Lower Duwamish Waterway Group

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

QUALITY ASSURANCE PROJECT PLAN ADDENDUM 4

Enhanced Natural Recovery/Activated Carbon Pilot Study

Lower Duwamish Waterway

Year 3 Monitoring Modifications

FINAL

Prepared for:

The U.S. Environmental Protection Agency
Region 10
Seattle, Washington

The Washington State Department of Ecology
Northwest Regional Office
Bellevue, Washington

Prepared by:

Wood Environment & Infrastructure Solutions, Inc.
Ramboll
Floyd|Snider
Geosyntec Consultants

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Year 3 Monitoring Modifications

Wood Environment & Infrastructure Solutions, Inc. Project Manager	Cliff Whitmus	February 20, 2020 Date
Wood Team Quality Assurance Manager	Gretchen Heavner	2/20/2020 Date
U.S. Environmental Protection Agency Project Manager	Ellen Hale Elly Hale	2/20/2020 Date
U.S. Environmental Protection Agency Quality Assurance Manager	Donald M. Brown	2/20/2020 Date
Washington State Department of Ecology Project Manager	Tamara Cardona-Marek for Ecology	2/20/2020 Date

DISTRIBUTION LIST

This list identifies all individuals to receive a copy of the approved Quality Assurance Project Plan, either in hard copy or electronic format, as well as any subsequent revisions.

Agency Team

Elly Hale, U.S. Environmental Protection Agency Project Manager

Tamara Cardona-Marek, Washington State Department of Ecology Project Manager

Donald Brown, U.S. Environmental Protection Agency Quality Assurance Manager

Consultant Team

Cliff Whitmus, Wood Environment & Infrastructure Solutions, Wood Team Project Manager

Gretchen Heavner, Floyd|Snider, Wood Team Quality Assurance Officer

Victor Magar, Ramboll, Wood Team Monitoring Lead

Jason Conder, Geosyntec Consultants, Wood Team Passive Sampling Expert

Lower Duwamish Waterway Group:

Joe Flaherty and Lindsey Erickson, The Boeing Company

Kathy Bahnick and Joanna Florer, Port of Seattle

Jeff Stern and Debra Williston, King County

Pete Rude, Dave Schuchardt, and Allison Crowley, City of Seattle

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ABBREVIATIONS AND ACRONYMS

cm	centimeter
DQO	data quality objective
Ecology	Washington State Department of Ecology
ENR	enhanced natural recovery
ENR+AC	enhanced natural recovery amended with activated carbon
EPA	U.S. Environmental Protection Agency
LDWG	Lower Duwamish Waterway Group
ng/L	nanograms per liter
PCB	polychlorinated biphenyl
PRC	Performance Reference Compound
QAPP	quality assurance project plan
SPI	Sediment Profile Imagery
SPME	solid-phase microextraction

QUALITY ASSURANCE PROJECT PLAN ADDENDUM 4
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1.0 PROJECT DESCRIPTION AND OBJECTIVES

This Quality Assurance Project Plan (QAPP) Addendum serves as an addendum to the *Quality Assurance Project Plan, Enhanced Natural Recovery/Activated Carbon Pilot Study, Lower Duwamish Waterway* (Pilot Study QAPP, AMEC et al., 2016) and details changes to the Year 3 monitoring approach.

The Lower Duwamish Waterway Group (LDWG) proposes making some minor modifications to solid-phase microextraction (SPME) samples and related procedures for the Year 3 monitoring event based on review of the Year 2 field activities and monitoring data. This Addendum documents only these minor modifications; where not superseded by the modifications presented in this Addendum, the original procedures presented in the Enhanced Natural Recovery/Activated Carbon ENR/AC Pilot Study QAPP, Addendum 1, Addendum 2, and Addendum 3 apply to the Year 3 monitoring program.

The modifications detailed in this Addendum Year 3 consist of:

- Discontinuing the deployment of the co-located 0 to 1 centimeter (cm) SPMEs at the scour and intertidal plots (modifications apply to procedures in QAPP Sections 3.1.2 and 3.2.5.2)
- Modifications to SPME deployments and bulk sediment collection due to deposition of new sediment at the scour plot (modifications apply to procedures in QAPP Sections 3.1.1.4, 3.2.4.1, 3.2.4.3, 3.2.5.2, and 3.2.5.3)
- Potential use of archive SPMEs for composites (modifications apply to procedures in QAPP Sections 3.1.2, 3.2.5.2, and 3.2.5.3)
- Increasing the number of SPME trip blanks (modifications apply to procedures in QAPP Section 3.5.2.2)

In November 2019, LDWG submitted to the U.S. Environmental Protection Agency (EPA) and Washington State Department of Ecology (Ecology) a memorandum (Proposed Changes to the Enhanced Natural Recovery/Activated Carbon Pilot Study Year 3 Monitoring, LDWG 2019) describing these changes. Subsequent to the submission of the memorandum EPA approved the changes detailed in the memorandum and requested a QAPP addendum be submitted for review and approval by EPA and Ecology.

