Puget Sound Regional Toxics Model: Evaluation of PCBs, PBDEs, PAHs, Copper, Lead, and Zinc

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Puget Sound Regional Toxics Model: Evaluation of PCBs, PBDEs, PAHs, Copper, Lead, and Zinc

by

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Abstract

The Puget Sound Regional Toxics Model (PSRTM) is a combined model of contaminant fate, transport, and bioaccumulation that was developed by the Washington State Department of Ecology in 2009. Initial modeling of polychlorinated biphenyls (PCBs) in Puget Sound identified critical data gaps that limited the usability of the PSRTM for evaluating source control strategies. To address the data gaps and reduce uncertainties in model inputs, monitoring projects were conducted between 2009 and 2011. These projects collected new data on contaminant concentrations in the marine water column, ocean boundary waters, and various species of biota, and also generated revised estimates of contaminant loading to Puget Sound via atmospheric deposition, surface runoff, wastewater treatment plants, and groundwater.

The present study was undertaken to (1) incorporate the recently collected monitoring data and loading estimates into the PSRTM and (2) expand the PCB model to provide the capability to simulate additional contaminants of concern, including polybrominated diphenyl ethers (PBDEs), selected polycyclic aromatic hydrocarbons (PAHs), copper, lead, and zinc.

The fate and transport component of the PSRTM was successfully modified to enable simulation of new organic contaminants and metals. However, the updated model tended to underestimate contaminant concentrations in water and sediment compared to observed data and also predicted rapidly declining trends that were not supported by the data. Using the model in "hindcast" mode, it was found that current estimates of contaminant loading from watershed sources, the ocean, or both, may be too low. Despite these issues, preliminary results provided information on the relative importance of source pathways and loss processes to the long-term fate of these contaminants in Puget Sound.

The updated bioaccumulation model was shown to be a useful tool for predicting the concentration of PCBs or PBDEs in species throughout the food web based on contaminant concentrations in the sediments and water column. Example scenarios demonstrated the model utility for identifying locations where organisms would be expected to bioaccumulate contaminants to levels that exceed adverse-effects thresholds and for estimating sediment and water concentrations necessary to ensure that biota thresholds would not be exceeded.

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  - Charles Pitz provided spreadsheets of the Phase 3 direct groundwater loading estimates.
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Executive Summary

Introduction

In 2009 the Washington State Department of Ecology (Ecology) developed numerical models to simulate (1) contaminant fate and transport in the waters and sediments of Puget Sound and (2) bioaccumulation of contaminants in aquatic organisms throughout the Puget Sound food web. The combined model, referred to as the Puget Sound Regional Toxics Model (PSRTM), was intended to be used as a tool for the evaluation of management alternatives for toxic chemicals, allowing comparison of the ecosystem response under potential source reduction strategies.

The initial modeling work by Pelletier and Mohamedali (2009) focused on polychlorinated biphenyls (PCBs) due to the relative abundance of data available at the time. However, a high degree of uncertainty was associated with some of the model inputs, which limited the usability of the model. Under the auspices of the Puget Sound Toxics Loading Analysis (PSTLA), several monitoring projects were conducted to fill the identified data gaps. Those projects collected new data on contaminant concentrations in the marine water column, ocean boundary waters, and various species of biota. Studies were also conducted to estimate contaminant loading to the Sound via surface runoff, wastewater treatment plants (POTWs), atmospheric deposition, and groundwater.

The present study was undertaken to update and expand the modeling work of Pelletier and Mohamedali (2009). The primary objectives were to:

- Modify the PSRTM to allow the simulation of contaminants beyond PCBs, including the fate and transport of polybrominated diphenyl ethers (PBDEs), selected polycyclic aromatic hydrocarbons (PAHs), copper, lead, and zinc and the bioaccumulation of PBDEs.
- Incorporate new loading estimates and recent regional data from the PSTLA projects and other readily available sources to improve model inputs and reduce uncertainty in the model predictions.

This report documents the implementation of these model enhancements and also describes efforts to test the utility of the updated PSRTM to evaluate management scenarios.

Puget Sound Regional Toxics Model

Pelletier and Mohamedali (2009) developed the PSRTM based on three previously published model applications:

- **Box model of water circulation and transport** (Babson et al., 2006). A model to predict transport of water between regions and between surface and deep layers of the water column.
- **Mass balance model of contaminant fate** (Davis, 2004). A model to predict contaminant concentrations in water and sediment in response to external loading and internal processes.
- **Food web bioaccumulation model** (Arnot and Gobas, 2004; Condon, 2007). A model to predict contaminant concentrations in biota in response to water and sediment concentrations.

The model domain of the PSRTM includes the marine waters of Puget Sound south of the outlets at Admiralty Inlet and Deception Pass. This area is divided into ten regions (Figure ES-1). Seven of the regions correspond to the principal basins: Admiralty Inlet, northern Hood Canal, southern Hood Canal, Main Basin, the Narrows, South Sound, and Whidbey Basin. Three additional regions represent urban bays: Commencement Bay, Elliott Bay, and Sinclair/Dyes Inlets. The ocean boundary to the model domain consists of the U.S. portions of the Straits of Juan de Fuca and Georgia.

The circulation and transport application is completely integrated with the contaminant fate application in the "fate and transport model" component of the PSRTM. The combined model predicts contaminant concentrations in the sediments and waters of each region through time in response to external loading, horizontal and vertical water movements (including inflow and outflow at the model boundary), and to processes such as volatilization, degradation, settling, resuspension, and burial.

In the "bioaccumulation model" component of the PSRTM, contaminant fluxes into and out of individual organisms are simulated, including uptake from water, feeding, and respiration and losses from metabolism, respiration, growth, and excretion. Species are linked through feeding interactions to represent the food web, and the model predicts the steady-state concentration of contaminant that would accumulate in each species due to long-term exposure to specific concentrations in the sediments and waters of the ecosystem.
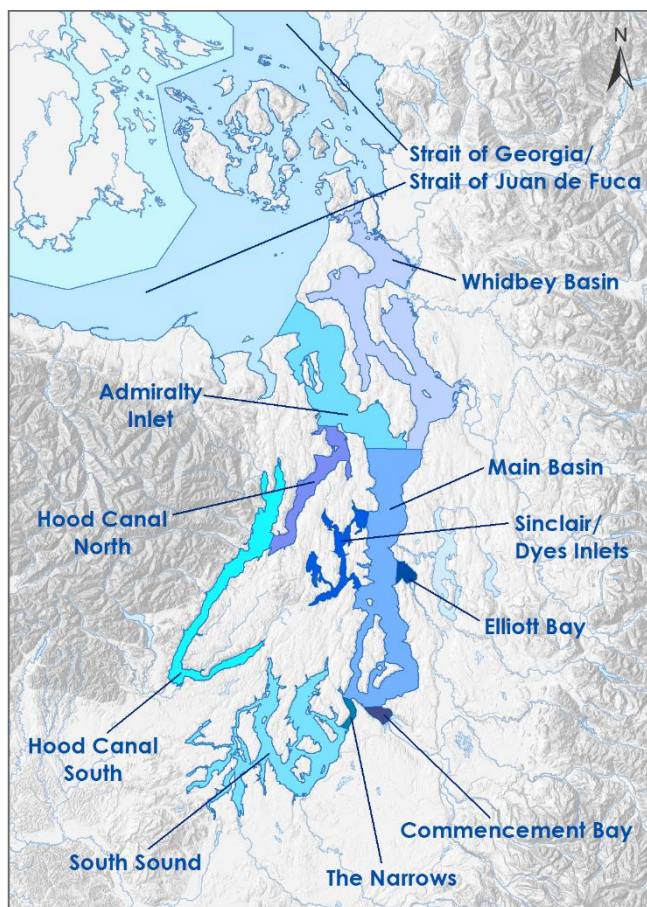
Figure ES-1. Map of Puget Sound showing model regions.

Project Tasks

To accomplish the project objectives, the following tasks were performed:

- Compiled recently collected data on concentrations of PCBs, PBDEs, PAHs, copper, lead, and zinc in the sediments and waters of Puget Sound and the Strait of Juan de Fuca to define model inputs and boundary conditions. Data on PCB and PBDE concentrations in Puget Sound biota were also summarized for comparison with bioaccumulation model predictions.

- Calculated contaminant loads to each model region via atmospheric deposition and watershed pathways (i.e., surface runoff, POTWs, and groundwater) using the data and methods that were employed in the development of the Puget Sound basin-wide loading estimates published in recent Ecology reports.

- Searched the literature to obtain contaminant-specific parameters describing chemical properties, partitioning, and rates of various processes. The modeling literature was also reviewed for biological parameters and feeding relationships for modeled species.

- Modified the PSRTM code to provide the capability to simulate fate and transport processes for PCBs, PBDEs, selected PAHs, copper, lead, and zinc, and the bioaccumulation of PCBs and PBDEs in the Puget Sound food web.

- Attempted to calibrate the fate and transport model to regional data for each of the modeled contaminants (including re-calibration for PCBs). The bioaccumulation model was calibrated so that predicted concentrations of PCBs and PBDEs across all species and regions gave the best possible match to observed data.

