90% Remedial Design Basis of Design Report

Appendix K
Chemical Fate and Transport Modeling to
Support Evaluations of Buried
Contamination, ENR/AC Pilot, and
Area-Specific Technology Locations

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### **ABBREVIATIONS**

µg/L micrograms per liter
AC activated carbon

BODR Basis of Design Report

cm centimeter

cm/yr centimeters per year

Ecology Washington State Department of Ecology

ENR enhanced natural recovery

ENR/AC Pilot Study pilot study to evaluate enhanced natural recovery amended with activated

carbon

EPA U.S. Environmental Protection Agency

FNC federal navigation channel foc fraction organic carbon g/cm³ grams per cubic centimeter GAC granular activated carbon

LDW Lower Duwamish Waterway
MLLW mean lower low water

mg/kg milligrams per kilogram

N/A not applicable OC organic carbon

PCB polychlorinated biphenyl
RAA remedial action area
RAL remedial action level
RD remedial design
ROD Record of Decision

TOC total organic carbon

USACE U.S. Army Corps of Engineers

# 1 Introduction and Approach

This appendix describes chemical transport modeling conducted to support the contaminated sediment remedial design (RD) for the upper reach of the Lower Duwamish Waterway (LDW). The purpose of this modeling was to evaluate the transport potential of dissolved phase polychlorinated biphenyls (PCBs) in the following areas and circumstances:

- Areas of contamination buried beneath cleaner sediment (i.e., sediment with concentrations less than remedial action levels [RALs]) that do not require remedial action
- Areas where a thin layer of sand/gravel were placed over contaminated sediment as part of a
  pilot study to evaluate enhanced natural recovery amended with activated carbon (referred to
  as the ENR/AC Pilot Study)
- Structural offset areas, where an area-specific technology in the form of a sandy gravel cover will be used

Section 2 of this appendix discusses the transport potential of dissolved phase PCBs in areas not requiring remedial action (i.e., RAL exceedances) but where contamination is potentially buried beneath cleaner surface sediments adjacent to remedial action areas (RAAs). This evaluation addressed two specific core locations, per U.S. Environmental Protection Agency (EPA) input, and two conservative representative locations where there is potential for buried contamination outside of the adjacent RAAs. This section also describes two sensitivity analyses that were conducted—the first to understand the impact of sedimentation and the second to identify the maximum theoretical buried contamination concentration that could exist without exceeding the RAL at the surface within 100 years.

Section 3 presents a similar evaluation of the ENR/AC Pilot Study area to assess the long-term effectiveness of a sand cover to attenuate contaminants and maintain concentrations at the surface within project remedial targets. The information presented in Sections 2 and 3 was presented to the EPA in a meeting on July 19, 2022.

Section 4 presents modeling that was conducted to evaluate whether a sandy gravel cover could address RAL exceedances at two locations adjacent to existing structures where dredging and enhanced natural recovery (ENR) technology cannot be used. Two locations adjacent to existing structures (RAA 24/25/26) have PCB concentrations that exceed the surface RAL ENR upper limit (three times the RAL). Dredging cannot occur at these locations due to their proximity to structures and risk of structural failure (area known as a dredge offset). Per the *Record of Decision* (ROD; EPA 2014), in areas with structural or access restrictions (e.g., under-pier areas and in the vicinity of dolphins or pilings, bulkheads, and riprapped or engineered shorelines), a location-specific cleanup technology can be applied. A sandy gravel cover was evaluated as an area-specific technology for these two locations in RAA 24/25/26, including the need for amendment.



The one-dimensional model of chemical transport within sediment caps, CapSim (version 3.8; Reible 2017),<sup>1</sup> was used for these evaluations. Although this model was initially developed to support design of sediment caps, it also can be used to simulate transport within uncapped sediments. This model simulates the time-variable fate and transport of chemicals (dissolved and sorbed phases) under the processes of advection, diffusion/dispersion, biodegradation, bioturbation/bioirrigation, and exchange with the overlying surface water within a vertical column of sediment and cap material (if present). Details on the model structure and underlying theory and equations are provided in Lampert and Reible (2009), Go et al. (2009), the EPA/USACE capping guidance (Appendix B of Palermo et al. 1998), and Shen et al. (2018).

<sup>&</sup>lt;sup>1</sup> A newer version of CapSim is available; however, the functionality of the model used in these evaluations has not changed in the newer version.



## 2 Buried Contamination Evaluation

For the purposes of this evaluation, buried contamination is defined as sediment having PCB concentrations greater than the RAL (12 milligrams per kilogram [mg/kg] organic carbon [OC]) that is buried beneath 60 centimeters (cm; 2 feet) or more of sediment with concentrations less than RALs in subtidal areas or that is buried beneath 45 cm (1.5 feet) or more of sediment with concentrations less than RALs in intertidal areas. The evaluation presented in this section assesses whether buried contamination is likely to migrate to the surface, resulting in exceedances of the RAL within the surface sediment (0 to 10 cm). This evaluation does not assess the physical processes that may result in exposure of the buried contamination (e.g., scour).<sup>2</sup> A number of factors can affect the transport of contaminants within subsurface and surface sediment and influence the resulting concentrations over time in the surface sediment (i.e., top 10 cm). Two key factors that affect the potential for buried contamination to recontaminate surface sediment over the long term due to chemical migration through the sediments are as follows:

- 1. The magnitude of the buried contaminant concentrations
- 2. The depth below the surface at which such concentrations are present

Higher PCB concentrations present in buried sediments have a greater potential to result in an increase in concentrations in the surface sediment over the long term due to upward transport (i.e., driven by groundwater seepage) as compared with lower PCB concentrations that are buried. Likewise, elevated PCB concentrations present closer to the surface have a greater potential to result in an increase in concentrations in the surface sediment as compared to those same concentrations buried more deeply.

