APPENDIX D

Year 2 and 3 Additional Studies

Year 2 and 3 Additional Studies

Enhanced Natural Recovery/Activated Carbon Pilot Study
Lower Duwamish Waterway

Table of Contents

List of Figures

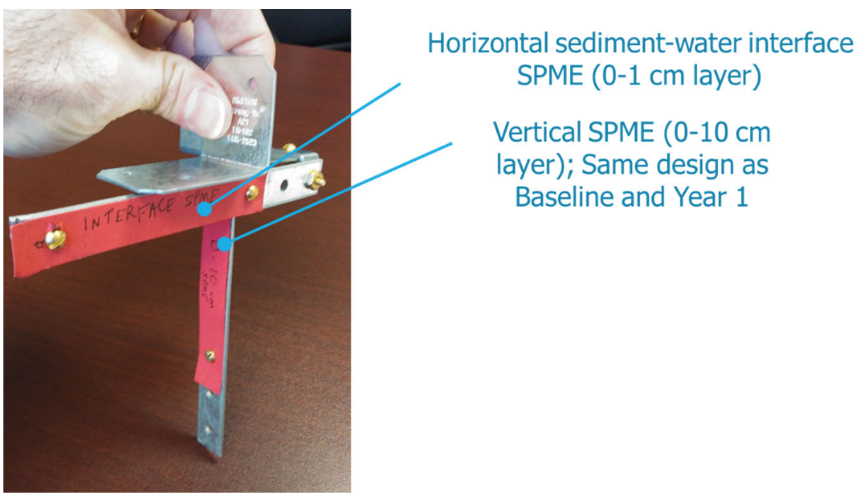
YEAR 2 AND 3 ADDITIONAL STUDIES
Enhanced Natural Recovery/Activated Carbon Pilot Study
Lower Duwamish Waterway

Year 2: 0 to 1 cm versus 0 to 10 cm SPME Samples in the Intertidal and Scour Plots

Introduction and Methods

As described in Quality Assurance Project Plan (QAPP) (Amec Foster Wheeler et al., 2016; Wood et al., 2020) and Section 2.4.4 and Appendix A of the main report, in Year 2, solid-phase micro extractions (SPMEs) were deployed in both 0 to 1 centimeter (cm; sediment-water interface) and 0 to 10 cm (surface sediment) layer at both intertidal and scour plots (**Figure D-1**).[1, 2] 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 to 10 cm) samples.

The sampler design for *in situ* deployment in Year 2 consisted of an additional horizontal SPME for deployment in sediment-water interface (0 to 1 cm layer) as shown below. A vertical SPME was also attached to the design for deployment in the top 10 cm of the sediment surface (0 to 10 cm layer). Both horizontal and vertical SPMEs had a length of 10 cm.



Thus, at each sample location, there were both 0 to 10 cm (S010) and sediment-water interface (SWWI; 0 to 1 cm) SPME fibers. The S010 and SWWI SPME fibers were used to create 0 to 10 cm (S010) and 0 to 1 cm (SWWI) composites for analysis using the same methodology described in Section 2.1 of main report.

[1] See Appendix A for SPME sampler design, deployment, retrieval, and analysis details.
[2] At the subtidal plot SPMEs were deployed *ex situ* so there are no 0 to 1 cm SPMEs.

Results

Year 2 data from the scour and intertidal plots indicated there was little difference in the total C_{free} PCBs in co-located 0 to 1 cm and 0 to10 cm SPMEs within each subplot (**Figure D-2**).

The lack of differences between the 0 to 1 cm and 0 to 10 cm results was consistent with the understanding of the two plots following Year 2 monitoring:

- At the intertidal plot, there was little deposition of fine-grained material; average 0.7-cm and 1.7-cm thick at Enhanced Natural Recovery (ENR) and ENR amended with activated carbon (ENR+AC), respectively (**Figure D-3**). 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 layers. 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 total C_{free} PCB measurements would be similar (**Figure D-2**).

- At the scour plot, a depositional layer was observed and averaged 4.7 cm and 2.6 cm at ENR and ENR+AC respectively (**Figure D-3**) but was found to be transient in nature.[3] 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 total C_{free} PCB results of the two SPME deployment depths in Year 2 yielded no differences in results. Additionally, the transient nature of the depositional layer lead to uncertainty with regard to the 0 to 1 cm measurement and how well it reflected total 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 were 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.[4]

Overall, these findings indicated that the 0 to 1 cm SPMEs at the intertidal and scour plots were not providing any additional information to the study. The 0 to 1 cm SPMEs were therefore discontinued in Year 3 per QAPP Addendum 4 (Wood et al., 2020).

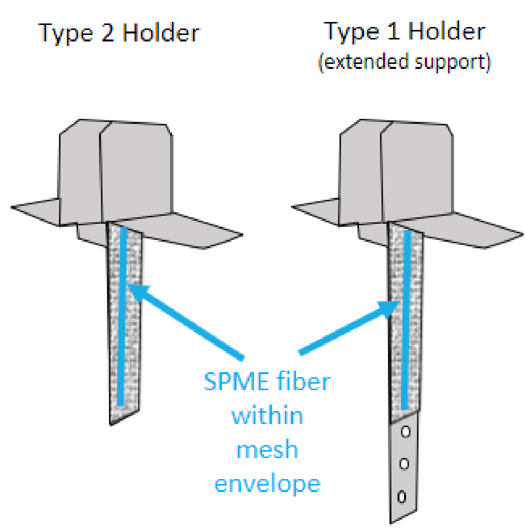
[3] Full Details in QAPP Addendum 4, Section 2.1.
[4] Understanding the influence of the depositional layer at the scour plot is relevant to the investigation; therefore, a plan to measure the C_{free} in the depositional layer from the scour plot was developed and provided in QAPP Addendum 4, Section 2.2.

Year 3: Type 1 versus Type 2 Samples in the Scour Plot

Methods

As described in Quality Assurance Project Plan (QAPP) Addendum 4 (Wood et al., 2020) and Section 2.4 of the main report, in Year 3, SPMEs deployment and sediment collection at the scour plot featured two different approaches conducted in parallel. The purpose of the parallel SPME deployments and sediment sampling was to examine the influence of silt deposits overlying the Enhanced Natural Recovery (ENR) and ENR amended with activated carbon (ENR+AC) surfaces on the porewater collected in the 0 to 10 centimeter (cm) interval. This test was initiated after observing silt deposition of up to 9 to 11 cm on the scour plot subareas during the Year 2 sampling event. It was hypothesized that the overlying silt deposits may be inflating concentrations in bulk and C_{free} measurements under the assumption that the overlying silt represents materials that may be depositing on the ENR and ENR+AC from adjacent, unremediated areas and upstream solids. Because this phenomenon would have much less effect on ENR or ENR+AC remedy areas once sediment remediation outlined in U.S. EPA's Record of Decision (U.S. EPA, 2014) is completed, the effect of the overlying silt was examined by implementing two types of SPME deployments and sediment collection approaches at each SPME/sediment sample location in the scour plot:

- **Type 1**: SPME deployments and sediment collection at Type 1 locations were handled in the same manner as in prior sampling events. That is, SPME fibers were deployed to measure total C_{free} PCB concentrations in the surface 10 cm of the sediment bed, regardless of the thickness of newly-deposited silt; similarly, sediment samples were collected from the surface 10 cm (**Figure D-4 and Figure D-5**). To enable the SPMEs to remain embedded (especially in locations in which silt was thick), the Type 1 SPME device featured a longer support rod than that of the Type 2 device (as shown below).



