Use of a Risk-Based Hydrogeologic Model To Set Remedial Goals for PCBs, PAHs, and TPH in Soils during Redevelopment of an Industrial Site

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One focus of approaches to developing cleanup levels for soils has been to protect groundwater from infiltrating that transports contaminants from overlying soils. During redevelopment of an industrial site along a Puget Sound shoreline, a hydrogeologic model was used in a risk-based, site-specific approach to set cleanup levels for subsurface soil chemicals that are protective of exposures of marine organisms to groundwater that has surfaced in waters of the Sound. Remedial goals for polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and total petroleum hydrocarbon (TPH) in subsurface soils were identified to protect marine receptors and their consumers. State and federal marine water quality criteria, or surrogate values, were the starting points in the model, and corresponding concentrations of chemicals in groundwater beneath the site were back-calculated through a hydrogeologic model. The model included a mixing zone component in the receiving bay and dilution/attenuation factors along the groundwater transport pathway that were determined from onsite groundwater and surface water chemical ion concentrations. A rearranged Summers equation was then applied to groundwater concentrations in a second back-calculation to determine corresponding chemical concentrations in subsurface soils. The Summers equation was based on calculated aquifer flow rates for the local watershed and rates of infiltration, calculated by the HELP model, for various surface cover materials. Concrete, asphalt, ballast, and a landfill geomembrane were modeled as soil surface cover material, which were planned to prevent direct contact with surface soils and attenuate infiltrating surface water. Results of the risk-based hydrogeologic model indicate that, depending on type of soil cover after site remediation, concentrations in subsurface soils of PCBs ranging from 2 to 1000 mg/kg, PAHs from 448 mg/kg for chrysene to saturation levels for less water soluble compounds, and TPH from 28 000 mg/kg to saturation concentrations would not result in risks to marine organisms or their consumers in the receiving water of Puget Sound.

Introduction

A major effort has been initiated in recent years to clean up and redevelop underused or abandoned industrial sites. Although many of these sites are not severely contaminated, state regulations for clean up of total petroleum hydrocarbon (TPH) in soils and groundwater frequently slow the process of regulatory approval, or private financing, for site cleanup and redevelopment. Recently, U.S. EPA funded the Brownfields Redevelopment Program (*1*) to help local agencies and industries develop conceptual and methodological approaches to clean up sites contaminated with industrial chemicals, particularly polychlorinated biphenyls (PCBs) and petroleum hydrocarbons measured as TPH. Several other organizations and government agencies are developing guidance to address issues related to environmental releases of petroleum chemicals (*2–4*).

A variety of approaches to developing cleanup levels (i.e., remedial action objectives) for soils has been compiled by U.S. EPA (*5*), and recent guidance (*6*, *7*) recommends numerous considerations for setting soil cleanup levels depending on site characteristics and overall site remediation goals. A major focus of most of these approaches is on protecting groundwater from contaminant transport from overlying soils via infiltrating water from the surface. For example, the Washington Department of Ecology (Ecology) in the past has recommended applying a factor of 100 to human health-based groundwater cleanup criteria to calculate cleanup levels for soils that are protective of underlying groundwater (*8*). This approach is similar to the dilution-attenuation factor (DAF) approach recommended by U.S. EPA for screening evaluations of soil contamination (*6*). More recent efforts by Ecology to develop soils standards for TPH include the surrogate chemical approach for fate and transport modeling (*4*) and the use of the narcosis model for developing standards for protection of surface water (*9*).

At an industrial site along the shoreline of Elliott Bay, Puget Sound, we developed a hydrogeologic model for use in a risk-based, site-specific approach to setting cleanup action levels for subsurface soil chemicals that are protective of exposures to subsequently contaminated groundwater. Specifically, the remedial goal that drove model design was to mitigate risks to receptors exposed to contaminated groundwater after it surfaces in marine waters of Puget Sound.

Site Description. The Port of Seattle is developing industrial property in the Duwamish River estuary along the shoreline of Elliott Bay (Figure 1) to expand existing container terminal facilities as part of the Southwest Harbor Project (SWHP). The site (105 acres) was operationally divided into four areas (Figure 2). Remediation area (RA) 1 consists of several small light industries and a railyard contaminated with petroleum-related chemicals. Remediation area 2 consists of a steel plant and assembly yard, contaminated with PCBs and slag from the steel plant. Remediation area 3 consists of an abandoned municipal landfill and a scrap metal recycling yard. The municipal landfill has been present for more than 50 years and inactive for over 25 years. The landfill and yard contain slag and other waste material from the steel plant, which is likely the source of metals and PCBs in soils and groundwater. Remediation area 4, a CERCLA