Several core profiles and buried contamination scenarios were evaluated with the model. These core profiles are based on concentrations in sediment within the federal navigation channel (FNC) that are considered conservatively high concentrations. The core profiles evaluated are as follows:

• Two specific core profiles having buried contamination of PCBs: LDW21-SC572 and LDW21-SC554 (Figure K2-1). Core LDW21-SC572 is located in RAA 14/15/16 (Figure 6-2c of the Pre-Final [90%] RD Basis of Design Report [BODR]) and Core LDW21-SC554 is located between RAA 4/5/6 and 12 (Figure 6-2b of the BODR). These two cores were selected because they represented worst-case buried contamination core profiles as discussed with EPA. LDW21-SC572 had an elevated PCB concentration at a depth of 30 cm (when overlying shoal sediment depth is conservatively ignored), and LDW21-SC554 had the highest buried PCB concentration, observed at a depth greater than 4 feet. Values for PCB concentration, total

<sup>&</sup>lt;sup>2</sup> EPA's 2014 ROD anticipates that subsurface buried contamination will remain in some areas, subject to the specific criteria defined in the ROD (EPA 2014). EPA's determination was based on a variety of analyses in the Feasibility Study, including the potential for scour from river flows and vessels. Therefore, EPA's ROD already accounts for likely exposure of buried contamination from potential scour associated with physical processes.



- organic carbon (TOC), dry bulk density, and porosity used in the model for these locations were based on the samples from each depth interval at each core location.
- Two generalized core profile scenarios were developed to be representative of potential buried contamination adjacent to the following: 1) RAA 1/2/3, as shown in Figure 6-2a of the BODR; and 2) RAA 14/15/16, as shown in Figure 6-2c of the BODR. The generalized core profiles for RAA 1/2/3 and RAA 14/15/16 are shown in Figures K2-2 and K2-3, respectively. These generalized core profiles were used to conservatively simulate buried contamination immediately beneath surface sediment that may be adjacent to those RAAs. They were configured to simulate 60 cm (2 feet) of sediment (below RAL concentrations) on top of the buried contamination as well as a worst-case thickness of 30 cm (1 foot; i.e., shorter distance) of surface sediment (below RAL concentrations) on top of the buried contamination (see panels on right side of Figures K2-2 and K2-3). The 30-cm thickness represents a hypothetical worst-case scenario in which some removal of the cleaner surface material may have occurred. This scenario is more conservative than the 60-cm thickness because it assumes the buried contamination is closer to the surface (i.e., shorter distance for contaminants to travel to the surface).

Concentrations associated with the layers of sediment for the generalized core profiles were based on shallow subsurface (0 to 60 cm) and deep subsurface (all depths beneath the shallow subsurface) sediment samples within and adjacent to the two groups of areas evaluated. Both maximum and average PCB concentrations from these local areas were evaluated to cover a range of conditions that may be observed in the generalized profiles. For the maximum scenario, the TOC, dry bulk density, and porosity associated with the sample that produced the maximum PCB concentration were used. For the average scenario, the TOC, dry bulk density, and porosity values were based on the average values from the samples that made up the average PCB concentration.

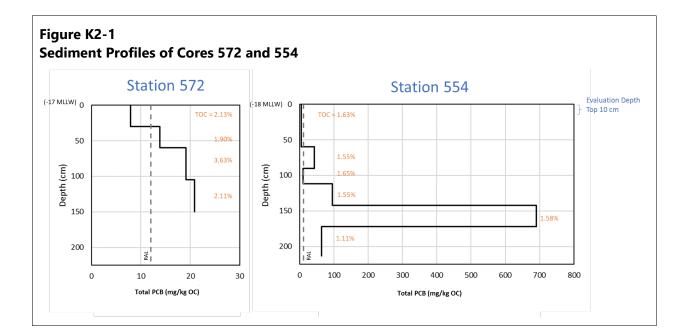


Figure K2-2 **Generalized Core Profiles for RAA 1/2/3** Maximum Shallow Subsurface and Deep Subsurface Concentration 2 ft Sediment Above 1 ft Sediment Above **Buried Contamination Interval Buried Contamination Interval** TOC = 1.6% TOC = 1.6%20 20 40 Depth (cm) Depth (cm) 1.5% 1.5% 80 80 100 100 40 80 80 20 **Total PCB Concentration Total PCB Concentration** (mg/kg OC) (mg/kg OC) Average Shallow Subsurface and Deep Subsurface Concentration 2 ft Sediment Above 1 ft Sediment Above **Buried Contamination Interval Buried Contamination Interval** OC = 2.1%TOC = 2.1%20 20 40 40 Depth (cm) Depth (cm) 60 60 1.5% 1.5% 80 100 100 120 120

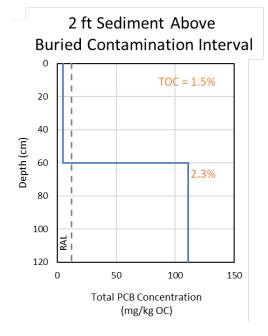
Total PCB Concentration (mg/kg OC)

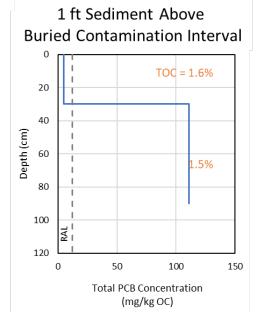
Total PCB Concentration

(mg/kg OC)

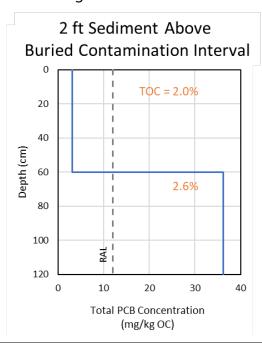
Figure K2-3
Generalized Core Profile for RAA 14/15/16

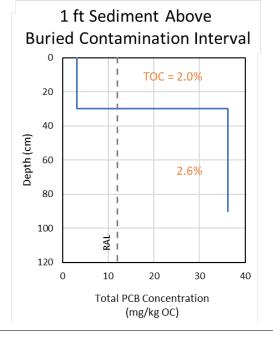
Maximum Shallow Subsurface and Deep Subsurface Concentration





Average Shallow Subsurface and Deep Subsurface Concentration





### 2.1 Buried Contamination Model Inputs

The model uses several input parameters that describe chemical-specific properties, sediment properties, and chemical mass transfer rates. Chemical-specific properties (e.g., molecular diffusivity and OC partition coefficients), bioturbation properties (depth and biodiffusion coefficients), reaction rates, and sedimentation (conservatively ignored), are consistent with the values used for the cap design modeling described in BODR Appendix I. As described in BODR Appendix I, the groundwater seepage rate (Darcy flux) in the upper reach is estimated to average 400 centimeters per year (cm/yr) and range from 100 cm/yr in the center of the channel up to 800 cm/yr nearshore. Because the areas being evaluated for buried contamination are located within the FNC and are not nearshore, this evaluation considered Darcy fluxes of 100 cm/yr and 400 cm/yr. A sensitivity analysis was conducted for the full range of groundwater seepage rates, including 800 cm/yr, to identify the maximum concentration that could exist in the LDW upper reach deep subsurface sediments before resulting in a RAL exceedance in surface (0 to 10 cm for intertidal and subtidal areas) and in the shallow subsurface (0 to 45 cm in the intertidal; Section 2.3.1).