2.0 CHANGES AND RATIONALE

The sections below describe the changes for Year 3 and the rationale for the changes.

2.1 DISCONTINUING THE 0 TO 1 CM SPMES

In Year 2, SPMEs were deployed in both 0 to 1 cm (sediment-water interface) and 0 to 10 cm (surface sediment) layer at both intertidal and scour plots. The 0 to 1 cm SPMEs were used to determine if newly deposited material has any effect on polychlorinated biphenyl (PCB) freely dissolved concentrations (C_{free}) in the surface layer (0-10 cm) samples.

2.1.1 QAPP Revision

Based on the findings of Year 2 as presented below, the 0 to 1 cm sediment-water interface SPMEs will not be collected in Year 3.

2.1.2 Rationale

In Year 2, SPMEs were deployed in both the 0 to 1 cm and 0 to 10 cm depths at the scour and intertidal pilot study plots.[1] Year 2 data from the scour and intertidal plots indicate there is little difference in the C_{free} concentrations of PCBs in co-located 0 to 1 cm and 0 to 10 cm SPMEs within each subplot (see Figure 2-1).

The lack of differences between the 0 to 1 cm and 0 to 10 cm results is consistent with the current understanding of the two plots:

- At the intertidal plot, there was little deposition of fine-grained material. The intertidal plot data suggests that the small amount of thin depositional material observed in some areas is not affecting the results for the 0 to 1 cm or the 0 to 10 cm layer. Since both the 0 to 1 cm and 0 to 10 cm layers still appear to be comprised of the same material (ENR or ENR+AC material that may have entrained some finer materials), it is reasonable that C_{free} measurements would be similar (Figure 2-1).

- At the scour plot, the depositional layer was thicker than the depositional layer measured in the intertidal plot but was found to be transient in nature (see Section 2.2). The transient, dynamic nature of the depositional layer at the scour plot led to some SPMEs becoming dislodged from the sediment or leaving the SPME completely exposed to overlying water and consequently resulted in poor SPME recoveries or not being usable. Both the 0 to 1 cm and 0 to 10 cm SPMEs that were recovered were exposed to a mix of the depositional layer and the ENR or ENR/AC material. This may explain why the C_{free} results for Year 2 were higher than in Year 1[2] as well as explain why the results of the two SPME deployment depths in Year 2 yield no differences in results. Additionally, the transient nature of the depositional layer leads

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[1] At the subtidal plot SPMEs were deployed *ex situ* so there are no 0 to 1 cm SPMEs.

[2] There was much less depositional material observed in Year 1 at the scour plot.

to uncertainty with regard to the 0 to 1 cm measurement and how well it reflects C_{free} PCB measurements in the 0 to 1 cm layer of the scour plot. For example, at locations where the depositional material was thickest, there was poor recovery of the SPME samplers. The poor recovery was due to the transient, dynamic nature of the depositional layer, which led to some SPMEs becoming dislodged from the sediment or leaving the SPME completely exposed to overlying water. Overall, the differences in the 0 to 1 cm and 0 to 10 cm C_{free} results are difficult to discern under these circumstances, and a difference may not necessarily be expected given the poor recovery of SPMEs deployed in areas with thicker depositional material.[3]