- Assessed the sensitivity of the fate and transport model to changes in individual parameters, as well as the influence of uncertainties in various model inputs on long-term model predictions. For the bioaccumulation model, the relative influence of contaminants in sediments versus water on the predicted concentration in each species was also evaluated.

- Conducted exercises to test the performance and assess the utility of the updated fate and transport model. Diagnostic exercises were also carried out to investigate inconsistencies between model results and actual conditions.

- Performed bioaccumulation model exercises to demonstrate the utility of the model for hypothetical management scenarios, including estimation of regional sediment and water concentrations needed to meet various biota endpoints. The biota endpoints (called Model Scenario Threshold Concentrations, or MSTCs) were adverse-effects concentrations from the literature or dietary thresholds based on Puget Sound Partnership targets.

Results

Fate and Transport Model

The fate and transport model tended to underestimate the concentration of contaminants in Puget Sound sediments and waters compared to observed data. The model also predicted rapid declining trends for all contaminants that were not supported by the observed data. Possible causes were explored with the model, and the results suggested that one or both of the following may explain the discrepancies between model predictions and the observed data:

- Contaminant loadings from watershed sources (including surface runoff, POTWs, and direct groundwater discharges) may have been underestimated in recently published studies. The model was used to back-calculate, or hindcast, how much higher the local sources would need to be in order to predict reasonable concentrations in Puget Sound. This analysis indicated that watershed loading sources would need to be approximately 5 to 10 times higher than current best estimates to match observed contaminant masses in the Sound.

- Contaminant concentrations in the waters of the Straits of Juan de Fuca and Georgia may have been underestimated in previously published studies. These waters represent the ocean boundary of the model and determine the magnitude of contaminant loading from the ocean to Puget Sound. The model was used to hindcast how much higher the boundary water concentrations would need to be in order to predict reasonable concentrations in Puget Sound. Ocean boundary concentrations would need to be approximately 2 to 4 times higher than the current best-estimate values to match observed contaminant masses in the Sound.

Based on preliminary model runs with all inputs and parameters set to the best currently available values, the relative importance of loss pathways and processes to the long-term fate of contaminants in Puget Sound differed by contaminant.

- The dominant loss pathway for most contaminants was export at the ocean boundary, which generally accounted for around half of the cumulative loss from the system.

- Burial was responsible for over 80% of the removal of lead and approximately half of the long-term losses of copper and zinc. Burial was also an important loss pathway for PCBs, accounting for about a third of the removal, but for other organic contaminants burial was not an important loss process.

- Degradation was a key loss process for some organic contaminants, accounting for around half of the long-term loss of PBDEs and PAHs. However, degradation only accounted for a small fraction of the long-term loss of PCBs from the system due to their much slower degradation rate (half-life of 56 years for PCBs compared to approximately 1 year for PBDEs and from several weeks to several years for PAH compounds).

- Volatilization played only a small role in the removal of organic contaminants relative to other loss processes. The metals addressed are not affected by volatilization.

Overall, the fate and transport model for PCBs in Puget Sound was successfully updated and expanded with the capability to simulate PBDEs, PAHs, copper, lead, and zinc. However, uncertainties remain that limit its utility as a tool for estimating the reduction in specific types of loading that would be needed to meet management targets for contaminants in sediment, water, or biota on a Puget Sound basin-wide scale.

Food Web Bioaccumulation Model

The calibrated model for the bioaccumulation of PCBs and PBDEs in the Puget Sound food web predicted biota concentrations with accuracy comparable to similar modeling studies. For PCBs, the model had an overall bias across all species and regions of 0.97, indicating excellent agreement with the observed data (perfect agreement would be 1.00). While the PBDE model tended to underestimate observed biota concentrations, the overall bias of 0.59 was within acceptable limits.

Scenario exercises demonstrated the utility of the bioaccumulation model for exploring hypothetical management questions.

- The model identified locations in Puget Sound where the observed PCB or PBDE concentrations in the sediments and waters were predicted to cause contaminants to bioaccumulate in organisms at concentrations exceeding adverse-effects levels or dietary thresholds. Figure ES-2 gives an example of such analyses, showing the predicted PCB concentration in the harbor seal pups of each region compared to an adverse-effects threshold concentration from the literature. Generally, the largest exceedances of biota thresholds were predicted in the urban bays (Commencement Bay, Elliott Bay, and Sinclair/Dyes Inlet). In the basins of Puget Sound, predicted biota concentrations were also above some of the thresholds but by much smaller magnitudes compared to the urban bays.

- The model was also used to determine how low environmental concentrations of PCBs or PBDEs would have to be in each region to ensure that various biota thresholds would not be exceeded. The model predicted that sediment concentrations would generally have to be near analytical detection limits to meet the most restrictive biota thresholds tested, while contaminants in water would have to be at or below minimum measured concentrations. In a management context, the sediment and water concentrations derived in this exercise could inform the development of ecologically-relevant targets or benchmarks for effectiveness monitoring.
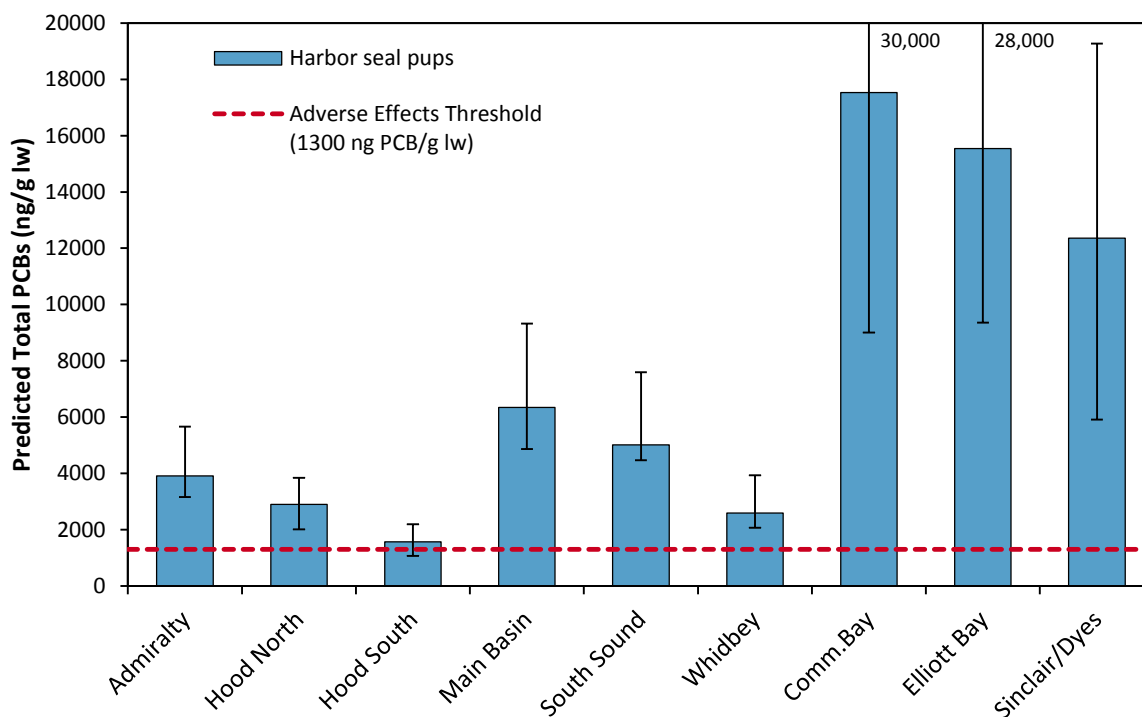
Figure ES-2. Predicted Total PCBs in harbor seal pups compared to an adverse-effects threshold.

Error bars show the range of predictions using 25th percentile (lower bars) and 75th percentile (upper bars) sediment and water concentrations in each region. Upper bars for Commencement and Elliott Bays extend to 30,000 and 28,000 ng/g lw, respectively.

Sensitivity tests for the bioaccumulation model indicated that predicted concentrations of contaminants in biota were more strongly influenced by changes to contaminant concentrations in the water column than by comparable changes in sediment concentrations, particularly in relatively uncontaminated regions where sediment concentrations were low. In contrast, the influence of sediments was greater in urban bays where sediment concentrations were typically much higher. Although the majority of PCB and PBDE mass in Puget Sound is stored in the sediments, these results indicate the importance of contaminants in water as an exposure route and driver of bioaccumulation in many areas. Efforts to decrease contaminant concentrations in Puget Sound marine waters (e.g., by actions to reduce loads and prevent releases) may therefore be a critical component of strategies to achieve ecosystem health goals. For the urban bays and regional "hot spots" where contaminants in the sediments are high, these results also underscore the importance of sediment cleanup activities for reducing the uptake and bioaccumulation of contaminants in the food web.

In sum, the food web bioaccumulation model was shown to be a useful tool for evaluation of the relationships between contaminant concentrations in water, sediment, and biota, and interactions among trophic levels in the Puget Sound ecosystem.

