

APPENDIX A. cPAH PASSIVE SAMPLER INFORMATION

The following table is an updated version of *Table 2. Schedule for cPAH passive sampler exposures, analysis, and reporting* included in the memorandum regarding rationale for re-exposure and re-analysis of cPAH passive samplers.

Event	Initiation date	Date Complete	Duration
Prepare PE passive samplers	October 3, 2018	October 16, 2018	2 weeks
<i>Ex situ</i> exposures	October 24, 2018	November 26, 2018	4 weeks
PE passive sampler analysis	December 7, 2018	January 17, 2019	6 weeks
Data validation	January 21, 2019	February 11, 2019	3 weeks
Data evaluation (either as an addendum or included in the draft final Data Evaluation Report, depending on the schedule of the draft final Data Evaluation Report)	February 12, 2019	March 12, 2019	4 weeks

cPAH – carcinogenic polycyclic aromatic hydrocarbon

EPA – US Environmental Protection Agency

PE – polyethylene

Memorandum Regarding Rationale for
Re-Exposure and Re-Analysis of
cPAH Passive Samplers

MEMORANDUM

To: Elly Hale, US Environmental Protection Agency
From: LDWG
Subject: cPAH passive samplers
Date: October 8, 2018

As part of the clam quality assurance project plan (QAPP) (Windward 2018), carcinogenic polycyclic aromatic hydrocarbon (cPAH) concentrations in co-located intertidal sediment (0–10 cm), clam tissue, and porewater were analyzed to assess the utility of porewater data in better understanding the clam tissue-sediment relationship. A total of 16 locations were sampled for clam tissue and sediment from May 15 through 18, 2018. Of these 16 sediment sampling locations, 10 were selected to assess the freely dissolved concentrations of individual cPAHs in porewater using passive samplers exposed to sediment *ex situ*. Integral Consulting Inc. (Integral) set up the polyethylene (PE) passive sampler exposures on May 25, 2018, and took them down on June 22, 2018. The passive samplers were extracted from the sediment and sent to SGS Axys Analytical Services Ltd. (Axys) on July 3, 2018, for analysis.

When Windward Environmental LLC (Windward) received preliminary data from Axys on August 30, 2018, the data were reviewed and the results for LDW18-PWPS-A07 were identified as anomalous. Specifically, no cPAHs were detected in the passive sampler, and there was little loss of the target performance reference compounds (PRCs). Windward contacted Axys and asked the laboratory to review the records for this passive sampler. During data validation, EcoChem, Inc. (EcoChem) contacted Windward to note that the exposure blank (LDW18-PWPS-ExpBlk-PAH) had elevated concentrations of cPAHs that would result in all of the passive sampler results being qualified as non-detected because of blank contamination.

In consultation with Axys, Windward determined that the passive samplers had been swapped at some point in the analytical process, either at Analytical Resources Inc. (ARI), where Integral had conducted the exposures, or at Axys. The passive sampler that had been analyzed as LDW18-PWPS-A07 was determined to be the exposure blank, and the passive sampler that had been analyzed as LDW18-PWPS-ExpBlk-PAH was determined to be a passive sampler exposed to Lower Duwamish Waterway (LDW) sediment.

When the exposures were set up in May, the mass of each passive sampler was recorded prior to sediment exposure. The passive sampler masses were also recorded at Axys prior to extraction. In general, the masses recorded at these two steps in the process were similar; any differences were consistent with those expected when measurements are made using different scales (Table 1). However, four passive samplers had mass differences that were statistical outliers, suggesting that some passive samplers may have been swapped at some point in the process. For example, the mass of the passive sampler analyzed as LDW18-PWPS-A07 was consistent with the measured mass of the exposure blank, suggesting strongly that this passive sampler was, in fact, the exposure blank. PRC data were also consistent with this interpretation (i.e., there was very little depletion of the PRCs from the passive sampler).

Table 1. Passive sampler masses recorded by Integral compared to the masses recorded by Axys

Windward Passive Sampler ID	Axys Passive Sampler ID	Integral PE Mass (g)	Axys PE Mass (g)	Mass Difference (g)
LDW18-PWPS-A01	L29627-1	0.0987	0.0984	-0.0003
LDW18-PWPS-A02	L29627-2	0.1076	0.1073	-0.0003
LDW18-PWPS-A03	L29627-3	0.1099	0.1093	-0.0006
LDW18-PWPS-A04	L29627-4	0.1026	0.1025	-0.0001
LDW18-PWPS-A05	L29627-5	0.1093	0.1093	0.0000
LDW18-PWPS-A06	L29627-6	0.1097	0.1091	-0.0006
LDW18-PWPS-A07	L29627-7	0.1090	0.1035	-0.0055
LDW18-PWPS-A08	L29627-8	0.1054	0.1085	0.0031
LDW18-PWPS-A09	L29627-9	0.1009	0.1006	-0.0003
LDW18-PWPS-A10	L29627-10	0.1073	0.1048	-0.0025
LDW18-PWPS-A11	L29627-11	0.1042	0.1047	0.0005
LDW18-PWPS-A11 Dup	L29627-12	0.1042	0.1036	-0.0006
LDW18-PWPS-A12	L29627-13	0.1017	0.1009	-0.0008
LDW18-PWPS-A13	L29627-14	0.1043	0.1042	-0.0001
LDW18-PWPS-A17	L29627-15	0.1062	0.1049	-0.0013
LDW18-PWPS-A18	L29627-16	0.1029	0.1025	-0.0004
LDW18-PWPS-A19	L29627-17	0.0996	0.0990	-0.0006
LDW18-PWPS-ExpBlk_PAH	L29627-18	0.1040	0.1065	0.0025

Shading indicates passive samplers with mass differences that Axys identified as statistical outliers.