- **Type 2**: SPME deployments and sediment collection at Type 2 locations involved limiting the thickness of silt deposits on the ENR and ENR+AC material surface in locations where the silt was thick. For locations where silt deposits were <3 cm thick, Type 2 SPME fibers were deployed in the same manner as Type 1, to measure C_{free} in the surface 10 cm of the sediment bed, and sediment samples were collected from the surface 10 cm (**Figure D-4**). For locations where silt deposits were ≥3 cm deep, divers brushed away the silt deposits to expose the ENR or ENR+AC layer surfaces before deploying SPMEs and collecting sediment samples. In this manner, PCB concentrations were measured in the top 10 cm of the newly-exposed sediment bed (**Figure D-5**).

Following the above Type 1 and Type 2 approaches, at locations with less than 3 cm of silt a single sediment core was taken for both Type 1 and Type 2 sampling, and Type 1 and Type 2 SPMEs were deployed (**Figure D-4**). The core sampled whatever combination of silt and underlying material that was present. This resulted in one set of cores with little or no silt present (**Figure D-6, left**). The core was split into two jars, one for the Type 1 composite, one for the Type 2 composite.

At scour plot sites with 3 cm of silt or more, both Type 1 and Type 2 SPMEs were deployed and two cores were collected for bulk sediment analyses. The Type 1 SPME was deployed in the top 10 cm, without modification. At the Type 2 SPME location, silt was cleared to expose the surface of the ENR or ENR+AC layer prior to insertion of the Type 2 SPME (**Figure D-5**). Two sediment cores were collected, one representing each respective condition (i.e., uncleared and cleared). One core was taken at the Type 2 sampling location after silt clearing and contained only underlying material, and another was taken at the Type 1 sampling location containing whatever combination of silt and underlying material that was present. This resulted in two sets of cores; at Type 2 set with no silt present and a Type 1 set with thick silt layers of 3 cm or more (**Figure D-6, right**).

Scour plot sediment core composites were created to match the Type 1 and 2 and SPME samples (**Figure D-7**); composites from each subplot were created as described in Section 2.1 of the main report. Type 1 cores ranged from little to no silt to thicker silt layers respective to amount of silt present at the sampling location. Type 2 cores contained either little or no silt (site was cleared) or contained minimal silt of less than 3 cm (site not cleared).

Results

Bulk PCB sediment results suggest that the samples for which the overlying silt was removed (Type 2 samples) were lower than those for which silt was not removed (Type 1 samples), as shown in **Figure D-8**. Bulk PCB concentrations for the Year 3 Type 2 samples (cleared) were approximately 10 to 20 micrograms per kilogram (µg/kg), lower than the Year 3 Type 1 samples (not cleared) which were similar to or higher than concentrations observed the in baseline and Year 2. Bulk measurements of percent fines, TOC, and AC/BC (inset table below, values corrected for gravel fraction) indicated that values were lower in the ENR subplot after clearing (by a factor of 5 to 7 on average). However, of percent fines, TOC, and AC/BC did not differ greatly between Type 2 and Type 1 samples (within a factor of 1 to 2 on average).

Sample	Sample Type	Percent Fines (%)	Total Organic Carbon (TOC, %)	Activated Carbon / Black Carbon (AC/BC, %)
ENR-A	Type 2	1.5	0.12	0.042 U
ENR-C	Type 2	2.1	0.21	0.037 U
ENR-D	Type 2	2.1	0.16	0.040 U

Sample	Sample Type	Percent Fines (%)	Total Organic Carbon (TOC, %)	Activated Carbon / Black Carbon (AC/BC, %)
ENR Type 2 (Cleared) Average		**1.9**	**1.9**	**Not detected (U)**
ENR-A	Type 1	9.8	0.74	0.120
ENR-C	Type 1	8.5	0.77	0.095
ENR-D	Type 1	22.3	1.10	0.250
ENR Type 1 (Not Cleared) Average		**13.5**	**13.5**	**0.155**
ENR+AC-A	Type 1	3.9	1.30	1.10
ENR+AC-B	Type 1	1.6	1.50	1.20
ENR+AC-C	Type 1	3.2	1.40	2.05
ENR+AC Type 2 (Cleared) Average		**2.9**	**2.9**	**1.450**
ENR+AC-A	Type 2	6.7	1.30	0.95
ENR+AC-B	Type 2	7.5	0.89	1.40
ENR+AC-C	Type 2	5.4	1.50	1.90
ENR+AC Type 1 (Not Cleared) Average		**6.5**	**6.5**	**1.417**
ENR	Silt	70.6	2.80	0.31
ENR+AC	Silt	45.7	5.00	2.20

Porewater concentration results suggest that the effect on porewater concentrations of the overlying silt layer present in Year 3 was minimal or unclear, but that the use of the Type 2 approach (in which thick silt layers was cleared prior to insertion of the SPME into the ENR/ENR+AC layers) is the most appropriate data for evaluating PCB bioavailability in ENR and ENR+AC layers without the effects of overlying silt. At the scour ENR subplot, Type 1 and Type 2 total C_{free} PCBs were both approximately 3 nanograms per liter (ng/L), and somewhat lower than a total C_{free} PCBs measurement in a single composite sample of silt (4.6 ng/L) that was collected from multiple locations in the scour ENR subplot and performed *ex situ* (**Figure D-9**).[5] In contrast, the Type 1 total C_{free} PCBs in the ENR+AC had a higher total C_{free} PCBs of 6.5 ng/L compared to the Type 2 (3.3 ng/L) – results were borderline statistically significant (p = 0.06). Total C_{free} PCBs measurement in the single composite sample of silt collected from multiple locations in the scour ENR+AC subplot was slightly lower (5.7 ng/L) than the geomean of the Type 1 SPMEs.

When incorporating the results of the total bulk sediment PCB measurements in the top 10 cm of material collected from the Type 1 and Type 2 locations, as well as the composite silt samples (**Figure D-10**), the overlying silt does not appear to have a consistent or clear effect on the results:

- At the ENR subplot, where 78% of the Type 2 locations were cleared, total bulk sediment PCB concentrations in samples were consistently lower (geomean of 8.1 µg/kg versus 52 µg/kg, **Figure D-8**) after silt was cleared. The total PCB concentration in the composite

[5] Silt was collected by divers from the sediment bed surface by manually moving silt material into a submerged sample jar. Sediment plumes generated during sampling suggest that some losses occurred during sampling, and those losses likely biased toward the loss of fines.

sample of the silt layer was only 9.7µg/kg, which was comparable to the Type 2 (cleared) bulk results. However, as noted above, total C_{free} PCBs remained relatively unchanged because of the clearing process in the ENR subplot. Sample collection procedures reported by the divers raised concern that the bulk overlying-silt composites lost a finer (potentially more contaminated) grain size component to the water column during collection; evidence for this observation include the plume of silt material created during sampling and the low total C_{free} PCBs results for the silt material. This component is present in the bulk Type 1 (uncleared sample), but does not greatly influence total C_{free} PCBs since the Type 1 and Type 2 results are similar.

