required to enhance the usability of the report will be inserted at this time.

10.0 QA REPORT REVIEW

A QA check of selected data validation reports within an individual delivery order will be reviewed by the QA department. A formal nonconformance report will be generated for any identified deficiencies. The deficiency will be addressed with the appropriate staff and corrected prior to submittal to senior management for final review and signature.

11.0 SENIOR MANAGEMENT REVIEW

The program/technical manager will perform an overall review of the final reports. He will sign the report cover letter and submit the report to the sample custodian for shipment to the client.

12.0 Archived Data Packages

LDC Validation Packages Archive Boxes are labeled as follows:

1. Box number is assigned in chronological order
2. LDC job number – Client/Project

12.1 Holding times for archived material

1. Data Packages received from client as hard copy will be held for 3 months.
2. Data Packages received from client electronically will be held for 30 days.

Laboratory Data Consultants, Inc. (LDC)

SOP #14.0.0 REV 1.0

January 16, 2020

3. Data Packages where client has requested Data to be returned, the data packages will be returned to client upon completed validation.

13.0 Electronic Data Deliverables (EDD)

This process will be initiated at step 1 with the receipt of disks or from the client or loading EDDs to LDC's secured Internet portal LDCAdvantage. After automated verification of the EDD format, content, and fields, the EDD will be populated with the manual review for importing of the final data qualifiers. The final approval of qualifiers will occur after step 5.

Appendix G

Sampling Location Details

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
Segment 1																										
100	3	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
101	3	1	subtidal	x		x	1	no	yes			x	Characterize the subtidal near the northern boundary.	yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
102	3	1	subtidal	x		x	1	no	yes	x			Reoccupy SD-PER205 (2015); total PCB EF of 1.8. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
103	3	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
104	3	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
105	3	1	intertidal		x		3	no	no	x			Reoccupy of RI core SC-47 with PCB EF of 9.2 in the 2 ft to 3 ft interval. Only the 0- to 45-cm sample will be collected because a co-located 0- to 10-cm sample was collected in 2018 and will be analyzed.	-	-	-	-	yes	yes	yes	a	-	-	-	-	
106	3.1	1	intertidal	x	x		3	no	no	x			Reoccupy B7a (2004); HCB EF of 5.	yes	yes	a	yes	yes	yes	yes	a	-	-	-	-	-
107	3.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
108	3.1	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
109	3.1	1	subtidal	x		x	1	no	yes	x			Reoccupy SD-DUW75 (1996); total PCB EF of 1.3.	yes	yes	yes	yes	-	-	-	-	-	yes	yes	yes	yes
110	3.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
111	3.1	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
112	3.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
113	3.1	1	subtidal	x		x	3	no	yes	x			Reoccupy SD-PER209 (2015); total PCB EF of 1.1. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-

Table G1
Rationale for Sediment Sampling Locations

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
114	3.1	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
115	3.1	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
116	3.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
117	3.1	1	subtidal	x		x	1	no	yes	x			Reoccupy SD-PER208 (2015); total PCB EF of 3.3. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
118	3.1	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
119	3.1	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
120	3.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	-
121	3.1	1	subtidal	x		x	3	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
122	3.2	2 (archive)	subtidal			x	1	no	yes	x	x		Reoccupy LDW18-SS-122 (2018); analyzed as part of composite (no RAL screen). Only the 0- to 60-cm sample will be collected because a co-located 0- to 10-cm sample was collected in 2018 and will be analyzed.	-	-	-	-	-	-	-	-	a	a	a	a	
123	3.2	1	subtidal	x		x	1	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
124	3.2	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	-
125	3.2	1	subtidal	x		x	1	no	yes	x			Reoccupy SD-PER210 (2015); no EFs > 1. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
126	3.2	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
127	3.2	1	intertidal	x	x		3	no	no	x			Reoccupy DR201 (1998); total PCB EF of 3.2.	yes	yes	yes	yes	yes	yes	yes	yes	-	-	-	-	-
128	3.2	2 (archive)	subtidal	x		x	3	no	yes		x			a	a	a	a	-	-	-	-	-	a	-	-	-
129	3.2	2 (archive)	subtidal	x		x	3	no	yes		x			a	a	a	a	-	-	-	-	-	a	-	-	-
130	3.2	1	subtidal	x		x	1	no	yes			x		yes	yes	yes	yes	-	-	-	-	-	yes	yes	yes	yes

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
131	3.2	2 (archive)	subtidal	x		x	3	no	yes		x			a	a	a	a	-	-	-	-	-	a	-	-	-
132	3.2	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
133	3.2	1	intertidal	x	x		3	no	no	x			Reoccupy SD-PER212 (2015); total PCB EF of 1.9. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	yes	yes	a	yes	yes	yes	yes	a	-	-	-	-	
134	3.3	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
135	3.3	1	subtidal	x		x	1	no	yes	x			Reoccupy SD-PER211 (2015); no EFs > 1. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
136	3.3	2 (archive)	subtidal			x	3	no	yes	x	x		Reoccupy LDW18-SS-124 (2018); analyzed as part of composite (no RAL screen). Only the 0- to 60-cm sample will be collected because a co-located 0- to 10-cm sample was collected in 2018 and will be analyzed.	-	-	-	-	-	-	-	-	-	a	-	-	-
137	3.3	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	
138	3.3	2 (archive)	subtidal	x		x	1	no	no		x			a	a	a	a	-	-	-	-	-	a	a	a	a
139	3.3	1	intertidal	x	x		3	no	no	x			Reoccupy LDW-SS106 (2005); total PCB EF of 1.8.	yes	yes	a	yes	yes	yes	yes	a	-	-	-	-	
140	3.3	1	subtidal	x		x	1	no	yes			x	Characterize scour area.	yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
141	3.3	2 (archive)	subtidal	x		x	3	no	yes	x	x		Reoccupy SD-PER213 (2015); no EFs > 1. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	a	a	a	a	-	-	-	-	-	a	-	-	-
142	3.3	1	subtidal	x		x	1	no	no			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
143	3.3	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	
144	3.3	1	subtidal	x		x	3	no	yes			x	Characterize area near core SB-5 with PCB exceedances in three intervals, 0-2.5 ft (EF 4), 2.5–5 ft (EF 11) and 5 – 7.5 ft (EF 3.5). SB-5 was collected to characterize sediment dredged for bridge construction.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
145	3.3	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	
146	3.3	1	intertidal	x	x		3	no	no			x		yes	yes	yes	yes	yes	yes	yes	yes	-	-	-	-	-
147	3.3	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	
148	3.3	1	subtidal	x		x	3	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
149	3.3	2 (archive)	subtidal	x		x	1	no	no		x			a	a	a	a	-	-	-	-	-	a	a	a	a
150	3.4	1	subtidal	x		x	1	no	no			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
151	3.3	1	intertidal	x	x		3	no	no			x		yes	yes	a	yes	yes	yes	yes	a	-	-	-	-	-
152	3.4	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	-
153	3.4	2 (archive)	subtidal	x		x	3	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
154	3.4	1	intertidal	x		x	2	no	no			x	Collect 0- to 60-cm interval subsurface samples rather than 0- to 45-cm samples because subtidal conditions are consistent with the intended use for the South Park Marina.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
155	3.4	1	subtidal	x		x	3	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
156	3.4	1	subtidal	x		x	3	no	yes			x	Characterize area between Boeing DSOA and shoal area.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
157	3.4	2 (archive)	subtidal	x		x	3	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
158	3.4	1	intertidal	x		x	2	no	no			x	See note for location 154 regarding sample intervals.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
159	3.4	1	intertidal	x		x	3	no	no			x	Characterize area near private storm drain. See note for location 154 regarding sample intervals.	yes	yes	yes	yes	-	-	-	-	-	yes	-	-	-
160	3.4	1	subtidal	x		x	3	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
161	3.5	1	intertidal			x	2	no	no	x			Collect only the 0- to 60-cm sample because there is a recent surface sample at this location. See note for location 154 regarding sample intervals.	-	-	-	-	-	-	-	-	-	yes	-	-	-
162	3.5	1	subtidal	x		x	3	no	yes			x	Characterize area between Boeing DSOA and shoal area.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
163	3.5	2 (archive)	subtidal	x		x	3	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
164	3.5	2 (archive)	intertidal	x		x	3	no	no		x		See note for location 154 regarding sample intervals.	a	a	a	a	-	-	-	-	-	a	-	-	-
165	3.5	2 (archive)	intertidal	x		x	2	no	no		x		See note for location 154 regarding sample intervals.	a	a	a	a	-	-	-	-	-	a	-	-	-
166	3.5	1	subtidal	x		x	3	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
167	3.5	1	intertidal	x		x	3	no	no		x		See note for location 154 regarding sample intervals.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
168	3.5	1	intertidal	x		x	2	no	no		x		See note for location 154 regarding sample intervals.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
169	3.5	1	intertidal	x		x	2	no	no		x		See note for location 154 regarding sample intervals.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
Segment 2																										
200	3.5	2 (archive)	intertidal	x	x		2	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	-
201	3.5	2 (archive)	subtidal	x		x	3	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
202	3.5	1	subtidal	x		x	1	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
203	3.6	1	subtidal	x		x	1	no	no	x			Reoccupy SD-PER308 (2015); total PCB EF of 1.8. Reoccupying post-FS perimeter monitoring location with temporal variation in RAL EF status.	yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
204	3.6	1	subtidal	x		x	3	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
205	3.6	2 (archive)	subtidal	x		x	1	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
206	3.6	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
207	3.6	2 (archive)	subtidal	x		x	1	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
208	3.6	1	subtidal			x	1	yes	yes	x			Re-occupy Jorgensen perimeter location PMN-1 with no EFs >1 in 2018. Only the 0- to 60-cm sample will be collected because of the proximity of this location to the Jorgensen Forge long-term	-	-	-	-	-	-	-	-	-	yes	yes	yes	yes