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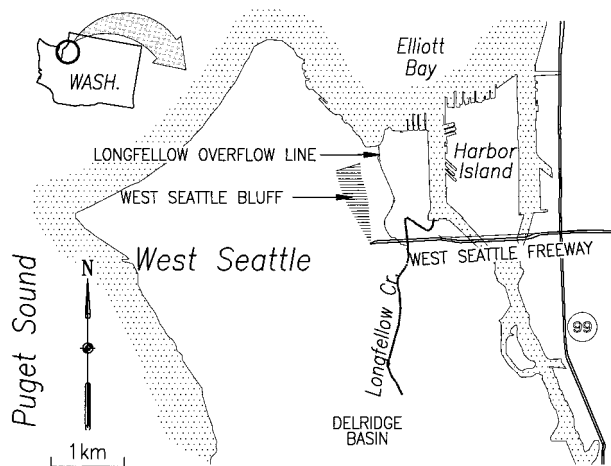§ Floyd & Snider, Inc.
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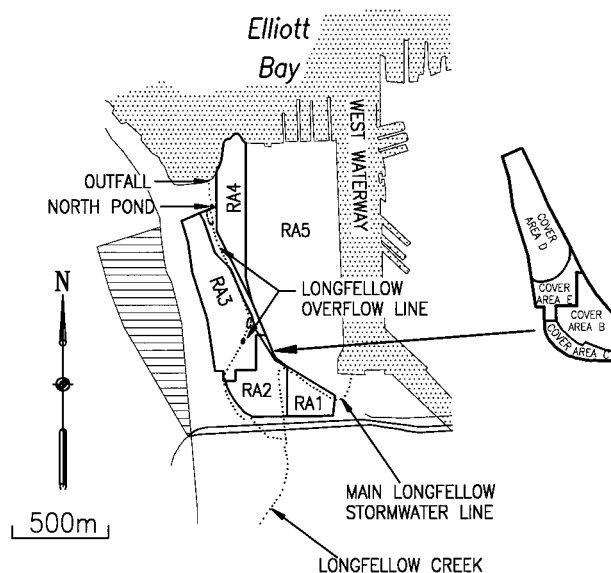
FIGURE 1. Site vicinity map.

FIGURE 2. Locations of remediation areas and soil covers. Soil cover locations (cover areas B, C, D, E) are shown for Remediation areas (RA) 2 and 3.

Superfund site, is a recently closed wood-treating facility contaminated with petroleum-related chemicals and metals in the area hydrologically connected to RAs 1, 2, and 3, and with pentachlorophenol in other areas. Remediation area 5 has undergone cleanup and is a covered area.

Although PAHs and TPH have been measured in soils and groundwater throughout much of the site, BETX chemicals (i.e., benzene, ethylbenzene, toluene, and xylenes) have not been observed. Soils at each of the four areas are being covered with various materials as part of the redevelopment plans for the site. Soil cover material consists of asphalt, concrete, and ballast, and a low permeable membrane cover for the landfill. The type of soil covers and their permeability to infiltrating surface water are critical components of the subsurface soil model.

Risk-Based Cleanup Approach. Remediation areas 1, 2, and 3 were investigated under Washington State's Model Toxics Control Act (MTCA) under guidance from Ecology. A risk assessment was performed on a site-wide basis for RAs 1, 2, and 3 to demonstrate the mitigation of risks to human health and the environment following site remediation and redevelopment. This "postremediation" approach to the risk assessment was consistent with Ecology policy, which discouraged performance of quantitative baseline risk assessments at MTCA sites. Although Ecology policy is

undergoing revision following recommendations of a multi-stakeholder policy advisory committee, the current policy provides a process to clean up hazardous waste sites whereby specific exposure parameters identified in MTCA are used to develop cleanup action levels in environmental media. The MTCA procedure is based on a back-calculation from regulatory risk levels to protective concentrations in environmental media. Specifically, risk-based cleanup levels are derived for exposures of humans by direct contact or ingestion of surface soils, groundwater, and surface water, and by inhalation of contaminants in air. (A similar approach to setting cleanup levels for protection of wildlife in Washington is presently under development.)

However, an exposure pathway analysis demonstrated that the remediation and redevelopment plans for the site eliminated the potential for human exposures to chemical contaminants via pathways that are addressed under MTCA. For example, the plans call for cover of all surface soils, consolidation of the landfill, and collection and treatment of landfill gases. In addition, the groundwater was recognized by Ecology as a nonpotable source. A potentially complete exposure pathway was found to consist of washing of soil chemicals into infiltrating water and mixing of infiltrating water with underlying groundwater, followed by transport of the contaminated groundwater downgradient to discharge to Elliott Bay. Marine organisms, principally shellfish and anadromous fish, and humans who consume them could then be exposed to groundwater contaminants that have discharged and mixed with marine surface waters.

Because of the lack of MTCA cleanup criteria for subsurface soils and because the MTCA procedure for identifying cross-media cleanup levels (i.e., for protection of groundwater) consisted of a screening-level procedure similar to the DAF approach, the objective of the SWHP risk assessment was to calculate site-specific criteria that would be protective of marine receptors exposed to soil contaminants transported in groundwater. The numerical criteria developed from this objective were based on the presumptive remedy of soil capping, which is expected to reduce or minimize infiltrating water and hence reduce washout of subsurface soil chemicals to groundwater. Because of the uncertainty in predicting metals partitioning in subsurface soils, the development of risk-based cleanup levels are reported only for PCBs, PAHs, and TPH.

Site Hydrogeology. The major hydrogeologic characteristic of the site is the Longfellow Overflow Line, which extends from the south boundary of the site to the discharge point at Elliott Bay (Figure 2). Formerly Longfellow Creek, the overflow line was constructed between 1961 and 1980 when local tideflats were filled. The original creek flow has been diverted to the West Waterway of the Duwamish River through the Longfellow Creek main line. Input to the Overflow Line consists of four main sources: overflow from the Longfellow Creek main line, stormwater runoff and cooling water discharge from the steel facility at RA 2, and groundwater infiltration throughout the site.