- At the ENR+AC subplot, where 22% of the Type 2 locations were cleared, total bulk sediment PCB concentrations in samples were slightly lower after silt was cleared (geomean of 14 µg/kg versus 24 µg/kg, **Figure D-8**). The PCB concentration in the composite sample of the silt layer was comparable to the silt measured at the Scour ENR Subplot (approximately 14 µg/kg). Also, as in the ENR subplot, total bulk sediment PCBs in silt (geomean of 14 µg/kg) was comparable to the Type 2 (cleared) bulk results. However, there is evidence that total C_{free} PCBs decreased slightly because of the clearing process. For two of the three ENR+AC samples, total C_{free} PCBs decreased from 7 to 8 ng/L in Type 1 to 3 to 4 ng/L in Type 2.

Overall, comparison of the Type 1, Type 2, and silt results indicates a slight or indeterminate effect of the overlying silt layer on the Year 3 results for the scour plot. The comparison of these results are likely complicated by several factors, including the potential loss of finer silt particles during sampling of the silt by the SCUBA divers, heterogeneity in the silt layers within and between the subplots, and the presence of silt from previous years (e.g., Year 2) already mixed into within the ENR/ENR+AC layers. Given that some tentative reductions in total C_{free} PCBs and concentrations of total bulk sediment PCB material may have been indicated by the scour ENR+AC data, the results support the use of the Type 2 results as the best available data for evaluating the conditions specific to the ENR/ENR+AC layers.

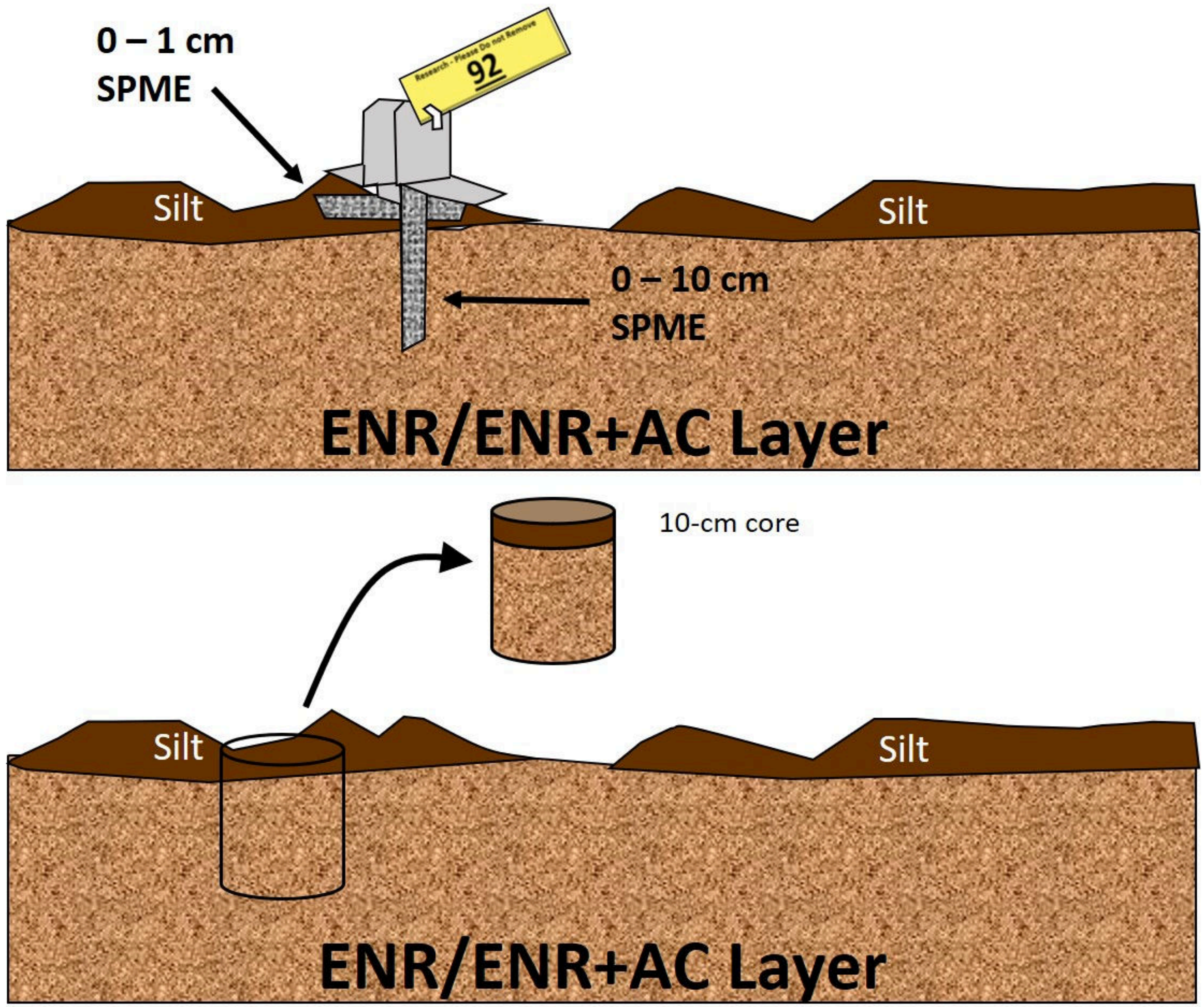
References

Amec Foster Wheeler Environment & Infrastructure, Inc., Dalton, Olmsted & Fuglevand, Inc., Ramboll Environ, Floyd|Snider, and Geosyntec Consultants (Amec Foster Wheeler et al.) 2016. Quality Assurance Project Plan, Enhanced Natural Recovery/Activated Carbon Pilot Study Lower Duwamish Waterway. Prepared on behalf of Lower Duwamish Waterway Group, Seattle, Washington. February.

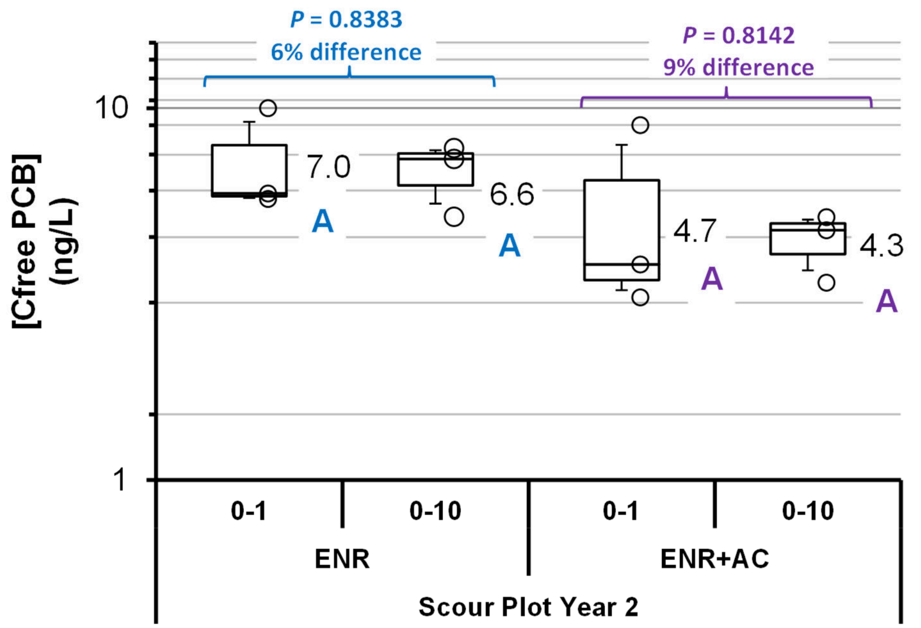
U.S. Environmental Protection Agency (U.S. EPA). 2014. Record of Decision, Lower Duwamish Waterway Superfund Site. November.