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
245	3.9	1	subtidal	x		x	1	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
246	3.9	2 (archive)	subtidal	x		x	3	yes	yes			x		a	a	a	a	-	-	-	-	-	a	a	a	a
247	3.9	1	intertidal	x	x		3	no	no			x		yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-
248	3.9	1	intertidal	x	x		1	no	no			x		yes	yes	a	yes	yes	yes	yes ³	a	yes	-	-	-	-
249	3.9	2 (archive)	subtidal	x		x	1	yes	yes			x		a	a	a	a	-	-	-	-	-	a	a	a	a
250	3.9	1	subtidal	x		x	1	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
251	3.9	1	subtidal	x		x	1	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
252	3.9	2 (archive)	intertidal	x	x		1	no	no			x		a	a	a	a	a	a	a	a	a	-	-	-	-
253	4	1	intertidal	x	x		1	no	no			x		yes	yes	a	yes	yes	yes	yes ³	a	yes	-	-	-	-
254	4	2 (archive)	subtidal	x		x	1	yes	yes			x		a	a	a	a	-	-	-	-	-	a	a	a	a
255	4	1	subtidal	x		x	1	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
256	3.9	2 (archive)	intertidal	x	x		2	no	no			x		a	a	a	a	a	a	a	a	-	-	-	-	-
257	3.9	1	intertidal	x	x		2	no	no	x	x		Reoccupy AN-019 (2006); total PCB EF of 4 in order to assess remedial technology in this area. Near location of AN-027 (2006) with a dioxin/furan TEQ of 20.6 ng/kg.	yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-
258	4	1	intertidal	x	x		2	no	no			x		yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-
259	4	2 (archive)	intertidal	x	x		2	no	no			x		a	a	a	a	a	a	a	a	-	-	-	-	-
260	4	2 (archive)	intertidal	x	x		2	no	no			x		a	a	a	a	a	a	a	a	-	-	-	-	-
261	4	1	subtidal	x		x	1	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes
262	4	2 (archive)	subtidal	x		x	1	no	yes			x		a	a	a	a	-	-	-	-	-	a	a	a	a
263	4	2 (archive)	intertidal	x	x		1	no	no			x		a	a	a	a	a	a	a	a	a	-	-	-	-
264	4	1	subtidal	x		x	1	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes

Table G1
Rationale for Sediment Sampling Locations

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample				
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	
265	4	2 (archive)	subtidal	x		x	3	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a	
266	4	1	intertidal	x	x		2	no	no	x	x		Reoccupy EST145 (1997); total PCB EF of 1.1.	yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-	
267	4	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	-	
268	4	1	intertidal	x	x		3	no	no			x	Characterize area near core AN-41 (2008) with PCB concentrations greater than the benthic cleanup level in the 0- to 1-ft interval.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-	
269	4	1	subtidal	x		x	3	yes	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes	
270	4	2 (archive)	subtidal	x		x	3	yes	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a	
271	4	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a	
272	4	1	intertidal	x	x		1	no	no			x		yes	yes	a	yes	yes	yes	yes ³	a	yes	-	-	-	-	
273	4	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a	
Segment 3																											
300	4	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	a	-	-	-	-	-
301	4	1	intertidal	x	x		3	no	no	x			Reoccupy core location SH-01 (2004) with PCB concentrations greater than the benthic cleanup level in 10- to 25-cm interval.	yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-	
302	4	1	intertidal	x	x		3	no	no	x			Reoccupy core location SH-02 (2004) with PCB concentrations greater than the benthic cleanup level in 10- to 25-cm interval.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-	
303	4	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-	
304	4	1	intertidal	x	x		3	no	no	x			Reoccupy IT-13 (2011); total PCB EF of 3.5 to assess remedial technology in this area.	yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-	
305	4	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-	
306	4.1	1	intertidal	x	x		3	no	no	x	x		Reoccupy core location RP-05 (2011) with PCB concentrations greater than the benthic cleanup level in the 2- to 3-ft interval.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-	

