

APPENDIX B  
CHEMICAL ISOLATION CAP DESIGN

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## LIST OF ACRONYMS AND ABBREVIATIONS

$\mu\text{g}/\text{kg}$	micrograms per kilogram
$\mu\text{g}/\text{L}$	micrograms per liter
B(a)A	benz(a)anthracene
B(a)P	benzo(a)pyrene
CAP	Cleanup Action Plan
cm	centimeter
cm/day	centimeters per day
cm/hr	centimeters per hour
cm/yr	centimeters per year
$\text{cm}^2/\text{s}$	square centimeters per second
$\text{cm}^2/\text{yr}$	square centimeters per year
Corps	U.S. Army Corps of Engineers
cPAH	carcinogenic polycyclic aromatic hydrocarbon
EDR	Engineering Design Report
foc	fraction organic carbon
$\text{g}/\text{cm}^3$	grams per cubic centimeter
$K_d$	chemical-specific equilibrium partition coefficient
$K_{oc}$	organic carbon partition coefficient
L/kg	liters per kilogram
MLLW	mean lower low water
MTCA	Model Toxics Control Act
ng/kg	nanograms per kilogram
SMA	Sediment Management Area
TEF	toxicity equivalency factor
TEQ	toxic equivalents quotient
TOC	total organic carbon
USEPA	U.S. Environmental Protection Agency
$\text{yr}^{-1}$	per year

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## 1 INTRODUCTION

This appendix describes design analyses for in situ chemical isolation and containment (i.e., capping) to ensure that surface cap materials that overlie contaminated sediments and/or buried creosote-treated piles that may remain in the former Port Gamble Bay wharf area (i.e., piles that cannot be practicably removed) are maintained below site-specific sediment cleanup levels. These analyses were performed in accordance with U.S. Environmental Protection Agency (USEPA) and U.S. Army Corps of Engineers (Corps) *Guidance for In-Situ Subaqueous Capping of Contaminated Sediments* (Palermo et al. 1998).

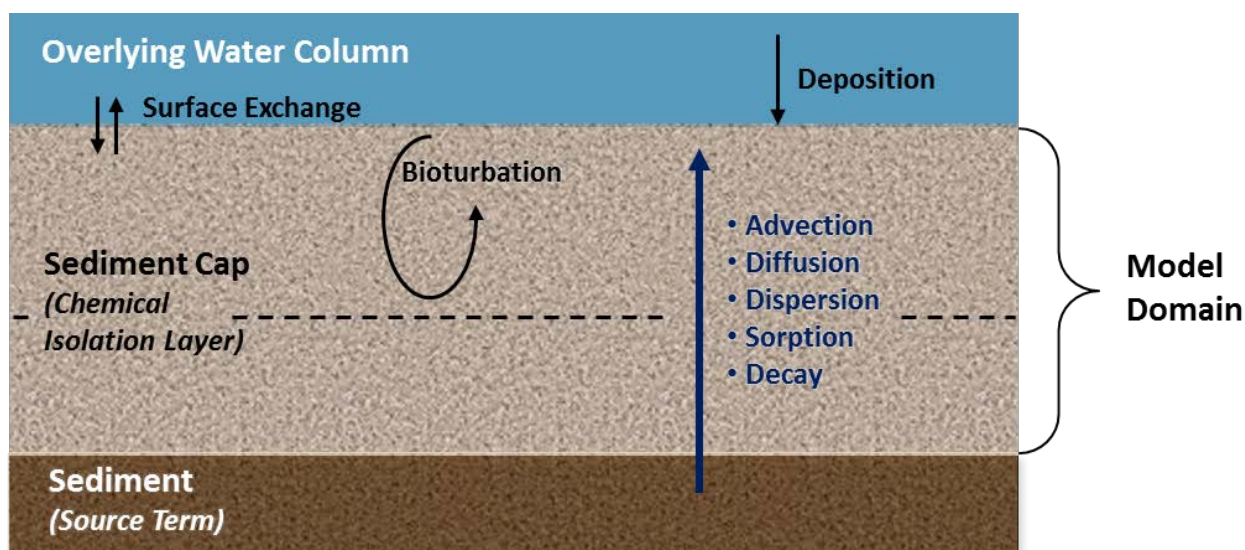
The primary goal of the cap design analyses described herein was to simulate the transport of carcinogenic polycyclic aromatic hydrocarbons (cPAHs) within the chemical isolation layer of sediment caps and to use the model to evaluate the long-term effectiveness of engineered caps to maintain concentrations within the upper 2 feet of sediments below 16 micrograms per kilogram ( $\mu\text{g}/\text{kg}$ ) toxic equivalents quotient (TEQ), the site-specific sediment cleanup level for Port Gamble Bay (“Site”) set forth in the *Final Cleanup Action Plan* (CAP; Ecology 2013a). In addition, although they were not identified in the CAP as a primary chemical of concern for human health, modeling evaluations were also performed to ensure that sediment caps at the Site are also protective with respect to dioxins/furans detected in adjacent nearshore sediments and soils at the former sawmill site, again to maintain concentrations within the upper 2 feet of sediments below the site-specific sediment cleanup level for dioxins/furans of 5 nanograms per kilogram ( $\text{ng}/\text{kg}$ ) TEQ, as set forth in the CAP.