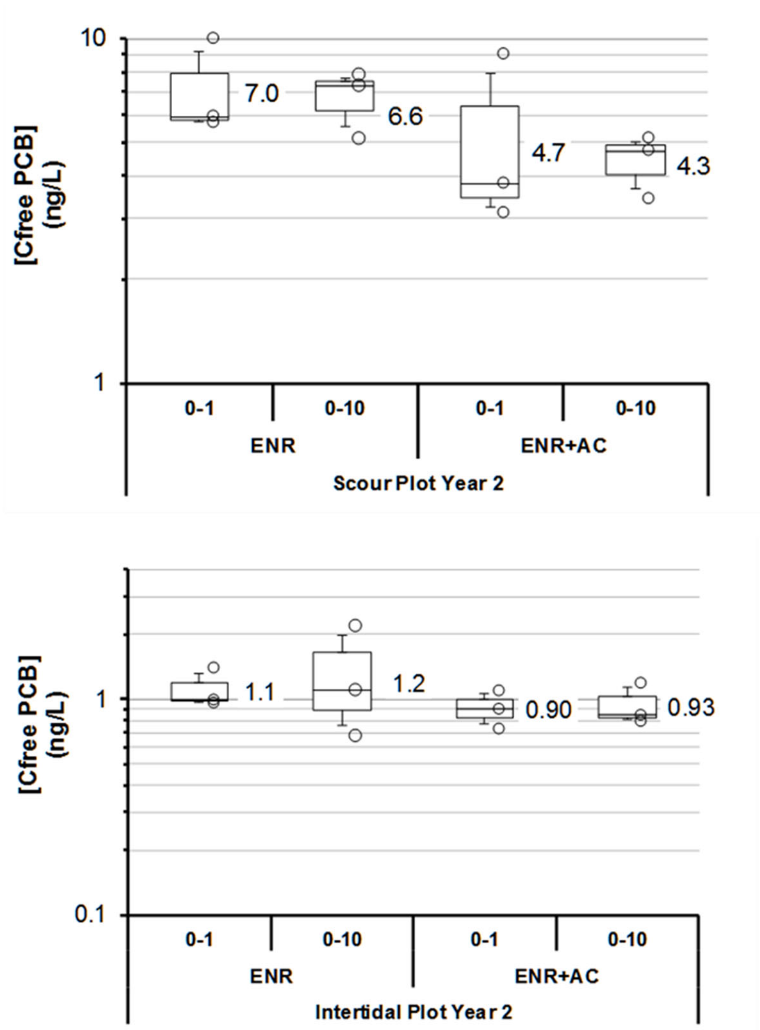

Figure 2-1 Year 2 C_{free} PCB Data for 0 to 1 cm and 0 to 10 cm SPME Deployments at the Scour and Intertidal Plots (ng/L = nanograms per liter).

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[3] Understanding the influence of the depositional layer at the scour plot is relevant to the investigation; therefore, a plan to measure the C_{free} in the depositional layer from the scour plot is provided in Section 2.2.

Overall, these findings indicate the 0 to 1 cm SPMEs at the intertidal and scour plots are not providing any additional information to the study. The 0 to 1 cm SPMEs will therefore be discontinued in Year 3. This approach is consistent with Section 3.1.1.4 of the QAPP, which states: "*LDWG may request to EPA and Ecology that the sediment-water interface PCB porewater measurement at Year 3 be omitted in the scour plot if evidence indicates that there is no sediment accumulation in Years 2 and 3 and Year 2 data indicate there is no difference in sediment-water interface SPME PCB concentrations in the ENR+AC versus ENR plots.*"

2.2 Modifications to SPME Deployments and Bulk Sediment Sample Collection due to Deposition of New Sediment at the Scour Plot

To address the issue with transient deposition at the scour plot, sample collection in the scour plot is changed.

2.2.1 QAPP Revision

Section 3.3.1 of the QAPP discusses the potential responses to significant buildup of fresh sediment at the study plots. The QAPP states:

> "*If a significant buildup of fresh sediment occurs at a plot as a distinct layer rather than mixing in with the ENR and ENR+AC layer, this material could impact the study results. Minor buildup is considered a normal condition and not a concern, although it will be noted on SPI interpretations and the surface sediment core logs if encountered….*
>
> *If a significant buildup of fresh sediment occurs across a plot, a composite of the material (one per subplot) will be collected and tested for PCB congeners, TOC, black carbon, and grain size. The physical observations of the depositional layer and the chemistry results will be shared with the EPA and Ecology and the DQOs reviewed.* ***If appropriate, modifications may be suggested, approved, and implemented in subsequent monitoring events based on this discussion****.* [emphasis added]"

To minimize and understand the potential confounding influence of transient depositional deposits on the porewater results, the following changes for the scour plot for Year 3 to be made are:

- Perform *ex situ* SPME exposures in the laboratory with the composited depositional material samples (one composite sample per subplot) to determine the C_{free} PCB concentrations in the depositional material. To enable this measurement, samples of depositional material (approximately 4-8 ounces) will be collected during scour plot SPME deployment at all SPME stations with an approximate 3 cm (or greater) thicknesses of depositional material. General collection procedures will be consistent with QAPP Section 3.2.4.1 and those used for collecting sediment in the Year 1 and Year 2 monitoring events. Specifically, divers will use hand coring methods to obtain an intact sediment core that will be brought to the sampling vessel, whereupon the depositional material will be sectioned from the top of the core and preserved for shipping and analysis. A composite sample of this material will be created for each scour subplot in the laboratory and then used for *ex situ* SPME exposure in the same manner as the *ex situ* SPMEs for the subtidal plot using the procedures described in the *Ex Situ SPME Sampling at the Subtidal Plot QAPP Addendum* (QAPP Addendum 1; AMEC et al., 2017).