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
307	4.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-	
308	4.1	1	intertidal	x	x		3	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
309	4.1	1	intertidal	x	x		3	no	no	x	x		Reoccupy core location RP-05 (2011) with PCB concentrations greater than the benthic cleanup level.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
310	4.1	1	intertidal	x	x		3	no	no	x			Reoccupy SB-12 (2004); cPAH EF ¹ of 1.2, other PAH EFs of 1.0 -1.1.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
311	4.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
312	4.1	1	intertidal	x	x		3	no	no	x			Reoccupy location SH-05 (2004); PCB EF of 9.6 to assess depth of contamination and assess remedial technology for this area, located near location IT-7 with a dioxin/furan TEQ of 14.3 ng/kg. The 0- to 10-cm sample will be archived.	a	a	a	a	yes	yes	a	yes	-	-	-	-	-
313	4.1	1	intertidal	x	x		3	no	no	x			Reoccupy location RP-10 (2010) with PCB EF of 5 to assess depth of contamination. The 0- to 10-cm sample will be archived.	a	a	a	a	yes	yes	a	a	-	-	-	-	-
314	4.1	2 (archive)	subtidal	x		x	3	no	yes		x			a	a	a	a	-	-	-	-	-	a	-	-	-
315	4.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
316	4.1	1	intertidal	x	x		3	no	no	x			Reoccupy RP-11 (2011) with PCB EF of 1.8. The 0- to 10-cm sample will be archived.	a	a	a	a	yes	yes	a	a	-	-	-	-	-
317	4.1	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
318	4.1	1	subtidal	x		x	3	no	yes	x			Reoccupy core location RP-23 (2012) with PCB concentrations greater than the benthic cleanup level.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
319	4.1	1	intertidal	x	x		3	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
320	4.1	1	intertidal	x	x		3	no	no	x			Reoccupy SH-06 (2004); total PCB EF of 1.6.	yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-
321	4.2	2 (archive)	intertidal	x	x		1	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-
322	4.2	1	subtidal	x		x	1	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
323	4.2	1	intertidal	x	x		3	no	no	x			Reoccupy core location SH-08 (2004) with PCB concentrations greater than the benthic cleanup level.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
324	4.1	1	subtidal	x		x	2	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
325	4.1	2 (archive)	intertidal	x		x	2	no	no		x		Collect 0- to 60-cm interval subsurface samples rather than 0- to 45-cm samples because subtidal conditions are consistent with the intended use of the Duwamish Yacht Club.	a	a	a	a	-	-	-	-	-	a	-	-	-
326	4.1	1	intertidal	x		x	2	no	no			x	See note for location 325 regarding sample intervals.	yes	yes	a	yes	-	-	-	-	-	yes	-	-	-
327	4.1	1	intertidal	x		x	2	no	no			x	See note for location 325 regarding sample intervals.	yes	yes	yes	yes	-	-	-	-	-	yes	-	-	-
328	4.1	2 (archive)	subtidal	x		x	2	no	yes		x		See note for location 325 regarding sample intervals.	a	a	a	a	-	-	-	-	-	a	-	-	-
329	4.1	2 (archive)	intertidal	x		x	2	no	no		x		See note for location 325 regarding sample intervals.	a	a	a	a	-	-	-	-	-	a	-	-	-
330	4.2	1	intertidal		x		3	no	no			x	Collect only the 0- to 45-cm sample because post-FS 0- to 10-cm samples exist in this location, LDW18-2100A-1 (2018) and LDW18-2100A-2 (2018).	-	-	-	-	yes	yes	a	yes	-	-	-	-	-
331	4.2	1	intertidal	x	x		3	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
332	4.2	1	intertidal	x	x		3	no	no	x			Reoccupy LDW-SS131 (2005); no EFs > 1, dioxin/furan TEQ of 22.7 ng/kg in the field dup.	yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-
333	4.2	2 (archive)	subtidal	x		x	1	no	Yes ²		x			a	a	a	a	-	-	-	-	-	a	a	a	a
334	4.2	1	intertidal		x		1	no	no	x		x	Reoccupy LDW18-DeltaMarine (2018) location for 0- to 45-cm coverage. Collect only the 0- to 45-cm sample because a 2018 0- to 10-cm sample exists at this location.	-	-	-	-	yes	yes	yes ³	a	yes	-	-	-	-
335	4.2	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
336	4.2	1	subtidal	x		x	1	no	yes			x		yes	yes	yes	yes	-	-	-	-	-	yes	yes	yes	yes
337	4.2	2 (archive)	subtidal	x		x	1	no	yes		x			a	a	a	a	-	-	-	-	-	a	a	a	a
338	4.2	1	subtidal	x			1	no	yes	x			Reoccupy DR176 (1998); benthic PAH EFs of 1.5 to 2.9. Collect only the 0- to 10-cm sample	yes	yes	a	yes	-	-	-	-	-	-	-	-	-

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample				
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	
354	4.3	2 (archive)	intertidal		x		3	no	no	x	x		Reoccupy LDW18-SS-150 (2018); analyzed as part of composite (no RAL screen). Only the 0- to 45-cm sample will be collected because a co-located 0- to 10-cm sample was collected in 2018 and will be analyzed.	-	-	-	-	a	a	a	a	-	-	-	-	-	
355	4.3	2 (archive)	intertidal	x		x	1	no	no		x			a	a	a	a	-	-	-	-	-	a	a	a	a	
356	4.3	1	intertidal	x	x		3	no	no			x		yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-	
357	4.3	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-	
358	4.3	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-	
359	4.3	1	intertidal	x	x		3	no	no	x			Reoccupy WIT258 (1997); total PCB EF of 1.8.	yes	yes	a	yes	yes	yes	yes	yes	yes	yes	yes	-	-	-
360	4.3	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-	
361	4.3	1	intertidal	x	x		1	no	no		x		Analyze the 0- to 45-cm interval as Tier 1 to characterize the area next to the navigation dredge area; the 0- to 10-cm sample will be archived.	a	a	a	a	yes	yes	yes ³	a	yes	-	-	-	-	
362	4.3	2 (archive)	subtidal			x	3	no	yes	x	x		Collect only the 0- to 60-cm sample because a co-located 0- to 10-cm sample was collected in 2018 and will be analyzed.	-	-	-	-	-	-	-	-	-	a	-	-	-	
363	4.3	2 (archive)	intertidal		x		3	no	no	x	x		Reoccupy LDW18-SS2089-D (2018) location to bound location 364.	-	-	-	-	a	a	a	a	-	-	-	-	-	
364	4.3	1	intertidal	x	x		3	no	no	x			Reoccupy R75 (1997); cPAH EF ¹ of 1.4.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-	
365	4.4	1	intertidal	x	x		1	no	no			x		yes	yes	a	yes	yes	yes	yes ³	a	yes	-	-	-	-	
366	4.4	2 (archive)	subtidal			x	3	no	yes	x	x		Reoccupy LDW18-SS-153 (2018); analyzed as part of composite (no RAL screen). Only the 0- to 60-cm sample will be collected because a co-located 0- to 10-cm sample was collected in 2018 and will be analyzed.	-	-	-	-	-	-	-	-	-	a	-	-	-	
367	4.4	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	a	-	-	-	-	-	
368	4.4	1	subtidal	x		x	1	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	yes	a	yes	
369	4.5	1	intertidal		x		3	no	no	x		x	Reoccupy LDW-SS2085-A (2011). Only the 0- to 45-cm sample will be collected for spatial	-	-	-	-	yes	yes	a	yes	-	-	-	-	-	