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## 2 APPROACH

Consistent with current USEPA (2005) Superfund guidance, this cap design evaluation used the one-dimensional models of chemical transport within sediment caps developed by Dr. Danny Reible (currently at Texas Tech University). There are two versions of the Reible cap model: one uses a steady-state analytical solution to the governing equations and the other is a numerical model that simulates transient (time-variable) conditions. The theory and governing equations for the steady-state model were published by Lampert and Reible (2009; see also Reible 2012). The theory and solution techniques associated with the transient numerical model are documented in Go et al. (2009). Details on the model structure and underlying theory and equations are provided by Lampert and Reible (2009) as well as in the USEPA/Corps capping guidance (Palermo et al. 1998; USEPA 2005). These models have been used to support the evaluation and design of sediment caps at numerous Superfund sediment cleanup sites throughout the United States, and have also recently been used at several Model Toxics Control Act (MTCA) cleanup sites in Washington.

The Reible model simulates the fate and transport of chemicals (dissolved and sorbed phases) under the processes of advection, diffusion, dispersion, biodegradation, bioturbation, and exchange with the overlying surface water, as generally depicted on Figure B-1.



**Figure B-1**  
**Model Domain, Cap Configuration, and Processes Simulated**

The goal of the modeling was to design a cap that would maintain concentrations of cPAHs and dioxin/furan TEQ below the sediment cleanup standards long-term (defined as greater than 1,000 years for this evaluation). To achieve this goal, the evaluation of cap performance consisted of a two-phased modeling approach. The initial evaluation was based on analytical steady-state modeling. Steady-state predictions provide a useful means of assessing long-term contaminant profiles within a subaqueous cap, although the time to reach the steady-state concentrations will vary depending on the chemical characteristics of the contaminant, sediment geochemical conditions, and subsurface hydrogeology. Steady-state predicted surface contaminant concentrations maintained below the sediment cleanup levels at steady-state, indicate the cap is effective in perpetuity and the second phase of the modeling approach was not necessary. Caps resulting in concentrations that may exceed the cleanup level at steady-state were subsequently evaluated under the second phase of the modeling, which consisted of repeating the simulations using the transient numerical model to evaluate long-term effectiveness under transient conditions. If necessary, cap designs were modified to ensure that caps were protective for at least 1,000 years.

For the purposes of optimizing the cap design, the Site was divided into two zones, based on differences in cPAH concentrations. The areas that contain creosote-treated piles at the Site (referred to herein as the Piling Zone) are characterized by higher cPAH concentrations and are therefore anticipated to require a more robust cap design. The remaining Site sediments that do not contain creosote-treated piles (referred to herein as the Non-Piling Zone) contain lower cPAH concentrations. Since intertidal sediment and nearshore soil cPAH and dioxin/furan TEQ concentrations are similar across Sediment Management Area (SMA)-1 and SMA-2, the Non-Piling Zone was evaluated on a SMA-wide basis.