Several groundwater flow studies have shown that the overflow line intercepts shallow groundwater flow and is the primary drain and outfall for shallow groundwater beneath RAs 1, 2, 3, and the upland portion of RA 4. Inflow to the overflow line occurs at unsealed joints and breaks, and active seeps to the line were observable at four open, unlined equalization basins. Thus, the line serves as a transport route for chemicals that wash from subsurface soils to groundwater, which drains into the line or into the line infrastructure and fill material and then discharges at an outfall to Elliott Bay. The single discharge point for upland site groundwater was a unique feature of the site hydrogeology that facilitated development of the risk-based model. Because the landfill, overflow drain, and other features of the site have been in
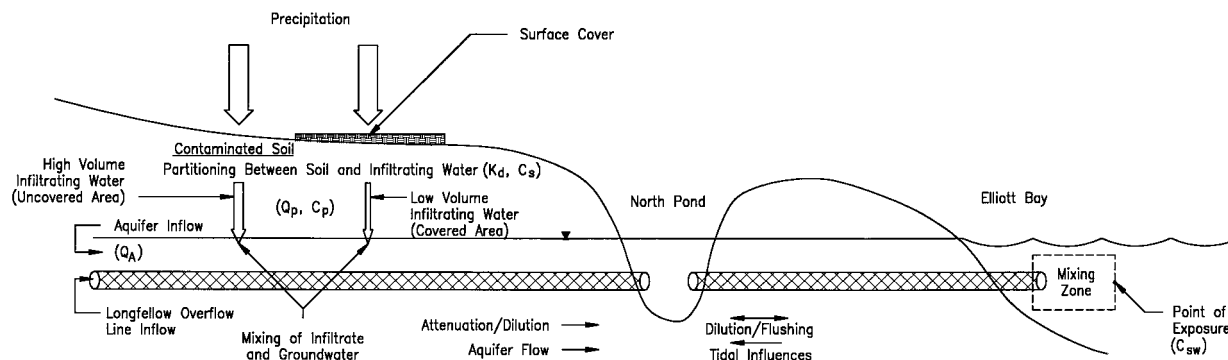
FIGURE 3. Conceptual diagram of surface water exposure model. Model parameter symbols are defined in Table 1.

TABLE 1. Model Parameters

parameter		value	step in model
total site area		3 834 600 ft^2 (356 246 m^2)	
chemical concentration in surface water	C_{sw}	water quality criterion	1
attenuation-dilution factor	AD	73	2
mixing zone dilution factor	MZ	76.4	2
chemical concentration in groundwater	C_{gw}	site-wide (μg/L)	2
soil cover percolation rate		HELP model	3
volumetric infiltration rate	Q_p	soil cover specific (ft^3/day or m^3/day)	3
total aquifer flow rate	Q_A	3900 ft^3/day (110 m^3/day) (modeled)	4
aquifer volumetric flow rate	Q_{Aadj}	cover area specific	4
chemical concentration in infiltrating water	C_p	soil cover specific (mg/L)	5
chemical partitioning	K_{oc}, K_d	chemical specific	6
chemical concentration in subsurface soils	C_s	soil cover specific (mg/kg)	7

place for many years and the present geochemical groundwater environment is a reducing state, no site activities are expected to change the present redox status of site environmental media.

Materials and Methods

Surface Water Protection Model. The approach to developing chemical cleanup criteria for subsurface soils consisted of back-calculations from allowable chemical concentrations in marine waters. The back-calculation model was based on the conceptual hydrogeologic model developed for groundwater movement at the site. The model uses water quality criteria that are protective of the health of marine organisms and humans that may consume them as the starting point. We call this approach a risk-based hydrogeologic "surface water protection model" for subsurface soils. The end result of the model is the development of concentrations of chemicals in subsurface soils that do not present a threat to marine surface waters. We call these concentrations "surface water protection values".

The surface water protection model is depicted conceptually in Figure 3. The figure illustrates the partitioning of subsurface soil contaminants to infiltrating water and percolation to underlying groundwater, which in turn transports along the Longfellow Overflow Line to discharge at Elliott Bay. The model assumes that groundwater is below the contaminated soils. Since the model predicts groundwater contamination from contaminated unsaturated soils, additional sources located in the saturated zone are not addressed. The amount of infiltrating water that moves to and mixes with the underlying groundwater is dependent on the type and amount of cover material over the soil. A representative soil cover is depicted in Figure 3 as decreasing the volume of infiltrating water compared to infiltrating water that passes through soil without a cover. The model assumes that the covers will remain intact through time. Thus, a highly impermeable soil cover will result in a low rate of water

infiltration and smaller amounts of chemicals washing out of the subsurface soils compared to other soil cover types. A highly impermeable soil cover will ultimately result in higher calculated surface water protection values (i.e., higher cleanup levels) for chemicals in subsurface soils of that area.

Model Procedure. In Figure 3, the surface water protection model works backward from chemical concentrations in Elliott Bay waters up the Longfellow Overflow Line to concentrations in infiltrating water at the site and then to concentrations in subsurface soils. Numerous conservative assumptions are inherent in the model design, and are explained below. Specific model parameters are listed in Table 1. The following steps describe the model.

1. Identify the Appropriate Risk-Based Marine Surface Water Chemical Concentrations (C_{sw}). Marine water quality criteria are used as surface water chemical concentrations (C_{sw}) to be protective of marine life and human consumers. Water quality criteria consist of Washington water quality standards for protection of aquatic life (Washington Administrative Code 173-201A-040) or U.S. EPA quality criteria for marine water and human consumption of fish [40 CFR Part 131.36(b) (1)], whichever is most stringent.