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample					
				0–10 cm	0–45 cm	0–60 cm				Reoccupiation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers		
386	4.7	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-			
387	4.8	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-			
388	4.7	1	intertidal	x	x		1	no	no		x			yes	yes	a	yes	yes	yes	yes ³	a	yes	-	-	-	-		
389	4.8	1	intertidal	x	x		3	no	no	x	x		Reoccupy B10a (2004); phenol EF of 1.3.	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	-	-	-	-
390	4.7	1	intertidal	x	x		3	no	no		x			yes	yes	a	yes	yes	yes	yes	a	-	-	-	-	-		
391	4.7	2 (archive)	intertidal	x	x		3	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-			
392	4.8	1	subtidal	x		x	3	no	yes			x		yes	yes	a	yes	-	-	-	-	-	yes	-	-	-		
393	4.8	1	intertidal	x			2	no	no			x	Collect only the 0- to 10-cm sample because of limited sediment depth at the location. Located near seep location with cPAHs and BEHP detections.	yes	yes	a	yes	-	-	-	-	-	-	-	-	-		
Segment 4																												
400	4.8	2 (archive)	intertidal	x	x		2	no	no		x			a	a	a	a	a	a	a	-	-	-	-	-			
401	4.9	1	intertidal	x	x		2	no	no	x			Reoccupy NFK304 (1995); total PCB EF of 1.5.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-		
402	4.8	2 (archive)	subtidal	x			2	no	no		x		No 0- to 60-cm sample will be collected because no subsurface RALs apply in Segment 4.	a	a	a	a	-	-	-	-	-	-	-	-			
403	4.9	2 (archive)	subtidal	x			2	no	no		x		No 0- to 60-cm sample will be collected because no subsurface RALs apply in Segment 4.	a	a	a	a	-	-	-	-	-	-	-	-			
404	4.9	1	subtidal	x			2	no	no	x			Reoccupy NFK307 (1995); total PCB EF of 4.2. No 0- to 60-cm sample will be collected because no subsurface RALs apply in Segment 4.	yes	yes	a	yes	-	-	-	-	-	-	-	-			
405	4.9	2 (archive)	subtidal	x			2	no	no		x		No 0- to 60-cm sample will be collected because no subsurface RALs apply in Segment 4.	a	a	a	a	-	-	-	-	-	-	-	-			
406	4.9	1	intertidal	x	x		2	no	no	x			Reoccupy NFK308 (1995); total PCB EF of 2.5.	yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	-		
407	4.9	1	intertidal	x			2	no	no	x			Reoccupy NFK311 (1995); total PCB EF of 1.7. Only the 0- to 10-cm sample will be collected because clamming is not possible because the location is not accessible, and clams are not expected because of low salinity in this area.	yes	yes	a	yes	-	-	-	-	-	-	-	-			
408	4.9	2 (archive)	subtidal	x			2	no	no		x		No 0- to 60-cm sample will be collected because no subsurface RALs apply in Segment 4.	a	a	a	a	-	-	-	-	-	-	-	-			

Table G1
Rationale for Sediment Sampling Locations

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample			
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers
409	4.9	1	intertidal	x	x		2	no	no			x		yes	yes	a	yes	yes	yes	a	-	-	-	-	-	
410	4.9	2 (archive)	intertidal	x	x		2	no	no			x		a	a	a	a	a	a	a	-	-	-	-	-	
411	4.9	1	intertidal	x	x		2	no	no	x			Reoccupy LDW-SS144 (2005); total PCB EF of 2.1.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
412	4.9	2 (archive)	subtidal	x			na	no	no			x	No 0- to 60-cm sample will be collected because no subsurface RALs apply in Segment 4. Norfolk EAA remediation addressed subsurface sediment contamination.	a	a	a	a	-	-	-	-	-	-	-	-	
413	4.9	1	intertidal	x			2	no	no			x	Collect only the 0- to 10-cm sample will be collected because clamming is not possible because the location is not accessible, and clams are not expected because of low salinity in this area.	yes	yes	a	yes	-	-	-	-	-	-	-	-	
414	4.9	2 (archive)	subtidal	x			na	no	no			x		a	a	a	a	-	-	-	-	-	-	-	-	
415	4.9	1	intertidal	x	x		2	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	
416	4.9	1	intertidal	x	x		na	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	
417	4.9	2 (archive)	intertidal	x	x		na	no	no	x	x		Reoccupy S2 (2017); total PCB EF of 3.3. Post-FS 0-10 cm location will be re-occupied to evaluate potential source.	a	a	a	a	a	a	a	a	-	-	-	-	-
418	4.9	1	intertidal	x	x		na	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	
419	4.9	1	intertidal	x	x		2	no	no			x		yes	yes	yes	yes	yes	yes	a	yes	-	-	-	-	
420	4.9	2 (archive)	subtidal	x			na	no	no			x		a	a	a	a	-	-	-	-	-	-	-	-	
421	4.9	1	intertidal	x	x		2	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	
422	4.9	2 (archive)	subtidal	x			na	no	no			x	No 0- to 60-cm sample will be collected because no subsurface RALs apply in Segment 4.	a	a	a	a	-	-	-	-	-	-	-	-	
423	4.9	1	intertidal	x	x		2	no	no	x			Reoccupy NFK004A (1994); total PCB EF of 2.9 and BBP EF of 1.1.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-
424	4.9	1	intertidal	x	x		2	no	no			x		yes	yes	a	yes	yes	yes	a	a	-	-	-	-	
425	5	2 (archive)	intertidal	x	x		2	no	no			x		a	a	a	a	a	a	a	a	-	-	-	-	
426	5	1	intertidal	x	x		2	no	no	x			Reoccupy NFK006 (1994); cPAH EF ¹ of 1.1.	yes	yes	a	yes	yes	yes	a	a	-	-	-	-	-

**Table G1
Rationale for Sediment Sampling Locations**

Location	RM	Tier	Category	Target Depth(s)			Recovery Category	Shoaling Area?	Potential Vessel Scour Area?	Rationale for Location Placement			Notes Regarding Location	Analytes for 0–10-cm Surface Sample				Analytes for 0–45-cm Subsurface Sample					Analytes for 0–60-cm Subsurface Sample				
				0–10 cm	0–45 cm	0–60 cm				Reoccupation	Bounding	Spatial Coverage Only		PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	cPAHs	Dioxins/ Furans	Other Benthic Risk Drivers	PCBs	Arsenic	Dioxins/ Furans	Other Benthic Risk Drivers	
427	5	2 (archive)	intertidal	x	x		2	no	no		x			a	a	a	a	a	a	a	a	a	-	-	-	-	-

Notes:

1. cPAH TEQ compared to ROD cPAH RAL. It is expected that there will be an explanation of significant differences issued by EPA based on the updated benzo(a)pyrene toxicity value with an updated cPAH RAL.
2. Area assumed to be within potential vessel scour areas based on surrounding areas. Updated bathymetry was not collected in 2019 at this location because of obstructions.
3. In Recovery Category 1 areas, cPAHs will be analyzed by EPA 8270 with the full SVOC list along with other benthic risk drivers. In Recovery Category 2 and 3 areas, cPAHs are the only SVOC analytes and will be analyzed by EPA 8270-SIM.