Recommendations

The analyses and findings of this study support the following recommendations:

Fate and Transport Model

Future efforts to model contaminant fate and transport in Puget Sound should focus on smaller geographic areas, such as individual urban bays or selected watersheds. This would help reduce uncertainties in critical model inputs such as local loading and would make it economically feasible to collect data to support the model. Examples of appropriate smaller scales for fate and transport modeling include the recent modeling work on PCBs in Lake Washington by King County (DeGasperi et al., 2014) and the ongoing multi-agency work on the Lower Duwamish Waterway for which modeling will be used in support of source control strategies.

If there is a desire to continue Puget Sound basin-wide modeling, the following data gaps and uncertainties should be addressed:

- Data on contaminant concentrations in the waters of the model's ocean boundary are needed (i.e., in the Strait of Juan de Fuca just beyond the sill at Admiralty Inlet). Model predictions are especially sensitive to the concentrations in the ocean boundary waters, and additional data would help to reduce uncertainty in this important model input.

- There is a gap in data on contaminants associated with suspended sediments in Puget Sound marine waters. The collection of such data would enable comparisons of model-predicted and observed contaminant concentrations in regional suspended sediments, thereby adding confidence to model predictions of contaminant partitioning in the environment.

- Loading from atmospheric deposition was significant for some contaminants (e.g., PBDEs). Because atmospheric deposition for some contaminants is correlated with development (Brandenberger et al., 2010), as human population increases it is likely that loads from

atmospheric deposition will also increase. Establishment of a sampling program to monitor contaminant deposition at stations around Puget Sound would be useful in conjunction with modeling to explain or interpret observed trends in contaminant concentrations in the waters and sediments of the Sound.

Food Web Bioaccumulation Model

The bioaccumulation component of the PSRTM was shown to perform well as a stand-alone model that can be used to explore how PCB and PBDE concentrations in Puget Sound biota respond to varying levels of these contaminants in the sediments and waters of the ecosystem. The following recommendations would further enhance the utility of the bioaccumulation model:

- Limited data were available on water column concentrations of PCBs and PBDEs in Puget Sound. Model sensitivity analyses showed that contaminant concentrations in the water column have a large influence on predicted biota concentrations in all regions, especially in areas where sediment concentrations are relatively low. New sampling to refine estimates of water column concentrations would help reduce uncertainties in this key model input.

- Additional monitoring should be conducted to fill data gaps on PCB and PBDE concentrations in species at all trophic levels in the Puget Sound food web. Such data would reduce uncertainties in the observed biota data, provide information on contaminants in additional species, and allow for better accounting of covariates such as organism size, age, and sex. Ideally, biota data would be sampled from multiple locations spanning the range of environmental conditions found in each region and would be coincident and co-located with sampling for contaminants in water and sediment. As new data on contaminants in biota are collected, organism-specific parameters can be refined and the model calibration can be improved.

- A next step in the development of the bioaccumulation model would be to create, in consultation with local biologists, region-specific food webs to account for differences in species and feeding relationships that may exist between the regions of Puget Sound.

Introduction

Background

Human activities introduce a wide range of contaminants into the Puget Sound ecosystem, many of which are environmentally persistent and harmful to humans and aquatic life. While not necessarily released at dangerous levels, toxic contaminants that enter the inland marine and estuarine waters of Puget Sound can remain for long periods of time due in part to the system's physical setting, which consists of deep and narrow interconnected basins separated by shallow sills that restrict exchange. As a result, these contaminants can accumulate in some embayments and inlets of Puget Sound, increasing their exposure to aquatic organisms.

Toxic contaminants in the water column and sediments of Puget Sound can cause adverse biological effects on the organisms that come into contact with them (PSP, 2006). These effects can range from chronic, sub-lethal problems that reduce an organism's ability to survive or reproduce (e.g., neurological problems, reproductive and developmental abnormalities, immune-response suppression, cancer, endocrine disruption) to outright death. Due to their lipophilic nature, some contaminants concentrate in animal tissues and magnify as they move up through the Puget Sound food web, accumulating in forage and bottom fish species (e.g., herring and English sole, respectively) and ultimately affecting salmon, seals, and orcas. These contaminants can also be a human health concern for consumers of fish and other aquatic organisms with high contaminant levels.

Despite cleanup efforts and targeted actions to reduce point and non-point sources, many locations in Puget Sound contain legacy toxic substances that were banned decades ago, such as polychlorinated biphenyls (PCBs) and some polybrominated diphenyl ethers (PBDEs). These and other contaminants that have not been banned, such as polycyclic aromatic hydrocarbons (PAHs) and metals (e.g., copper, lead, and zinc), continue to enter the Sound via stormwater and surface runoff, municipal and industrial wastewater, groundwater discharges, and atmospheric deposition. As such, the problem of toxic contaminants in the Puget Sound ecosystem remains an ongoing challenge and a priority for environmental managers and the general public (PSP, 2014: Action Agenda Priority C).

From 2006 to 2011, the Washington State Department of Ecology (Ecology) worked in collaboration with the Puget Sound Partnership (PSP) and other state and federal agencies to conduct a multi-phase Puget Sound Toxics Loading Analysis (PSTLA[1]). The overall goal of the PSTLA was to provide scientific information to guide decisions about how best to direct resources and prioritize strategies for controlling toxic contaminants in the Puget Sound basin. To that end, PSTLA studies aimed to improve understanding of the sources, delivery pathways, and hazards of selected chemicals entering Puget Sound, as well as their transport and fate in the ecosystem.

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[1] Ecology's website for the PSTLA, from which all project publications can be accessed, is at
http://www.ecy.wa.gov/programs/wq/pstoxics/index.html.

Phase 2 of the PSTLA included an Ecology study to develop numerical models to simulate the movement of toxic contaminants within and between Puget Sound waters, sediments, and aquatic organisms. Such models are useful tools for the evaluation of management alternatives, allowing comparison of the ecosystem response under various source control scenarios. In that study, Pelletier and Mohamedali (2009) developed the Puget Sound Regional Toxics Model (PSRTM; previously called the "Puget Sound Toxics Box Model" or "Ecology box model") by integrating three previously published model applications:

- Box model of water circulation and transport (Babson et al., 2006).
- Mass balance model of contaminant fate (Davis, 2004).
- Food web bioaccumulation model (Arnot and Gobas, 2004; Condon, 2007).

Pelletier and Mohamedali (2009) performed initial Puget Sound modeling simulations with PCBs due to the relative abundance of data. Model input values were derived from actual data collected from Puget Sound to the extent possible and were supplemented with default values from the literature for parameters that could not be estimated from observed data.

A high degree of uncertainty was associated with some of the model inputs because regional toxics data were lacking or limited for a number of ecosystem components. These uncertainties limited the usability of the model for evaluating source control strategies. Pelletier and Mohamedali (2009) recommended that additional data on contaminant concentrations in the marine water column, ocean boundary waters, various species of biota, and external loads to Puget Sound were needed to improve calibration of the model and to reduce uncertainty in the model predictions. Several projects were carried out in Phase 3 of the PSTLA to collect regional toxics data to fill the identified data gaps.

Project Description

The present study was undertaken to update and expand the modeling work of Pelletier and Mohamedali (2009). The primary objectives were to:

- Modify the Puget Sound Regional Toxics Model to allow the simulation of contaminants beyond PCBs, including PBDEs, selected PAHs, copper, lead, and zinc.

- Incorporate new loading estimates and recent regional data from Phase 3 of the PSTLA and other readily available sources to improve model inputs and reduce overall uncertainty in the model predictions.

The enhanced model was intended to reliably forecast concentrations of the selected contaminants in the waters, sediments, and biota of the Puget Sound ecosystem. In this way, the PSRTM would have broader utility as a tool for exploring how the ecosystem might respond to potential contaminant source reduction strategies.

The project QAPP (Osterberg and Pelletier, 2012) outlined the following specific tasks that were to be carried out in support of the project goals:

- Compile recently collected data on concentrations of PCBs, PBDEs, selected PAHs, copper, lead, and zinc in regional sediments, waters, and biota for model inputs and boundary conditions.

- Review the modeling literature to obtain contaminant-specific model parameters.

- Update the PSRTM code to provide the capability to simulate fate and transport processes for PCBs, PBDEs, selected PAHs, copper, lead, and zinc, and the bioaccumulation of PCBs and PBDEs in the Puget Sound food web.

- Calibrate the PSRTM to regional data for each of the modeled contaminants (including re-calibration for PCBs after the incorporation of newly collected data).

- Evaluate the sensitivity and uncertainty of model predictions to various input parameters and boundary conditions for each of the modeled contaminants.

- Identify *model scenario threshold concentrations* (MSTCs) for each modeled contaminant to describe concentrations in water, sediment, or biota above which the health of the ecosystem or humans (or both) may be harmed or adversely affected.

- Conduct exercises to demonstrate the utility of the model for the evaluation of management scenarios:
    - Estimate numeric reductions in contaminant loadings or environmental concentrations needed to meet MSTC endpoints.
    - Estimate the time required to achieve MSTCs under various loading reductions.