A listing of model input parameters that differ from those reported in BODR Appendix I are provided in Table K2-1. These inputs describe the scenario-specific characteristics of the sediment simulated with the model and include PCB concentrations (converted to porewater concentrations by homolog group<sup>3</sup> based on partition coefficients, consistent with the cap design modeling), porosity, dry bulk density, and fraction organic carbon (foc).

<sup>&</sup>lt;sup>3</sup> PCB concentrations were measured using an Aroclor-based method. To account for the range in mobility of the PCB congeners that make up an Aroclor, reported Aroclor PCB concentrations in sediment were converted to homolog concentrations based on the average fraction of each homolog group associated with each Aroclor developed from several published studies (Rushneck et al. 2004; Schulz-Bull et al. 1989; Frame et al. 1996; EPA 1995).



Table K2-1
Buried Contamination Modeling Input Parameter Values

	PCB Homolog Porewater Concentration (μg/L)										Dry Bulk			
Core Location	Depth Interval (cm)	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca	Porosity	Density (g/cm³)	f <sub>oc</sub>
	0 to 60	6.5E-06	7.5E-05	4.6E-04	7.2E-04	5.7E-04	2.8E-04	8.0E-05	8.0E-06	4.6E-07	1.9E-08	0.66	0.90	0.016
	60 to 90	4.8E-05	3.1E-04	1.4E-03	2.3E-03	3.1E-03	3.0E-03	1.1E-03	1.2E-04	6.9E-06	2.8E-07	0.63	0.95	0.016
LDW24 CC554	90 to 112	1.4E-05	1.7E-04	1.1E-03	1.7E-03	1.2E-03	5.5E-04	1.5E-04	1.5E-05	8.4E-07	3.4E-08	0.65	0.92	0.017
LDW21-SC554	112 to 142	1.8E-04	3.0E-03	2.2E-02	2.7E-02	1.1E-02	2.5E-03	4.0E-04	3.5E-05	2.0E-06	8.4E-08	0.59	1.07	0.016
	142 to 172	7.6E-04	5.3E-03	2.5E-02	4.3E-02	5.3E-02	4.8E-02	1.7E-02	1.8E-03	1.0E-04	4.3E-06	0.59	1.06	0.016
	172 to 213	1.0E-04	1.6E-03	1.1E-02	1.5E-02	7.3E-03	2.2E-03	4.5E-04	4.3E-05	2.5E-06	1.0E-07	0.54	1.19	0.011
	0 to 30	9.5E-06	1.0E-04	6.2E-04	9.8E-04	8.2E-04	4.4E-04	1.3E-04	1.3E-05	7.7E-07	3.1E-08	0.67	0.86	0.021
LDW24 CC572	30 to 60	1.8E-05	2.4E-04	1.5E-03	2.3E-03	1.6E-03	6.5E-04	1.6E-04	1.6E-05	9.0E-07	3.6E-08	0.64	0.94	0.019
LDW21-SC572	60 to 105	3.0E-05	4.5E-04	3.1E-03	4.1E-03	2.2E-03	7.1E-04	1.5E-04	1.4E-05	8.0E-07	3.3E-08	0.56	1.14	0.036
	105 150	2.8E-05	3.9E-04	2.5E-03	3.7E-03	2.4E-03	9.3E-04	2.2E-04	2.2E-05	1.2E-06	5.0E-08	0.58	1.09	0.021
DAA 4/2/2/	Surface <sup>1</sup>	1.2E-05	1.2E-04	7.0E-04	1.1E-03	9.1E-04	6.2E-04	2.1E-04	2.1E-05	1.2E-06	5.0E-08	0.67	0.85	0.016
RAA 1/2/3 (maximum)	Subsurface <sup>2</sup>	7.7E-05	1.0E-03	6.6E-03	1.1E-02	8.5E-03	2.9E-03	5.9E-04	5.5E-05	3.2E-06	1.3E-07	0.65	0.92	0.015
DAA 1/2/2 (	Surface <sup>1</sup>	8.9E-06	1.0E-04	6.2E-04	9.3E-04	7.0E-04	3.8E-04	1.1E-04	1.1E-05	6.7E-07	2.7E-08	0.67	0.86	0.021
RAA 1/2/3 (average)	Subsurface <sup>2</sup>	5.4E-05	6.7E-04	4.2E-03	6.6E-03	5.2E-03	2.2E-03	5.6E-04	5.5E-05	3.2E-06	1.3E-07	0.61	1.01	0.015
DAA 44/45/46/	Surface <sup>1</sup>	7.0E-06	9.2E-05	6.1E-04	8.3E-04	4.9E-04	2.2E-04	6.2E-05	6.2E-06	3.6E-07	1.5E-08	0.60	1.03	0.015
RAA 14/15/16 (maximum)	Subsurface <sup>2</sup>	1.7E-04	2.5E-03	1.7E-02	2.4E-02	1.4E-02	4.1E-03	7.3E-04	6.6E-05	3.8E-06	1.5E-07	0.66	0.893	0.023
DAA 14/15/16/	Surface <sup>1</sup>	4.7E-06	6.4E-05	4.3E-04	5.8E-04	3.4E-04	1.4E-04	3.8E-05	3.8E-06	2.2E-07	8.9E-09	0.60	1.05	0.020
RAA 14/15/16 (average)	Subsurface <sup>2</sup>	5.3E-05	7.8E-04	5.3E-03	7.4E-03	4.3E-03	1.4E-03	2.9E-04	2.7E-05	1.6E-06	6.4E-08	0.63	0.96	0.026

#### Notes:

1. Generalized core profiles were configured to simulate the surface as 2 feet of cleaner sediment on top of the buried contamination (i.e., depth interval of 0 to 60 cm) as well as 1 foot of cleaner surface sediment (i.e., 0 to 30 cm).

2. The generalized core profiles were configured to have 60 cm of sediment beneath the surface. For the case where the surface interval is 60 to 120 cm. For the case where the surface represents the 1 foot of cleaner material, the subsurface interval is 30 to 90 cm.

