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Appendix C
Relationship Between Surface and Subsurface COC Concentrations

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FIGURES

1 Introduction

This appendix was prepared to address a US Environmental Protection Agency (EPA) request to compare co-located surface and subsurface sediment contaminant of concern (COC) concentrations collected as part of the Pre-Design Investigation (PDI) in the upper reach (river mile [RM] 3.0 to RM 5.0]) of the Lower Duwamish Waterway (LDW).

This comparison was conducted for the four human health risk drivers (polychlorinated biphenyls [PCBs], carcinogenic polycyclic aromatic hydrocarbons [cPAHs], dioxins/furans, and arsenic). COC concentrations in co-located surface sediment (0–10 cm) and subsurface sediment (0–45 cm or 0–60 cm) were compared at all locations where both surface and subsurface sediment samples were collected during the same sampling event. Samples were considered co-located if they had been collected within 10 ft of one another.

The comparison was conducted with samples collected for the upper reach PDI in 2020 and 2021. The purpose of the PDI was to delineate areas with remedial action level (RAL) exceedances to support remedial design. The dataset was not designed to provide the basis for establishing relationships between surface and subsurface intervals for the site, nor to evaluate the site conceptual site model (CSM); therefore, these comparisons should be considered exploratory. The evaluation of co-located surface and subsurface concentrations for specific recovery categories had the following limitations:

- Fewer co-located samples were analyzed for cPAHs, dioxins/furans, and arsenic than for PCBs, the COC with the most RAL exceedances.
- Fewer locations with co-located surface and subsurface samples were needed within Recovery Category 1 areas to address design needs.
- The co-located dataset did not include locations where just one of the intervals was analyzed in Tier 1 and was above the RAL, as analysis of the other interval was not necessary to determine the need for remedial action. This could have biased the dataset toward areas with lower concentrations.
- The shoaling cores were not included in the co-located dataset because of the variability in the subsurface intervals in these cores. The top interval of the core was determined by the depth of the shoaled material; the intervals varied between 0–31 cm and 0–81 cm.

Data assessed in this appendix are summarized in Attachment C1.

2 Comparison of Surface Sediment (0–10 cm) to Subsurface Intertidal Sediment (0–45 cm)

2.1 Co-located Sample Interval Evaluation

PCB concentrations and cPAH toxic equivalents (TEQs) for surface sediment and subsurface intertidal sediment are compared in Figure C-1, with results shown separately by recovery category. The limited numbers of Recovery Category 1 locations (n=8 for PCBs and n=7 for cPAHs) restricts the ability to make conclusive statements about any differences between recovery categories in the patterns and correlations observed among the co-located samples. Instead, the data across all recovery categories were combined for the evaluation of these relationships. The two datasets (0–10 cm and 0–45 cm) are significantly correlated for dry weight PCB concentrations (non-parametric Spearman's rank correlation rho=0.53, $p << 0.001$, n=97), organic carbon (OC)-normalized PCB concentrations (rho=0.48, $p << 0.001$, n=73), and cPAH TEQs (rho = 0.52, $p < 0.001$, n=40).

The deviations in concentrations between the two sampling intervals were calculated, with positive values indicating that 0–45-cm concentrations were greater than 0–10-cm concentrations. A sign test was used to determine if the median value of these deviations was significantly different from zero, indicating a tendency for one sampling interval to have higher or lower concentrations than the other. By definition, half the samples have deviations above the median value, so a positive median value would indicate that there are more samples with 0–45-cm concentrations greater than 0–10-cm concentrations. The sign test counts the number of pairs with positive and negative deviations (i.e., the "sign" for the deviation) and considers only the direction—not the magnitude—of the differences in concentrations. The frequency distribution of the magnitude of these deviations between the surface (0–10 cm) and subsurface intertidal (0–45 cm) PCB concentrations and cPAH TEQs is shown in Figure C-2. Values near zero indicate that concentrations in the two intervals are similar. Figure C-2 illustrates that the majority of the locations have deviations near zero (i.e., 75% of the locations have PCB concentration deviations within +/- 200 µg/kg dry weight [dw], and 73% have cPAH TEQ deviations within +/- 100 µg/kg dw). The sign tests did not reject the null hypothesis ($p < \alpha = 0.05$) that the median values were zero (PCBs: median deviation = 9 µg/kg dw and 1.2 mg/kg OC, sign test p = 0.13, n=97 [dry weight]; sign test p = 0.06, n=73 [OC normalized]; cPAH: median deviation = -4 µg/kg dw, sign test p = 0.87, n=40). These results indicate that there was no consistent bias for the surface concentrations to be greater or less than the subsurface concentrations for PCBs and cPAH TEQs in this dataset.