This report documents the implementation of these model enhancements and describes efforts to test the utility of the updated PSRTM in a hypothetical management capacity.

Study Area and Model Domain

Puget Sound is the largest estuarine fjord system in the contiguous United States. Located between the Olympic and Cascade mountain ranges in Washington State, the estuary is an arm of the Pacific Ocean that extends inland where it meets 19 different river watersheds. The Puget Sound watershed covers more than 16,800 square miles ($43,400 \text{ km}^2$) of land and water, with approximately 2,800 square miles ($7,250 \text{ km}^2$) of inland marine waters bounded by 2,500 miles (4,025 km) of complex shorelines (Hart Crowser et al., 2007).

The hydrography of Puget Sound consists of a series of interconnected basins separated by relatively shallow ridges, or sills. The three major branches of Puget Sound include the Main Basin and South Sound (separated by a sill and constriction at the Narrows), Hood Canal, and Whidbey Basin. Admiralty Inlet links the three branches of the Sound together and serves as the primary outlet to the Straits of Juan de Fuca (SJF) and Georgia (SOG) and ultimately the Pacific Ocean. The only other outlet to SJF/SOG is the shallow and extremely narrow Deception Pass located at the northern end of Whidbey Basin.

The model domain includes the marine waters of Puget Sound south of the outlets at Admiralty Inlet and Deception Pass. The model domain is divided into ten regions based on the locations of sills and data stations (Figure 1). Seven of the regions correspond to the principal basins: Admiralty Inlet, northern Hood Canal, southern Hood Canal, Main Basin, the Narrows, South Sound, and Whidbey Basin. Three additional regions represent urban bays: Commencement Bay, Elliott Bay, and Sinclair/Dyes Inlets. The ocean boundary to the model domain consists of the U.S. portions of the Straits of Juan de Fuca and Georgia.
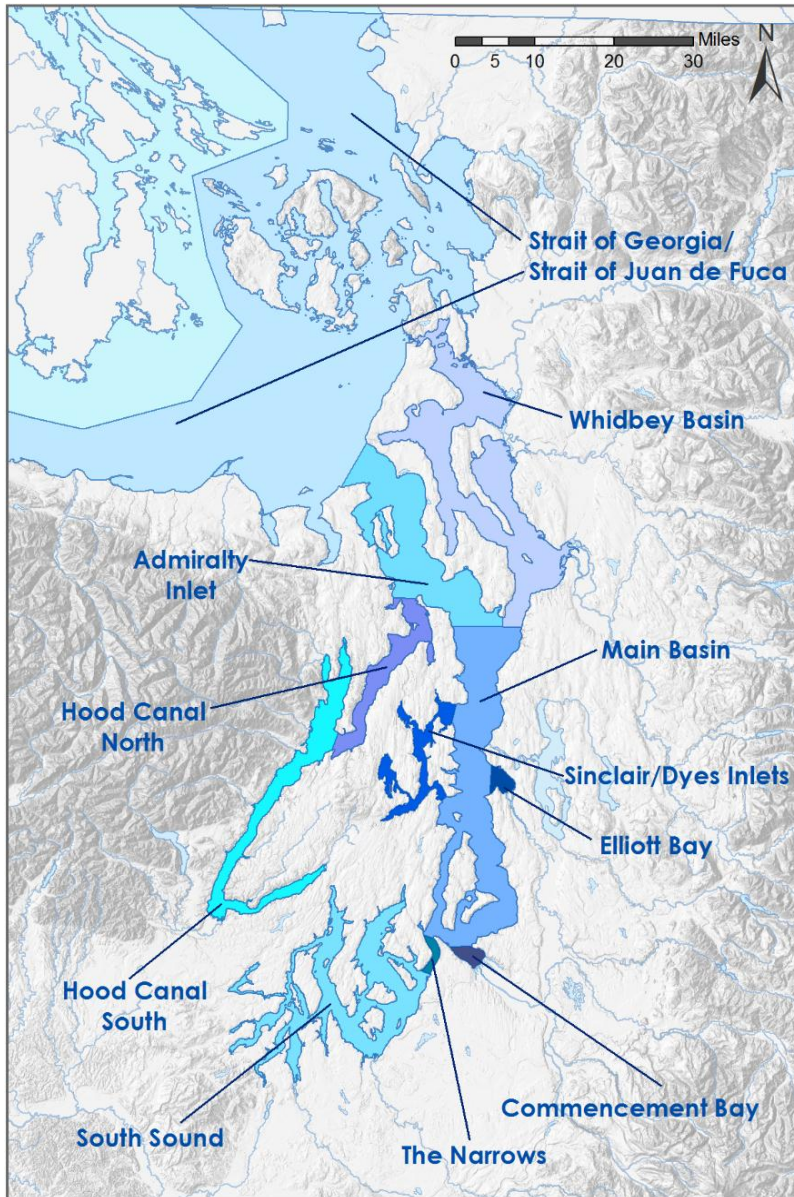
Figure 1. Map of Puget Sound showing model regions.

Model Components

The numerical modeling approach for this project involved three sub-models to simulate water circulation and transport, contaminant fate in the ecosystem, and contaminant bioaccumulation in the food web. While the combined model is referred to as the Puget Sound Regional Toxics Model, the manner in which the sub-models were linked by Pelletier and Mohamedali (2009) is most accurately described as having two major components: (1) a "contaminant fate and transport model" that completely integrates the circulation and transport sub-model with the contaminant fate sub-model, and (2) a "food web bioaccumulation model." To a large extent these components are independent, but they can be used in concert to explore how contaminant dynamics in the physical ecosystem affect the accumulation of contaminants in aquatic organisms (i.e., predicted contaminant concentrations in sediment and water from the "fate and transport model" can be set as inputs for the "bioaccumulation model").

The following sections provide brief descriptions of the three sub-models, their integration into the PSRTM by Pelletier and Mohamedali (2009), and their application for the present study. The reader is referred to the original publications for more detailed discussions of the theory and equations supporting each model.

Contaminant Fate and Transport Model

Water Circulation and Transport

A previously published box model (Babson et al., 2006) for simulating water circulation in Puget Sound was adapted for the PSRTM by Pelletier and Mohamedali (2009). The model theory is described in Babson et al. (2006) and Li et al. (1999). Briefly, circulation is assumed to be driven primarily by density differences between freshwater river inputs and salty marine water at the seaward boundaries of the Sound. The model approximates this circulation as two-layer exchange flow, with mean flow seaward at the surface and landward at depth.

The ten regions of the model domain (Figure 1) are "boxes" between which water exchange occurs in the model. The water column in each region of the model is further divided vertically into a surface layer and a deep layer, resulting in a total of twenty boxes. The thickness of the water column layer varies by region and is determined by the depth of no motion where the tidally averaged velocity between the seaward-flowing surface layer and the landward-flowing deep layer is zero (Table 1). A schematic of the circulation box model is presented in Figure 2.

Model equations are based on the conservation of mass and salt. Forcing of the system is primarily due to freshwater inputs from the major rivers to the surface waters of the Sound and the entrainment of deep saline water at the Admiralty Inlet seaward boundary. The model estimates salinity for each box and calculates transports of salt and water between boxes due to vertical mixing and horizontal and vertical advection. In this way, the model is capable of predicting seasonal and inter-annual variations of water residence times and transports.
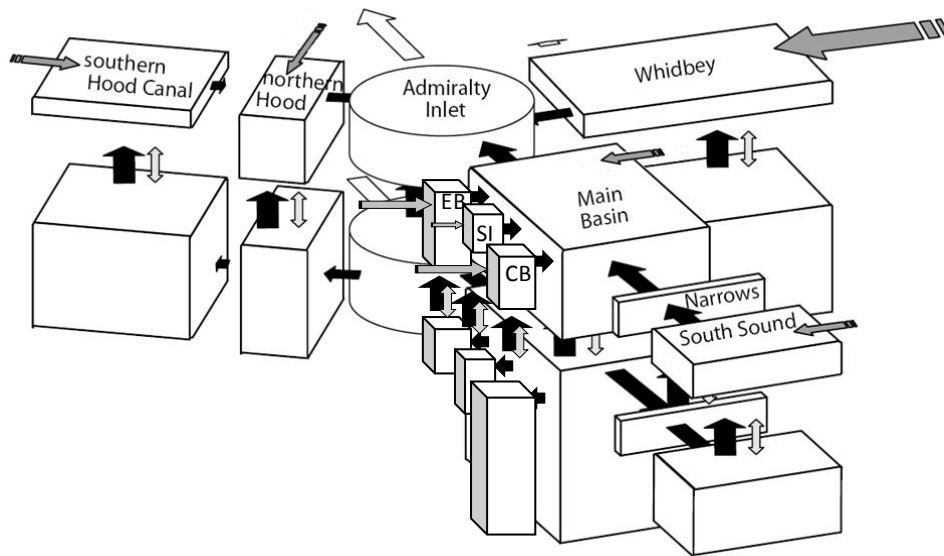
Figure 2. Schematic diagram of the box model of water circulation and transport in Puget Sound (after Babson et al., 2006).