For TPH, water quality criteria are not available. Instead, the MTCA organoleptic-based drinking water criterion of 1 mg/L was used to derive a surrogate toxicity value. A single value for TPH was preferred over a surrogate chemical approach, such as the use of representative toxicities of hydrocarbon fractions (4) or narcotic endpoints (9), because of the need to address state regulatory requirements for TPH cleanup levels. An uncertainty factor of 1000 was applied to the drinking water criterion, assuming that it adequately accounted for extrapolating from an acute aesthetic criterion to a chronic toxicity criterion, and from humans to aquatic organisms. The resulting surrogate marine water quality criterion for TPH is 1.0 μg/L.

2. Back-Calculate from the Surface Water Chemical Concentration to a Corresponding Concentration in

Groundwater (C_{gw}) beneath the Site. The concentration of a chemical in groundwater is back-calculated by including dilution in a mixing zone in Elliott Bay and attenuation and dilution during transport along the Longfellow Overflow Line:

$$C_{gw} = C_{sw}(MZ \times AD)$$

where

C_{gw} = corresponding groundwater concentration
$$(\mu g/L)$$

C_{gw} = surface water quality criterion ($\mu g/L$)
$$\text{(from step 1)}$$

MZ = mixing zone dilution factor in Elliott Bay (76.4)
$$\text{(unitless)}$$

AD = attenuation-dilution factor for the Longfellow Overflow Line (73) (unitless)

Mixing Zone Dilution (MZ). A mixing zone is defined as an area around a discharge point where contaminant concentrations may exceed water quality criteria. The Longfellow Overflow Line outfall met the Washington State criteria for a mixing zone.

The Longfellow Overflow Line outfall is tidally active and fluctuates between an inflow and outflow over the tidal cycle. In addition, the depth of water at the outfall fluctuates from near zero to more than 15 feet (4.6 m) over the period of tidal fluctuations experienced in Elliott Bay. Because of the relatively shallow depth of the outfall, the mixing zone dilution calculations were performed with a U.S. EPA model for nearshore environments (*10*). The model input calculations conservatively did not include any stormwater discharges, and assumed that the effluent concentration and flow rate were constant over the tidal cycle. The outfall pipe geometry used in the mixing zone calculations accounted for the presence of sediment in the line, which will be removed during site remediation. The results of the dilution model showed that greater dilution occurs if the future, sediment-free outfall is used in the analysis. To be conservative and to account for the possibility that sediment redeposition may occur in the future, the present pipe geometry with partial sediment filling was used in our analysis. Results of the model calculations (*12*) indicated a mixing zone dilution factor (MZ) of 76.4 at 200 feet (61 m) from the outfall.

In-Line Attenuation-Dilution (AD). The in-line attenuation-dilution factor (AD) is based on two components.

A. Mixing of Groundwater Inflow with Existing Nontidal, Low Flow in the Overflow Line. Nontidal flow in the overflow line that comes into the site consists of National Pollutant Discharge Elimination System (NPDES) discharges from an upgradient steel plant. Groundwater at the site includes groundwater inflow and infiltration of precipitation and enters the Longfellow Overflow Line through cracks in the line and through discharge to onsite equalization basins that are within the overflow line. A hydrologic, or water balance, evaluation of this mixing (*12*) yielded an attenuation-dilution factor of 7.3. The water balance analysis compared measured surface water flows to groundwater inflows predicted from a groundwater flow model of the site.

B. Mixing of Flow with Elliott Bay Water Introduced in the Line over the Tidal Cycle. A hydrochemical evaluation (*12*) showed that water in the Longfellow Overflow Line contains a gradient of increasing seawater concentration from the upgradient station to the downgradient station (sampled at the North Pond as representative of the downgradient aquifer, see Figures 2 and 3). Results indicated a marine water dilution factor in the North Pond of 10. The hydro-

chemical evaluation consisted of ion balance analysis at two stations, one upgradient with little seawater influence and one downgradient with significant seawater influence. The ion balance was used to estimate the proportions of seawater and freshwater mixing in the overflow line.

The attenuation dilution modeling did not account for stormwater discharge and conservatively assumed that all groundwater entering the site boundaries and all infiltration water at the remedial areas entered the Longfellow Overflow Line. As an additional conservative measure, the calculations of the dilution factor for the tide-induced mixing at the North Pond did not account for additional mixing or flushing from the North Pond to Elliott Bay. The two components together yield an in-line attenuation-dilution factor of 73 for the Longfellow Overflow Line. Combination of the in-line attenuation-dilution factor (73) and the mixing zone dilution factor (76.4) gives an overall attenuation-dilution factor of 5577.2.

3. Identify Volumetric Infiltration Flow Rates (Q_p) for Each Cover Parcel Area (ft^3/day or m^3/day). Volumetric infiltration flow rates (Q_p) are generated by multiplying the percolation rate for each cover by the square footage of the respective parcel area,

$$Q_p = \text{percolation rate} \times \text{area}$$

where

Q_p = volumetric infiltration flow rate
$$(ft^3/day \text{ or } m^3/day)$$

percolation rate = vertical permeability
$$(ft/day \text{ or } m/day)$$

area = area of soil cover (ft^2 or m^2)

Maps of soil cover areas for RAs 2 and 3 are shown in Figure 2. Although soils at RAs 1 and 4 are also planned for cover, this study focuses on the range of permeabilities of the 4-in. asphalt, 24-in. ballast, and geomembrane covers of RAs 2 and 3 (Table 3). For each of these cover areas, a percolation rate was calculated using the U.S. EPA Hydrologic Protection of Landfill Performance (HELP) model (*13*). The program models the effects of hydrologic processes, including precipitation, surface storage, runoff, infiltration, percolation, evapotranspiration, soil moisture storage, and lateral drainage, on various soil cover types. Since the permeability of asphalt is largely due to cracking rather than movement through pore spaces as in soil, the HELP model was used like a groundwater flow model that predicts flow in fractured rock, where the model predicted infiltrating flow for a given density of fractures over the asphaltic area.