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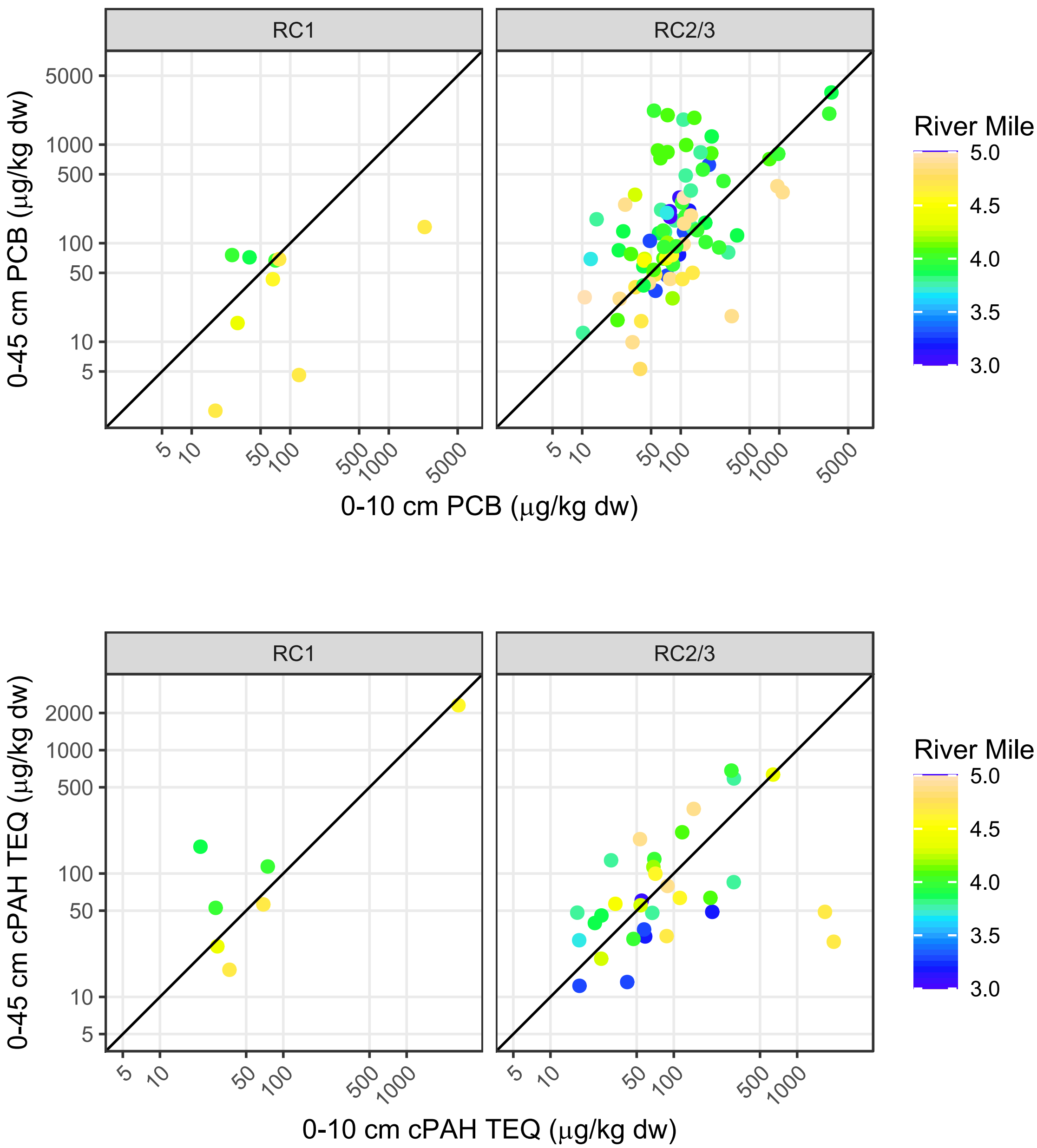
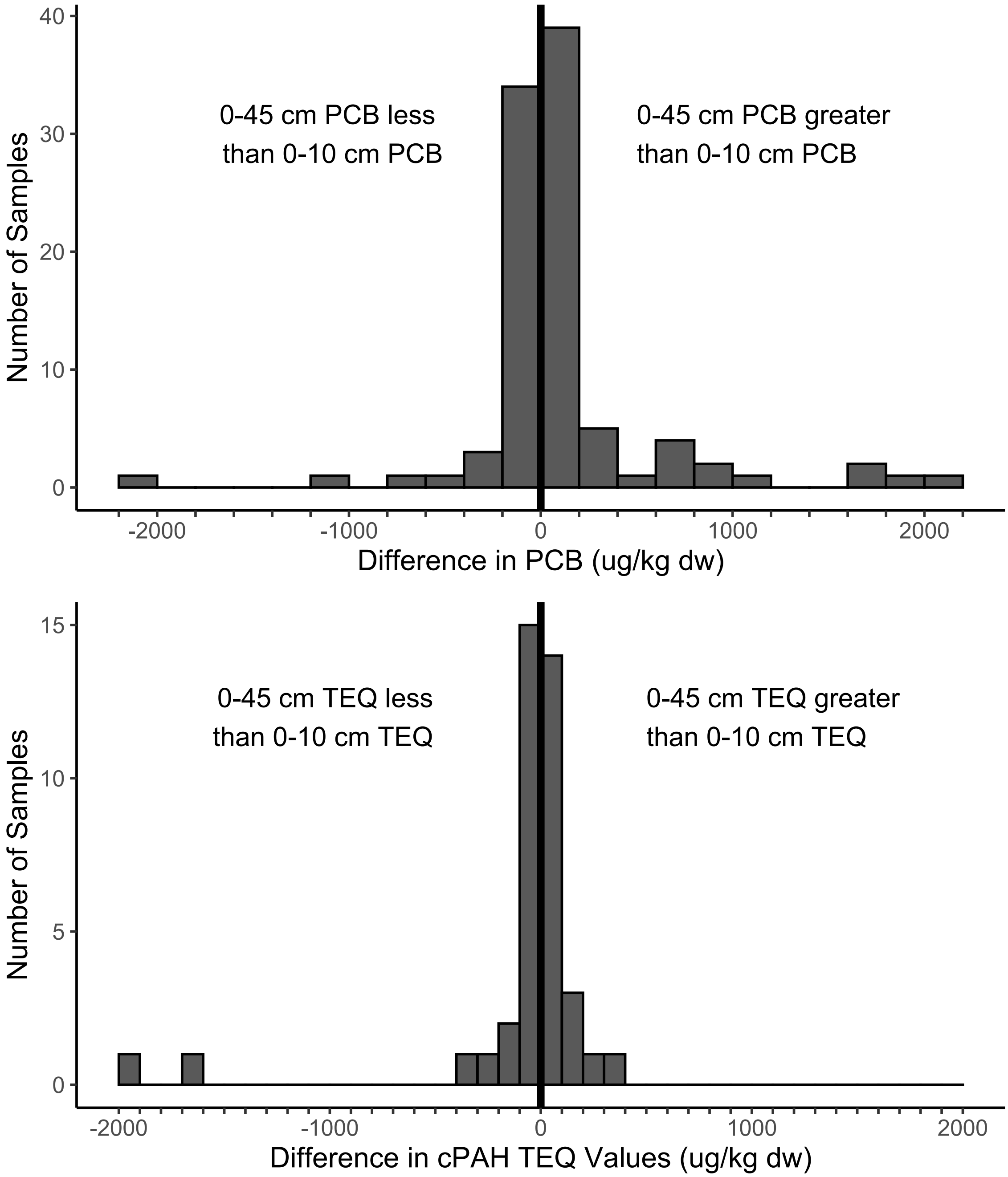
Figure C-1
Scatterplots of Total PCBs and cPAH TEQ Values in Surface (0–10 cm) Versus Subsurface Sediment (0–45 cm) in the Intertidal, Shown Separately for Recovery Category 1 and Recovery Categories 2/3



Points color coded by river mile. Black line is the 1:1 line; points above this line have subsurface concentrations greater than those in the surface.

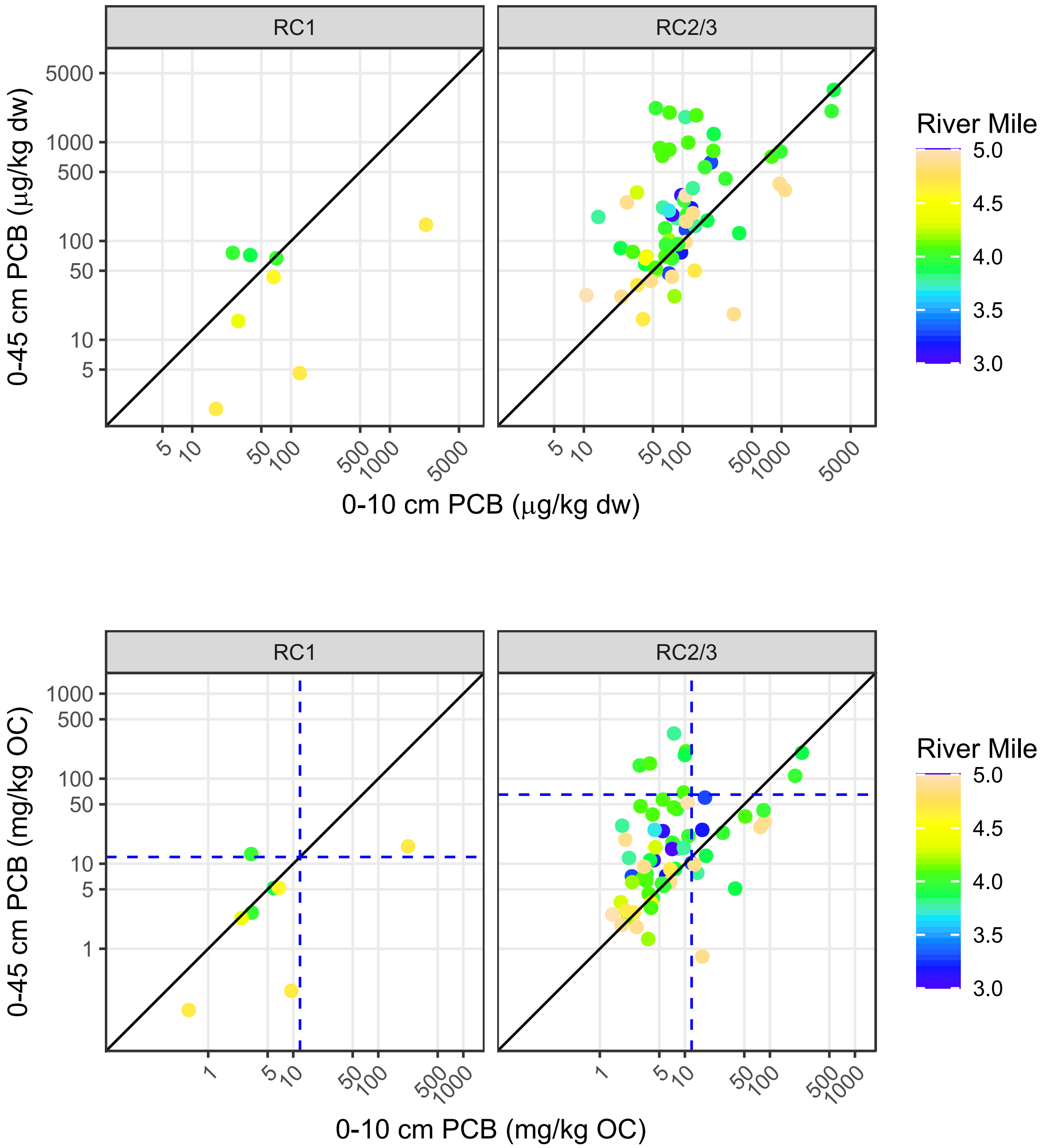
Figure C-2
Frequency Distribution of PCB Concentrations and cPAH TEQs in Subsurface Sediment (0–45 cm) in the Intertidal minus those in Surface Sediment (0–10 cm) at the Same Sampling Locations