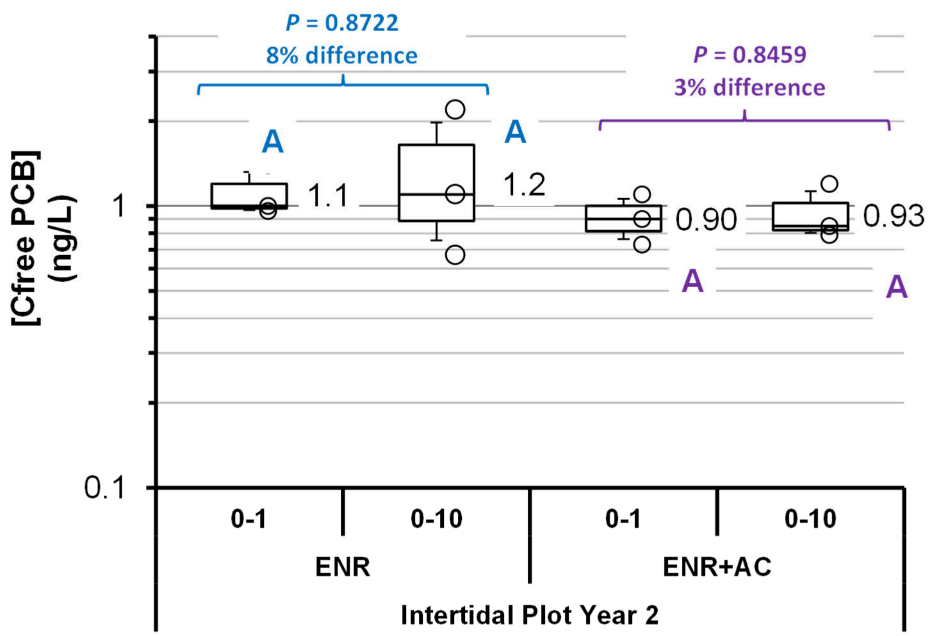
Wood Environment & Infrastructure Solutions, Inc.; Ramboll; Floyd|Snider; Geosyntec Consultants; and Dalton, Olmsted & Fuglevand, Inc. (Wood et al.). 2020. Quality Assurance Project Plan Addendum 4, Enhanced Natural Recovery/Activated Carbon Pilot

FIGURES



Lower Duwamish Waterway Group Port of Seattle / City of Seattle / King County / The Boeing Company	**ENR/AC Pilot Study** **Year 3 Monitoring Report** **Lower Duwamish Waterway**	Figure D-1 Year 2 Scour and Intertidal Plot SPME and Sediment Core Sampling

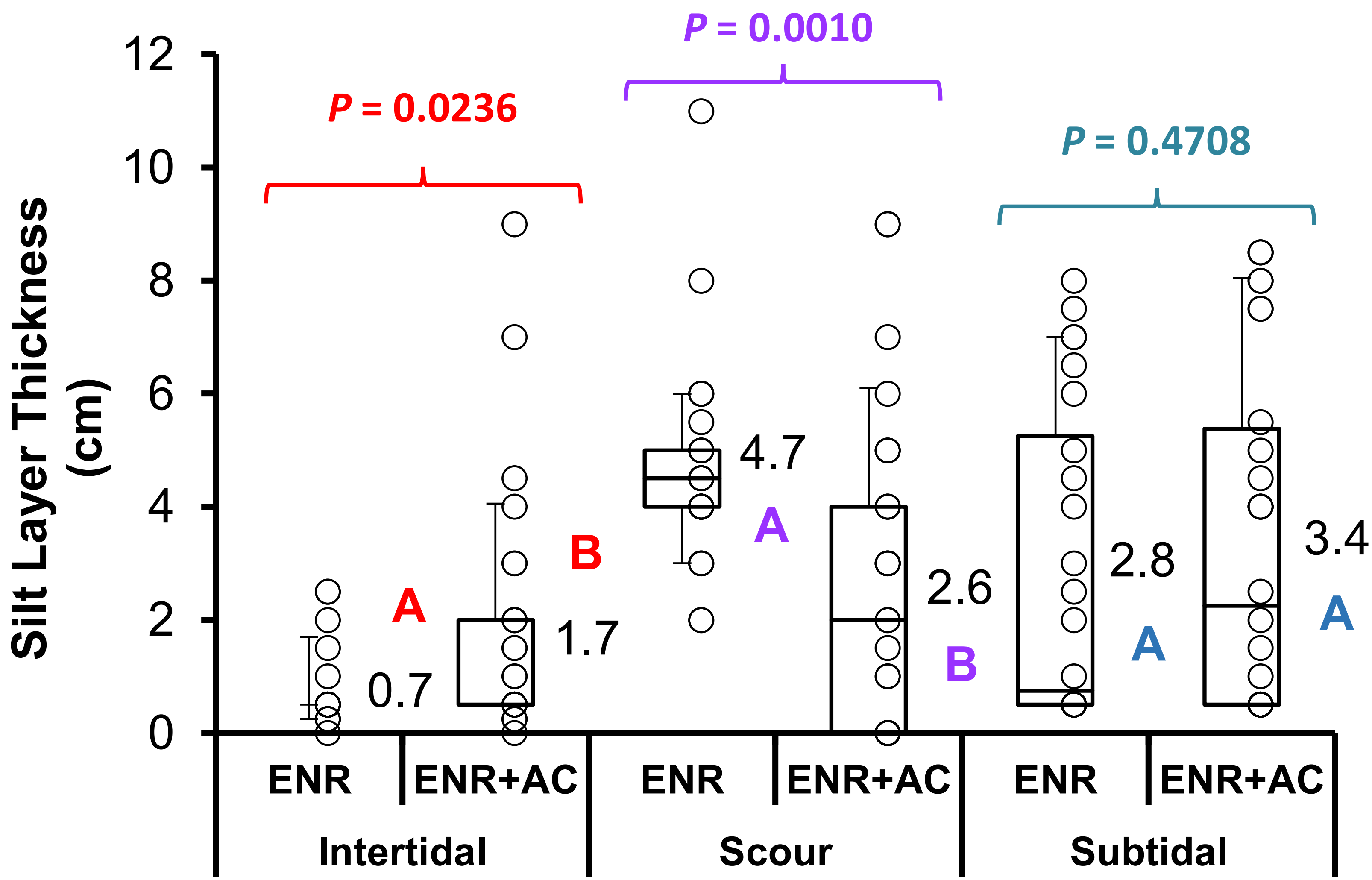




Note: Results within each subplot are compared statistically such that if results for 0-1 and 0-10 for are plot are labeled the same letter, the results are not statistically different