- At each SPME deployment location (both ENR and ENR+AC subplots), two SPMEs will be deployed:
  - SPME1 will be deployed so that the SPME fiber is exposed to the top 10 cm of whatever substrate material is present, as in previous events (Baseline, Year 1, Year 2). SPME1 will be deployed with a longer support rod that will better anchor the SPME in the ENR or ENR+AC substrate. This will improve the chances that the SPME will not become dislodged if the surface depositional layer interval is eroded, leaving the opportunity for the portion of the SPME still in contact with the sediment to be included in the composite sample. On retrieval, any significant portion of the SPME that is exposed to overlying water will be trimmed and not added to the composite, following the approach used in the both Year 1 and 2 monitoring events.[4]
  - SPME2 will be deployed directly in the ENR or ENR+AC material to avoid exposing the SPME to the potentially-transient depositional material present on top of the ENR or ENR+AC material. The standard length of the support rod will be used (consistent with previous monitoring events). The focus of this adjustment is to reduce the potential influence of the transient depositional layer on the C_{free} result, allowing an emphasis on measurements of C_{free} within the ENR and ENR+AC materials (a primary line of evidence to address the study data quality objective (DQO) evaluating the effect of AC on availability). Prior to insertion of the SPME, the SCUBA diver will remove fine-grained material present to visually uncover the ENR or ENR+AC layer at a small area. SPME2 will be deployed in the ENR substrate so that the SPME contacts the top 10 cm interval of the ENR or ENR+AC layer that may, in some cases, be mixed with newly-deposited material. The results of the SPME2 sample will be emphasized in the study when addressing DQO-3 (Assess Changes in Bioavailability in ENR+AC Compared to ENR Alone).

Bulk sediments samples will be collected from each of the same depth intervals as the SPME1 and SPME2 deployment depths (i.e., two separate bulk samples per SPME location). The comparison

[4] In the Year 1 event, for individual SPME fibers that *were observed to be exposed to more than approximately 2.5 cm (or more) of overlying water* during the *in situ* exposures (i.e., only the lower 7.5 cm of the fiber was found to be full inserted within the sediment at the time of retrieval), the portion of the fiber exposed to the overlying water (rounded up to the nearest cm) was removed and excluded prior to compositing the remainder (lower portion) of the fiber. These procedures were planned for implementation in Year 2, although no SPME fibers were observed to be exposed to more than approximately 2.5 cm (or more) of overlying water (so there was no need for sectioning and exclusion of the fibers).

of SPME1 and SPME2 composite results for each scour subplot will provide additional information to evaluate the transient depositional layer in context of the data quality objectives.

2.2.2 Rationale

Substantial deposition of new fine-grained sediment was documented in the scour plot during Year 2 monitoring. However, based on observations noted during Sediment Profile Imagery (SPI) work, SPME deployment, and SPME retrieval, it appears that some of the sediment deposition is transient. The thickness of the deposition layer varied several centimeters within the timespan of a few weeks over much of the scour plot. Figures 2-2 and 2-3 list the thickness of the depositional layer measured during the three different sampling activities in Year 2. Each grid cell lists the depositional layer thickness (in cm) measured during:

- The SPI survey, which took place in March 2019; these measurements are indicated in the upper left of each sample cell;
- SPME deployment, which took place in May 2019; these measurements are indicated in the upper right of each sample cell; and
- SPME retrieval, which took place in June 2019; these measurements are indicated in the lower middle of each sample cell.

Grid cells with only two measurements did not have SPI measurements or the SPME was not retrieved (not recovered or found out of the sediment laying on the surface). The red circles on the figures indicate grid cells with 3 cm or more change in depositional layer thickness among these measurements.

These figures show that the differences among depositional layer thickness measurements over the 3-month period were as high as 9 cm (both gains and losses), indicating that the depositional layer is transient and variable at the scour plot. The depositional layer was observed as a distinct layer in some grid cells and partially mixed in others. This depositional layer may affect the ability to compare C_{free} between the ENR and ENR+AC subplots, or between the monitoring events at each subplot in the scour plot.

Additionally, SPMEs deployed in a location with a thick layer of depositional material can result in poor recovery of the deployed SPMEs. For example, if the depositional layer is resuspended or eroded during the SPME deployment period, this causes a significant portion of the top of the SPME to be exposed to overlying water rather than the sediment, which is the focus of the measurement. Including measurements of the overlying water in the SPME would not be useful for evaluating the project data quality objectives. In some cases, the erosion is so significant that it causes the SPME to become dislodged, leaving the SPME completely exposed to overlying water.