a: archive

AC: activated carbon

BEHP: bis(2-ethylhexyl) phthalate

cPAH: carcinogenic polycyclic aromatic hydrocarbon

EAA: Early Action Area

EF: exceedance factor

ENR: enhanced natural recovery

EPA: US Environmental Protection Agency

FS: feasibility study

na: not applicable, no recovery category assigned to EAA

PAH: polycyclic aromatic hydrocarbon

PCB: polychlorinated biphenyl

RAL: remedial action level

RM: river mile

SIM: selective ion monitoring

SVOC: semivolatile organic compound

**Table G2
Sediment Sampling Locations**

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
100	3	subtidal	2 (archive)	x		x		yes	-	-	1273310	197775	-122.319473	47.532473
101	3	subtidal	1	x		x		no	-	-	1273249	197679	-122.319710	47.532206
102	3	subtidal	1	x		x		yes	-	-	1273379	197719	-122.319189	47.532323
103	3	subtidal	2 (archive)	x		x		yes	-	-	1273334	197665	-122.319367	47.532172
104	3	subtidal	2 (archive)	x		x		yes	-	-	1273450	197657	-122.318895	47.532157
105	3	intertidal	1		x			no	-	-	1273347	197447	-122.319297	47.531576
106	3.1	intertidal	1	x	x			no	-	-	1273379	197419	-122.319165	47.531501
107	3.1	intertidal	2 (archive)	x	x			no	-	-	1273412	197453	-122.319035	47.531596
108	3.1	subtidal	2 (archive)	x		x		yes	-	-	1273548	197559	-122.318492	47.531893
109	3.1	subtidal	1	x		x		yes	-	-	1273586	197487	-122.318333	47.531698
110	3.1	intertidal	2 (archive)	x	x			no	-	-	1273472	197364	-122.318783	47.531355
111	3.1	subtidal	2 (archive)	x		x		no	-	-	1273585	197394	-122.318331	47.531444
112	3.1	intertidal	2 (archive)	x	x			no	-	-	1273526	197276	-122.318560	47.531117
113	3.1	subtidal	1	x		x		no	-	-	1273587	197311	-122.318315	47.531216
114	3.1	subtidal	2 (archive)	x		x		yes	-	-	1273695	197426	-122.317889	47.531535
115	3.1	subtidal	2 (archive)	x		x		yes	-	-	1273705	197341	-122.317841	47.531305
116	3.1	intertidal	2 (archive)	x	x			no	-	-	1273624	197239	-122.318160	47.531020
117	3.1	subtidal	1	x		x		yes	-	-	1273793	197347	-122.317484	47.531325
118	3.1	subtidal	2 (archive)	x		x		yes	-	-	1273791	197243	-122.317484	47.531039
119	3.1	subtidal	2 (archive)	x		x		yes	-	-	1273870	197277	-122.317168	47.531137
120	3.1	intertidal	2 (archive)	x	x			no	-	-	1273735	197120	-122.317702	47.530699
121	3.1	subtidal	1	x		x		no	-	-	1273805	197128	-122.317420	47.530725
122	3.2	subtidal	2 (archive)			x		yes	-	-	1273877	197160	-122.317131	47.530818
123	3.2	subtidal	1	x		x		yes	-	-	1273927	197209	-122.316929	47.530955
124	3.2	intertidal	2 (archive)	x	x			no	-	-	1273840	197017	-122.317270	47.530422
125	3.2	subtidal	1	x		x		yes	-	-	1273945	197086	-122.316849	47.530618
126	3.2	subtidal	2 (archive)	x		x		yes	-	-	1273999	197146	-122.316634	47.530784
127	3.2	intertidal	1	x	x			no	-	-	1273911	196942	-122.316975	47.530221
128	3.2	subtidal	2 (archive)	x		x		no	-	-	1273964	196988	-122.316764	47.530350
129	3.2	subtidal	2 (archive)	x		x		yes	-	-	1274069	196989	-122.316338	47.530357
130	3.2	subtidal	1	x		x		yes	-	-	1274133	197026	-122.316083	47.530465

**Table G2
Sediment Sampling Locations**

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
131	3.2	subtidal	2 (archive)	x		x		no	-	-	1274111	196888	-122.316160	47.530085
132	3.2	subtidal	2 (archive)	x		x		yes	-	-	1274211	196936	-122.315761	47.530222
133	3.2	intertidal	1	x	x			no	-	-	1274128	196821	-122.316087	47.529901
134	3.3	subtidal	2 (archive)	x		x		no	-	-	1274198	196753	-122.315798	47.529719
135	3.3	subtidal	1	x		x		yes	-	-	1274299	196841	-122.315397	47.529965
136	3.3	subtidal	2 (archive)			x		no	-	-	1274271	196754	-122.315503	47.529724
137	3.3	intertidal	2 (archive)	x	x			no	-	-	1274225	196679	-122.315684	47.529516
138	3.3	subtidal	2 (archive)	x		x		yes	-	-	1274371	196778	-122.315101	47.529796
139	3.3	intertidal	1	x	x			no	-	-	1274280	196614	-122.315456	47.529342
140	3.3	subtidal	1	x		x		no	-	-	1274332	196649	-122.315248	47.529441
141	3.3	subtidal	2 (archive)	x		x		no	-	-	1274380	196679	-122.315056	47.529525
142	3.3	subtidal	1	x		x		yes	-	-	1274451	196708	-122.314771	47.529610
143	3.3	intertidal	2 (archive)	x	x			no	-	-	1274343	196540	-122.315195	47.529141
144	3.3	subtidal	1	x		x		no	-	-	1274453	196591	-122.314753	47.529288
145	3.3	intertidal	2 (archive)	x	x			no	-	-	1274416	196551	-122.314900	47.529175
146	3.3	intertidal	1	x	x			no	-	-	1274398	196493	-122.314971	47.529016
147	3.3	intertidal	2 (archive)	x	x			no	-	-	1274469	196456	-122.314678	47.528919
148	3.3	subtidal	1	x			x	yes	82	3	1274584	196519	-122.314220	47.529096
149	3.3	subtidal	2 (archive)	x		x		yes	-	-	1274650	196597	-122.313957	47.529314
150	3.4	subtidal	1	x		x		yes	-	-	1274712	196539	-122.313701	47.529158
151	3.3	intertidal	1	x	x			no	-	-	1274557	196390	-122.314318	47.528743
152	3.4	intertidal	2 (archive)	x	x			no	-	-	1274606	196331	-122.314116	47.528584
153	3.4	subtidal	2 (archive)	x			x	yes	122	4	1274711	196408	-122.313695	47.528800
154	3.4	intertidal	1	x		x		no	-	-	1274727	196260	-122.313621	47.528396
155	3.4	subtidal	1	x			x	yes	101	4	1274815	196328	-122.313267	47.528585
156	3.4	subtidal	1	x		x		yes	-	-	1274905	196312	-122.312904	47.528547
157	3.4	subtidal	2 (archive)	x			x	yes	27	2	1274967	196234	-122.312647	47.528337
158	3.4	intertidal	1	x		x		no	-	-	1274874	196129	-122.313013	47.528045
159	3.4	intertidal	1	x		x		no	-	-	1274860	196054	-122.313063	47.527838
160	3.4	subtidal	1	x			x	yes	186	4	1275005	196142	-122.312483	47.528087
161	3.5	intertidal	1			x		no	-	-	1274943	196000	-122.312725	47.527694