Abbreviations:
Cfree: freely dissolved concentration
ENR: Enhanced natural recovery
ENR+AC: Enhanced natural recovery amended with activated carbon
ng/L: nanograms per liter
PCB: polychlorinated biphenyl

Lower Duwamish Waterway Group Port of Seattle / City of Seattle / King County / The Boeing Company	**ENR/AC Pilot Study** **Year 3 Monitoring Report** **Lower Duwamish Waterway**	Figure D-2 Year 2 Total C_{free} PCB Data for 0 to 1 cm and 0 to 10 cm SPME



Notes:
Results within each plot are compared statistically (t test) such that if results for ENR and ENR+AC for a plot are labeled with the same colored letter, the results are not statistically different.

Abbreviations:
cm = centimeter(s)
ENR = Enhanced natural recovery
ENR+AC = Enhanced natural recovery amended with activated carbon

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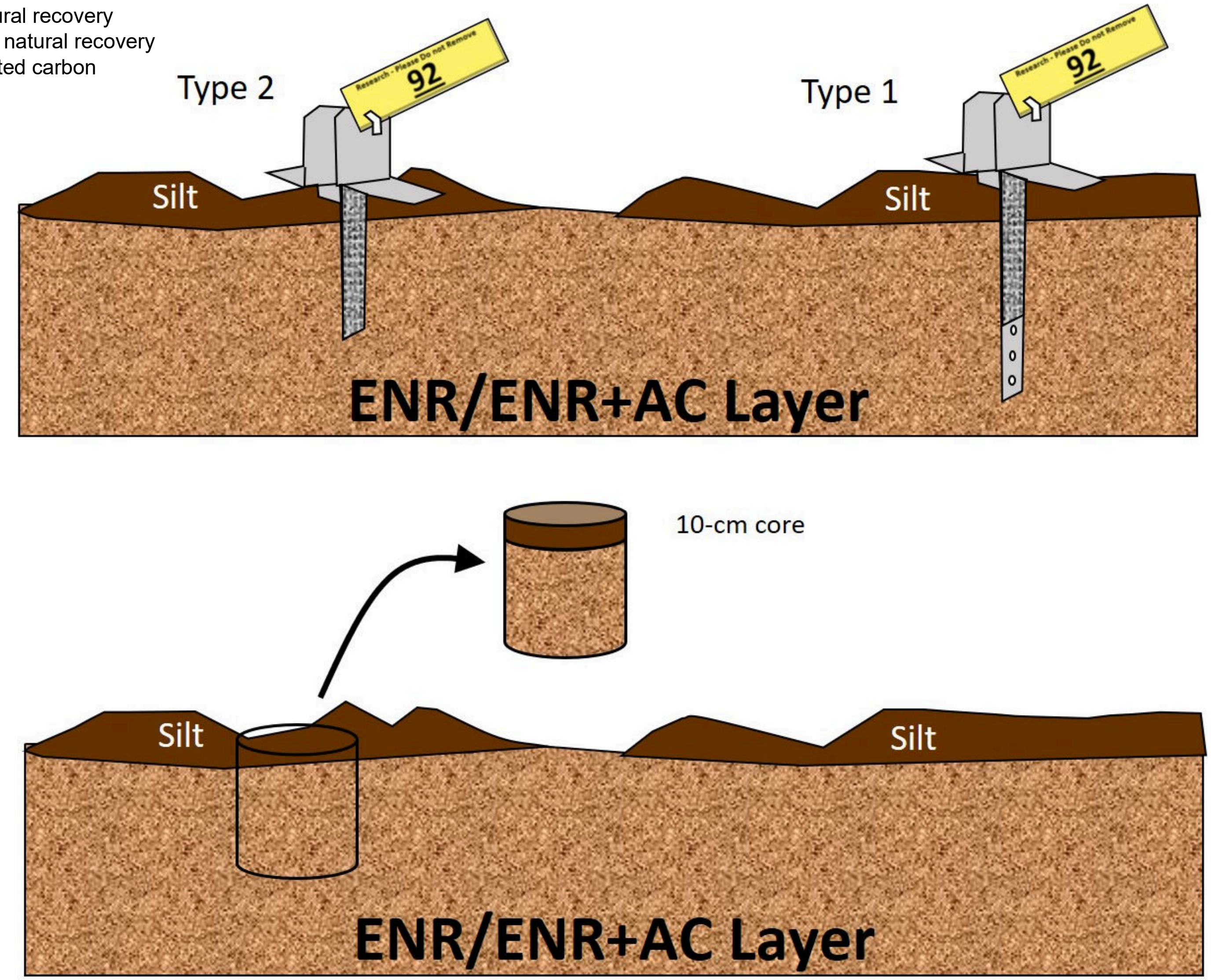
Year 3 Monitoring Report
Lower Duwamish Waterway

Figure D-3
Year 2 Silt Layer Thickness

Abbreviations:
cm = centimeter(s)
ENR = Enhanced natural recovery
ENR+AC = Enhanced natural recovery amended with activated carbon