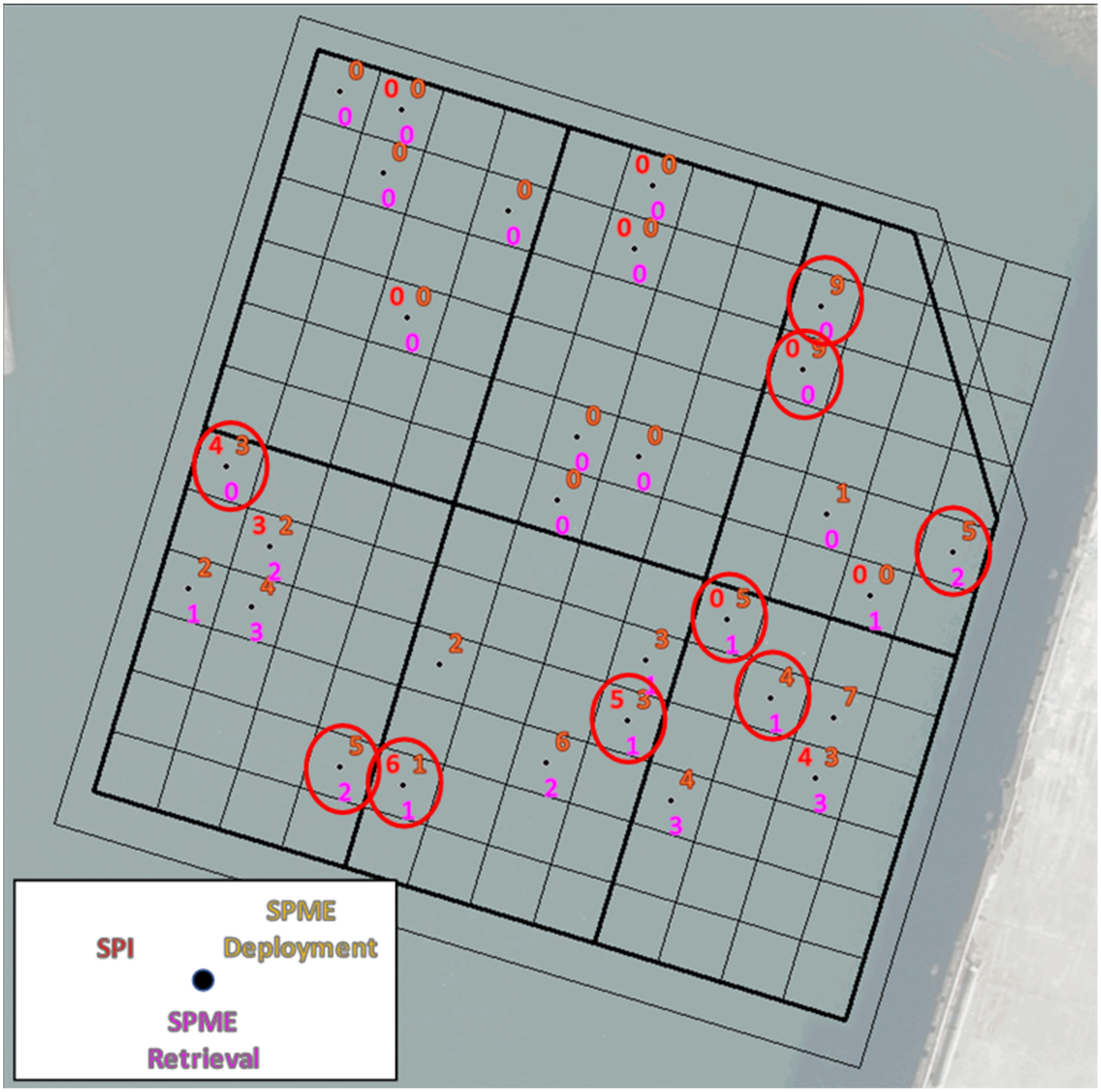

Figure 2-2 Depositional Layer Thickness (in cm) Measured in the Scour ENR+AC Subplot during the Year 2 Monitoring Event (SPI Survey, SPME Deployment, SPME Retrieval).