All of the samples used in this evaluation had cPAH TEQ values below the applicable RALs presented in the explanation of significant differences (ESD) (EPA 2021). For PCBs, the relationships among

OC-normalized concentrations in 0–10-cm and 0–45-cm samples were plotted along with the RALs presented in Table 28 of the 2014 Record of Decision (ROD) (EPA 2014) (Figure C-3). Results for locations in Recovery Category 1 areas (n=8) and results for locations in Recovery Categories 2/3 areas (n=65) are shown separately. The data in this figure are restricted to those samples with total organic carbon values ≥ 0.5% and ≤ 3.5% for comparison to the OC-normalized RALs. There are no notable differences between the patterns and the correlations based on dry weight concentrations (top row; Figure C-3) and the patterns and correlations based on OC-normalized concentrations (bottom row; Figure C-3). The limited number of Recovery Category 1 locations restricts the ability to make conclusive statements about any differences between recovery categories in the patterns and correlations observed for the co-located samples.

Figure C-3
Scatterplots of Dry Weight and OC-normalized PCBs in Surface Sediment (0–10 cm) Versus Subsurface Sediment (0–45 cm) in the Intertidal, Shown Separately for Recovery Category 1 and Recovery Categories 2 and 3

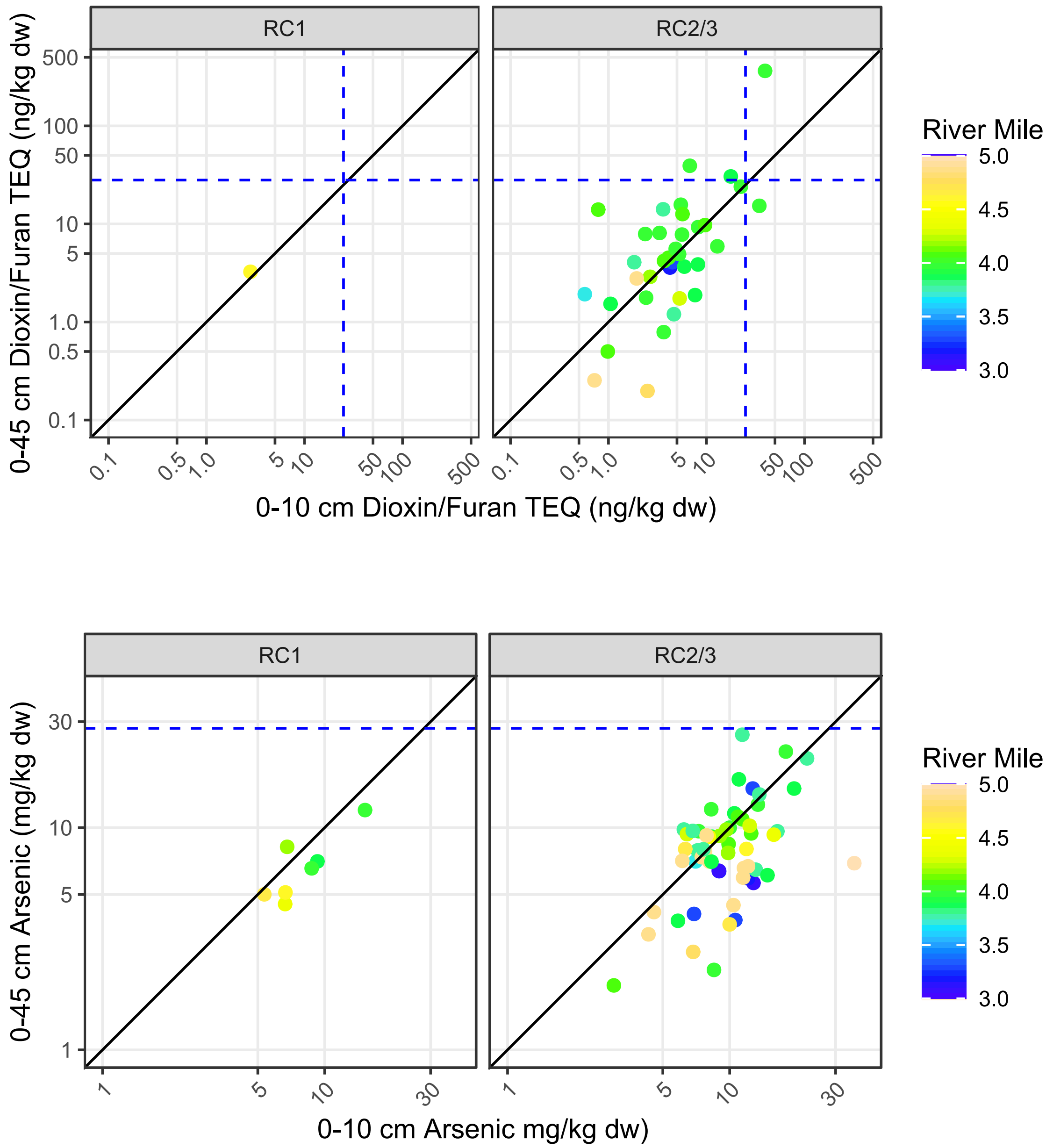


Points color coded by river mile. Black line is the 1:1 line; points above this line have subsurface concentrations greater than those in the surface. On the bottom row, the dashed blue lines indicate the surface and subsurface PCB RALs.

Similar results are shown for dioxin/furan TEQ values and arsenic concentrations (Figure C-4), with results shown separately by recovery categories. There are an insufficient number of samples in Recovery Category 1 areas (n=1 for dioxin/furan TEQs and n=7 for arsenic) to adequately compare relationships between recovery categories. Consequently, the data across all recovery categories were evaluated together, with statistically significant Spearman's rank correlations within both datasets (dioxin/furan TEQ rho = 0.60, $p < 0.001$, n=37; arsenic rho = 0.45, $p < 0.001$, n=67). All of the samples used in this evaluation had arsenic concentrations below the applicable RALs in Table 28 of the ROD. For dioxin/furan TEQs, there were two 0–10-cm surface samples in Recovery Category 2/3 that exceeded the RAL in Table 28 of the ROD and three 0–45-cm samples (Recovery Category 2/3) that exceeded the RAL (Figure C-4).