μg/L: micrograms per liter
cm: centimeter
f<sub>oc</sub>: fraction organic carbon
g/cm³: grams per cubic centimeter
PCB: polychlorinated biphenyl
RAA: remedial action area

### 2.2 Buried Contamination Model Results

The purpose of this buried contamination modeling was to evaluate whether buried contamination has the potential to recontaminate surface sediments (0 to 10 cm) in the FNC to a concentration greater than the RAL in the future (i.e., over a 100-year simulation) through dissolved phase transport driven by groundwater seepage (as well as diffusion/dispersion and bioturbation). Conservatively, sedimentation was ignored in this evaluation, despite the fact that sedimentation in the FNC is ongoing, necessitating periodic maintenance dredging. Model-predicted concentrations in the top 10 cm (surface) of the sediment were compared to the surface RAL (0 to 10 cm) to evaluate whether buried contamination could result in RAL exceedances in the surface sediment within 100 years. PCB homologs were modeled separately to account for differences in transport properties and summed to calculate total PCB concentrations for comparison to the total PCB RAL of 12 mg/kg OC. Model-predicted total PCB concentrations in the top 10 cm of the sediment are shown in Table K2-2 for both Darcy flux values evaluated.

Table K2-2
Buried Contamination Model Results: Model-Predicted Concentrations in Top 10 cm of Sediment at Year 100

	Scenario			Propertie	?S			
		Surface Layer	Depth from Model Mudline Layer (feet)	Depth from	Initial Total PCB	Model-Predicted Surface Sediment (top 10 cm) Total PCB Concentration at Year 100 (mg/kg OC)		
Area	PCB Concentration Statistic Modeled	Thickness (feet)			Concentration (mg/kg OC)	100 cm/yr Darcy Flux	400 cm/yr Darcy Flux	
Specific Core	Profiles							
	A (-18 to -20 feet MLLW)		1	0–2	5.28			
	B (-20 to -21 feet MLLW)		2	2–3	42.8	3.5	3.7	
C 554	C (-21 to -22 feet MLLW)	2	3	3–3.7	11.0			
Core 554	D (-22 to -23 feet MLLW)	2	4	3.7–4.7	95.5			
	E (-23 to -24 feet MLLW)		5	4.7–5.7	690			
	F (-24 to -25 feet MLLW)		6	5.6–7	63.7			
	C (-17 to -18 feet MLLW)		1	3.6–4.6	7.93	5.7		
Core 572*	D (-18 to -19 feet MLLW)	2	2	4.6–5.6	13.8		6.0	
Core 572*	E (-19 to -20 feet MLLW)	2	3	5.6–6.6	19.2		6.0	
	G (-21 to -22 feet MLLW)		4	7.5–8.5	20.9			

	Scenario		Properties					
		Surface Layer		Depth from Mudline (feet)	Initial Total PCB	Model-Predicted Surface Sediment (top 10 cm) Total PCB Concentration at Year 100 (mg/kg OC)		
Area	PCB Concentration Statistic Modeled	Thickness (feet)	Model Layer		Concentration (mg/kg OC)	100 cm/yr Darcy Flux	400 cm/yr Darcy Flux	
Generalized C	ore Profiles							
	Martin	2	1	0–2	10.2	7.0	7.3	
	Maximum	2	2	2–4	64.6	7.0	7.3	
		1	1	0–1	10.2	6.9	7.6	
DAA 1/2/2	Maximum	1	2	1–3	64.6			
RAA 1/2/3	Average Average	2	1	0–2	6.97	4.9	5.1	
			2	2–4	44.2			
		1	1	0–1	6.97	4.9	5.2	
			2	1–3	44.2			
	Maximum	2	1	0–2	4.75	3.1	2.2	
	iviaximum	2	2	2–4	111		3.3	
	Maximum	1	1	0–1	4.75	2.4	4.0	
RAA	iviaximum	I	2	1–3	111	3.1	4.0	
14/15/16	Average	2	1	0–2	3.18	2.2	2.3	
	Average	2	2	2–4	36.2	2.2	2.3	
	Average	1	1	0–1	3.18	2.2	2.4	
	Average	1	2	1–3	36.2	2.2	2.4	

#### Notes:

Core 572 is within a shoal area and is a location within the FNC where the bed elevation is higher than the authorized navigation depth, Intervals A and B are shoal intervals and include sediment from elevation -13.4 to -17 MLLW; these shoal intervals did not exceed PCB RAL of 12 mg/kg OC.

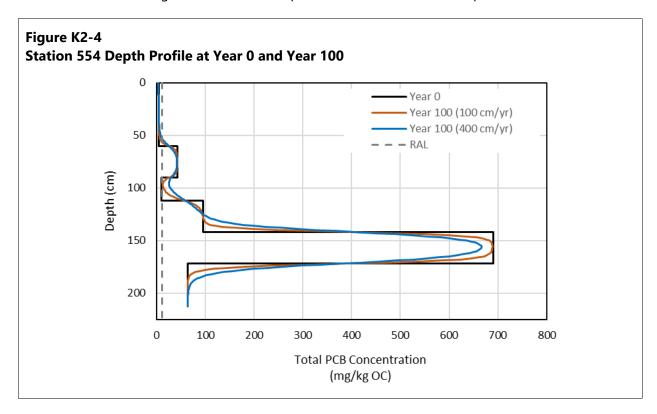
cm: centimeter OC: organic carbon

cm/yr: centimeters per year PCB: polychlorinated biphenyl mg/kg: milligrams per kilogram RAA: remedial action area MLLW: mean lower low water RAL: remedial action level



Model results in Table K2-2 show that PCB concentrations in the top 10 cm of the sediment are predicted to remain less than the surface RAL of 12 mg/kg OC for more than 100 years in all scenarios. Because buried contamination beneath 30 or 60 cm of sediment that is less than the surface RAL results in concentrations in the top 0 to 10 cm that remain below the surface RAL, these results also indicate that a 45-cm shallow subsurface layer that is less than the RALs would also result in the surface (top 10 cm) remaining below the surface RAL of 12 mg/kg OC for more than 100 years at groundwater seepage rates of 100 and 400 cm/yr. Because PCBs partition relatively strongly to sediments, they do not migrate quickly through the sediments in dissolved phase; therefore, contamination that is buried beneath cleaner sediment remains buried.

An example of this predicted lack of migration is shown for Core 554 in Figure K2-4. The black line represents the initial concentrations in sediment (Year 0). The orange and blue lines represent the concentrations predicted at Year 100 for the Darcy fluxes of 100 and 400 cm/yr, respectively. Although the PCBs are predicted to migrate upward to a very slight extent, the transport is not significant enough to impact the surface sediments. The model also predicts some smoothing of vertical concentrations gradients due to the processes of diffusion and dispersion.