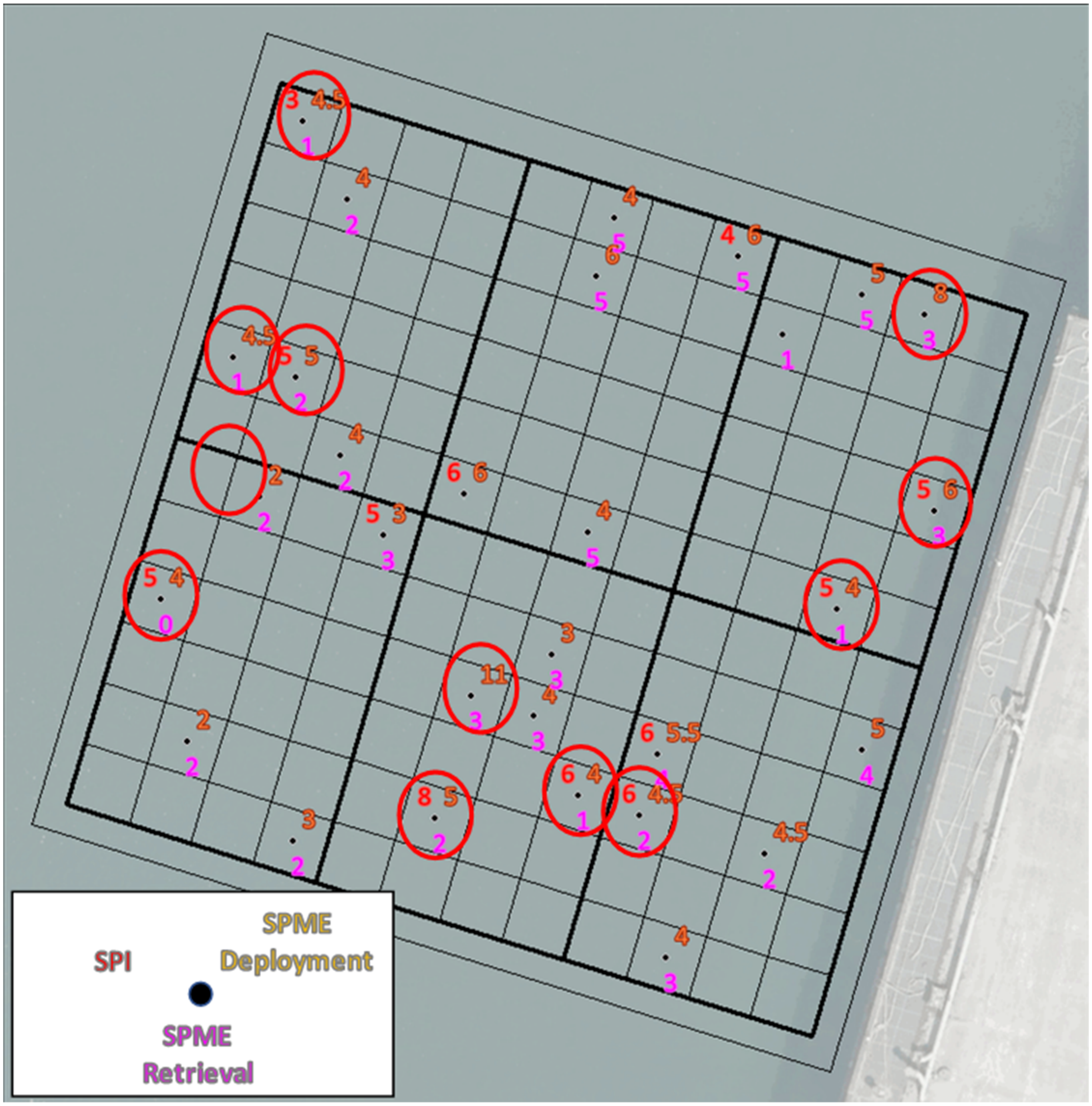

Figure 2-3 Silt Layer Thickness (in cm) Measured in the Scour ENR Subplot during the Year 2 Monitoring Event (SPI Survey, SPME Deployment, SPME Retrieval).

2.3 Potential Use of Archive SPMEs and Associated Bulk Sediment for Composites

Additional SPMEs and associated bulk sediment samples are collected and archived in both scour and intertidal plots so that additional samples (composites D and E) are available if statistical power analysis suggest they should be analyzed.

2.3.1 QAPP Revision

During Year 3, if SPMEs are lost from the A, B, or C composites, the D and E SPMEs will be used to try to maintain the six SPME locations per composite, if EPA and Ecology agree at the time sample composites are formed. Only one D or E archive sample will be utilized from each of the six grid cells within the subplot such that the grid cells will not be over-represented by the altered compositing approach. For example, if “A” SPMEs (blue cells in Figure 2-4) are not recovered from Grid Cells 1 and 2 (leaving only 4 “A” SPMEs available for the composite), the first option to supplement the “A” composite would be to use the “D” SPMEs from Grid Cell 1 and Grid Cell 2, rather than use the “D” and “E” SPMEs from Grid Cell 1. The latter approach would lead to the composite containing 2 SPMEs from Grid Cell 1, which may over-represent this spatial area in the composite.