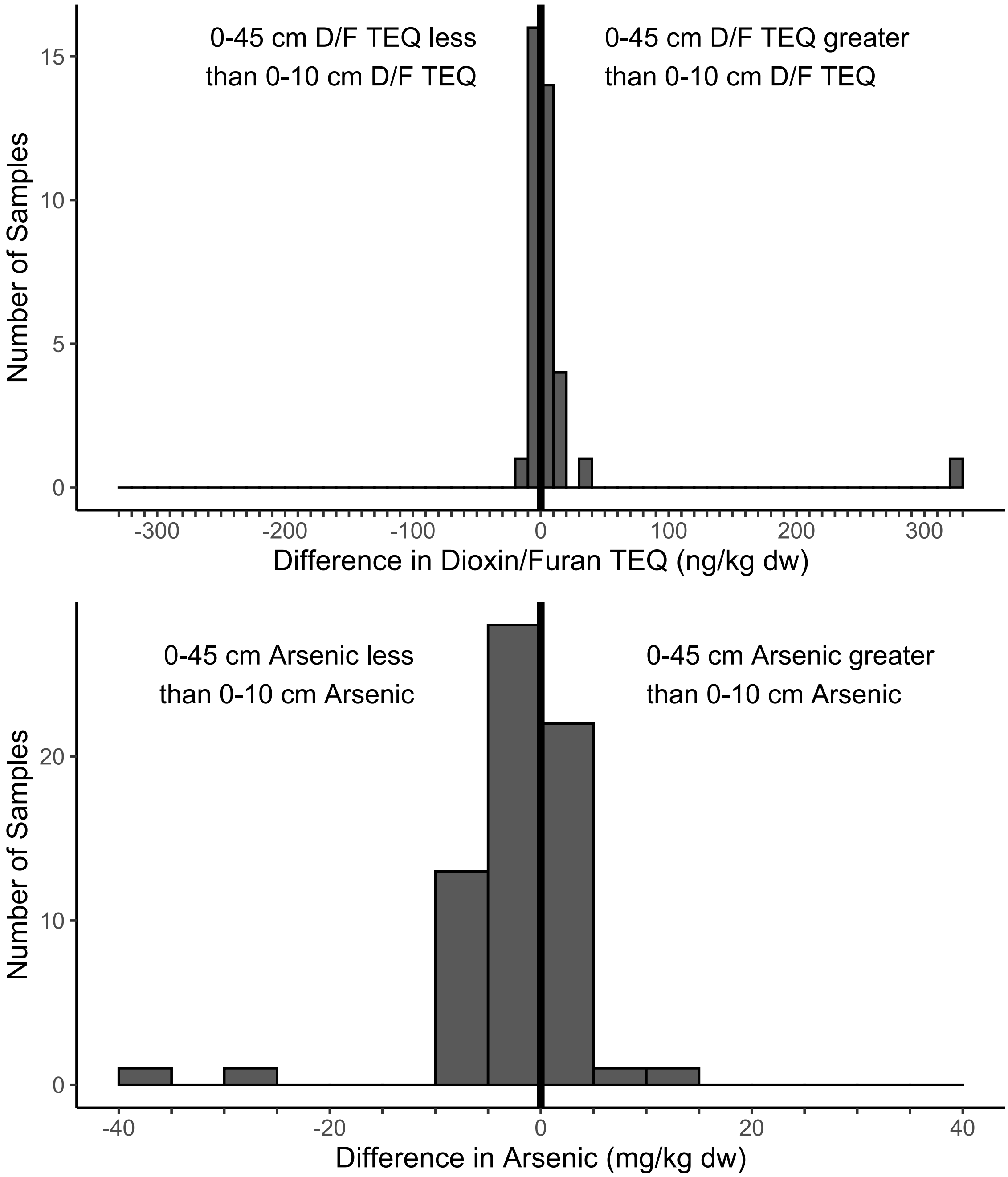
The distributions of deviations between concentrations in the 0–45-cm sample and the 0–10-cm sample are shown in Figure C-5; the sign test was not rejected for dioxin/furan TEQs (median deviation = 0.44 ng/kg dw; p=0.32, n=37), indicating there was no tendency for concentrations in the 0–45-cm samples to be greater or less than those in the 0–10-cm interval. The majority of the locations have deviations near zero; the exception is location 302, which had a dioxin/furan TEQ approximately 10 times higher in the 0–45-cm sample than in the 0–10-cm sample (364 ng/kg and 39.6 ng/kg, respectively). The deviations for arsenic are skewed slightly negative (Figure C-5). The results of the sign test are statistically significant (p = 0.036, n=67), indicating arsenic concentrations for 0–45 cm tended to be slightly lower than for the 0–10-cm interval, with a median difference of -1.06 mg/kg dw. Since arsenic concentrations were less than RALs and average concentrations in co-located surface and subsurface sediment were generally similar to background concentrations, this result is not contrary to the CSM.

Figure C-4
Scatterplot of Dioxin/Furan TEQs and Arsenic Concentrations in Surface Sediment (0–10 cm) Versus Subsurface Sediment (0–45 cm) in the Intertidal, Shown Separately for Recovery Category 1 and Recovery Categories 2/3



Points color coded by river mile. Black line is the 1:1 line; points above this line have subsurface concentrations greater than those in the surface. The dashed blue lines indicate the surface and subsurface RALs. The surface RAL for arsenic is not shown because it is greater than the maximum concentration shown on the plot.

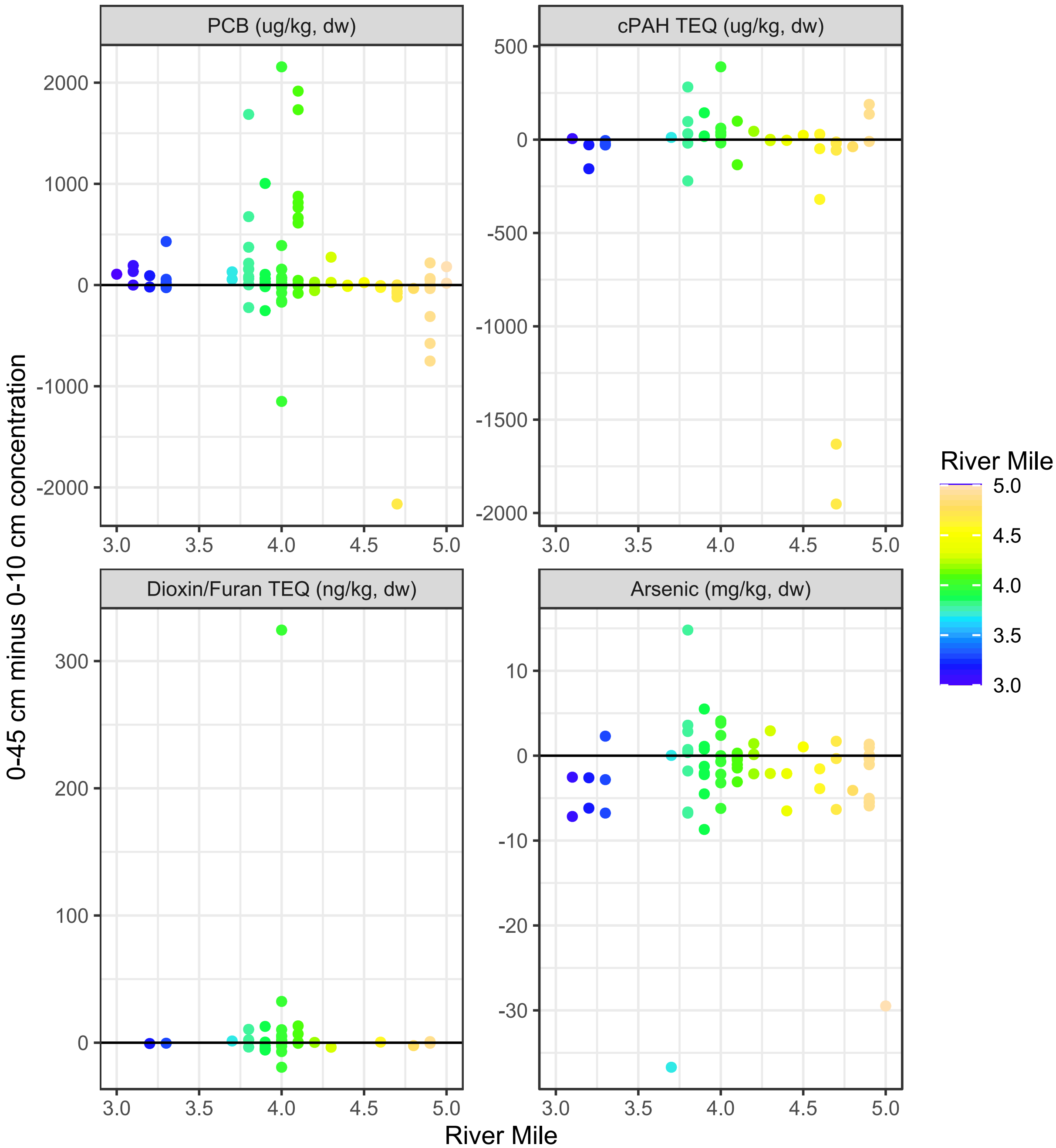
Figure C-5
Histogram of Dioxin/Furan TEQ and Arsenic Concentrations in Subsurface Sediment (0–45 cm) in the Intertidal minus those in Surface Sediment (0–10 cm) at the Same Sampling Location