**Table G2
Sediment Sampling Locations**

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
162	3.5	subtidal	1	x		x		yes	-	-	1275115	196143	-122.312038	47.528095
163	3.5	subtidal	2 (archive)	x			x	yes	165	4	1275106	196060	-122.312070	47.527866
164	3.5	intertidal	2 (archive)	x				no	-	-	1275007	195908	-122.312458	47.527446
165	3.5	intertidal	2 (archive)	x				no	-	-	1275084	195939	-122.312151	47.527534
166	3.5	subtidal	1	x			x	yes	165	4	1275177	195999	-122.311779	47.527704
167	3.5	intertidal	1	x		x		no	-	-	1275051	195863	-122.312275	47.527323
168	3.5	intertidal	1	x		x		no	-	-	1275130	195889	-122.311959	47.527398
169	3.5	intertidal	1	x		x		no	-	-	1275185	195857	-122.311736	47.527315
200	3.5	intertidal	2 (archive)	x	x			no	-	-	1275240	195866	-122.311515	47.527343
201	3.5	subtidal	2 (archive)	x			x	yes	165	4	1275326	195858	-122.311164	47.527325
202	3.5	subtidal	1	x		x		yes	-	-	1275392	195928	-122.310903	47.527519
203	3.6	subtidal	1	x		x		yes	-	-	1275486	195832	-122.310515	47.527262
204	3.6	subtidal	1	x			x	yes	122	4	1275453	195766	-122.310642	47.527078
205	3.6	subtidal	2 (archive)	x			x	yes	37	3	1275563	195693	-122.310191	47.526885
206	3.6	subtidal	2 (archive)	x		x		yes	-	-	1275695	195649	-122.309656	47.526772
207	3.6	subtidal	2 (archive)	x			x	yes	30	3	1275649	195589	-122.309835	47.526605
208	3.6	subtidal	1				x	yes	12	2	1275776	195554	-122.309319	47.526516
209	3.6	subtidal	2 (archive)	x		x		yes	-	-	1275791	195501	-122.309254	47.526372
210	3.6	subtidal	1	x			x	yes	30	3	1275710	195467	-122.309579	47.526274
211	3.7	subtidal	1			x		yes	-	-	1275826	195385	-122.309104	47.526054
212	3.7	subtidal	1	x			x	yes	37	3	1275766	195326	-122.309341	47.525889
213	3.7	subtidal	2 (archive)	x			x	yes	21	2	1275860	195222	-122.308952	47.525609
214	3.7	subtidal	1	x		x		no	-	-	1275727	195178	-122.309488	47.525482
215	3.7	intertidal	1	x	x			no	-	-	1275689	195053	-122.309631	47.525138
216	3.7	subtidal	2 (archive)	x			x	yes	110	4	1275780	195087	-122.309268	47.525236
217	3.7	subtidal	1	x			x	yes	15	2	1275902	195100	-122.308766	47.525277
218	3.7	intertidal	2 (archive)		x			no	-	-	1275730	194977	-122.309461	47.524931
219	3.7	subtidal	1	x			x	yes	110	4	1275811	194972	-122.309133	47.524922
220	3.7	subtidal	1	x			x	yes	40	3	1275945	194924	-122.308586	47.524799
221	3.8	intertidal	2 (archive)	x	x			no	-	-	1275766	194755	-122.309297	47.524326
222	3.8	subtidal	1	x			x	yes	82	3	1275870	194776	-122.308877	47.524387

**Table G2
Sediment Sampling Locations**

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
223	3.8	subtidal	1	x			x	yes	40	3	1275975	194785	-122.308454	47.524419
224	3.8	intertidal	1	x	x			no	-	-	1275822	194662	-122.309064	47.524073
225	3.8	subtidal	2 (archive)	x			x	yes	82	3	1275903	194632	-122.308733	47.523996
226	3.8	subtidal	1	x				yes	-	-	1276014	194687	-122.308289	47.524151
227	3.8	intertidal	2 (archive)	x	x			no	-	-	1276107	194659	-122.307910	47.524080
228	3.8	intertidal	1	x	x			no	-	-	1276145	194673	-122.307758	47.524121
229	3.8	intertidal	2 (archive)	x	x			no	-	-	1276160	194630	-122.307692	47.524004
230	3.8	subtidal	1	x			x	yes	55	3	1276023	194576	-122.308245	47.523846
231	3.8	subtidal	2 (archive)				x	yes	76	3	1275934	194525	-122.308601	47.523702
232	3.8	intertidal	1	x	x			no	-	-	1275845	194515	-122.308958	47.523670
233	3.8	intertidal	2 (archive)	x	x			no	-	-	1275848	194398	-122.308937	47.523349
234	3.8	subtidal	2 (archive)	x			x	yes	82	3	1275953	194424	-122.308515	47.523428
235	3.8	subtidal	1	x			x	yes	64	3	1276051	194459	-122.308123	47.523527
236	3.8	intertidal	1	x	x			no	-	-	1276153	194504	-122.307711	47.523657
237	3.9	subtidal	2 (archive)	x			x	yes	104	4	1275965	194333	-122.308459	47.523179
238	3.9	subtidal	1	x			x	yes	70	3	1276080	194346	-122.307997	47.523219
239	3.9	intertidal	2 (archive)	x	x			no	-	-	1275860	194228	-122.308876	47.522886
240	3.9	intertidal	1	x	x			no	-	-	1275879	194153	-122.308793	47.522681
241	3.9	subtidal	2 (archive)	x			x	yes	67	3	1276019	194184	-122.308228	47.522773
242	3.9	subtidal	2 (archive)	x			x	yes	79	3	1276133	194201	-122.307769	47.522825
243	3.9	intertidal	1	x	x			no	-	-	1276201	194243	-122.307497	47.522945
244	3.9	intertidal	1	x	x			no	-	-	1276216	194193	-122.307433	47.522807
245	3.9	subtidal	1	x			x	yes	73	3	1276136	194138	-122.307753	47.522653
246	3.9	subtidal	2 (archive)	x			x	yes	85	3	1276032	194073	-122.308168	47.522469
247	3.9	intertidal	1	x	x			no	-	-	1275950	194058	-122.308500	47.522424
248	3.9	intertidal	1	x	x			no	-	-	1275909	193966	-122.308659	47.522170
249	3.9	subtidal	2 (archive)	x			x	yes	58	3	1276094	194010	-122.307915	47.522300
250	3.9	subtidal	1	x			x	yes	85	3	1276173	193997	-122.307591	47.522268
251	3.9	subtidal	1	x		x		no	-	-	1276031	193878	-122.308159	47.521936
252	3.9	intertidal	2 (archive)	x	x			no	-	-	1275947	193849	-122.308493	47.521850
253	4	intertidal	1	x	x			no	-	-	1275933	193729	-122.308541	47.521522