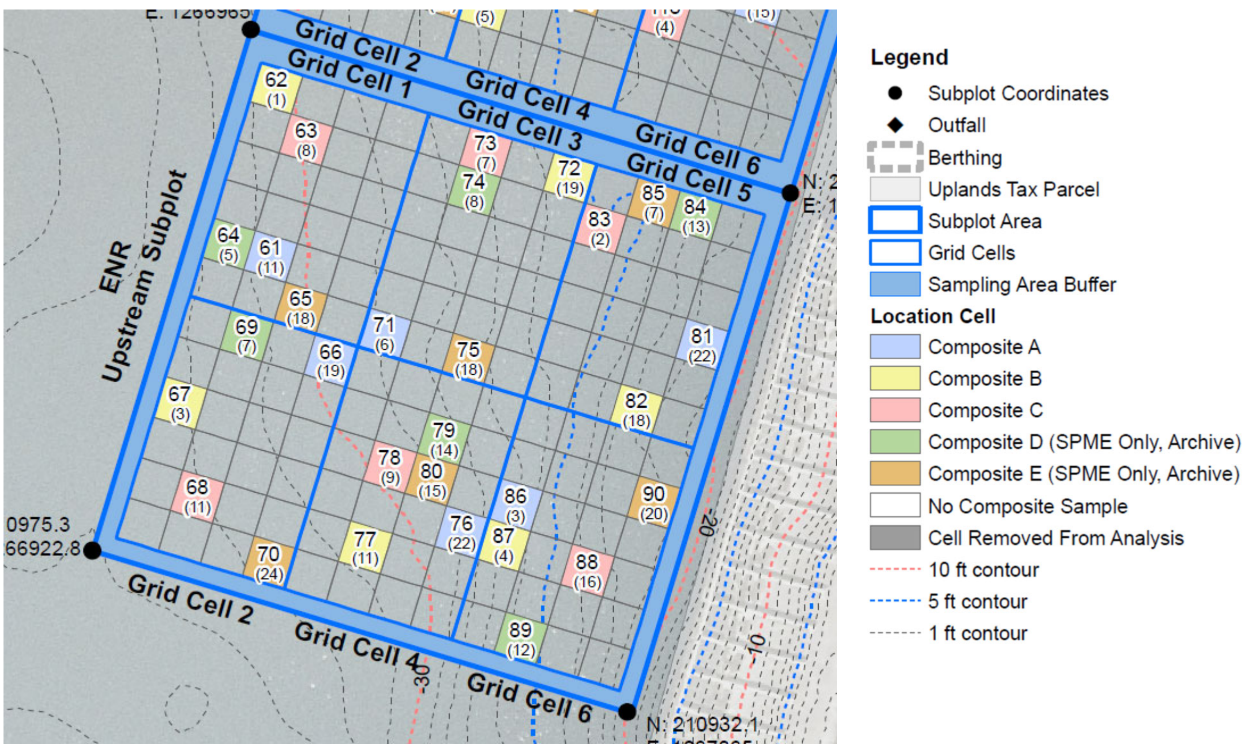

Figure 2-4 Planned SPME Stations and Compositing Approach for the Scour ENR Subplot (Year 2).

2.3.2 Rationale

During Year 2 sampling, there was a higher loss rate (compared to baseline and Year 1 events) of SPMEs at some locations in the scour subplots. This resulted in some sample composites having less than six SPME fibers per composite. Although this did not affect the quality of the data, the project team and EPA wishes to strive to attain six SPMEs per composite (per the QAPP) to the extent practicable.

The study design calls for deploying 30 SPMEs within each subplot to create five sample composites (A, B, C, D, and E) made up of six SPMEs per composite. For example, six "A" SPMEs are deployed in six different locations spanning a particular subplot (the subplot is divided into six grid cells with one SPME deployed at a random location within each grid cell). After retrieval, the SPMEs are composited together, extracted, and the single extract is analyzed for the estimation of C_{free}. Assuming all SPMEs in a subplot are recovered, each SPME sample A, B, C, D, and E are composited (e.g., all "A" SPMES are composited to create the "A" composite). After composite preparation, composites A, B, and C are submitted, whereas the D and E composites are archived pending analysis of the statistical power of the A, B, and C composites. The Baseline, Year 1, and Year 2 sampling events have had sufficient statistical power; therefore, analysis of the D and E composites has not been required.

In Year 2, recovery of SPMEs in the scour plot was low such that it became necessary to create one of the composite samples using recoverable SPMEs from both A and D locations (i.e., two SPMEs from A locations plus 2 SPMEs from D locations). To ensure spatial coverage across the subplot, the A and D SPMEs included in the composite originated from four of the six grid cells in the subplot (i.e., each SPME in the composite originated from different grid cells). If SPMEs are lost from the A, B, or C composites, the D and E SPMEs can be used to try to maintain the six SPME locations per composite.

For example, as shown in the below table, if the "A" SPME from grid cell 3 in the scour ENR+AC subplot is not recovered, the D SPME from grid cell 3 can be combined with the other five A SPMEs to create the A composite (compositing SPMEs from A1, A2, D3, A4, A5, and A6).

This approach may result in reducing the number of SPMEs that could be composited for the archived D and E samples, as indicated in the below hypothetical example table. Results should still be acceptable with fewer than six SPMEs, however, as consistent results and acceptable detection limits were found for Year 2 composite samples with fewer than six SPMEs. It should be noted that the risk of needing to analyze the D and E samples is low because the Baseline, Year 1, and Year 2 results have had sufficient statistical power for addressing the data quality objectives.