2.2 Spatial Trend Evaluation

The presence of a spatial trend was assessed by plotting the deviations for each sample by river mile for each COC (Figure C-6). For PCBs, cPAH TEQ, and dioxin/furan TEQ, the largest positive differences between 0–45-cm samples and 0–10-cm samples were for locations between approximately RM 3.8 and RM 4.1. The majority of the co-located samples in this area were collected from the intertidal area on the east side of the LDW. The higher concentrations in the 0–45-cm intervals (relative to the 0–10-cm results) are consistent with known historical sources in this portion of the LDW and with the Recovery Category 2/3 designations.

Figure C-6
COC Concentrations in Subsurface Sediment (0–45 cm) in the Intertidal minus those in Surface Sediment (0–10 cm) at the same sampling locations by River Mile



2.3 Summary

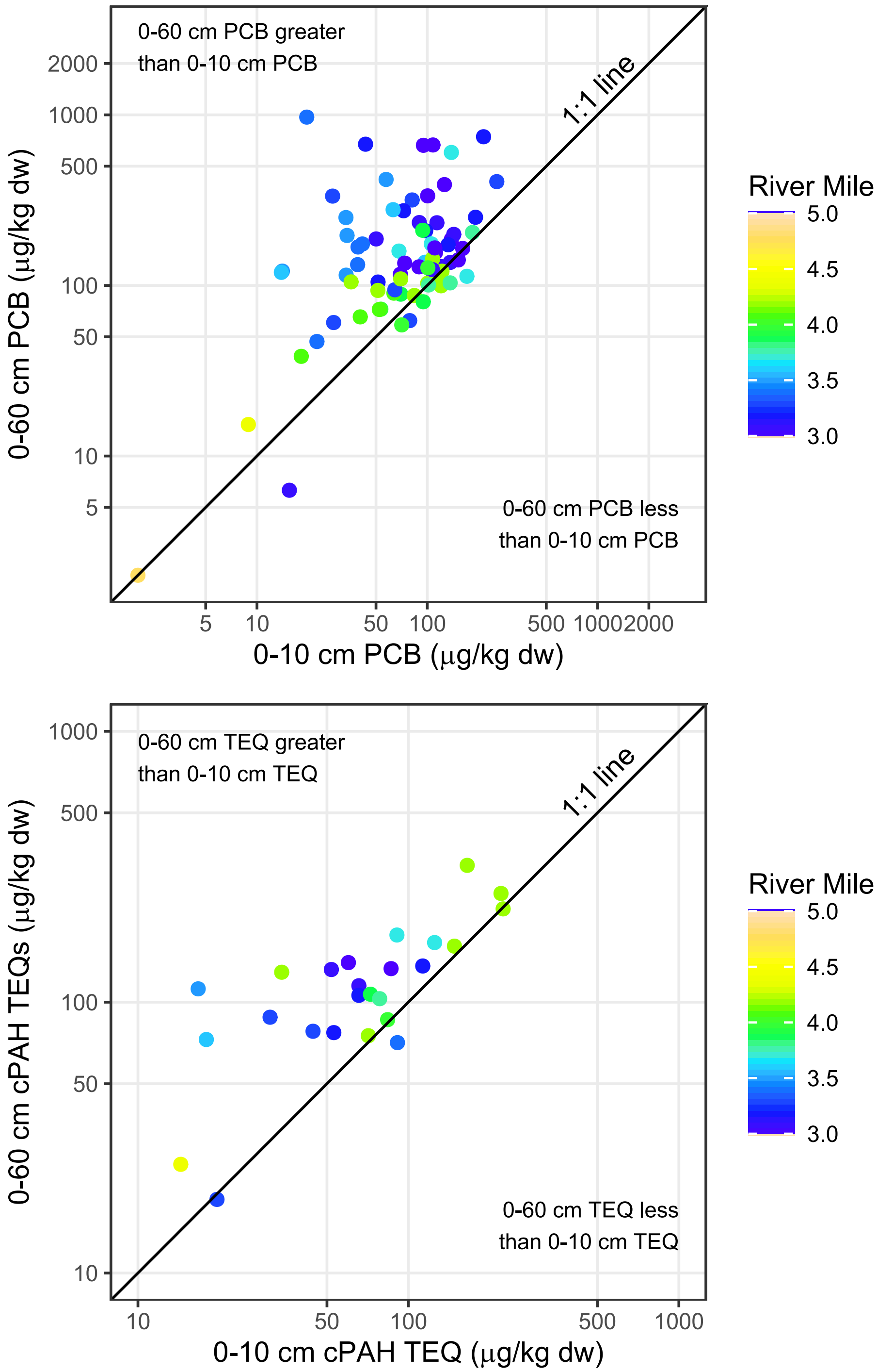
- A significant correlation was observed between co-located 0–10-cm concentrations and the 0–45-cm concentrations of PCBs, dioxin/furan TEQs, and cPAH TEQs, but there were no consistent or significant trends to indicate that concentrations tended to be higher in one sampling interval compared to the other. The OC-normalized PCB concentrations showed similar patterns to the dry weight concentrations.
- The arsenic concentrations in the 0–45-cm samples tended to be slightly lower than those in the 0–10-cm samples. All of the arsenic concentrations were less than the applicable RALs, and the mean concentrations for the 0–10-cm samples (10.9 mg/kg) and 0–45-cm samples (8.7 mg/kg) were similar to the natural background arsenic concentration 11 mg/kg (Ecology 2021).
- The spatial trend evaluation identified the intertidal area on the east side of the LDW between approximately RM 3.8 and RM 4.1 as an area where the 0–45-cm PCB concentrations, dioxin/furan TEQs, and cPAH TEQs tended to be higher than the 0–10-cm concentrations.