## 2.3 Sensitivity Analyses

In addition to evaluating a range of concentrations and a range of Darcy fluxes, two additional sensitivity analyses were conducted. The first sensitivity analysis was conducted to predict the

maximum PCB concentration that could exist beneath the shallow subsurface in the FNC before resulting in a RAL exceedance in the surface (0 to 10 cm) sediment. The second sensitivity analysis evaluated the impact of sedimentation on the model results. These two sensitivity analyses are discussed in the following subsections.

### 2.3.1 Hypothetical Maximum Subsurface Concentration

Additional modeling was conducted to identify the maximum concentration that could exist in the LDW upper reach deep subsurface sediments before resulting in a RAL exceedance in surface (0 to 10 cm for intertidal and subtidal areas) and in the shallow subsurface (0 to 45 cm in the intertidal). Starting with the generalized core profiles from RAA 1/2/3, and assuming the maximum concentration in the shallow subsurface (10.2 mg/kg OC), the deep subsurface concentration represented in the model was increased iteratively until the total PCB concentration predicted in the surface sediment (top 10 cm) was just below the PCB RAL of 12 mg/kg OC and, in the intertidal area, a PCB RAL of 65 mg/kg OC in the shallow subsurface (0 to 45 cm). Generalized core profiles, assuming 2 feet (60 cm), 1.5 feet (45 cm), and 1 foot (30 cm) of sediment (below RAL concentrations) on top of the buried contamination, were evaluated. Darcy fluxes of 100 and 400 cm/yr were assumed in the subtidal areas, and Darcy fluxes of 400 and 800 cm/yr were assumed in the intertidal areas.

EPA's Estimation Programs Interface Suite for Microsoft Windows indicates a wide range of solubility limits for PCB Aroclor mixtures, although it could be as high as 100 micrograms per liter ( $\mu$ g/L) for the Aroclors detected in site sediments. The current maximum subsurface porewater total PCB concentration from the generalized core profiles evaluated (Area 1, 2, and 3 maximum) is 0.03  $\mu$ g/L; 100  $\mu$ g/L is just over 3,000 times the current maximum subsurface total PCB concentration from the generalized core profile). Thus, modeling did not consider total PCB porewater concentrations greater than 100  $\mu$ g/L, which corresponds to a dry weight concentration of almost 3,000  $\mu$ g/kg.

Consistent with the modeling discussed in Sections 2.1 and 2.2, sedimentation was ignored. Through this modeling, it was determined that, in the subtidal areas, PCB concentrations beneath the surface could be as high as 3,000 times the current maximum subsurface total PCB concentration from the generalized core profiles when assuming 100 cm/yr Darcy flux and 2 feet of sediment (not exceeding RALs) on top of the buried contamination. This concentration is close to solubility limits for Aroclor PCBs (i.e., theoretical maximum dissolved phase concentration). The maximum concentration that could be present in buried contamination was predicted to be 10 times greater than the current concentration when assuming the Darcy flux of 400 cm/yr and only 1 foot of cleaner sediment on top of the buried contamination, which is considered a worst-case scenario. In the intertidal area, the maximum PCB concentration that could be present in buried contamination was predicted to be 130 mg/kg OC assuming 1 foot of cleaner sediment on top of the buried contamination or 452 mg/kg OC assuming 1.5 feet of cleaner sediment on top of the buried contamination. The results are shown in Table K2-3.



Table K2-3
Results of Hypothetical Maximum Subsurface Concentration Sensitivity Analysis

Sediment Thickness Above		Subsurface Sediment Total PCB Concentration (mg/kg OC)				
Buried Contamination Interval <sup>1</sup>	Averaging Depth (cm)	100 cm/yr Darcy Flux <sup>2</sup>	400 cm/yr Darcy Flux	800 cm/yr Darcy Flux <sup>3</sup>		
		Subtidal Zone				
2 feet	0–10	>193,800 mg/kg OC (> 3,000X Area 1, 2, 3 Maximum Porewater)	>25,800 mg/kg OC (>400X Area 1, 2, 3 Maximum Porewater)	N/A		
1 foot	0–10	>38,800 mg/kg OC (>600X Area 1, 2, 3 Maximum Porewater) >650 mg/kg OC (>10X Area 1, 2, 3 Maximum Porewater)		N/A		
		Intertidal				
1.5 feet	0–10	N/A	>5,430 mg/kg OC (>84X Area 1, 2, 3 Maximum Porewater)	>711 mg/kg OC (>11X Area 1, 2, 3 Maximum Porewater)		
1.5 feet	0–45	N/A	>711 mg/kg OC (>11X Area 1, 2, 3 Maximum Porewater)	>452 mg/kg OC (>7X Area 1, 2, 3 Maximum Porewater)		
1 foot	0–10	N/A	>650 mg/kg OC (>10X Area 1, 2, 3 Maximum Porewater)	>194 mg/kg OC (>3X Area 1, 2, 3 Maximum Porewater)		
1 foot	0–45	N/A	>130 mg/kg OC (>2X Area 1, 2, 3 Maximum Porewater)	>130 mg/kg OC (>2X Area 1, 2, 3 Maximum Porewater)		

#### Notes:

Value in parenthesis is factor above maximum subsurface sediment concentration from RAA 1/2/3.

- 1. 2-foot thickness represents sediment above buried contamination in the subtidal zone. 1.5-foot thickness represents sediment above buried contamination in the intertidal zone. 1-foot thickness represents a hypothetical worst-case scenario, in which some removal of the cleaner surface material may have occurred.
- 2. 100 cm/yr Darcy flux not relevant to the intertidal areas.
- 3. 800 cm/yr Darcy flux not relevant to the subtidal areas.