4. Calculate the Adjusted Aquifer Flow Rate (Q_{Aadj}) for Each Parcel Area. The adjusted aquifer flow rate reflects the portion of the site aquifer beneath the respective soil cover area, and is generated by multiplying the site aquifer flow rate (Q_A) by the ratio of each soil parcel area to the total area of the site:

$$Q_{Aadj} = Q_A \times (\text{parcel area/total site area})$$

where

Q_{Aadj} = adjusted aquifer flow rate for each cover parcel area (ft^3/day or m^3/day)

Q_A = volumetric flow rate of groundwater in the aquifer (3900 ft^3/day or 110 m^3/day)

total site area is 3 834 600 ft^2 (356 246 m^2)

TABLE 2. Chemical Parameter Values

chemical	C_{sw}, water quality criterion (μg/L)[a]	K_{oc}, organic carbon partition coefficient (cm³/g)[b]	K_d, water/soil partition coefficient (L/kg)
PCBs	0.000 05	530 000	5830[c]
TPH	1[d]	NA[f]	4300[e]
PAHs			
benzo[a]anthracene	0.031	1 380 000	15 180[c]
benzo[b]fluoranthene	0.031	550 000	6050[c]
benzo[k]fluoranthene	0.031	550 000	6050[c]
benzo[a]pyrene	0.031	5 500 000	60 500[c]
benzo[ghi]perylene	300	1 600 000	17 600[c]
chrysene	0.031	200 000	2200[c]
dibenzo[a,h]anthracene	0.031	3 300 000	36 300[c]
fluoranthene	370	38 000	418[c]
indeno[1,2,3-cd]pyrene	0.031	1 600 000	17 600[c]
naphthalene	2350	1300	14.3[c]
phenanthrene	4.6	14 000	154[c]

[a] Most stringent value of Washington Department of Ecology, Chapter 173-201A, Washington Administrative Code, or U.S. EPA Marine Water Quality Criteria (11). [b] U.S. EPA (15, 16) or Washington Department of Ecology for naphthalene (8). [c] Calculated from the fraction soil organic carbon (f_{oc}), measured at 0.011. [d] MTCA Groundwater Protection Standard for aesthetic properties, modified by dividing by an uncertainty factor of 1000. [e] Field-based effective partition coefficient, calculated from co-located groundwater ($n = 4$) and soil ($n = 11$) sampling data. [f] NA, not available.

TABLE 3. Surface Water Protection Values for Subsurface Soils

cover designation		cover B		cover C		cover D	
cover type		4" asphalt		24" ballast		landfill geomembrane	
area of cover parcel (ft²)		631 816		237 103		1 306 800	
(m²)		58 700		22 028		121 406	
aquifer volumetric flow rate (Q_{Aadj}, ft³/day)[a]		643		241		1329	
(m³/day)[a]		18		6.8		37.6	
infiltration flow rate (Q_p, ft³/day)[b]		9.16		1351		2.18	
(m³/day)[b]		0.26		38.3		0.062	

chemical	C_{gw}[c] (μg/L)	C_p[d] (mg/L)	C_s[e] (mg/kg)	C_p[d] (mg/L)	C_s[e] (mg/kg)	C_p[d] (mg/L)	C_s[e] (mg/kg)
PCBs	0.28	0.02	116	0.0003	1.92	0.2	994
TPH	5577	397	$>1 \times 10^6$ [f]	7	28 261	3409	$>1 \times 10^6$
PAHs							
benzo[a]anthracene	173	12.3	186 713	0.2	3093	106	$>1 \times 10^6$
benzo[b]fluoranthene	173	12.3	74 415	0.2	1233	106	639 352
benzo[k]fluoranthene	173	12.3	74 415	0.2	1233	106	639 352
benzo[a]pyrene	173	12.3	744 146	0.2	12 326	106	$>1 \times 10^6$
benzo[g,h,i]perylene	$>1 \times 10^6$	154 904	$>1 \times 10^6$	2566	$>1 \times 10^6$	$>1 \times 10^6$	$>1 \times 10^6$
chrysene	173	12.3	27 060	0.2	448	106	232 492
dibenzo[a,h]anthracene	173	12.3	446 487	0.2	7396	106	$>1 \times 10^6$
fluoranthene	$>1 \times 10^6$	146 805	$>1 \times 10^6$	2432	$>1 \times 10^6$	$>1 \times 10^6$	$>1 \times 10^6$
indeno[1,2,3-cd]pyrene	173	12.3	216 479	0.2	3586	106	$>1 \times 10^6$
naphthalene	$>1 \times 10^6$	$>1 \times 10^6$	$>1 \times 10^6$	20 784	297 207	$>1 \times 10^6$	$>1 \times 10^6$
phenanthrene	34 523	2456	378 228	40.7	6265	21 102	$>1 \times 10^6$

[a] Q_{Aadj} (ft³/day or m³/day) = product of aquifer flow rate (Q_A) multiplied by the fraction of total site area (step 4). [b] Q_p (ft³/day or m³/day) = product of parcel area multiplied by the infiltration rate, determined by HELP model (step 3). [c] C_{gw} (μg/L) = modeled as site-wide groundwater concentration (step 2). [d] C_p (mg/L) = modeled concentration in infiltrating water (step 5). [e] C_s (mg/kg) = modeled concentration in subsurface soils (step 7). [f] Note that the model does not account for upper limits of solubility in groundwater (C_{gw}) or infiltrating water (C_p) or saturation of soils (C_s). The model also does not account for nonlinearity in K_d values at high concentrations nor the influence cosolutes may have on K_d values.