Example (Hypothetical) Year 3 SPME Recovery at the Scour ENR+AC Subplot

Grid Cell	Composites				
	A	B	C	D	E
1	☑ A1	☑ B1	Not found	☑ D1	☑ E1
2	☑ A2	☑ B2	☑ C2	☑ D2	☑ E2
3	Not found	☑ B3	Not found	☑ D3	☑ E3
4	☑ A4	☑ B4	☑ C4	☑ D4	☑ E4
5	☑ A5	☑ B5	Not found	Not found	Not found
6	☑ A6	☑ B6	Not found	Not found	☑ E6
SPMEs to Composite	↓	↓	↓	↓	↓
	A1, A2, D3, A4, A5, & A6	B1, B2, B3, B4, B5, & B6	D1, C2, E3, C4, & E6	D2 & D4	E1, E2, & E4

Additionally, if the D and E SPMEs are used to make up the A, B, and C composites, the corresponding sediment samples from those locations will be used for the sediment composite according to the same composting approach. LDWG will consult with EPA and Ecology before compositing Year 3 samples by showing tables similar to the one shown in the above hypothetical example.

2.4 Increasing the Number of SPME Trip Blanks

SPME trip blanks are analyzed to ensure that the samples do not become contaminated prior to or after deployment and to provide the initial concentrations of Performance Reference Compounds (PRCs) present in SPMEs.

2.4.1 QAPP Revision

The number of trip blanks will be increased from three to four to ensure precision and confidence in the C_{free} calculation process; increasing the number of SPME trip blanks ensure robust data for Year 3.

2.4.2 Rationale

In Year 2, one of the three trip blank samples indicated much lower-than-expected values for PRCs. PRCs in the trip blanks, along with PRCs in each SPME deployed in the field, are used to calculate the sampling rate for each field-deployed SPME. This sampling rate is used in turn to calculate C_{free} values. The issue with the Year 2 trip blanks was successfully addressed by removing the trip blank sample in question from the calculation process.

Although unlikely this may happen again in Year 3, adding an additional trip blank helps to ensure triplicate results. Thus, four SPME trip blank samples (instead of three) will be analyzed. This modification will improve precision and confidence in the C_{free} calculation process.

2.5 SUMMARY OF CHANGES

A summary of the Year 3 changes are detailed below.

At the intertidal plot:

- 0 to 1 cm sediment-water interface SPME will not be deployed; only the 0 to 10 cm SPME sample will be deployed and collected.
- Use archive SPME and sediment samples as necessary to achieve the goal of six locations per composite for the three primary samples (A, B, and C).

At the scour plot:

- 0 to 1 cm sediment-water interface SPME will not be deployed; only the 0 to 10 cm SPME sample will be deployed and collected.
- Two SPMEs will be deployed at each location as indicated below:
  - SPME1 will be deployed from 0 to 10 cm in whatever material is present. SPME1 will be deployed using a longer support rod on the SPME device.
  - SPME2 will be deployed in the top 10 cm of the ENR/ENR+AC material (i.e., below the depositional layer if present; the diver will clear depositional material before deployment if necessary). A longer support rod will not be used for this SPME device.
- Bulk sediment samples will be collected at locations corresponding with SPME1 and SPME2.
- Depositional material from each subplot will be collected at each SPME deployment location with ≥ 3 cm silt deposition to create a composite sample for bulk sediment chemical testing.
- C_{free} *ex situ* in composited depositional material samples will be measured in the lab (one composite for each subplot).
- Archive SPME and co-located sediment samples will be used as necessary to achieve the goal of six locations per composite for the three primary samples (A, B, and C).

At the Subtidal plot:

- No changes.

Trip Blanks:

- Four (instead of three) trip blank SPME composite samples will be created and analyzed.

3.0 REFERENCES

AMEC et al. (Amec Foster Wheeler; Dalton, Olmsted & Fuglevand, Inc.; Ramboll Environ; Floyd|Snider; and Geosyntec Consultants). 2016. Quality Assurance Project Plan, Enhanced Natural Recovery/Activated Carbon Pilot Study, Lower Duwamish Waterway. Lower Duwamish Waterway Group, Seattle, WA. February 22.

AMEC et al. (Amec Foster Wheeler; Dalton, Olmsted & Fuglevand, Inc.; Ramboll Environ; Floyd|Snider; and Geosyntec Consultants). 2017. Quality Assurance Project Plan Addendum 1, Enhanced Natural Recovery/Activated Carbon Pilot Study, Lower Duwamish Waterway, Ex Situ SPME Sampling at the Subtidal Plot. Lower Duwamish Waterway Group, Seattle, WA. February 15.

Lower Duwamish Waterway Group (LDWG). 2019. Proposed Changes to the Enhanced Natural Recovery/Activated Carbon Pilot Study Year 3 Monitoring. Memorandum to E. Hale (EPA), T. Cardona-Marek and Jing Liu (Ecology). November 26.