3 Comparison of Surface Sediment (0–10 cm) to Subsurface Subtidal Sediment (0–60 cm)

3.1 Co-located Interval Evaluation

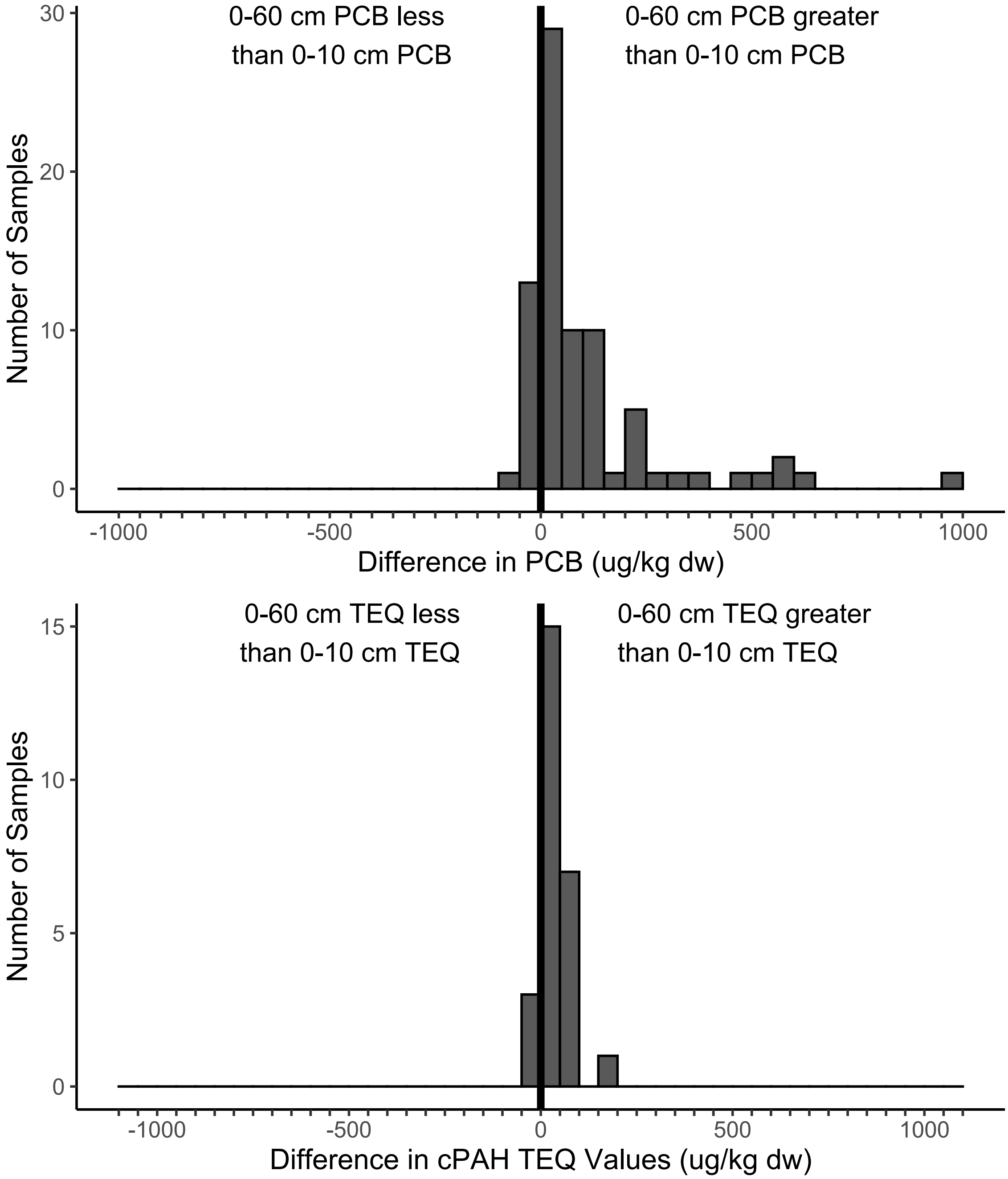
PCB concentrations and cPAH TEQs in subtidal subsurface sediment (0–60 cm) were similar to or greater than concentrations in surface sediment (0–10 cm) (Figure C-7). The Spearman's rank correlations were statistically significant for dry weight PCBs (rho = 0.33, p = 0.003, n = 78), OC-normalized PCBs (rho=0.52, p << 0.001, n=63), and cPAH TEQ (rho = 0.71, p << 0.001, n = 26). The majority of the sampling locations plot above the 1:1 line (Figure C-8), indicating that the 0–60-cm subsurface sediment PCB concentrations and cPAH TEQs tend to be greater than the surface sediment results (i.e., both sign tests were statistically significant, p << 0.001, with median deviations of 41 µg/kg dw for dry weight PCB concentrations, 3.3 mg/kg OC for OC-normalized PCB concentrations, and 34 µg/kg dw for cPAH TEQ). Higher PCB concentrations and cPAH TEQs in the 0–60-cm interval than in the 0–10-cm interval is consistent with the CSM, because the 0–60-cm interval integrates sediment deposited over a much longer time period.

Figure C-7
Scatterplots of PCB Concentrations and cPAH TEQ Values in Surface (0–10 cm) Versus Subsurface Sediment (0–60 cm) in the Subtidal



Points color coded by river mile. Black line is the 1:1 line; points above this line have subsurface concentrations greater than those in the surface.

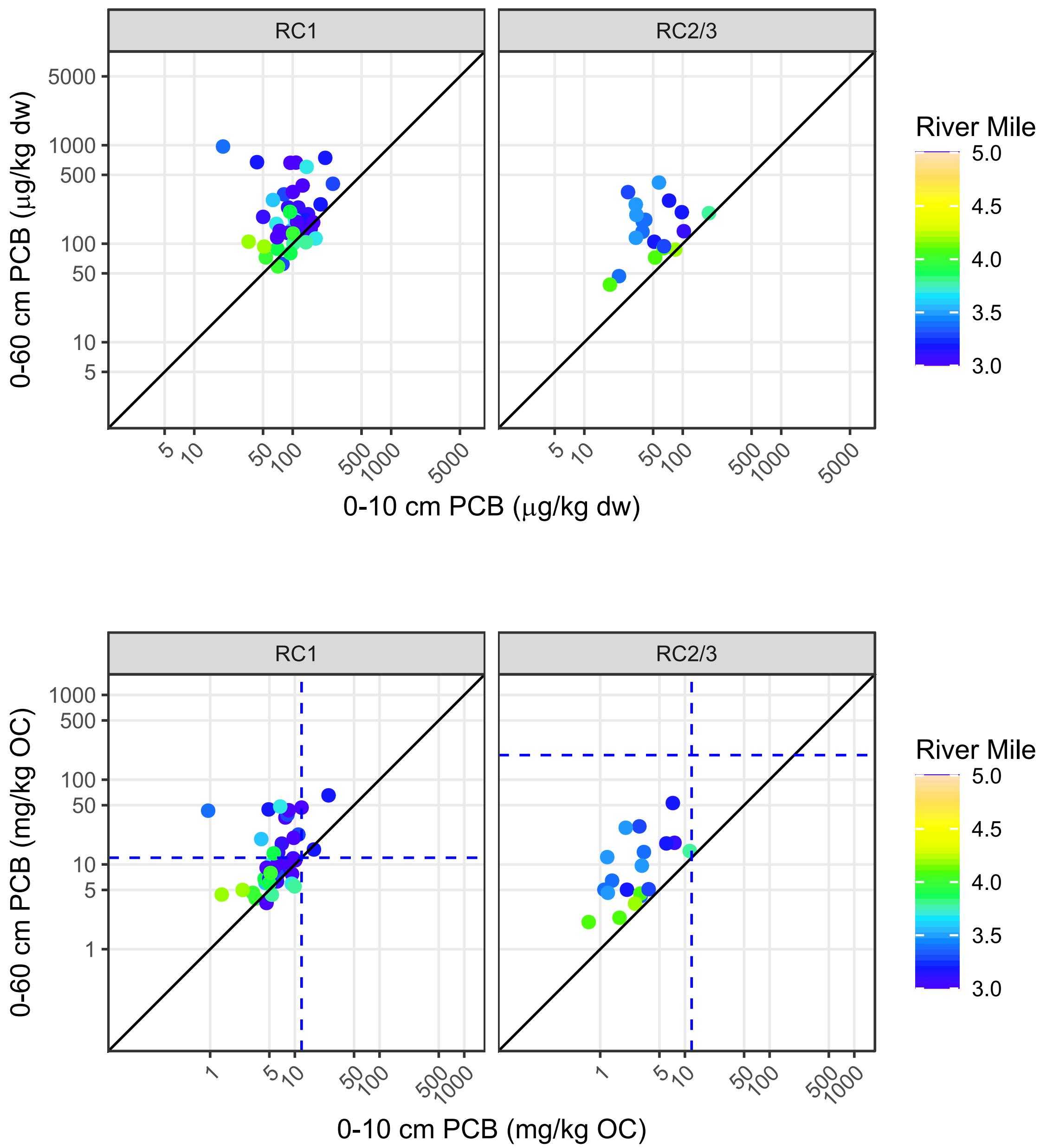
Figure C-8
Histogram of Differences in PCB and cPAH TEQ Values in Subsurface Sediment (0–60 cm) in the Subtidal minus Surface (0–10 cm) at the Same Sampling Locations