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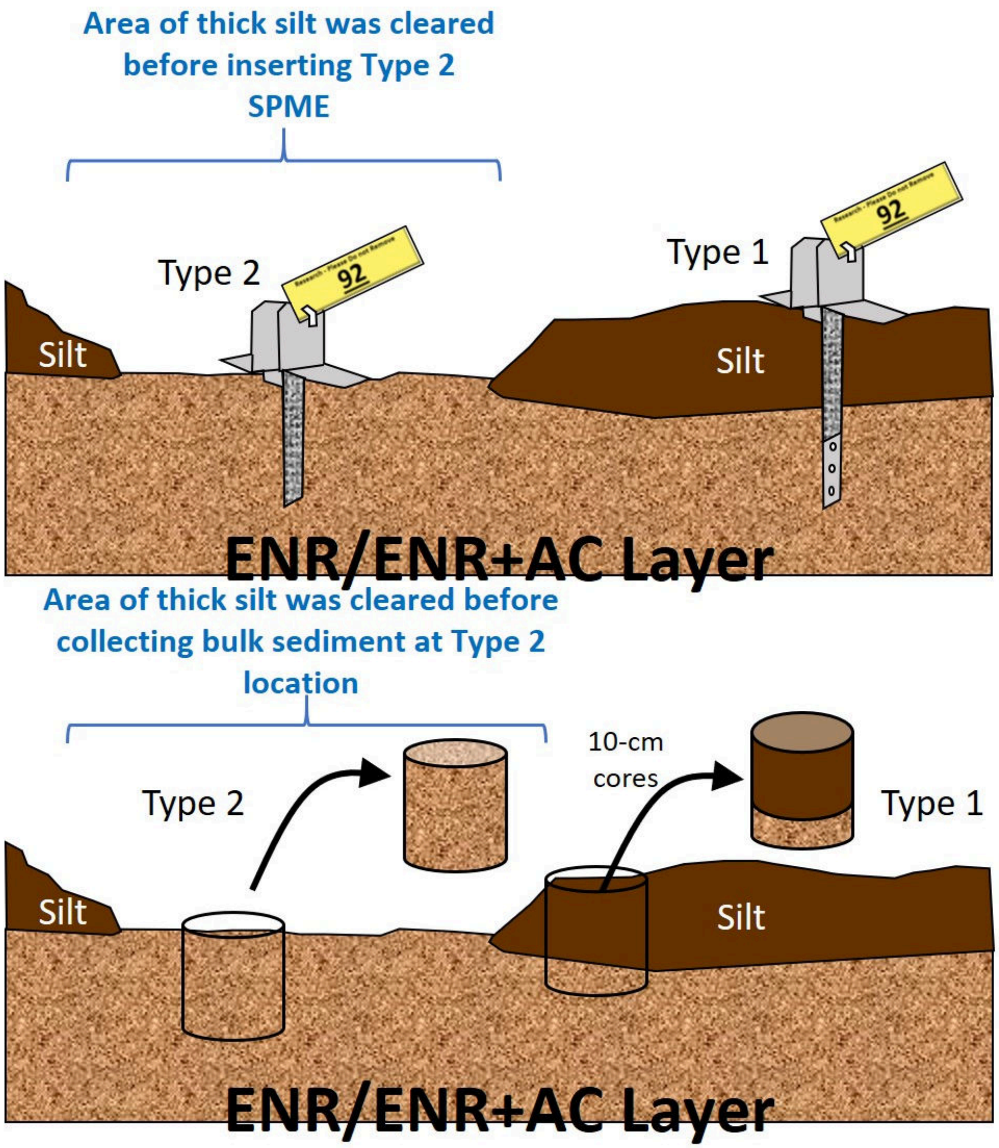
Abbreviations:
cm = centimeter(s)
ENR = Enhanced natural recovery
ENR+AC = Enhanced natural recovery amended with activated carbon
SPME = solid-phase micro extraction



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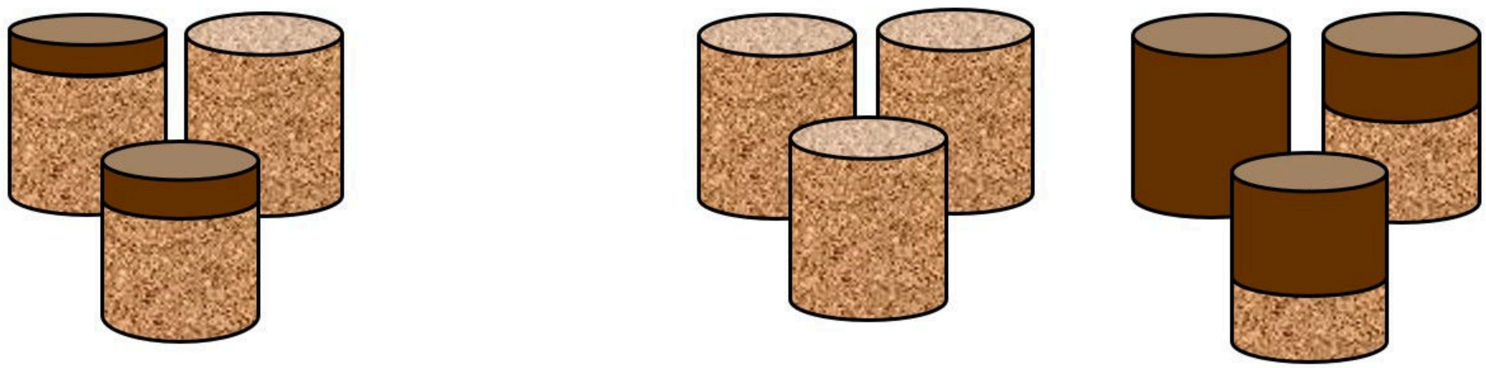
Scour Stations with < 3 cm of Silt

Cores from Type 1 and Type 2 Locations (not cleared) have no/little silt present

Scour Stations with ≥ 3 cm of Silt

Cores from Type 2 Locations (cleared) are as close to "silt free" as we can get

Cores from Type 1 Locations have thicker silt (≥ 3 cm)



One set of cores collected for Type 1 and 2 composites

Abbreviations:
- cm = centimeter(s)
- ENR = Enhanced natural recovery
- ENR+AC = Enhanced natural recovery amended with activated carbon

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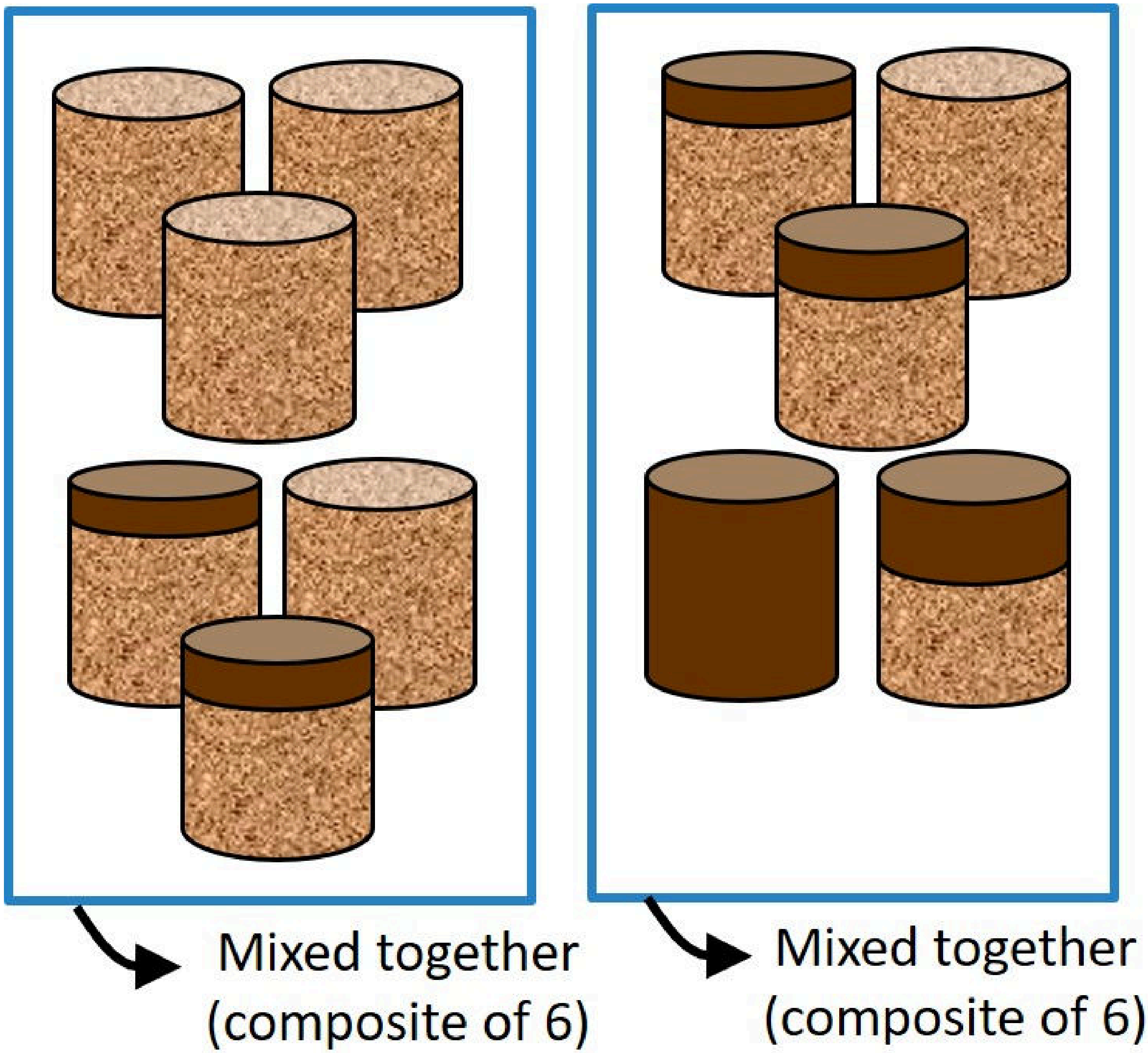