As discussed in Sections 6.4 and 7.4 of the accompanying Engineering Design Report (EDR), the cap designs evaluated herein are configured as follows:

- Non-Piling Zone: A 2-foot-thick layer consisting of a mixture of sand, gravel, and cobble, similar to the existing sediment substrate present in the former wharf area. These cap materials provide physical separation from underlying sediments, and also limit diffusive flux of chemicals by reducing the concentration gradient within the cap, improving cap effectiveness.

- **Piling Zone:** To ensure the protectiveness of caps that are overlying buried creosote-treated piles that cannot be practicably removed, the Piling Zone cap also includes a layer containing an adsorptive amendment in the form of bulk sand blended with organoclay (50% by weight organoclay). That layer will underlie a 2-foot layer of sand, gravel, and cobble consistent with that described for the Non-Piling Zone.

Based on discussions with the Washington State Department of Ecology, for sediments within the SMA-1 and SMA-2 intertidal areas, the point of compliance with site-specific sediment cleanup standards is the top 2 feet of the cap. The model was used to evaluate the effectiveness of the above chemical isolation cap designs to maintain surface cPAH and dioxin/furan TEQ concentrations below sediment cleanup levels on a long-term basis, which for the purpose of this evaluation was defined as more than 1,000 years.

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### 3 MODEL INPUTS

The Reible models summarized above use several input parameters that describe site-specific conditions, chemical-specific properties, cap material properties, and chemical mass transport rates. These input parameters were based on site-specific data, information from literature, and cap designs successfully constructed at other similar sites. Details on several key input parameters are provided in Sections 3.1 through 3.4, and a full listing of model inputs is provided in Table B-1. The same inputs were used for the steady-state modeling and transient modeling, except where otherwise noted.

#### 3.1 Partitioning

Partitioning of contaminants between porewater and sorbed (cap material) phases is described in the Reible models (Lampert and Reible 2009; Reible 2012) by a chemical-specific equilibrium partition coefficient ( $K_d$ ), using the customary  $K_d = f_{oc} * K_{oc}$  approach, where  $K_{oc}$  is the compound's organic carbon partition coefficient and  $f_{oc}$  is the organic carbon content of the cap material. For this analysis, the average cPAH  $K_{oc}$  was calculated based on the relative contributions of the PAH compounds that contribute to cPAH TEQ in creosote-treated piles, primarily benz(a)anthracene (B[a]A;  $K_{oc}$  of  $10^{5.55}$  liters per kilogram [L/kg]) and benzo(a)pyrene (B[a]P;  $K_{oc}$  of  $10^{5.98}$  L/kg; Parametrix 2011; Ecology 2013b, Table 747-1). The resulting effective cPAH  $K_{oc}$  used in the cap design model was  $10^{5.90}$  L/kg. The  $K_{oc}$  for individual dioxin/furan congeners detected in SMA-1 and SMA-2 intertidal sediments and nearshore soils was based on the octanol-water partition coefficients ( $K_{ow}$ ) reported in USEPA's KOWWIN database (USEPA 2013), converted to  $K_{oc}$  using the relationship developed by Di Toro (1985).

For the sorptive organoclay amendment incorporated into the Piling Zone cap,  $K_d$  values were based on laboratory studies of the adsorption of PAHs onto organoclay (Reible et al. 2011). For modeling the organoclay-amended sand layer in the Piling Zone, the  $K_d$  of the cPAH was calculated as a function of the compound's  $K_{ow}$  (USEPA 2003), using the relationship shown in Equation B-1. This equation accounts for the percent by dry weight of organoclay within the bulk mixture (which essentially ignores the sorptive capacity of the sand in the mixture).