The volumetric flow rate in the aquifer (Q_A) describes the groundwater that enters the site. For the SWHP, the groundwater inflow occurs along the western boundary of the site (i.e., from the West Seattle bluff) and from south of Spokane Street (the Delridge Basin) (Figure 1). The site is bounded on the east and north by the Duwamish River and Elliott Bay, respectively, and vertically by a lower silt/clay unit.

For the Delridge Basin contribution, groundwater inflow was based on Darcy's equation for groundwater flow, with the hydraulic conductivity (5.6×10^{-3} cm/s), hydraulic gradient (0.001), and cross-section of the Delridge Basin aquifer (12 000 ft² or 1115 m²) taken at Spokane Street along the south boundary of the project area. The groundwater flow to the SWHP from the Delridge Basin was estimated at 130 ft³/day (3.7 m³/day).

The contribution of groundwater flow from the West Seattle bluffs was derived from an existing model developed by the local county for a dewatering analysis of the bluff, which used the USGS groundwater flow package MODFLOW calibrated to both winter and summer conditions. The model demonstrated that the West Seattle bluff flow at 3770 ft³/day (107 m³/day) is the major component of groundwater at the site.

From the water balance analysis used in step 2 (12), the total nontidal dry weather inflow to the site was estimated at 37 300 ft³/day (1056 m³/day). Dry weather flow was used as a conservative representation of the low flow in Longfellow Creek, which results in the lowest dilution factor between surface water and groundwater inflows. Of the total inflow, the aquifer volumetric flow rate (Q_A) was estimated at 3900

ft^3/day (110 m^3/day), i.e., the sum of flows from the Delridge Basin and West Seattle bluffs.

5. Calculate the Corresponding Concentration in Infiltrating Water (C_p) for Each Cover Parcel Area. In back-calculating the corresponding concentration in infiltrating water, a number of assumptions are made: (1) a percentage of the rainfall at the site will infiltrate and desorb chemical contaminants from the soil; (2) infiltrating water transports these chemicals to the underlying groundwater; (3) chemical contaminants are contained in the pore water of soil; (4) contaminants are adsorbed to soil particles at equilibrium; (5) contaminants are not attenuated during transport; and (6) infiltrating water mixes completely with background inflowing water.

Chemical concentrations in infiltrating water are determined by rearrangement of the Summers et al. (*14*) equation for predicting groundwater contamination, as described in U.S. EPA (*4, 6*):

$$C_p = \frac{[C_{gw}(Q_p + Q_{Aadj}) - (Q_{Aadj}C_A)]CF}{Q_P}$$

where

C_p = chemical concentration in the infiltrate (mg/L)

C_{gw} = chemical concentration in the groundwater (μg/L) (from step 2)

C_A = background concentration of chemical in the aquifer (μg/L)

Q_p = volumetric flow rate of the infiltration (ft^3/day or m^3/day) (from step 3)

Q_{Aadj} = adjusted volumetric flow rate of groundwater in the aquifer (ft^3/day or m^3/day) (from step 4)

CF = conversion factor (1 mg/1000 μg).

6. Develop Partition Coefficients (K_d) for Pore Water to Soils. Pore water to soil solids partition coefficients are calculated for organic chemicals based on partitioning to organic carbon:

$$K_d = K_{oc}\, f_{oc}$$

where

K_d = chemical pore water to soil solids partition coefficient (mL/g, converted to L/kg)

K_{oc} = organic carbon partition coefficient (cm^3/g)

f_{oc} = fraction of organic carbon in site soil (unitless)

Organic carbon partition coefficients (K_{oc}) for PAHs and PCBs were taken from U.S. EPA (*15, 16*) and are shown in Table 2. For TPH, an effective partition coefficient (K_d) was calculated from concentrations in soil borings divided by concentrations in groundwater monitoring wells from the same locations and depths (Table 2). This approach is consistent with U.S. EPA (*6, 7*) guidance on setting groundwater protection values at hazardous waste sites. The effective partition coefficient for TPH was calculated at a mean value of 4300 L/kg (range of 4200−5500 L/kg), which is less than one-half of the mean of K_d values for the PAHs in Table 2.

7. Calculate Concentrations of Chemicals in Soils from Infiltrating Water Concentrations. The concentration of a

chemical in subsurface site soil that corresponds to the protective concentration in surface water of Elliott Bay (C_{sw}) is calculated from the concentration in infiltrating water:

$$C_s = C_p K_d$$

where

C_s = concentration of chemical in soil (mg/kg)

C_p = concentration of chemical in infiltration water (mg/L) (from step 5)

K_d = pore water to soil solids partition coefficient (L/kg) (from step 6)

The final step thus calculates chemical concentrations for subsurface soils in the areas of the site that drain to the Longfellow Overflow Line, which correspond to the water quality criteria for marine receptors in Elliott Bay.