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ENR/AC Pilot Study
Year 3 Monitoring Report
Lower Duwamish Waterway

Figure D-7
Year 3 Scour Plot Sediment Core Compositing

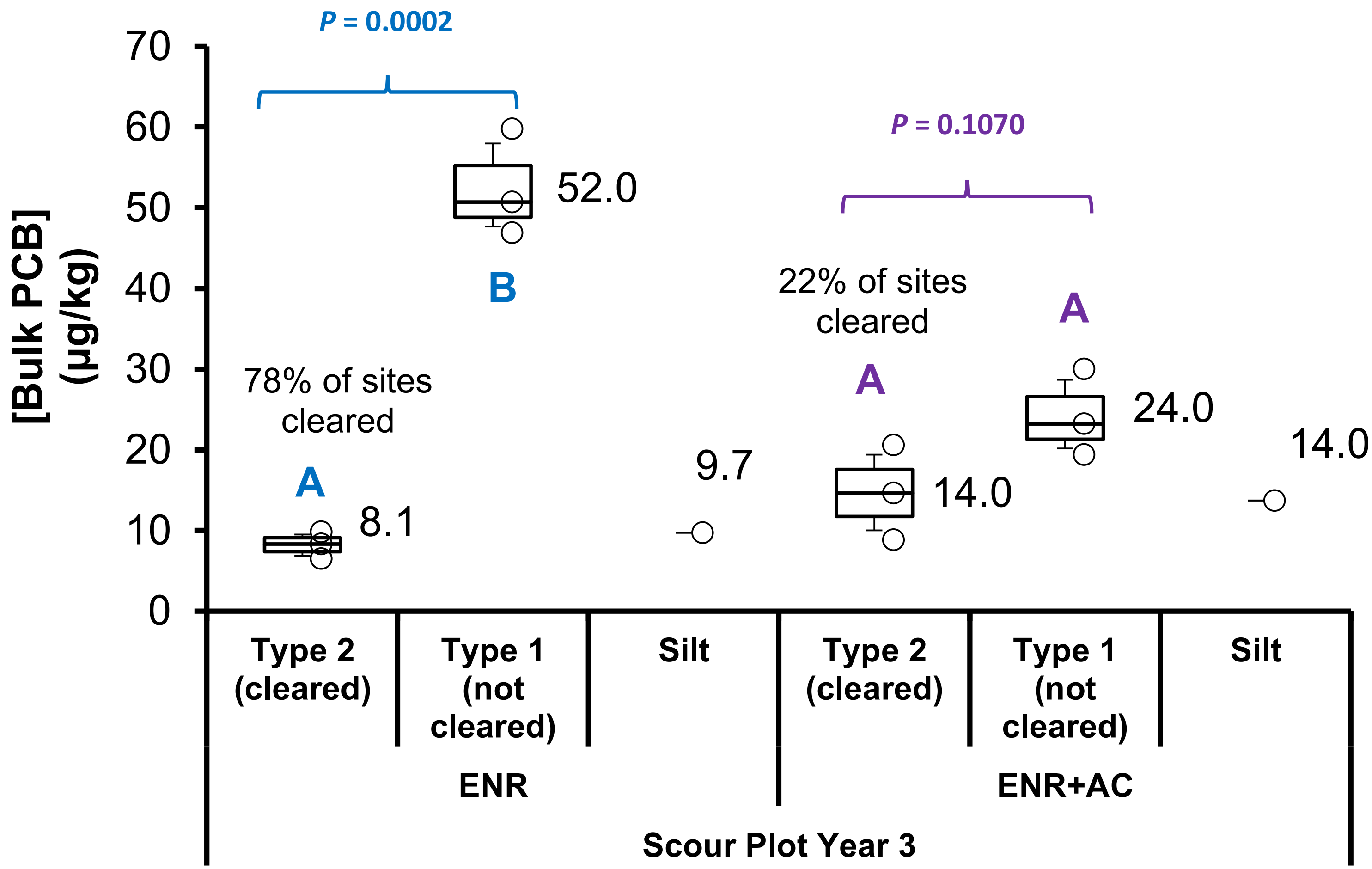
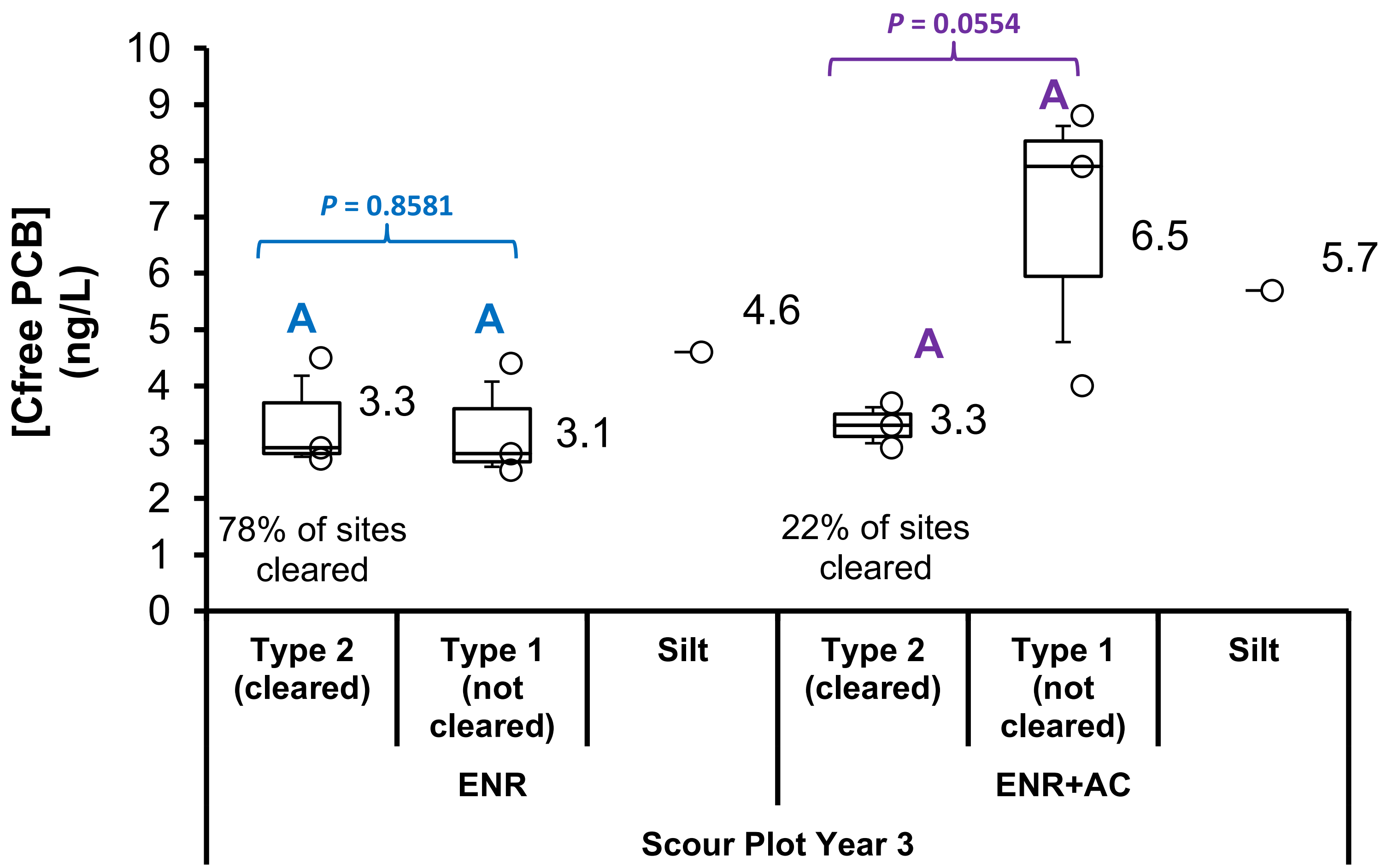