$$\log K_d = \%Organoclay * (1.20 * \log K_{ow} - 0.467) \quad (B-1)$$



### 3.2 Underlying Porewater Concentrations

Porewater chemical concentrations underlying the cap based on site-specific data in the Piling Zone and were calculated from partitioning theory using the average sediment chemical concentrations in the Non-Piling Zone, as follows:

- cPAHs in the Piling Zone: Parametrix (2011) conducted studies of leached cPAH concentrations from piles that are considered representative of a cut pile face exposed to water. Based on data from those studies at 7°C and a 96- to 336-hour exposure period (Parametrix 2011, Table 3), a cPAH TEQ concentration of 54 micrograms per liter (µg/L) was selected for model simulations of the Piling Zone.
- cPAHs in the Non-Piling Zone: Based on the pre-design sampling data (see Appendix A, Attachment 3 of the EDR), subsurface intertidal sediments and adjacent nearshore soils in SMA-1 and SMA-2 that are not influenced by the creosote-treated piles have an average cPAH TEQ concentration of approximately 280 µg/kg and an average total organic carbon (TOC) content of 1.48% (dry weight basis). The calculated equilibrium partitioning porewater cPAH TEQ concentration based on these values is 0.02 µg/L.
- Dioxins/furans in the Non-Piling Zone: Based on the pre-design sampling data (Appendix A, Attachment 3 of the EDR), subsurface intertidal sediments and adjacent nearshore soils in SMA-1 and SMA-2 have an average (congener-weighted) dioxin/furan TEQ concentration of approximately 36 ng/kg and an average TOC content of 1.48% (dry weight basis). The calculated toxicity equivalency factor (TEF)-weighted equilibrium partitioning porewater dioxin/furan TEQ concentration is 1.5E-07 µg/L.

These values were used as the (infinite source) porewater concentration directly beneath the cap in the model.

### 3.3 Groundwater Velocity

The groundwater velocity used in the cap model design calculations was calculated using the DuPuit solution<sup>1</sup> for steady-state unconfined flow (Fetter 2001), based on hydraulic conductivity and hydraulic head measurements from upland wells at the Site, as shown in Equation B-2:

$$q' = \frac{1}{2}K \left( \frac{h_1^2 - h_2^2}{L} \right) \quad (\text{B-2})$$

where:

- $q'$  = flow per unit width
- $K$  = hydraulic conductivity (68 feet/day based on mid-point measured in the upper sand/gravel aquifer at the former mill site; Anchor QEA and EPI 2012)
- $h_1$  = average saturated thickness of 18.4 feet overlying the silt aquitard (based on the top elevation of the aquitard being at -10 feet mean lower low water [MLLW]) at upland well MW-4 (Anchor Environmental and EPI 2008)
- $h_2$  = average saturated thickness of 16.1 feet overlying the silt aquitard at the shoreline (Anchor Environmental and EPI 2008)
- $L$  = horizontal distance of 190 feet between MW-4 and the mid-point of groundwater discharge into the shoreline area (i.e., the seepage face is present from +6 to -10 feet MLLW based on site-specific porewater sampling in the former wharf area; Attachment 2 of Appendix A of the EDR)

The flow per unit width calculated by the DuPuit solution was converted to a Darcy velocity (i.e., flow per unit area) by considering that groundwater in the wharf area discharges along approximately 60 linear feet of the exposed water-bearing sand unit along the

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<sup>1</sup> The DuPuit solution is analogous to the well-known Darcy's Law, with the difference being that Darcy's Law is applicable to confined flow conditions and the DuPuit solution is applicable to unconfined flow conditions (Fetter 2001).

intertidal/shallow subtidal beach (average slope = 3.5H:1V), below the average tidal water level, and above the silt aquitard. The resulting calculated average groundwater Darcy velocity in the wharf areas used in the cap design modeling was 0.23 foot/day (7.1 centimeters per day [cm/day]).