Sensitivity Analysis and Model Verification. A sensitivity analysis of the model input parameters was performed by iterations of the model with a range of input parameter values. The sensitivity analysis was designed to identify the input parameters that impact model output and to demonstrate the conservativeness of the parameter values selected for the model. A range of values for the input parameters of each model step was used in the iterative model runs. For example, for the mixing zone dilution factor (MZ), model iterations were run on diffusion function (i.e., the relationship between diffusion and distance from the outfall), outfall width and depth, current velocity, and discharge rate; additional input parameter variations included groundwater inflow rates, partition coefficients, and hydraulic conductivity in the calculation of infiltration rates.

A limited verification of the model was performed to determine its predictive quality. The verification consisted of forward calculations from measured subsurface soil concentrations to chemical concentrations in infiltrating water and subsequently to groundwater, and comparison of predicted groundwater concentrations with measured concentrations in groundwater. Due to the possible confounding influence of other sources contributing to downgradient chemical concentrations in groundwater, the forward calculations were run only to predict groundwater chemical concentrations beneath site soils and not concentrations further downgradient or in the receiving waters. For the forward calculations, values for surface soil infiltration flow rates representative of current (i.e., preremediation) conditions at the site were used in place of the postremediation infiltration rates proposed for site development.

Results

Subsurface Soil Concentrations Protective of Marine Receptors. The concentrations of chemicals in subsurface soils (C_s) that are considered protective of marine receptors are presented for three cover parcel areas in Table 3. Cover parcel areas were selected to represent the range of cover types and percolation rates for the site. They include an asphalt cover, a ballast cover, and a geomembrane cover for the landfill at RA 3.

The PCB group had the lowest risk-based concentrations in soils (C_s, Table 3) and was influential in setting overall soil remedial goals for the site. The low concentrations were due primarily to the low water quality criterion for PCBs. The PCB water quality criterion is based on a 1×10^{-6} cancer risk level associated with a lifetime of consuming fish (at 6.5 g/day) that live at the boundary of the mixing zone (*17*). Since migrating salmon are the fish generally taken and consumed from Elliott Bay and their residence time in the

TABLE 4. Comparison of Observed with Modeled Groundwater Chemical Concentrations

chemical	mean soil concentration (mg/kg)	observed mean groundwater concentration[a] (μg/L)	frequency of groundwater detection	modeled groundwater concentration current conditions[b] (μg/L)	modeled groundwater concentration postremediation[c] (μg/L)
		Ballast and Asphalt Cover Areas			
TPH	975	256 (250U−1300)[d]	1/9	192	67.6
total PCBs[e]	4.1	0.9 (0.1U−3.0)	6/12	0.99	0.35
		Landfill Area (Geomembrane Cover)			
TPH	9762	182	3/4	1857	3.72
total PCBs	41.3	ND	0/8	5.79	0.012

[a] Values for chemicals with low frequency of detections may not be representative of actual groundwater concentrations. Means include one-half detection limits for undetected values. [b] Calculated by running the Surface Water Protection Model in a forward direction using the mean soil chemical concentration for the uncovered (i.e., premediated) areas. Volumetric flow rate of infiltration (Q_p) for uncovered areas of RA 2 = 4961 ft^3/day (140 m^3/day). Volumetric flow rate of aquifer (Q_{Aadj}) for RA 2 = 884 ft^3/day (25 m^3/day). Volumetric flow rate of infiltration (Q_p) for the premediated landfill = 5973 ft^3/day (170 m^3/day). Volumetric flow rate of aquifer (Q_{Aadj}) for the premediated landfill = 1329 ft^3/day (38 m^3/day). [c] Calculated by running the Surface Water Protection Model in a forward direction using the mean soil chemical concentrations for covered (i.e., postremediated) areas. Volumetric flow rate of infiltration (Q_p) = 375 ft^3/day (11 m^3/day) (average of infiltration rates for the ballast and asphalt covers, weighted for the respective surface areas). Volumetric flow rate of aquifer (Q_{Aadj}) = 884 ft^3/day (25 m^3/day). Volumetric flow rate of infiltration (Q_p) for the landfill = 2.18 ft^3/day (0.06 m^3/day), calculated with the HELP model. Volumetric flow rate of aquifer (Q_{Aadj}) for the landfill area = 1329 ft^3/day (38 m^3/day). [d] Values are means with range in parentheses; "U" qualifier for lower values denotes detection limit. [e] Total PCBs include Aroclors 1016, 1242, 1221, 1232, 1248, 1254, 1260.

Bay is usually less than 3 days, the basis of the PCB criterion is considered conservative for this model.

Subsurface soil concentrations of TPH calculated to be protective of marine receptors at this site are relatively high (Table 3), a result of both high surrogate water quality criterion compared to PAHs and PCBs and high binding to site soils (i.e., a high K_d value), which results in less release to infiltrating water. The high soil concentrations calculated for TPH are consistent with the high concentrations calculated for the less water soluble PAHs (Table 3), for the same reasons.

The surface water protection values (C_s) for many of the PAHs and TPH were calculated by the model to exceed unity (i.e., >1 × 10^6 mg/kg, Table 3), as were some of the groundwater and infiltrating water concentrations (C_{gw} and C_p, respectively). Exceedances of unity resulted from model design, since the chemical concentrations in the mass balance equation and soil/water partitioning relationship do not include solubility or saturation limits. Although the model shows that concentrations of petroleum hydrocarbons less than free phase flow would be protective of marine waters after site remediation and redevelopment, the model does not account for nonlinearity in K_d values at high concentrations and may not accurately reflect the influence of very high concentrations of petroleum chemicals on the mobility of other organic chemicals, such as PCBs. In addition, low-density hydrocarbons could be present as free product at lower concentrations. However, no free phase product or high concentrations of TPH or PAHs were found in soils or groundwater at the site.