Boxes are scaled to show relative volumes and arrows are scaled to show transports. Black arrows represent advection, two-way gray arrows represent mixing, and white arrows are boundary exchanges. Gray arrows with dashed ends represent river inputs and are proportional on a log scale. The three boxes separated from the Main Basin represent urban bays (EB: Elliott Bay; CB: Commencement Bay; and SI: Sinclair/Dyes Inlets). EB and CB are located on the eastern side of the Main Basin, but their boxes are shown on the western side for visualization purposes.

Table 1. Depth at which the upper (surface) and lower (deep) water column layers are divided for each region of the PSRTM.

Model Region	Depth of surface/ deep division (meters)
Admiralty Inlet	37.0
Commencement Bay	20.0
Elliott Bay	40.0
Hood Canal North	19.8
Hood Canal South	13.0
Main Basin	50.2
The Narrows	21.5
South Sound	29.9
Sinclair/Dyes Inlet	23.0
Whidbey Basin	9.1

Contaminant Fate

A mass balance model of contaminant fate is joined with the circulation and transport model. Based on the work of Mackay et al. (1994) and Gobas et al. (1995), the fate model was developed by Davis (2004) to simulate PCBs in the San Francisco Bay ecosystem. Although the model was originally created for PCBs, the modeled processes are applicable for other hydrophobic organic contaminants (HOCs); for example, Oram et al. (2008) adapted the model for PBDEs in San Francisco Bay.

The fate model theory is explained in detail in Davis (2004). Briefly, the model estimates inputs, outputs, and changes of HOC concentrations in water and sediment compartments. Sediments are divided into two compartments: an "active sediment" layer that is in contact with the water column, and deep "buried" sediment.

Pelletier and Mohamedali (2009) integrated the Davis model with the circulation model to create a "fate and transport model" for PCBs in Puget Sound. The combined model adopted the two-layer water column of the circulation model, and so horizontal and vertical exchanges occur between the ten regions and two water layers of the PSRTM domain. Additionally, Pelletier and Mohamedali (2009) provided the ability to simulate the transport of sediment from the shallow margins to deeper areas, classifying two sub-areas of active sediment (Figure 3): (1) sediments that are below the surface water layer, and (2) sediments that are below the deep water layer.

The major processes that add or remove HOCs from water or sediment in the combined "fate and transport model" include (Figure 4):

- External loading (e.g., atmospheric deposition, surface runoff, wastewater discharges, groundwater discharges).
- Partitioning of dissolved and particulate forms.
- Volatilization.
- Diffusion (water-to-sediment and sediment-to-water).
- Solids settling and resuspension.
- Degradation in water and in sediment.
- Burial of deep sediments.
- Transport exchanges between regions and layers, including inflow and outflow at the model boundaries.

In sum, the fate model gives the PSRTM the ability to predict HOC concentrations in regional water and sediment layers in response to external loading and internal processes.
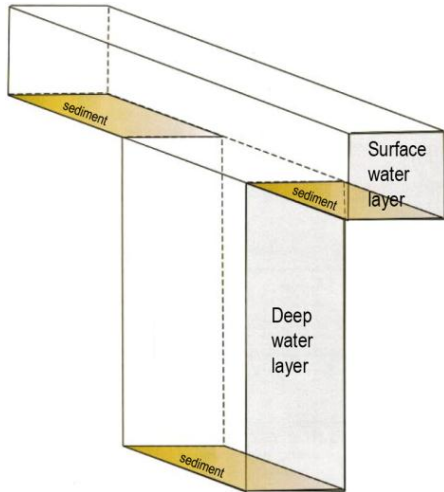
Figure 3. Conceptual representation of water column layers for the fate and transport model showing areas of active sediment.
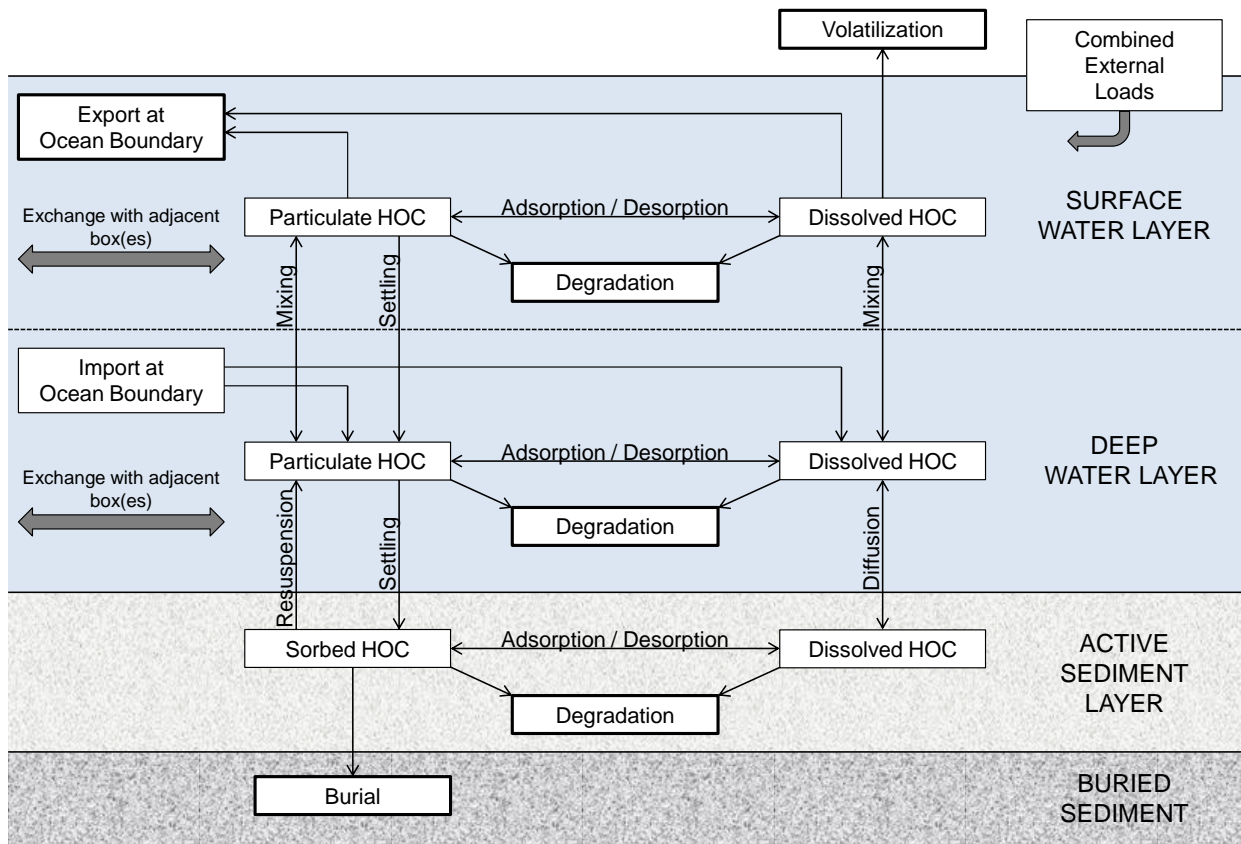
Figure 4. Diagram of the contaminant fate and transport model for HOCs (after Davis, 2004).

Arrows represent mass fluxes; thick gray arrows are mass fluxes of both particulate and dissolved forms; heavy outlines indicate sinks (i.e., removal from the system). The fate and transport of metals is identical except degradation and volatilization processes are omitted. In shallow areas the deep water layer is absent and the surface water layer is in direct contact with the active sediment layer (see Figure 3).

Food Web Bioaccumulation Model

A generalized bioaccumulation model for aquatic ecosystems was developed by Arnot and Gobas (2004) to simulate uptake and bioaccumulation of HOCs from sediment and water to the food web. Condon (2007) applied the Arnot and Gobas (2004) model in the Pacific Northwest, evaluating concentrations of PCBs in the biota at various trophic levels of the Strait of Georgia. Pelletier and Mohamedali (2009) linked the Condon (2007) model to the fate and transport model of the PSRTM and incorporated additional species to simulate fluxes of PCBs from sediments and water to biota in Puget Sound.

The theory for the food web bioaccumulation model is given in detail in Condon (2007) and Arnot and Gobas (2004). The model describes the principal feeding relationships of the aquatic food web and simulates the movement of HOCs through sediments and water, primary producers (phytoplankton and other plants), secondary producers (herbivores), forage species (carnivores), and top predators via bioaccumulation[2].

Each species or representative organism class in the model food web is described as a single compartment in terms of exchange with the surrounding environment. Tissue concentrations of HOCs are predicted by simulation of the fluxes into and out of each organism, including:

- Direct uptake from water.
- Uptake from feeding.
- Uptake and loss from respiration.
- Loss due to metabolism.
- Dilution due to growth.
- Loss due to diffusion.
- Loss due to fecal egestion (excretion).
- Loss due to reproduction and nursing.