### 3.4 Dispersion and Surface Exchange

The surface exchange coefficient and dispersivity values used in the cap design modeling were obtained from the literature to represent the large degree of tidal mixing that occurs at the Site driven by the large tidal range and relatively porous surface sediments that characterize the wharf area (which are also similar to the cap design specification). Based on site-specific porewater sampling performed in the former wharf area (Attachment 2 of Appendix A of the EDR), relatively large fluctuations of near-surface (2 feet below the sediment surface) porewater salinity (e.g., from 15 to 30 parts-per-thousand) occur over a tidal cycle, indicating a large degree of porewater exchange with the overlying surface water. Thus, the values selected for the dispersion and surface exchange coefficients in the model were reflective of this observed mixing, as follows:

- A surface exchange coefficient of 2 centimeters per hour (cm/hr) was used for the cap design modeling, based on upper-end of the range of values measured in laboratory and other (non-tidal) field sites, which are in the range of 0.01 to 2 cm/hr (e.g., Thibodeaux et al. 2001; Erickson et al. 2005). This value is appropriate, and likely conservative, given the large tidal range and associated exchange with surface water observed at the Site.
- The dispersivity value used to model contaminant transport in porous media at the Site was 50% of the model domain length, which is at the high end of the range for modeling transport in groundwater (e.g., Gelhar et al. 1985), again reflecting the relatively high tidal exchange in the Site area. Representing tidal mixing with an increased dispersion coefficient is a common approach in groundwater modeling (e.g., La Licata et al. 2011).

The selected values for dispersion and surface exchange coefficients are consistent with those used for cap design modeling at other sites with a similarly large degree of tidal mixing.

### 3.5 Input Parameter Summary

Input parameter values used for the cap design modeling and the source(s) from which they were derived are provided in Table B-1.

**Table B-1**  
**Input Parameter Values for the Chemical Isolation Cap Model**

Model Input Parameter	Value	Data Source
<b>Chemical-specific Properties</b>		
cPAH $K_{oc}$ (L/kg)	$10^{5.9}$	cPAH TEQ weighted average $K_{oc}$ from B(a)A and B(a)P (Ecology 2013b, Table 747-1; Parametrix 2011)
Dioxin/furan $K_{oc}$ (L/kg)	$10^{7.2}$	Dioxin/furan TEF weighted average $K_{oc}$ based on $K_{ow}$ reported in USEPA's KOWWIN database (USEPA 2013) converted to $K_{oc}$ by relationship developed by Di Toro (1985)
cPAH $K_{ow}$ (L/kg)	$10^{6.0}$	cPAH TEQ weighted average $K_{ow}$ from B(a)A and B(a)P (USEPA 2003)
cPAH Water diffusivity ( $cm^2/s$ )	$5.7E-06$	Calculated based on the molecular weight of B(a)A using the correlation identified by Schwarzenbach et al. (1993)
Dioxin/furan water diffusivity ( $cm^2/s$ )	$4.3E-06$	Calculated based on the TEF-weighted average molecular weight of dioxins/furan congeners using the correlation identified by Schwarzenbach et al. (1993)
Chemical biodegradation rate ( $yr^{-1}$ )	0	No degradation assumed (i.e., conservative assumption) for both cPAH and dioxins/furans
Underlying cPAH porewater concentration ( $\mu g/L$ )	Piling Zone: 54 Non-Piling Zone: 0.02	Piling Zone: cPAH concentrations calculated from Parametrix (2011) piling leaching study (see Section 3.2) Non-Piling Zone: Average porewater concentration based on sediment B(a)A and B(a)P concentrations measured in Puget Sound creosote-treated piles (Parametrix 2011) and in subsurface intertidal sediments and adjacent nearshore soils in SMA-1 and SMA-2 (Appendix A, Attachment 3 of the EDR), and equilibrium partitioning calculations (see Section 3.2)
Underlying Dioxin/Furan porewater concentration ( $\mu g/L$ )	$1.5E-07$	Average porewater concentration based on sediment concentrations measured in subsurface intertidal sediments and adjacent nearshore soils in SMA-1 and SMA-2 (Appendix A, Attachment 3 of the EDR), and equilibrium partitioning calculations (see Section 3.2)