**Table G2
Sediment Sampling Locations**

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
254	4	subtidal	2 (archive)	x			x	yes	61	3	1276130	193835	-122.307753	47.521822
255	4	subtidal	1	x			x	yes	98	4	1276212	193861	-122.307424	47.521899
256	3.9	intertidal	2 (archive)	x	x			no	-	-	1276286	193911	-122.307130	47.522039
257	3.9	intertidal	1	x	x			no	-	-	1276327	193924	-122.306963	47.522076
258	4	intertidal	1	x	x			no	-	-	1276353	193856	-122.306851	47.521890
259	4	intertidal	2 (archive)	x	x			no	-	-	1276316	193843	-122.307001	47.521855
260	4	intertidal	2 (archive)	x	x			no	-	-	1276330	193778	-122.306939	47.521675
261	4	subtidal	1	x			x	yes	82	3	1276216	193734	-122.307396	47.521550
262	4	subtidal	2 (archive)	x		x		no	-	-	1276097	193686	-122.307876	47.521412
263	4	intertidal	2 (archive)	x	x			no	-	-	1275991	193567	-122.308294	47.521081
264	4	subtidal	1	x		x		no	-	-	1276076	193588	-122.307951	47.521142
265	4	subtidal	2 (archive)	x			x	yes	88	3	1276244	193636	-122.307275	47.521284
266	4	intertidal	1	x	x			no	-	-	1276358	193714	-122.306822	47.521502
267	4	intertidal	2 (archive)	x	x			no	-	-	1276363	193627	-122.306795	47.521265
268	4	intertidal	1	x	x			no	-	-	1276428	193599	-122.306529	47.521191
269	4	subtidal	1	x			x	yes	98	4	1276271	193487	-122.307156	47.520876
270	4	subtidal	2 (archive)	x			x	yes	76	3	1276226	193416	-122.307332	47.520677
271	4	subtidal	2 (archive)	x		x		no	-	-	1276116	193416	-122.307779	47.520673
272	4	intertidal	1	x	x			no	-	-	1276023	193394	-122.308151	47.520608
273	4	subtidal	2 (archive)	x		x		no	-	-	1276102	193341	-122.307826	47.520465
300	4	intertidal	2 (archive)	x	x			no	-	-	1276471	193521	-122.306348	47.520980
301	4	intertidal	1	x	x			no	-	-	1276626	193525	-122.305722	47.520998
302	4	intertidal	1	x	x			no	-	-	1276644	193476	-122.305646	47.520865
303	4	intertidal	2 (archive)	x	x			no	-	-	1276579	193424	-122.305904	47.520719
304	4	intertidal	1	x	x			no	-	-	1276499	193435	-122.306229	47.520745
305	4	intertidal	2 (archive)	x	x			no	-	-	1276417	193388	-122.306556	47.520611
306	4.1	intertidal	1	x	x			no	-	-	1276638	193346	-122.305660	47.520508
307	4.1	intertidal	2 (archive)	x	x			no	-	-	1276527	193297	-122.306104	47.520367
308	4.1	intertidal	1	x	x			no	-	-	1276603	193291	-122.305798	47.520356
309	4.1	intertidal	1	x	x			no	-	-	1276656	193250	-122.305580	47.520247
310	4.1	intertidal	1	x	x			no	-	-	1276488	193172	-122.306254	47.520023

**Table G2
Sediment Sampling Locations**

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
311	4.1	intertidal	2 (archive)	x	x			no	-	-	1276589	193161	-122.305842	47.520000
312	4.1	intertidal	1	x	x			no	-	-	1276691	193156	-122.305431	47.519990
313	4.1	intertidal	1	x	x			no	-	-	1276611	193086	-122.305751	47.519793
314	4.1	subtidal	2 (archive)	x		x		no	-	-	1276458	193015	-122.306361	47.519593
315	4.1	intertidal	2 (archive)	x	x			no	-	-	1276549	193030	-122.305998	47.519638
316	4.1	intertidal	1	x	x			no	-	-	1276702	193064	-122.305381	47.519739
317	4.1	intertidal	2 (archive)	x	x			no	-	-	1276666	192983	-122.305517	47.519516
318	4.1	subtidal	1	x		x		no	-	-	1276521	192947	-122.306105	47.519407
319	4.1	intertidal	1	x	x			no	-	-	1276598	192915	-122.305787	47.519323
320	4.1	intertidal	1	x	x			no	-	-	1276761	192921	-122.305129	47.519350
321	4.2	intertidal	2 (archive)	x	x			no	-	-	1276670	192854	-122.305494	47.519161
322	4.2	subtidal	1	x		x		no	-	-	1276532	192780	-122.306046	47.518951
323	4.2	intertidal	1	x	x			no	-	-	1276796	192834	-122.304981	47.519113
324	4.1	subtidal	1	x		x		no	-	-	1276015	193166	-122.308169	47.519982
325	4.1	intertidal	2 (archive)	x		x		no	-	-	1276052	193059	-122.308009	47.519691
326	4.1	intertidal	1	x		x		no	-	-	1276185	193028	-122.307468	47.519613
327	4.1	intertidal	1	x		x		no	-	-	1276086	192859	-122.307854	47.519143
328	4.1	subtidal	2 (archive)	x		x		no	-	-	1276017	192814	-122.308132	47.519019
329	4.1	intertidal	2 (archive)	x		x		no	-	-	1276188	192803	-122.307438	47.518996
330	4.2	intertidal	1		x			no	-	-	1276058	192701	-122.307958	47.518710
331	4.2	intertidal	1	x	x			no	-	-	1276162	192694	-122.307537	47.518697
332	4.2	intertidal	1	x	x			no	-	-	1276246	192701	-122.307196	47.518720
333	4.2	subtidal	2 (archive)	x		x		no	-	-	1276262	192565	-122.307120	47.518347
334	4.2	intertidal	1	x	x			no	-	-	1276283	192341	-122.307019	47.517735
335	4.2	subtidal	2 (archive)	x		x		no	-	-	1276596	192471	-122.305761	47.518107
336	4.2	subtidal	1	x		x		no	-	-	1276658	192584	-122.305519	47.518421
337	4.2	subtidal	2 (archive)	x		x		no	-	-	1276715	192501	-122.305284	47.518197
338	4.2	subtidal	1	x				no	-	-	1276777	192598	-122.305040	47.518465
339	4.2	subtidal	2 (archive)	x		x		no	-	-	1276784	192699	-122.305020	47.518743
340	4.2	subtidal	1	x		x		no	-	-	1276869	192749	-122.304679	47.518884
341	4.2	intertidal	1	x				no	-	-	1276916	192563	-122.304474	47.518376

Table G2
Sediment Sampling Locations

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
342	4.2	subtidal	1	x		x		no	-	-	1277032	192803	-122.304026	47.519042
343	4.2	subtidal	2 (archive)	x		x		no	-	-	1277075	192740	-122.303845	47.518870
344	4.2	intertidal	2 (archive)	x	x			no	-	-	1277219	192706	-122.303261	47.518784
345	4.2	subtidal	1	x		x		no	-	-	1277273	192764	-122.303046	47.518946
346	4.2	subtidal	1	x		x		no	-	-	1277189	192819	-122.303390	47.519093
347	4.2	subtidal	1	x				no	-	-	1277209	192892	-122.303315	47.519294
348	4.2	subtidal	1	x		x		no	-	-	1277315	192933	-122.302889	47.519412
349	4.2	subtidal	1	x		x		no	-	-	1277358	192837	-122.302707	47.519151
350	4.2	intertidal	1	x				no	-	-	1277452	192822	-122.302328	47.519115
351	4.2	subtidal	1	x		x		no	-	-	1277485	192933	-122.302201	47.519421
352	4.2	subtidal	1	x				no	-	-	1277422	192973	-122.302459	47.519527
353	4.2	subtidal	1	x		x		no	-	-	1277431	193028	-122.302427	47.519678
354	4.3	intertidal	2 (archive)		x			no	-	-	1276711	192334	-122.305288	47.517737
355	4.3	intertidal	2 (archive)	x		x		no	-	-	1276710	192213	-122.305282	47.517405
356	4.3	intertidal	1	x	x			no	-	-	1276783	192207	-122.304986	47.517394
357	4.3	intertidal	2 (archive)	x	x			no	-	-	1276829	192128	-122.304791	47.517180
358	4.3	intertidal	2 (archive)	x	x			no	-	-	1276422	192130	-122.306438	47.517164
359	4.3	intertidal	1	x	x			no	-	-	1276343	192109	-122.306758	47.517102
360	4.3	intertidal	2 (archive)	x	x			no	-	-	1276371	191985	-122.306634	47.516764
361	4.3	intertidal	2 (archive)	x	x			no	-	-	1276477	191906	-122.306198	47.516554
362	4.3	subtidal	2 (archive)			x		no	-	-	1276734	191902	-122.305158	47.516554
363	4.3	intertidal	2 (archive)	x				no	-	-	1276901	191906	-122.304484	47.516575
364	4.3	intertidal	1	x	x			no	-	-	1276931	191853	-122.304359	47.516431
365	4.4	intertidal	1	x	x			no	-	-	1276517	191754	-122.306024	47.516138
366	4.4	subtidal	2 (archive)			x		no	-	-	1276607	191549	-122.305645	47.515580
367	4.4	intertidal	2 (archive)	x	x			no	-	-	1276868	191451	-122.304583	47.515326
368	4.4	subtidal	1	x		x		no	-	-	1276610	191341	-122.305616	47.515012
369	4.5	intertidal	1	x	x			no	-	-	1276950	191330	-122.304242	47.514999
370	4.5	subtidal	2 (archive)	x		x		no	-	-	1276655	191188	-122.305423	47.514595
371	4.5	intertidal	2 (archive)	x	x			no	-	-	1276991	191127	-122.304060	47.514445
372	4.5	intertidal	1	x	x			no	-	-	1277046	190939	-122.303823	47.513932