cm: centimeter

cm/year: centimeters per year mg/kg: milligrams per kilogram

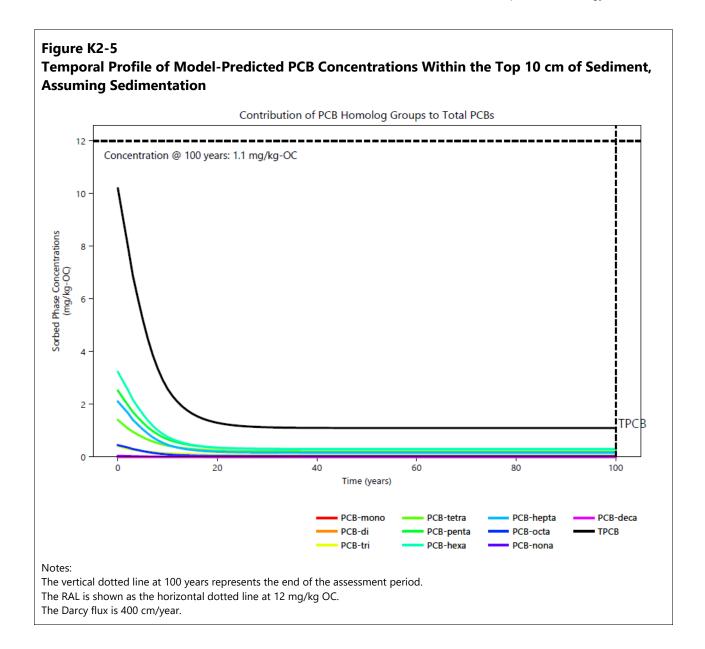
N/A: not applicable OC: organic carbon

PCB: polychlorinated biphenyl RAA: remedial action area

### 2.3.2 Sedimentation Sensitivity

The modeling discussed in Sections 2.1 and 2.2 ignored the effects of sedimentation. Although no sedimentation was assumed, based on feasibility study evaluations (AECOM 2012), it is expected that sedimentation will occur in the future. In addition, it is known that sedimentation occurs in the LDW upper reach. Therefore, a sensitivity analysis was conducted to evaluate the effects of sedimentation on the model results. Starting with the generalized core profile for RAA 1/2/3, using the maximum concentration in the surface and subsurface and a Darcy flux of 400 cm/yr, the modeling was repeated, with the inclusion of sedimentation. Sedimentation rates in intertidal and subtidal areas were estimated to range from 0.2 to greater than 2 cm/yr. Sedimentation rates in the LDW upper reach exceed 2 cm/yr (AECOM 2012). For this evaluation, a sedimentation rate of 1 cm/yr was assumed. The total PCB concentration of the depositing sediment was assumed to be 1.1 mg/kg OC for this sensitivity analysis. This is consistent with the incoming PCB concentrations measured upstream in the Green River (e.g., 20 micrograms per kilogram PCB and 1.8% TOC; Windward 2020).

Model results are shown in Figure K2-5. Model-predicted concentrations within the top 10 cm of the sediment decrease for approximately 20 years, until reaching a steady-state concentration of 1.1 mg/kg OC (i.e., the value specified for the depositing sediment). These results show that the exclusion of sedimentation from the base case modeling is conservative and that even a low amount of sedimentation would produce a situation in which the surface sediment concentrations are controlled by the concentrations of the depositing sediment and that upward transport from buried contamination would be negligible. If total PCB concentrations depositing on sediments in this area end up being greater than 1.1. mg/kg due to potentially uncontrolled PCB sources, then the surface sediments would equilibrate to those higher concentrations. This is an important consideration for setting expectations during long-term monitoring.



### 3 ENR/AC Pilot Area Evaluation

ENR consists of the placement of a thin cover layer of clean sand or sand/gravel atop contaminated sediment to accelerate natural recovery processes. ENR immediately provides a new surface substrate of clean sediments and reduces contaminant concentrations in surface sediments more quickly than would happen by natural sedimentation processes alone. Under order amendment with EPA and the Washington State Department of Ecology (Ecology), LDWG performed a pilot study (ENR/AC Pilot Study) to assess whether ENR material amended with activated carbon (AC) was more effective than ENR alone in reducing the bioavailability of PCBs in contaminated sediments of the LDW. Pilot study construction occurred in late 2016 through early 2017, and monitoring of three pilot study plots continued through 2020.

Results from 3 years of monitoring indicate that the application of ENR material alone resulted in decreases in baseline PCB bioavailability of approximately 90% or more in many cases (Wood et al. 2021). The study did not show measurable differences between ENR and ENR amended with AC, except for minor difference in intertidal plot. EPA and Ecology concluded there is no clear benefit in adding AC to ENR material in the LDW. Therefore, AC amendment was not included in ENR as part of the Pre-Final (90%) RD. Although the 3-year monitoring results are favorable, PCB concentrations in sediments beneath the placed ENR layer are greater than the upper limit for ENR in some samples of the intertidal plot. Therefore, contaminant transport modeling was conducted to evaluate the long-term effectiveness of the ENR layer in the ENR/AC Pilot area to maintain PCB concentrations in the surface sediments (top 10 cm) at levels less than the surface PCB RAL of 12 mg/kg OC.

## 3.1 ENR Model Inputs

The model was configured to simulate the cover material, as placed, which was, on average, 30 cm of sand/gravel overlying the surface sediment.

Chemical-specific properties (e.g., molecular diffusivity and OC partition coefficients), bioturbation properties (depth and biodiffusion coefficients), and reactions used in the ENR modeling were consistent with the values used for the buried contamination evaluations discussed in Section 2 and the cap modeling described in Appendix I of the BODR. As described in Appendix I of the BODR, the Darcy flux in the upper reach is estimated to average 400 cm/yr and range from 100 cm/yr in the center of the channel up to 800 cm/yr nearshore. The pilot study areas are located in different energy conditions and water depths, so the full range of Darcy fluxes (100 cm/yr to 800 cm/yr) was considered for these evaluations.

Human health RAOs are applied on an area-wide basis; therefore, the average PCB concentration in sediments beneath the cover material in the sand/gravel only pilot plots (41.9 mg/kg OC) was used



to represent the source of PCBs to the surface sediments in the modeling. Benthic RAOs are applied on a point-by-point basis; therefore, the maximum concentration (107 mg/kg OC, nearly 9 times the surface RAL) was also evaluated to demonstrate the effectiveness of ENR in this location, even though some sediment samples in the original surface concentrations exceeded the ROD ENR upper limit of 3 times the RAL. Pre-placement surface sediment concentrations within the pilot study areas and concentrations in the sediment immediately beneath the ENR cover material that were measured post-placement were used for this evaluation. The sediment PCB concentrations, fOC, and site-specific partition coefficients were used to estimate the porewater concentrations beneath the ENR layer (i.e., source term to the model), consistent with the cap design modeling presented in Appendix I of the BODR. A listing of PCB homolog concentrations used for model inputs is provided in Table K3-1.