Model Input Parameter	Value	Data Source
<b>Cap Properties</b>		
Cap thickness (cm)	Non-Piling Zone: 60.96  Piling Zone: 91.44	2 feet of sand and gravel in the Non-Piling Zone  0.5 foot of bulk sand/organoclay overlain by 2 feet of sand and gravel in the Piling Zone
Isolation Layer Amendment Content (% by weight)	50%	Piling Zone
Particle density (g/cm <sup>3</sup> )	2.6	Typical value for sand and gravel particles (e.g., Domenico and Schwartz 1990)
Porosity	0.4	Typical value for sand and gravel cap materials (e.g., Parsons and Anchor QEA 2012)
Bioturbation zone thickness (cm)	60.96	CAP (Ecology 2013). This value is considered conservative because the existing sediments and the cap surface consist of relatively coarse sand, gravel, and cobble material, which limits the extent of bioturbation
f <sub>oc</sub> of bioturbation zone (%)	0.02	Typical value for sand and gravel cap material
<b>Mass Transport Properties</b>		
Boundary layer mass transfer coefficient (cm/hr)	2	Literature value reflecting tidal exchange at the Site (see Section 3.4)
Groundwater seepage Darcy velocity (cm/day)	7.1	Calculated using DuPuit solution (see Section 3.3)
Depositional velocity (cm/yr)	0	Assumed no net sedimentation (i.e., conservative assumption)
Dispersion length (% of domain length)	50	Value reflecting tidal exchange at the Site (see Section 3.4)
Biodiffusion coefficients (cm <sup>2</sup> /yr)	100 (porewater) 1 (particle)	Parameters represent bioturbation rates applied to dissolved phase (porewater) and particulate phase in the model; values are typical values used for capping design (e.g., Reible 2012)

## Notes:

µg/L – micrograms per liter

B(a)A – benz(a)anthracene

B(a)P – benzo(a)pyrene

CAP – Cleanup Action Plan

cm – centimeter

cm/day – centimeters per day

cm/hr – centimeters per hour

cm/yr – centimeters per year

cm<sup>2</sup>/s – square centimeters per second

cm<sup>2</sup>/yr – square centimeters per year

cPAH – carcinogenic polycyclic aromatic hydrocarbon

f<sub>oc</sub> – organic carbon content

g/cm<sup>3</sup> – grams per cubic centimeter

K<sub>oc</sub> – organic carbon partition coefficient

L/kg – liters per kilogram

TEQ – toxic equivalents quotient

TOC – total organic carbon

yr<sup>-1</sup> – per year

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## 4 MODEL RESULTS

The results of the steady-state and transient modeling are summarized below.

- cPAH in Non-Piling Zone: Results of the steady-state model reveal that subsurface (below cap) groundwater inputs will result in long-term cPAH TEQ concentrations in the top 2 feet of the SMA-1 and SMA-2 intertidal sediment caps of approximately 3 µg/kg, well below the 16 µg/kg site-specific cleanup standard.
- Dioxin/Furan in Non-Piling Zone: Results of the steady-state model reveal that subsurface (below cap) groundwater inputs will result in long-term dioxin/furan TEQ concentrations in the top 2 feet of the SMA-1 and SMA-2 intertidal sediment caps of approximately 0.3 ng/kg, well below the 5 ng/kg site-specific cleanup standard.
- cPAH in Piling Zone: Results of the transient model reveal that placing 6 inches of sand amended with 50% organoclay (by weight) above cut creosote-treated piles (i.e., those that cannot be practicably removed) and below the sand/gravel cap, will maintain cPAH TEQ concentrations in the top 2 feet of the SMA-1 and SMA-2 intertidal sediment caps below the 16 µg/kg site-specific sediment cleanup standard for greater than 1,000 years.

These model results verify the protectiveness of the chemical isolation cap designs for both the Non-Piling and Piling Zones for Site chemicals of potential concern (cPAHs and dioxins/furans).

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