Figure D-8
Year 3 Scour Plot Bulk Sediment PCB



Notes:
Type 1 and Type 2 results within each plot are compared statistically (t test) such that if results are labeled with the same colored letter, the results are not statistically different.

Abbreviations:
C_{free} = freely dissolved concentrations
ENR = Enhanced natural recovery
ENR+AC = Enhanced natural recovery amended with activated carbon
ng/L = nanogram(s) per liter
PCB = polychlorinated biphenyl
SPME = solid-phase micro extraction

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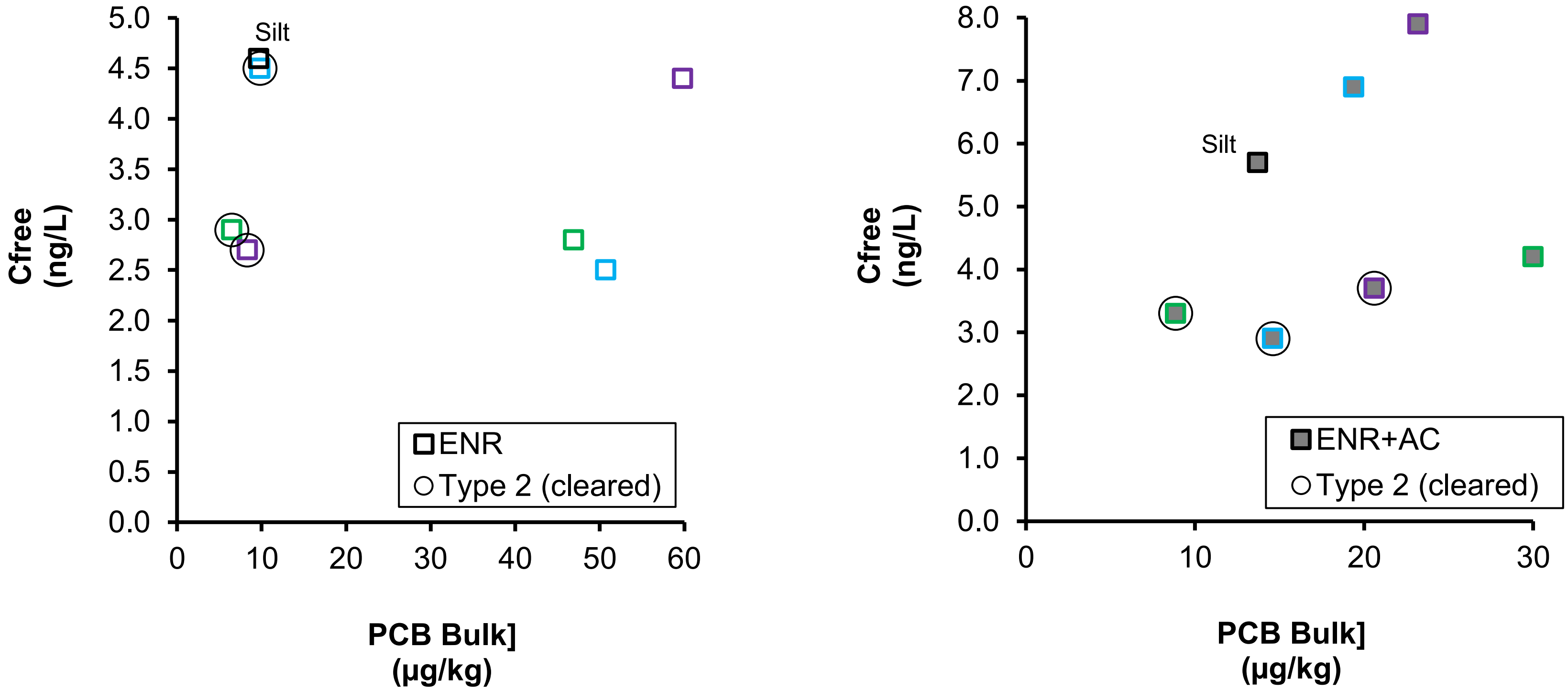
Year 3 Monitoring Report
Lower Duwamish Waterway

Figure D-9
Year 3 Comparison of Total C_{free} PCBs Type 2 and Type 1 SPME in Silt and Sediment



Notes:

Circled symbols indicate measurements at the Type 2 locations, where silt was cleared (if ≥ 3 cm thick). Symbols of the same color (green, blue, or purple) indicate the Type 1/Type 2 location pair (i.e., the circled green symbol indicates the Type 2 result adjacent to the result obtained at the adjacent Type 1 location, which is indicated by the uncircled green symbol).

Abbreviations:

- C_{free} = freely dissolved concentrations
- ENR = Enhanced natural recovery
- ENR+AC = Enhanced natural recovery amended with activated carbon
- ng/g = nanogram(s) per gram
- ng/L = nanogram(s) per liter
- PCB = polychlorinated biphenyl

Lower Duwamish Waterway Group Port of Seattle / City of Seattle / King County / The Boeing Company	**ENR/AC Pilot Study** **Year 3 Monitoring Report** **Lower Duwamish Waterway**	Figure D-10 Year 3 Comparison of Bulk PCBs and Total C_{free} PCBs in Silt and Sediment at Scour ENR and ENR+AC