The relationships between surface and subsurface intervals in different recovery categories were evaluated for PCBs because cPAH TEQ, arsenic, and dioxin/furan TEQ do not have subsurface RALs in Recovery Category 2/3 areas. The relationships between OC-normalized PCB concentrations in 0–

10-cm and 0–60-cm samples were plotted along with the RALs (Figure C-9), with separate panels for Recovery Category 1 (n=44) and Recovery Categories 2/3 (n=19). The data in this figure are restricted to those samples with total organic carbon values ≥0.5 and ≤ 3.5%. The patterns and correlations are similar between concentrations on a dry weight basis (top row) and those on an OC-normalized basis (bottom row; Figure C-9). In addition, the patterns and correlations are similar for the Recovery Category 1 locations and the Recovery Category 2/3 locations.

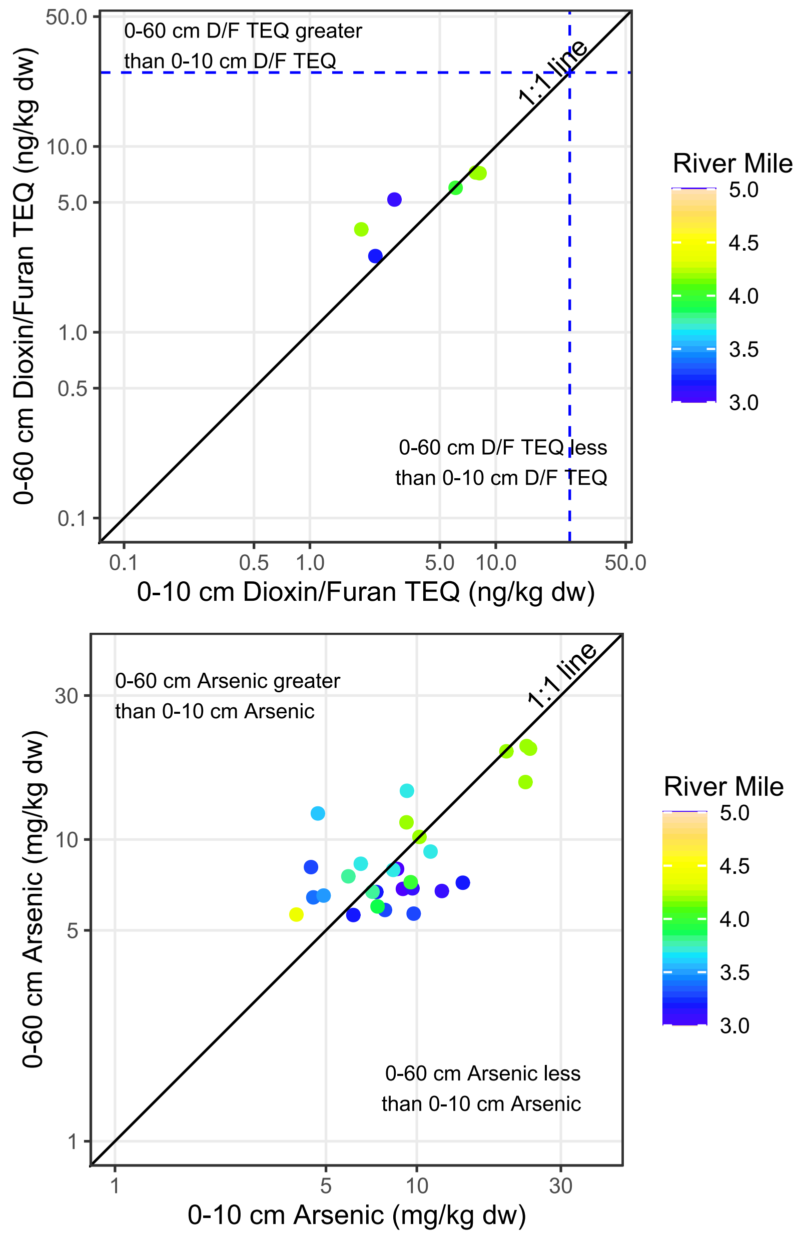
Figure C-9
Scatterplots of Dry Weight and OC-normalized PCB Concentrations in Surface (0–10 cm) versus Subtidal Subsurface Sediment (0–60 cm) Separated by Recovery Category



Points color coded by river mile. Black line is the 1:1 line; points above this line have subsurface concentrations greater than those in the surface. The dashed blue lines indicate the RALs; if not shown, the RAL exceeds the maximum value shown on the plot.

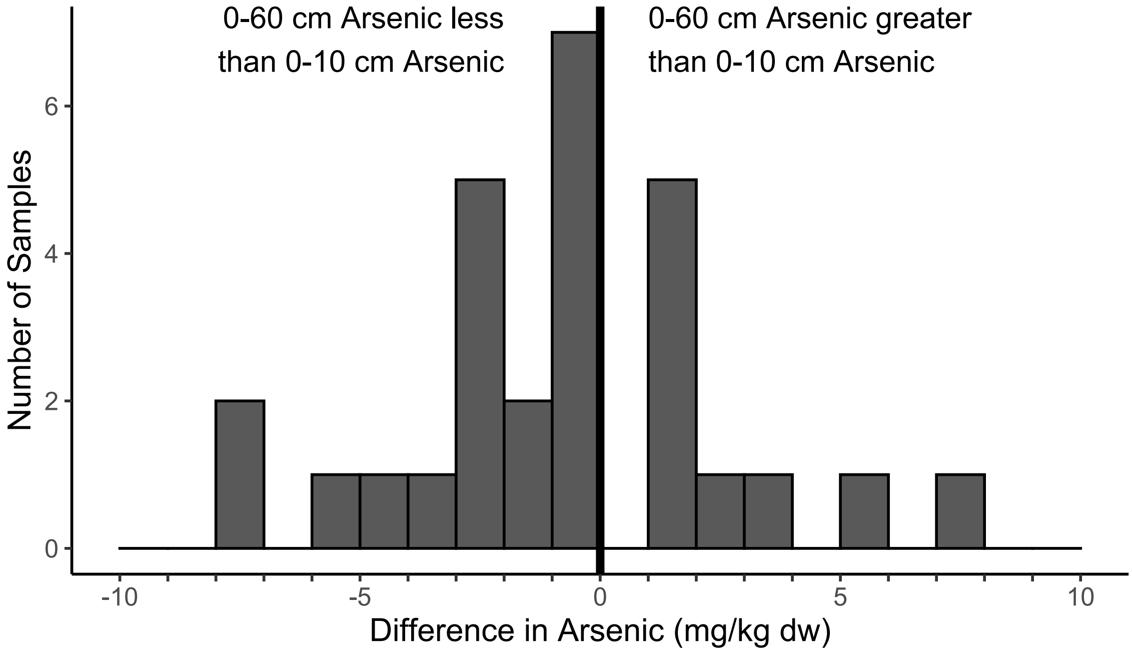
The data were insufficient to adequately assess the relationship for dioxin/furan TEQs (n = 6, Figure C-10), whereas arsenic had no consistent tendency for surface sediment concentrations to be greater or less than subsurface (0–60 cm) sediment concentrations in the subtidal samples (Figures C-10 and C-11). This correlation was statistically significant (with Spearman's rank correlation rho = 0.52, p = 0.005, n=28), and the sign test failed to reject the null hypothesis of a median difference of zero (median difference = -0.6 mg/kg dw, p = 0.12, n=28).