Table K3-1
Porewater Concentrations Representing the Source Term for ENR Modeling

	Concentration of Porewater Beneath Cover (µg/L)				
Chemical Name	Average	Maximum			
PCB-Mono	1.2E-04	4.8E-05			
PCB-Di	1.6E-03	5.4E-04			
PCB-Tri	9.8E-03	2.5E-03			
PCB-Tetra	1.7E-02	5.4E-03			
PCB-Penta	1.5E-02	5.9E-03			
PCB-Hexa	5.0E-03	2.2E-03			
PCB-Hepta	9.8E-04	4.3E-04			
PCB-Octa	9.0E-05	3.9E-05			
PCB-Nona	5.1E-06	2.2E-06			
PCB-Deca	2.1E-07	8.9E-08			

Notes:

µg/L: micrograms per liter ENR: enhanced natural recovery PCB: polychlorinated biphenyl

### 3.2 ENR Model Results

Model-predicted PCB concentrations within the surface of the ENR Layer (0 to 10 cm) were compared to the total PCB surface RAL (12 mg/kg OC) throughout the 100-year simulations. Model results indicate that PCBs in the surface of the ENR layer are predicted to remain less than 12 mg/kg OC for more than 100 years for both the average and maximum concentrations measured beneath the ENR pilot area plot (both subplots) and for each of the three Darcy flux values simulated

(Table K3-2). Thus, the use of ENR in the ENR/AC pilot plot will be protective even for concentrations that exceed the ROD ENR upper limit.

Table K3-2
ENR Model Results: Model-Predicted Concentrations in Top 10 cm of ENR Layer Within ENR/AC Pilot Study Intertidal Plot at Year 100

	Measured PCB Concentrations in	Model-Predicted PCB Concentration in the Top 10 cm of the ENR Layer at Year 100 (mg/kg OC)				
Scenario	Sediment Beneath ENR Layer (mg/kg OC)	100 cm/yr Darcy Flux	400 cm/yr Darcy Flux	800 cm/yr Darcy Flux		
Average	41.9	0.07	1.3	3.7		
Maximum	107	0.25	4.0	11		

Notes:

cm: centimeter

cm/yr: centimeters per year ENR: enhanced natural recovery mg/kg: milligrams per kilogram

OC: organic carbon

PCB: polychlorinated biphenyl

The results of this evaluation ignore the impacts of future sedimentation. As described in Section 2.3.2, sedimentation, even at a modestly low rate, can have a large impact on the future surface sediment concentrations. Therefore, the results of this evaluation are conservative and represent a worst-case scenario. In addition, the ENR/AC Pilot Study intertidal plot area will be included in the long-term monitoring plan for the site.

# 4 Area-Specific Technology Evaluation of Cover in Dredge Offset Areas

At sample locations IT627 and SS646 (RAA 24/25/26), which are within dredge offset areas, an area-specific technology in the form of a sandy gravel cover will be applied to address PCB RAL exceedances.

Chemical fate and transport modeling was conducted to evaluate the composition (thickness and amendment needs, if any) of a cover to maintain PCB concentrations less than the surface PCB RAL of 12 mg/kg OC for more than 100 years at each of these two locations. The model was configured to simulate a 15-cm-thick sandy gravel cover overlying the surface sediment, which is considered a minimum cover thickness that would be applied. The simulations were conducted in an iterative manner, increasing the thickness of the cover, and adding a sorptive amendment in the form of TOC as necessary to meet the RAL long term. When simulating the addition of amendments to the cover, the amendment was assumed to be mixed throughout the full thickness of the cover.

### 4.1 Cover Model Inputs

Chemical-specific properties (e.g., molecular diffusivity and OC partition coefficients), bioturbation properties (depth and biodiffusion coefficients), and reactions used in the modeling of the sandy gravel cover were consistent with the values used for the cap modeling described in BODR Appendix I. Location-specific values were developed for porewater concentrations in the sediments beneath the cover (discussed in the next paragraph), and the porosity and bulk density of the cover material, which were assumed to be 0.35 and 1.69 grams per cubic centimeter (g/cm³), respectively, based on typical geotechnical characteristics of sand cover. As described in BODR Appendix I, the Darcy flux in the upper reach is estimated to average 400 cm/yr and range from 100 cm/yr in the center of the channel to 800 cm/yr nearshore. Locations IT627 and SS646 are located closer to shore, so Darcy fluxes of 400 cm/yr and 800 cm/yr were used for these evaluations.

The surface sediment concentrations measured in these areas were used to represent the source of PCBs to the cover. The sediment PCB concentrations, foc, and site-specific partition coefficients were used to estimate the porewater concentrations beneath the cover (i.e., source term to the model), consistent with the cap design modeling presented in BODR Appendix I. A listing of the PCB homolog porewater concentrations is provided in Table K4-1.

Table K4-1
Porewater Concentrations Representing the Source Term to the Cover in Dredge Offset Areas

	Concentration of Porewater Beneath Cover (µg			
Chemical Name	Location IT627	Location SS646		
PCB-Mono	1.1E-04	1.4E-04		
PCB-Di	1.0E-03	1.1E-03		
PCB-Tri	3.0E-03	3.0E-03		
PCB-Tetra	2.0E-02	1.9E-02		
PCB-Penta	3.2E-02	3.2E-02		
PCB-Hexa	1.1E-02	1.3E-02		
PCB-Hepta	1.6E-03	2.6E-03		
PCB-Octa	1.3E-04	2.4E-04		
PCB-Nona	7.3E-06	1.4E-05		
PCB-Deca	2.8E-07	5.4E-07		

Notes:

μg/L: micrograms per liter PCB: polychlorinated biphenyl

### 4.2 Cover Model Results

Model-predicted PCB concentrations within the surface of the cover (0 to 10 cm) were compared to the total PCB surface RAL (12 mg/kg OC) throughout the 100-year simulations. Table K4-2 shows the range of cover configurations (thickness and amendment content) and the time before the surface PCB RAL of 12 mg/kg OC is predicted to be exceeded for each configuration. Model results indicate that at both locations, a 12-inch cover with 1% TOC or a 6-inch cover with 1.5% TOC would be sufficient to maintain the PCB concentration in the surface of the cover at values less than 12 mg/kg OC for more than 100 years for both Darcy flux scenarios. Amendments such as granular activated carbon (GAC) could be added to the cover material to achieve the equivalent of 1% to 1.5% TOC within the cover, if necessary. GAC has been shown to be at least 10 times more sorptive than other sources of TOC for PCBs (Arp et al. 2009, Hale et al. 2010); therefore, a conservative minimum dose of 1% GAC by weight, to ensure even distribution of GAC throughout the cover, would provide greater sorptive capacity than the required 1% to 1.5% TOC. The results of this evaluation ignore the impacts of future sedimentation. As described in Section 2.3.2, sedimentation, even at a modestly low rate, can have a large impact on the future surface sediment concentrations. Therefore, the results of this evaluation are conservative and represent a worst-case scenario.