The model assumes steady-state[3] conditions, with contaminant concentrations at equilibrium in sediment, water, and biota. This assumption is reasonable for situations in which an organism is exposed to contaminants over a long period of time (i.e., throughout its entire life). Contaminant concentrations in tissues fluctuate slowly compared to exposures, and so body burden tends to reflect the average concentration to which an organism was exposed over time (Arnot and Gobas, 2004).

A diagram of the selected species and trophic linkages in the Puget Sound aquatic food web developed by Pelletier and Mohamedali (2009) is presented in Figure 5.

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[2] *Bioaccumulation* is the process by which the chemical concentration within an organism achieves a level that exceeds that in its environment as a result of chemical uptake through all possible routes of exposure (e.g., dietary, dermal, respiratory) (Gobas and Morrison, 2000).

[3] At *steady-state* the total flux into a given organism is equal to the total flux out, resulting in no net change in mass or concentration of the contaminant.
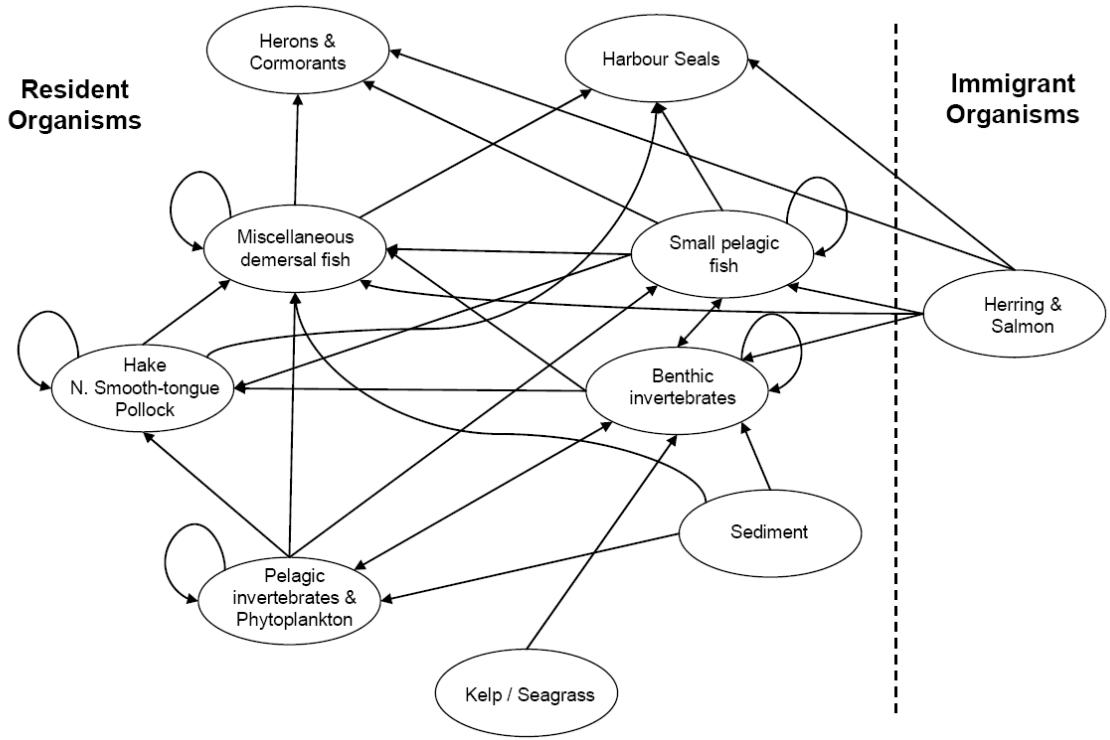
Figure 5. Diagram of trophic linkages for the major feeding groups in the food web bioaccumulation model (after Condon, 2007).

Modeled Toxic Contaminants

Initial development and testing of the PSRTM by Pelletier and Mohamedali (2009) focused solely on the simulation of polychlorinated biphenyls (PCBs); however, it was anticipated that the model would be adapted to additional contaminants at a later time. In Phase 3 of the PSTLA, studies were undertaken to fill data gaps for PCBs and also to collect similar environmental data for other contaminants of concern (COCs). The COCs targeted by the PSTLA studies were chosen for their (1) documented history of presence in Puget Sound, (2) capacity to harm or threaten the ecosystem, and (3) potential to represent, or serve as an indicator for, a particular class of chemicals in environmental media (Ecology, 2011). In general, these contaminants are highly persistent in the environment and can have toxic effects on aquatic organisms, and some have high bioaccumulation potential.

A subset of the PSTLA contaminants was selected for the present study based on the availability of recent data, modeling precedent in similar ecosystems (thus, availability of chemical-specific parameters and rates), and management interest (i.e., contaminants for which control strategies might benefit from an improved understanding of long-term fate processes). The COCs chosen for modeling were PCBs, polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), copper, lead, and zinc.

Polychlorinated Biphenyls (PCBs)

PCBs are a class of manmade organic compounds composed of two connected benzene rings with 1 to 10 chlorine atoms. There are 209 individual forms of PCBs, known as congeners, that have different chemical and physical properties based on the degree of chlorine substitution and arrangement on the biphenyl molecule. PCBs are also referred to by trade names given to various commercial mixtures of congeners, the most familiar being "Aroclors" in North America (manufactured by the Monsanto Corporation).

Commercial production of PCBs in North America spanned from 1929 to 1977 for use in a wide variety of applications requiring chemical stability and low flammability. The largest use was for heat transfer fluids in electrical transformers and capacitors, but PCBs were also used for plasticizers, hydraulic fluids, wax and pesticide extenders, lubricants, and adhesives. Many of the properties that made PCBs commercially desirable, such as their stability and resistance to degradation, make them extremely persistent in the environment where they bind strongly to sediment and soil particles and bioaccumulate in aquatic organisms.

PCBs were shown to have toxic effects to the immune, reproductive, nervous, and endocrine systems in humans and other animals. Furthermore, they have been found to cause cancer in animals and are considered likely to cause cancer in humans. The use of PCBs was restricted in the 1970s as their negative health and environmental impacts became apparent, and their manufacture was finally banned in 1979 under the Toxic Substances Control Act (TSCA; 44 FR 31514).

Although the sale and production of PCBs have been banned for over three decades, they continue to be found in environmental media and have become one of the most ubiquitous of all

environmental contaminants. Studies of fish tissue and sediment concentrations of PCBs in many areas of North America indicate that the initial post-ban rate of decline appears to have slowed or halted completely (Van Metre et al., 1998; Hickey et al., 2006; Bhavsar et al., 2007). Present sources of PCB releases to the environment include hazardous waste sites, illegal or improper disposal of industrial wastes and consumer products, leaks from old electrical transformers, municipal and industrial effluents, runoff from contaminated surfaces (e.g., building caulks and sealants in older structures), leachates from unsecured landfills, burning of some wastes in incinerators, and atmospheric deposition.

Once in the environment, the persistence of PCB congeners varies substantially by the degree of chlorination. Resistance to metabolization, degradation, and volatilization increases with increasing chlorination, while lipid solubility (i.e., the ability to accumulate in the lipids of animals) generally decreases with increasing degree of chlorination (Mabey et al., 1982). The toxic potential of PCBs also varies widely by congener and may differ by as much as a factor of 10,000 (Ahlborg et al., 1994).

Polybrominated Diphenyl Ethers (PBDEs)

PBDEs are another class of manmade organic compounds that, like PCBs, include 209 possible congeners. Individual PBDE congeners vary by the number and position of bromine atoms on the molecule, and "homolog" groups consist of congeners with the same number of bromines. Commercial PBDE mixtures generally contain congeners from a given homolog group, the most common being penta-, octa-, and deca-brominated diphenyl ethers (referred to as Penta, Octa, and Deca, respectively).

Manufacturers of many different materials and consumer products have used PBDEs as flame retardant additives since the 1960s (e.g., electronic equipment, plastic housings, polyurethane foams, and textiles). In the late 1990s, concern began to emerge over the accumulation in human and animal tissues, potential toxicity, and environmental persistence of PBDEs. Pressure to limit or ban PBDEs mounted until manufacturers of Penta and Octa voluntarily ceased production in 2004; in Washington State, the manufacture, import, and sale of Deca was banned as of the end of 2012.

Unlike most COCs, nearly all PBDEs are released in closed systems (i.e., indoors) due to the use, wear, and degradation of consumer products; such PBDE-containing products may therefore represent diffuse sources of PBDEs to the environment during the remainder of their life-cycle or during disposal and recycling (Hale et al., 2003). The pathways by which PBDEs get into the physical environment are not fully understood (Alcock et al., 2003), but volatilization to the air may be an important mechanism of release since PBDEs are not chemically bonded to the matrices of those materials or consumer products (Lorber and Cleverly, 2010).

Once in the environment, the fate and toxicity of different PBDE congeners vary widely. The heavier congeners with higher numbers of bromines tend to be less volatile and bind more strongly to solids and dust. Heavier congeners may also degrade to lighter, lower-brominated congeners that are more bioaccumulative (i.e., build up more in animals) and more toxic (Kelley et al., 2008).