Axys – SGS Axys Analytical Services Ltd.

ID – identification

PE – polyethylene

Integral and Axys reviewed their respective passive sampler-handling protocols, which both required that only one PE passive sampler be transferred at a time. In addition,

both Integral and Axys pre-labelled the containers. No evidence was found to indicate when or how the passive samplers were switched. This issue only impacts the passive sampler results. The quality assurance (QA) sample tracking protocols for the tissue and sediment samples were followed and there is no evidence of sample switching for these matrices.

Because there was no way to definitively identify the passive samplers that had been affected, the Lower Duwamish Waterway Group (LDWG) and US Environmental Protection Agency (EPA) agreed that the passive sampler dataset was compromised. As a result, the *ex situ* exposures will be redone using sediment from the 10 locations that has been archived, frozen, at ARI. These sediments are the remaining sediment in the analytical jars used in the cPAH and TOC analyses. The frozen sediment will be shipped to Dr. Upal Ghosh, who will oversee the passive sampler exposures. Axys will prepare the PE passive samplers following the procedures outlined in the QAPP (Windward 2018) and then ship the passive samplers to Dr. Ghosh. At the conclusion of the exposures, the PE passive samples will be removed from the sediment slurries and shipped to Axys for cPAH analysis. The laboratories will follow their respective passive sampler-handling protocols and document all passive sampler transfers with photographs showing both jar labels prior to sample transfer for every sample at both laboratories.

The resulting cPAH porewater data will not be provided in the clam data report, which will be submitted before the data are available. Instead, the data will be provided and interpreted in an addendum to the data evaluation report, according to the schedule provided in Table 2.

Table 2. Schedule for cPAH passive sampler exposures, analysis, and reporting

Event	Initiation date	Date Complete	Duration
Prepare PE passive samplers	October 3, 2018	October 16, 2018	2 weeks
<i>Ex situ</i> exposures	October 22, 2018	November 19, 2018	4 weeks
PE passive sampler analysis	November 26, 2018	December 31, 2019	5 weeks
Data validation	January 1, 2019	January 21, 2019	3 weeks
Data evaluation report addendum to EPA	January 21, 2019	February 19, 2019	4 weeks

cPAH – carcinogenic polycyclic aromatic hydrocarbon
 EPA – US Environmental Protection Agency
 PE – polyethylene

REFERENCES

Windward. 2018. Lower Duwamish Waterway clam collection and chemical analyses - quality assurance project plan. Final. Windward Environmental LLC, Seattle, WA.

Selection of cPAH Passive Samplers for Analysis

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Subject: Selection of cPAH porewater samples
Date: Thursday, June 28, 2018 2:37:05 PM
Attachments: [sed-tissue scatterplots - total and individual cPAHs.docx](#)

Hi Elly – Attached are the follow-up plots requested for the sediment sample selection for the cPAH porewater investigation. The summary table is below. Please let us know if you have any concerns with the recommended samples. It would be good to get this settled by July 4 if possible. Thanks!

Table 1. Sediment and clam tissue TEQs, sorted by sediment TEQ (µg/kg dw) showing samples proposed for porewater analysis.

Location	Sediment cPAH TEQ (µg/kg)	Tissue cPAH TEQ (µg/kg)	TOC (%)	lipid (%dw)	cPAHs detection frequency in tissue
LDW18-SSCL-A02	10.1	4.71	0.74	0.45	4/7
LDW18-SSCL-A04	18.4	4.40	0.5	0.63	1/7
LDW18-SSCL-A12	25.9	ND	0.61	0.26	0/7
LDW18-SSCL-A06	46.6	4.44	0.53	0.56	4/7
LDW18-SSCL-A09	47.9	4.47	0.77	0.35	4/7
LDW18-SSCL-A10	56.0	4.73	0.4	0.45	4/7
LDW18-SSCL-A13	76.6	4.40	0.68	0.34	2/7
LDW18-SSCL-A19	80.8	4.44	0.84	0.26	1/7
LDW18-SSCL-A11	90.1	4.54	1.39	0.68	4/7
LDW18-SSCL-A05	107.1	4.47	1.26	0.39	4/7
LDW18-SSCL-A07	125.2	4.55	1.9	0.42	3/7
LDW18-SSCL-A08	194.2	4.54	0.57	0.47	3/7
LDW18-SSCL-A17	207.6	4.48	1.05	0.4	4/7
LDW18-SSCL-A01	875.1	6.28	0.64	0.52	5/7
LDW18-SSCL-A18	1393.1	6.37	0.77	0.42	6/7
LDW18-SSCL-A03	11571.3	52.84	1.78	0.45	7/7

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Following plots show results for clam tissue composites and co-located sediments. All plots exclude the outlier (Station A03 with Total cPAH value of 40,500 $\mu\text{g}/\text{kg}$ in sediments, and 186 $\mu\text{g}/\text{kg}$ in tissues). Only individual cPAHs with 4 or more detects in tissue samples are shown in plots.

cPAH	Detection Frequency in Tissues	Detection Frequency in Sediments
Benzo(a)anthracene	12/16	16/16
Chrysene	13/16	16/16
Benzo(b)fluoranthene	15/16	16/16
Benzo(k)fluoranthene	10/16	16/16
Benzo(a)pyrene	3/16	16/16
Indeno(1,2,3-cd)pyrene	2/16	16/16
Dibenzo(a,h)anthracene	1/16	15/16