Table G2
Sediment Sampling Locations

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
373	4.5	intertidal	2 (archive)	x	x			no	-	-	1276562	190728	-122.305765	47.513329
374	4.6	intertidal	1		x			no	-	-	1276576	190583	-122.305697	47.512932
375	4.6	intertidal	2 (archive)	x	x			no	-	-	1276679	190609	-122.305283	47.513008
376	4.6	intertidal	2 (archive)	x	x			no	-	-	1277046	190785	-122.303813	47.513511
377	4.6	intertidal	1	x	x			no	-	-	1277144	190834	-122.303418	47.513649
378	4.6	intertidal	2 (archive)	x	x			no	-	-	1277188	190742	-122.303233	47.513400
379	4.6	intertidal	1	x	x			no	-	-	1277333	190612	-122.302635	47.513050
380	4.7	subtidal	2 (archive)	x		x		no	-	-	1277354	190522	-122.302547	47.512805
381	4.7	subtidal	1			x		no	-	-	1277371	190426	-122.302469	47.512544
382	4.7	intertidal	2 (archive)	x	x			no	-	-	1276992	190050	-122.303971	47.511492
383	4.7	intertidal	1	x	x			no	-	-	1277150	189888	-122.303321	47.511057
384	4.7	intertidal	2 (archive)	x	x			no	-	-	1277231	189852	-122.302990	47.510964
385	4.7	intertidal	2 (archive)	x	x			no	-	-	1277226	190006	-122.303023	47.511384
386	4.7	intertidal	2 (archive)	x	x			no	-	-	1277405	190132	-122.302308	47.511739
387	4.8	intertidal	2 (archive)	x	x			no	-	-	1277633	190135	-122.301387	47.511760
388	4.7	intertidal	1	x	x			no	-	-	1277514	190058	-122.301860	47.511543
389	4.8	intertidal	1	x	x			no	-	-	1277627	190001	-122.301400	47.511391
390	4.7	intertidal	1	x	x			no	-	-	1277558	189941	-122.301675	47.511224
391	4.7	intertidal	2 (archive)	x	x			no	-	-	1277492	189847	-122.301936	47.510962
392	4.8	subtidal	1	x		x		no	-	-	1277675	190427	-122.301240	47.512562
393	4.8	intertidal	1	x				no	-	-	1277742	190519	-122.300975	47.512817
400	4.8	intertidal	2 (archive)	x	x			no	-	-	1278186	190432	-122.299170	47.512601
401	4.9	intertidal	1	x	x			no	-	-	1278219	190415	-122.299037	47.512557
402	4.8	subtidal	2 (archive)	x				no	-	-	1278189	190388	-122.299158	47.512483
403	4.9	subtidal	2 (archive)	x				no	-	-	1278214	190320	-122.299049	47.512298
404	4.9	subtidal	1	x				no	-	-	1278241	190354	-122.298943	47.512391
405	4.9	subtidal	2 (archive)	x				no	-	-	1278269	190318	-122.298827	47.512295
406	4.9	intertidal	1	x	x			no	-	-	1278298	190362	-122.298713	47.512416
407	4.9	intertidal	1	x				no	-	-	1278327	190299	-122.298591	47.512245
408	4.9	subtidal	2 (archive)	x				no	-	-	1278316	190262	-122.298631	47.512143
409	4.9	intertidal	1	x	x			no	-	-	1278135	190122	-122.299355	47.511750

**Table G2
Sediment Sampling Locations**

Location	RM	Category	Tier	Sample Type(s)				In FNC?	Est. Shoal Thickness (cm)	No. Subsurface Samples at Shoaling Locations	Target Coordinates			
				Surface (0–10 cm)	Intertidal Subsurface (0–45 cm)	Subtidal Subsurface (0–60 cm)	Subtidal Subsurface in Shoaling Area ¹				X	Y	Longitude	Latitude
410	4.9	intertidal	2 (archive)	x	x			no	-	-	1278372	190346	-122.298412	47.512377
411	4.9	intertidal	1	x	x			no	-	-	1278412	190348	-122.298251	47.512384
412	4.9	subtidal	2 (archive)	x				no	-	-	1278410	190303	-122.298256	47.512260
413	4.9	intertidal	1	x				no	-	-	1278388	190239	-122.298341	47.512084
414	4.9	subtidal	2 (archive)	x				no	-	-	1278438	190254	-122.298138	47.512126
415	4.9	intertidal	1	x	x			no	-	-	1278474	190295	-122.297996	47.512241
416	4.9	intertidal	1	x	x			no	-	-	1278509	190247	-122.297851	47.512112
417	4.9	intertidal	2 (archive)	x	x			no	-	-	1278533	190248	-122.297753	47.512117
418	4.9	intertidal	1	x	x			no	-	-	1278537	190221	-122.297734	47.512041
419	4.9	intertidal	1	x	x			no	-	-	1278565	190218	-122.297623	47.512034
420	4.9	subtidal	2 (archive)	x				no	-	-	1278508	190171	-122.297848	47.511903
421	4.9	intertidal	1	x	x			no	-	-	1278413	189965	-122.298219	47.511335
422	4.9	subtidal	2 (archive)	x				no	-	-	1278600	190086	-122.297471	47.511677
423	4.9	intertidal	1	x	x			no	-	-	1278622	190172	-122.297388	47.511912
424	4.9	intertidal	1	x	x			no	-	-	1278654	190105	-122.297253	47.511731
425	5	intertidal	2 (archive)	x	x			no	-	-	1278671	190051	-122.297179	47.511583
426	5	intertidal	1	x	x			no	-	-	1278712	190048	-122.297014	47.511577
427	5	intertidal	2 (archive)	x	x			no	-	-	1278725	189992	-122.296959	47.511424

Notes:
1. Depth of samples intervals varies.
FNC: federal navigation channel
RM: river mile