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a class of nonpolar hydrophobic compounds characterized by two or more fused aromatic rings composed of carbon and hydrogen. There are hundreds of such compounds, but most Ecology studies have focused on sixteen PAH compounds designated as "priority pollutants" in the federal Clean Water Act[4] (Table 2). Individual compounds are classified based on the number of fused carbon rings as low molecular weight (LPAHs, with three or fewer rings) or high molecular weight (HPAHs, with four or more rings). Carcinogenic compounds from either group are commonly referred to as cPAHs.

Table 2. Classification of sixteen "priority pollutant" PAHs by molecular weight.

LPAHs	HPAHs
Acenaphthene Acenaphthylene Anthracene Fluorene Naphthalene Phenanthrene	Benz(a)anthracene* Benzo(a)pyrene* Benzo(b)fluoranthene* Benzo(g,h,i)perylene Benzo(k)fluoranthene* Chrysene Dibenzo(a,h)anthracene* Fluoranthene Indeno(1,2,3–c,d)pyrene* Pyrene

* Designated as probable human carcinogen (cPAH) by EPA.

PAHs have both natural and anthropogenic sources, but those of natural origin are produced at very low rates (Blumer, 1976). PAHs are formed mainly as a result of incomplete combustion of fossil fuels and other organic materials (e.g., garbage, tobacco, and meat), and they are also constituents of petroleum and its derivatives (Neff, 1979). Sources of anthropogenic PAH releases to the environment include wood-burning stoves, vehicle emissions (including tire wear and motor oil leaks), forest fires, coal tar sealants, oil spills, residential trash burning, and industrial emissions. In addition, creosote-treated wood (e.g., marine pilings, railroad ties, and utility poles) and pole-treating operations have historically been major sources of PAHs to Puget Sound.

While PAHs are widespread in terrestrial, atmospheric, and aquatic environments throughout the world, their fate and persistence varies considerably by compound. Generally, PAHs are hydrophobic and have a strong affinity for particulates in air and water. As such, they are capable of being transported long distances in the atmosphere, and in aquatic systems they tend to settle out into the sediments. Volatilization plays an important role in the transport and distribution of LPAHs, but it is less significant for heavier molecular weight forms. Photolysis, hydrolysis, and microbial degradation are more important loss processes for PAHs compared to PCBs or PBDEs. These processes tend to be slower for HPAHs than for LPAHs (i.e., HPAHs

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[4] See Appendix A to 40 CFR Part 423. The current list of 126 "priority pollutants" is available from EPA at http://water.epa.gov/scitech/methods/cwa/pollutants.cfm.

are more resistant to these degradation processes), and so LPAHs typically have faster ecosystem loss rates than HPAHs.

Due to their lipophilic nature, PAHs can become concentrated in the fat tissues of animals. Some animals (especially vertebrates) have the ability to metabolize and eliminate PAHs, but those that are incapable (e.g., many invertebrates) may bioaccumulate PAHs and ultimately transfer the contaminant burden to predators. Many PAH compounds and mixtures are toxic to animals and humans to some degree[5], causing adverse effects such as immunosuppression, reduced growth, reproductive problems, and cancer. Despite their known toxicity, PAHs are not strictly regulated due in part to the large number and diversity of sources.

Copper

Copper is a metal that occurs naturally in the earth's crust. In addition to natural sources, anthropogenic releases of copper to the environment can occur from abrasion of vehicle brake pads, leaching from roofing materials, leaching of vessel anti-fouling paint, pesticide and micronutrient use in agricultural applications, and pesticide use in urban areas (Ecology, 2011). Such releases result in elevated copper concentrations in surface waters at locations where they are most likely to occur (e.g., adjacent to commercial/industrial areas, agricultural areas, and high-density urban areas) and in nearshore marine waters.

In the aquatic environment, copper exists in the dissolved form as cupric ions (Cu^{+2}), complexed with inorganic anions or organic ligands, or adsorbed to suspended or settled particles. Copper in the form of the cupric ion is the most bioavailable form. Because copper is an essential micronutrient for all living organisms it is readily accumulated by plants and animals, but it does not biomagnify in food webs.

Although copper is generally not toxic to humans and terrestrial wildlife at typical environmental concentrations, it can be highly toxic to aquatic organisms at low concentrations. Even trace amounts of copper can cause significant biological effects such as avoidance behaviors, altered sensory capacity, and sub-lethal neurotoxicity. In the Pacific Northwest, the disruptive effects of copper on salmonids are well documented (e.g., Tierney et al., 2010; Sandahl et al., 2007; Baldwin et al., 2003) and include reduced olfactory function, impaired olfactory-dependent behaviors (e.g., homing in spawning streams), and impaired behavioral responses to alarm pheromones (i.e., predator avoidance behaviors).

Lead

Lead is another naturally occurring metal that enters the environment through both natural processes and human activities. Natural sources are small relative to anthropogenic lead releases from historical sources such as lead-based paint, leaded gasoline, and lead-arsenate pesticides. Additional ongoing sources include lead mining, ammunition, fishing sinkers, wheel weights, lead-acid batteries, vehicle brake pads and tires, roofing materials, residential plumbing components, fertilizer applications, and emissions from the combustion of aviation fuel

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[5] LPAHs tend to be more acutely toxic but less carcinogenic than HPAHs.

(Ecology, 2011). Once released to the environment, lead is persistent and does not degrade to other substances.

Lead in the aquatic environment exists in the dissolved form as plumbous ions (Pb^{+2}), complexed with inorganic anions or organic ligands, or adsorbed to suspended or settled particles. Much of the lead in the marine environment is strongly adsorbed onto particles, and so the transport of lead is closely linked with the movement of particles. Lead accumulated in the sediments can be a significant reservoir, as adsorbed lead may dissolve and replenish interstitial and overlying waters. The dissolved ion is the most bioavailable form of lead for primary producers, but consumers also take up lead from contaminated food.

Unlike copper, lead is not an essential element for any known plant or animal. In fact, lead is highly toxic and causes many different types of health problems to both people and wildlife. In humans, lead most notably affects the development of the nervous system in children and causes problems with the cardiovascular, immune, and reproductive systems in adults. Exposed animals that do not die from acute lead exposure may face similar chronic effects that can reduce their ability to survive or reproduce. In aquatic environments, lead has been shown to accumulate in fish, particularly in bony material, but it does not biomagnify in the food web to any meaningful extent (Eisler, 1988; WHO, 1995).

Zinc

The final modeled contaminant, zinc, is a naturally occurring metal that is abundant in the earth's crust and is nearly always present at detectable concentrations in water and sediments from freshwater and marine environments. Anthropogenic sources of zinc include mining activities, metal smelters, vessel coatings (for protection against corrosion), roofing materials, vehicle tire and brake pad wear, fertilizers, residential plumbing components, and industrial emissions (Ecology, 2011). Once in the aquatic environment, zinc is highly mobile and exists in dissolved form as zinc ions (Zn^{+2}), complexed with inorganic anions, or adsorbed to particles.

Zinc is a biologically essential element, but in excess of cellular requirements it becomes toxic to humans and animals. For salmonids, exposure to high concentrations can be lethal, as zinc accumulates on the gills and impairs the ability to regulate relative levels of ions in the body (Skidmore, 1970). Sub-lethal effects for salmonids may include the avoidance of rearing habitat, physiological stress, and reduced immune response.

Fate and Transport Model

Model Setup

As developed by Pelletier and Mohamedali (2009), the fate and transport component of the PSRTM was configured to predict concentrations of a single hydrophobic organic contaminant (HOC) in the regional waters and sediments of Puget Sound. This approach allows the direct simulation of a specific congener or compound; however, to simulate an entire chemical class (e.g., Total PCBs, which encompass 209 congeners), a set of generalized chemical properties must be used to represent the group.

Both Davis (2004) and Pelletier and Mohamedali (2009) used the chemical properties of a single "representative" congener, PCB-118, to simulate the mass fluxes of Total PCBs. The selection of PCB-118 as the representative congener was based on its intermediate chemical properties and level of chlorination, abundance in the ecosystem, chemical similarity to the most toxic congener to humans (PCB-126), and data availability. The present work followed the previous modeling precedent and used PCB-118 properties to simulate Total PCBs. Chemical parameters for PCB-118 were updated with recent values from the literature whenever possible.

Expansion of the PSRTM to additional organic contaminants required similar decisions. For PBDEs, congener-specific chemical property information was scarce in the literature, but general properties for PBDE homologs were available. Tetra-BDEs had chemical properties that were intermediate among the PBDE homologs and were found to comprise a large fraction of the PBDE mass in Puget Sound sediments (see Figure B-12); Total PBDEs were therefore simulated using the chemical parameters of tetra-BDEs for the present study.