Table K4-2 ENR Model Results: Model-Predicted Concentrations in Top 10 cm of Cover Material at Year 100

	Measured PCB Concentrations in			Time to Exceed Surface PCB RAL of 12 mg/kg OC (years)		
Scenario	Sediment Beneath Cover (mg/kg OC)	Thickness of Cover (cm)	Amendment	400 cm/yr Darcy Flux	800 cm/yr Darcy Flux	
		15	None	87	41	
		15	1% TOC	>100	95	
IT627	191	15	1.5% TOC	>100	>100	
		30	None	>100	94	
		30	1% TOC	>100	>100	
		15	None	84	40	
		15	1% TOC	>100	95	
SS646	214	15	1.5% TOC	>100	>100	
		30	None	>100	94	
		30	1% TOC	>100	>100	

Notes:

cm: centimeter

cm/yr: centimeters per year mg/kg: milligrams per kilogram

OC: organic carbon

PCB: polychlorinated biphenyl RAL: remedial action level TOC: total organic carbon

### 5 Conclusions

Evaluations were conducted to evaluate transport potential of dissolved phase PCBs in areas of contamination buried beneath cleaner sediment, areas where thin layer of sand/gravel were placed over contaminated sediment as part of the ENR/AC Pilot Study, and dredge offset areas, where an area-specific technology in the form of a sandy gravel cover will be used. The results showed that for each of these scenarios, model-predicted PCB concentrations within the surface of the sediment or cover (0 to 10 cm) are expected to remain less than the surface RAL for more than 100 years.

The results of these evaluations ignore the impacts of future sedimentation. As described in Section 2.3.2, sedimentation, even at a modestly low rate, can have a large impact on the future surface sediment concentrations. Therefore, the results of this evaluation are conservative and represent a worst-case scenario. Further, should long-term monitoring results show areas with higher PCB concentrations within the surface, it should be considered that the elevated PCB concentrations may be due to sediments depositing on the sediments/cover material due to uncontrolled PCB sources rather than from chemical transport from subsurface layers.

### 6 References

- AECOM, 2012. Final Feasibility Study, Lower Duwamish Waterway. Submitted to EPA October 2012.
- Arp, H.P.H., G.D. Breedveld, and G. Cornelissen, 2009. "Estimating the In Situ Sediment-Porewater Distribution of PAHs and Chlorinated Aromatic Hydrocarbons in Anthropogenic Impacted Sediments." *Environmental Science & Technology* 43(15):5576-5585.
- EPA (U.S. Environmental Protection Agency), 1995. *Phase 2 Report Review Copy. Further Site Characterization and Analysis. Database Report.* Hudson River PCBs Reassessment RI/FS. Prepared by TAMS Consultants, Inc., for EPA, Region 2, New York. October 1995.
- EPA, 2014. *Record of Decision*. Lower Duwamish Waterway Superfund Site. United States Environmental Protection Agency Region 10. November 2014.
- Frame, G.M., J.W. Cochran, and S.S. Bøwadt, 1996. "Complete PCB Congener Distributions for 17 Aroclor Mixtures Determined by 3 HRGC Systems Optimized for Comprehensive, Quantitative, Congener-Specific Analysis." *Journal of High Resolution Chromatography* 19(12):657–668.
- Go, J., D.J. Lampert, J.A. Stegemann, and D.D. Reible, 2009. "Predicting Contaminant Fate and Transport in Sediment Caps: Mathematical Modeling Approaches." *Applied Geochemistry* 24(2009):1347–1353.
- Hale, S.E., S. Kwon, U. Ghosh, D. Werner, 2010. "Polychlorinated Biphenyl Sorption to Activated Carbon and the Attenuation Caused by Sediment." *Global NEST Journal* 12(3):318–326.
- Lampert, D.J. and D. Reible, 2009. "An Analytical Modeling Approach for Evaluation of Capping of Contaminated Sediments." *Soil and Sediment Contamination: An International Journal* 18(4):470–488.
- Palermo, M., S. Maynord, J. Miller, and D. Reible, 1998. *Guidance for In-Situ Subaqueous Capping of Contaminated Sediments*. EPA 905-B96-004, Chicago: Great Lakes National Program Office.
- Reible, D., 2017. *CapSim 3.5 Quick-Start Manual*. Available at: https://www.depts.ttu.edu/ceweb/groups/reiblesgroup/downloads/CapSim%203.6%20Quick%20Start%20Manual.docx.
- Rushneck D.R., A. Beliveau, B. Fowler, et al., 2004. "Concentrations of Dioxin-Like PCB Congeners in Unweathered Aroclors by HRGC/HRMS Using EPA Method 1668A." *Chemosphere* 54:79–87.
- Schulz-Bull, D., G. Petrick, and J.C. Duinker, 1989. "Complete Characterization of PCB Congeners in Commercial Aroclor and Clophen Mixtures by Multidimensional Gas Chromatography–Electron Capture Detection." *Environmental Science and Technology* 23(7):852–859.



- Shen, X., D. Lampert, S. Ogle, and D. Reible, 2018. "A Software Tool for Simulating Contaminant Transport and Remedial Effectiveness in Sediment Environments." *Environmental Modelling and Software* 109:104–113. DOI: 10.1016/j.envsoft.2018.08.014.
- Windward (Windward Environmental, LLC), 2020. Lower Duwamish Waterway Pre-Design Studies Data Evaluation Report (Task 6). Prepared for Lower Duwamish Waterway Group. June 26, 2020.
- Wood (Wood Environment & Infrastructure Solutions, Inc.), Ramboll, Floyd|Snider,
  Geosyntec Consultants, and Integral Consulting), 2021. Final Year 3 Monitoring Report,
  Enhanced Natural Recovery/Activated Carbon Pilot Study. Lower Duwamish Waterway.
  Prepared for U.S. Environmental Protection Agency Region 10 and The Washington State
  Department of Ecology, Northwest Regional Office. October 2021.