Figure C-10
Scatterplot of Dioxin/Furan TEQ Values and Arsenic Concentrations in Surface (0–10 cm) Versus Subtidal Subsurface Sediment (0–60 cm)



Points color coded by river mile. Black line is the 1:1 line; points above this line have subsurface concentrations greater than those in the surface. The dashed blue lines indicate the RALs; if not shown, the RAL exceeds the maximum value shown on the plot.

Figure C-11
Histogram of Differences in Arsenic Concentrations in Subsurface Sediment (0–60 cm) in the Subtidal minus Surface (0–10 cm) at the Same Sampling Locations

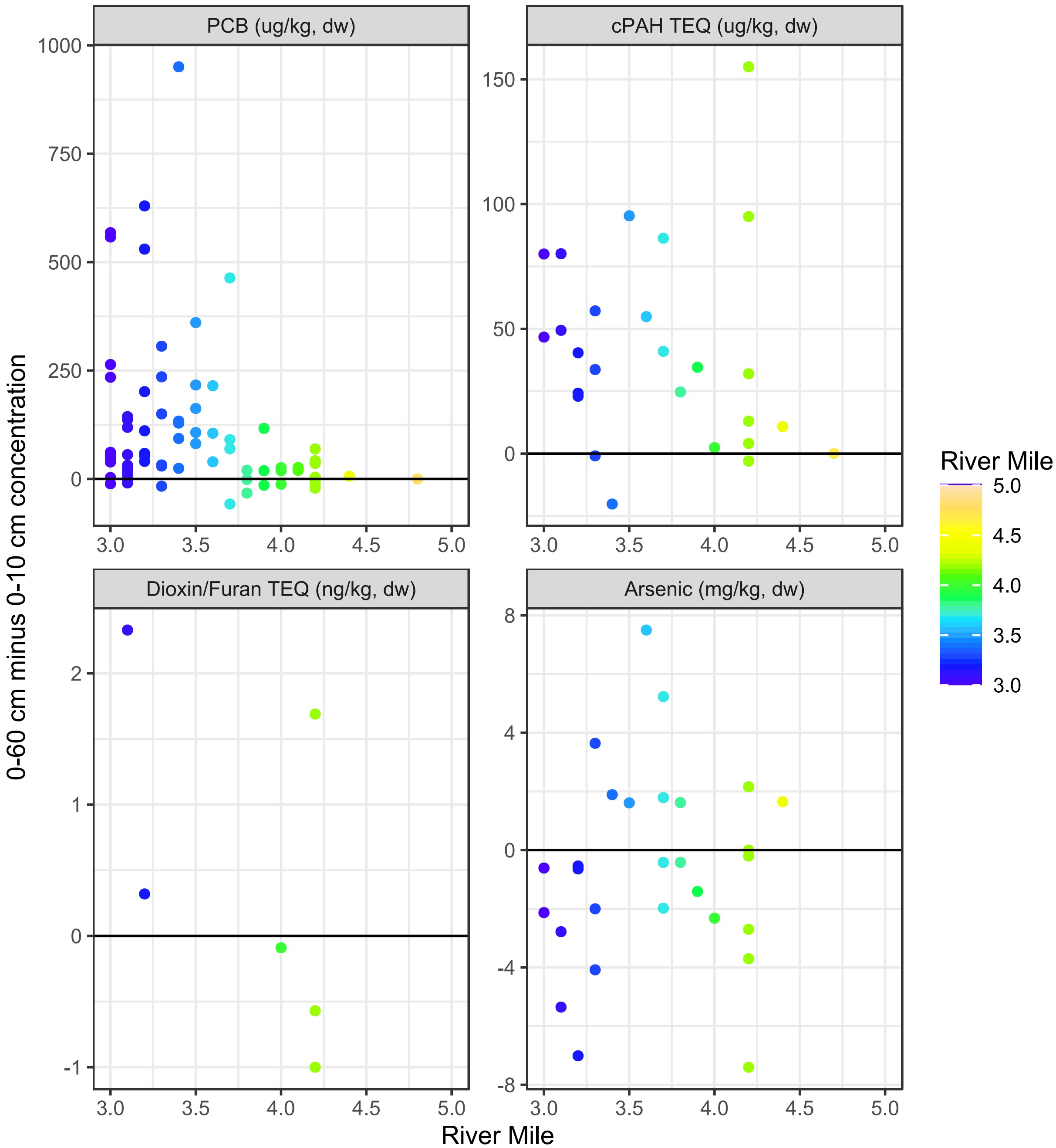


3.2 Spatial Trend Evaluation

The presence of a spatial trend was assessed by plotting the deviations for each location by river mile for each COC (Figure C-12). The locations with both the 0-10-cm and 0-60-cm sampling intervals were not evenly distributed throughout the upper reach. The locations with both sampling intervals were predominantly located between RM 3.0 and RM 4.2.[1] The differences in PCB concentrations between 0–60-cm samples and 0–10-cm samples were generally higher in the areas downstream of RM 3.5. Similar trends were seen for cPAH TEQs. This is consistent with the distribution of listed upland cleanup sites, as well as the deposition of upstream solids in the upper portion of the upper reach, which requires regular maintenance dredging of the navigation channel between RM 4.0 and RM 4.65. Arsenic concentrations displayed no apparent spatial trend, and dioxin/furan TEQ data were too sparse to assess.

[1] The Federal Navigation Channel between RM 4.0 and RM 4.65 was not sampled as part of the PDI, because this area is regularly sampled for dredge material characterization (including Z-samples to -19 ft mean lower low water) associated with maintenance dredging. North of the bridge at RM 4.8, there are no areas with 0–60-cm RALs because the bridge prevents vessel traffic in this area.

Figure C-12
Differences in COC Concentrations in Subtidal Subsurface Sediment (0–60 cm) minus Surface (0–10 cm) at the same sampling locations by River Mile



3.3 Summary

- PCB concentrations and cPAH TEQs in the 0–60-cm samples tended to be higher than those in the 0–10-cm samples, which is consistent with the CSM. Co-located data were insufficient to assess the dioxin/furan TEQs.
- The patterns and correlations for PCB concentrations were similar to those for dry weight concentrations and OC-normalized concentrations. The results for Recovery Category 1 locations and Recovery Category 2/3 locations were similar.
- There was no significant trend between co-located 0–10-cm concentrations and the 0–60-cm arsenic concentrations.
- The spatial trend evaluation identified higher PCB concentrations and cPAH TEQs in the 0–60-cm than in the 0–10-cm concentrations at downstream locations.

4 References

Ecology. 2021. Sediment cleanup user's manual. Guidance for implementing the cleanup provisions of the sediment management standards, Chapter 173-204 WAC. Third revision December 2021. Pub. No. 12-09-057. Toxics Cleanup Program, Washington State Department of Ecology, Olympia, WA.

EPA. 2014. Record of Decision. Lower Duwamish Waterway Superfund Site. US Environmental Protection Agency.

EPA. 2021. Proposed explanation of significant differences. Draft for public comment. Lower Duwamish Waterway Superfund site. US Environmental Protection Agency Region 10, Seattle, WA.

Attachments

Attachment C1 Data Assessed