Note that for the ballast cover (cover C) of RA 2, where the attenuation of infiltrating water is much smaller, risk-based chemical concentrations for PAHs do not exceed unity (Table 3). The ballast soil cover has a greater permeability than the asphalt or landfill covers and allows for more infiltrating water and hence more potential for transferring chemicals in soil to underlying groundwater.

Sensitivity Analysis and Model Verification. Iterative runs of the model with ranges of input values demonstrated the sensitivity of the model output to various input parameters (data not shown). The mixing zone dilution factor (MZ) was most sensitive to the discharge flow rate along the Longfellow Line, and increased in a log−log relationship with a decrease in discharge rate. The in-line attenuation-dilution factor (AD) was based on site-specific data, and was not included in the sensitivity analysis. Groundwater inflow (Q_A) from off-site is factored into a number of model steps (e.g.,

attenuation-dilution factor, mixing zone dilution factor, calculation of C_{gw}, and calculation of C_p), and influences the model output in opposing directions. The effect of variation of the aquifer inflow rate was nearly canceled by these opposing directions, and the resulting change in model output is slight. An increase in infiltration rate (Q_p) at low realistic values (e.g., 1 ft^3/day to 2000 ft^3/day, equivalent to 0.028−56 m^3/day) results in an essentially linear increase in chemical concentrations in groundwater (C_{gw}), but at higher infiltration rates, C_{gw} approaches C_p (i.e., the chemical concentration in groundwater approaches the concentration in infiltrating water at very high rates of infiltration). Infiltration rates are log−log related to the protective concentrations of chemicals in soil (C_s), such that decreases in infiltration rates below 20 ft^3/day (about 0.6 m^3/day) for low permeable (e.g., geomembrane) soil covers or below 200 ft^3/day (about 6 m^3/day) for high permeable (e.g., ballast) soil covers result in dramatic rises in respective C_s values. The protective soil concentrations (C_s) are directly related to chemical partition coefficients (K_d), which for TPH was based on site-specific data. Of the above model parameters, results of the sensitivity analysis indicate that the hydrogeologic model was most sensitive to changes in infiltration rates (Q_p) and partition coefficients (K_d).

Results of the limited model verification are presented in Table 4. Mean concentrations of PCBs and TPH measured in site soils were used in forward modeling to predict corresponding groundwater concentrations under current conditions and under planned soil covers (i.e., postremediation conditions). Because of the limited soil and groundwater data available for portions of the site, the ballast and asphalt cover areas are combined in the forward calculations of the model. Comparison of the modeled groundwater concentrations under current conditions with the means of measured groundwater concentrations at the two areas shows that the model achieves reasonable accuracy given the limitations of the data. For example, for the ballast and asphalt cover areas (Table 4), the modeled groundwater chemical concentrations fall within the ranges of detection limits and detected values for both chemical groups. The larger variations from measured values occurred where groundwater data were limited to three or fewer samples. The variations are considered unsurprising given the uncertainties about whether additional sources of groundwater contamination may be located in the saturated zone of upgradient site soils.

In the presence of soil covers, data on chemical concentrations modeled in groundwater under postremediation conditions (Table 4) demonstrate the degree of predicted attenuation of soil contaminant transfer to underlying groundwater from the presence of soil covers. In particular, the presence of a geomembrane over the landfill area was predicted to reduce the transfer of chemicals to underlying groundwater by an order of magnitude compared to the ballast and asphalt covers.

Discussion

The surface water protection model developed for the SWHP successfully demonstrated that remediation and development plans for the site would adequately protect human health and the environment from subsurface soil chemical contaminants, at PCB concentrations as high as 1000 mg/kg soil and PAH and TPH concentrations up to saturation levels, depending on soil cover type. The model is a novel integration of a risk-based approach for PAHs and PCBs, a conceptual model of site hydrogeology and contaminant transport, and the Summers model for predicting groundwater contamination from soil chemicals. The Summers model is one of a number of methods to evaluate soil contaminant transfer and has been used to identify potential soil cleanup levels for chlorinated pesticides in Washington (*18*).

Because of the limited sample data and the likelihood of additional sources of groundwater contamination at the SWHP that are not accounted for in the model, a typical model calibration could not be performed. Instead, a comparison of predicted chemical concentrations in groundwater beneath the site with measured values was performed as a limited model verification. Within the uncertainties of the limited sampling data, the concentrations developed from the forward model calculations closely predicted measured groundwater concentrations at the site in most cases. These results demonstrate that regardless of the type of cover, large errors in the model outcome did not occur. This verification further showed that any fractures, utilities, or other compounding factors that may exist in the site soils did not significantly affect the prediction of downgradient concentrations of chemicals in site groundwater.

To meet regulatory agency concerns about the degree of protectiveness of the modeled soil concentrations to groundwater resources at the site, the assumptions used in the model calculations were deliberately conservative. The sensitivity analysis identified chemical partition coefficients (K_d) and surface water infiltration rates (Q_p) as the most sensitive parameters for calculating protective soil concentrations (C_s). The sensitivity of the model to infiltration rates (Q_p) was the focus of iterative computations to determine the optimal (i.e., effective yet cost sensitive) geomembrane cover for the landfill and to ensure optimal design of the covers for the other soil areas. In this way, the model successfully guided the selection of appropriate soil cover permeabilities for the site redevelopment. Finally, the model was used to establish remediation plans for the site that achieved the state regulatory agency's goal of protecting human health and the environment by all potential exposure pathways.

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