For PAHs, the model configuration provided the ability to simulate the sixteen compounds of interest individually and as groups of compounds (e.g., Total PAHs). Compound-specific chemical properties obtained from the literature were sufficient to support the simulation of all sixteen compounds; of the sixteen, seven compounds were chosen for the project's scenario exercises. For the simulation of Total PAHs, Fluoranthene was selected as a representative compound as it comprised the largest mass in Puget Sound sediments (see Figure B-13) and had chemical properties near the middle of the LPAH to HPAH range.

The following sections describe modifications that were made to the model code to facilitate simulation of the new contaminants of concern (COCs), and the development of model inputs to prepare the model for performance testing runs.

Model Code Updates

The computer code used to execute the calculations for the PSRTM's fate and transport component was written in Microsoft Excel's Visual Basic for Applications (VBA) programming language. Although Pelletier and Mohamedali (2009) used the model for PCB simulations, the framework and modeled processes were designed to be applicable to other hydrophobic organic contaminants (HOCs). As such, adaptation of the model to simulate PBDEs and PAHs did not require modification of the VBA code.

The processes that govern the fate and transport of metals in the ecosystem differ from those dictating the movement of organic contaminants. For example, most metals are conservative and do not have a gaseous phase, and so degradation mechanisms (e.g., biodegradation, photolysis) and volatilization do not apply (Chapra, 1997). Consequently, changes to the fate and transport model code were required so that only those processes applicable to metals were simulated. Switches were added to the fate and transport model code to bypass the degradation and volatilization loss processes during metals simulations. The partitioning of metals into dissolved, solids-sorbed, and DOC-sorbed forms was also incorporated into the code with guidance from the EPA WASP model (Wool et al., 2003) and Allison and Allison (2005).

Other code changes that were made to update or improve the model included the following:

- Added the capability to input atmospheric deposition loads (kg/yr) in addition to fluxes ($ng/m^2/yr$).

- Added water-air exchange functions for HOCs. Previously, the model used constant water- and air-side mass transfer coefficients from Davis (2004). The new functions compute the mass transfer coefficients at each time step based on the instantaneous water temperature, salinity, and wind speed. See Appendix D for details.

- Updated wind inputs with recent monthly averages from regional weather stations. See Appendix E for details.

- Added dynamic adjustment (i.e., at each time step) of partitioning coefficients to ambient temperature and salinity.

- Added the option to use 3-phase partitioning of HOCs in the water column, with contaminants in dissolved form, adsorbed to suspended particulates, or adsorbed to DOC. DOC-sorbed HOCs in the water column were made to be unavailable for volatilization and settling (Arnot and Gobas, 2004; DeGasperi et al., 2014).

- Fixed an error with the calculation of contaminant resuspension from the active sediments. Previously, the mass of resuspended contaminant was derived using the fraction of dissolved contaminant in the water column; the updated function uses the fraction in the active sediments. This change generally resulted in more rapid depletion of HOC from the active sediments and higher water column concentrations of HOC.

Model Inputs

The fate and transport model allows users to set environmental variables that describe contaminant loads to the ecosystem, initial concentrations in the sediments and marine waters throughout the model domain and boundary, chemical properties, and rate constants for modeled processes. While some attributes are independent of the modeled contaminant (e.g., sediment deposition and burial rates), most model inputs are contaminant-specific. Inputs for PCBs were updated from those used by Pelletier and Mohamedali (2009) whenever possible, and new suites of inputs were developed for the simulation of PBDEs, PAHs, and metals.

Data from a variety of sources was used to estimate ranges of possible contaminant loadings and concentrations in regional sediments and water layers, and to determine "best-estimate[6]" values for use as model inputs. No field sampling was conducted for the present project, but Phase 3 of the PSTLA included several studies designed specifically to provide new data for loading and concentration inputs. Information from those recent studies was supplemented by data from existing repositories (e.g., long-term monitoring program databases), the peer-reviewed literature, and communications with experts.

Once acquired, data quality was assessed and screening criteria were applied to remove data that were not appropriate for the purposes of the model. While different screening criteria were applicable for specific types of data (e.g., sediment data versus water data), there were general conditions required of all data. The following acceptance criteria were evaluated for all data used in the development and testing of the fate and transport model:

- *Data Reasonableness*. The quality of the available data was evaluated graphically and through review of written reports to the extent possible. Statistical summaries were used to identify erroneous or extreme outlier data; if there was a known reason to doubt their validity, these observations were removed from the data sets.

- *Data Representativeness*. Data that were reasonably complete and representative of typical conditions at the location under consideration (e.g., model region, water column layer, and watershed) were used. Data from contaminated "hot spots" were included if they were representative of current conditions; however, data collected prior to a known or suspected cleanup action were not used.

- *Data Comparability*. Sample collection and analysis methods were variable between and sometimes within data sources (e.g., due to project-specific resources and objectives, as well as the laboratory techniques and detection limits achievable at the time). A review of the available metadata and documentation was conducted and records that used obviously inappropriate or anomalous methods were removed from the data sets[7].

Model parameters for chemical properties and processes were derived from Puget Sound data when possible or were obtained from closely related modeling studies found in the literature. If data or published guidance for a particular parameter value were not available for Puget Sound (or a region thereof), then published values from similar aquatic systems were considered.

The following sub-sections describe the acquisition, assessment, and summarization of the environmental data and parameters used for model inputs. Uncertainties and potential biases of these inputs are also discussed.

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[6] Following Pelletier and Mohamedali (2009), median values from the data sets were generally used as model inputs because they were considered to be the best measure of central tendency.

[7] For metals data, the documentation of "total" versus "total recoverable" results was found to be unreliable and so both were included in the project data sets. For PCB Aroclor data in sediments, Aroclor sums were converted to equivalent sums of congeners to make all PCB sums in the sediment data set comparable (see Sediment Properties section for details).

External Contaminant Loads

Contaminants enter the model domain via (1) the inflow of deep boundary waters from the Straits of Juan de Fuca and Georgia to Admiralty Inlet, (2) atmospheric deposition to the marine water surface, and (3) delivery to the surface water column layer from external sources such as surface runoff, wastewater discharges, and groundwater. The flux of COCs at the ocean boundary is computed by the model from the contaminant concentration in the boundary waters and the volume exchange across the boundary, while the atmospheric and surface layer loadings are user-defined model inputs.

The Phase 2 modeling work by Pelletier and Mohamedali (2009) used atmospheric deposition loads for PCBs based on fluxes measured at two stations in British Columbia by Noel (2007). They obtained surface runoff loading estimates from Hart Crowser et al. (2007) and EnviroVision et al. (2008); however, an error was discovered in the flow calculation method of the latter study, and Pelletier (2010) updated the PCB modeling analyses using re-calculated loadings from Herrera (2010). Estimates of PCB loadings from wastewater and groundwater discharges were not available to Pelletier and Mohamedali (2009) or Pelletier (2010) and so were not included in their model inputs for external loadings from watershed sources.

Several studies were conducted during Phase 3 of the PSTLA to fill gaps and improve estimates of COC loads to Puget Sound via the following pathways:

- Atmospheric deposition to the marine water surface[8] (Brandenberger et al., 2010).
- Surface water runoff (Herrera, 2011).
- Publicly-owned treatment works (Ecology and Herrera, 2010).
- Direct groundwater discharge (Pitz, 2011).

The results from these studies were intended to be used "off the shelf" as model inputs; however, for the purposes of the present study the published loads were of limited usability due to region definition errors, incompatible or conflicting data rules, and other issues. As such, extensive re-calculations were necessary. A brief description of the Phase 3 loading studies, the rationale for re-calculating the published loads, and details of the load regeneration process are documented in Appendix A. In most cases the same procedures employed in the Phase 3 studies were adopted for the load regeneration calculations, as those methods had been peer-reviewed and approved. Comparisons of the published Phase 3 loads and the regenerated loads are given in Tables A-2, A-4, A-6, and A-8.

Table 3 presents the median regenerated loads to each model region via atmospheric deposition, surface runoff, POTWs, and direct groundwater discharges. These regenerated Phase 3 loads represent the best available estimates of pathway-specific loadings to the model regions, and were therefore used as model inputs for the present study. Estimates of the 25th and 75th percentile loads (presented in Table A-9) provide some indication of the uncertainty in the loading estimates. For model inputs, the external load to the surface water column layer in each region was set to the sum of the median regional loading estimates for the surface runoff,

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[8] Brandenberger et al. (2010) estimated direct atmospheric deposition to Puget Sound marine waters; the atmospheric deposition of contaminants on the watershed (and the mobilization and transport therefrom) is implicit in the surface runoff loads.

Table 3. Median regenerated loads (kg/yr) to model regions.

See Appendix A for details of the re-calculation process. See Table A-9 for regenerated estimates of 25th and 75th percentile loads.

Contaminant	Loading Pathway	Admiralty Inlet	Hood Canal North	Hood Canal South	Main Basin	The Narrows	South Sound	Whidbey Basin	Comm. Bay	Elliott Bay	Sinclair/Dyes Inlet	Puget Sound Total
Copper	Atmospheric Deposition	126	33.5	58.7	250	56.0	276	298	77.3	85.1	37.0	1299
	Surface Runoff	303	325	2285	2039	0.00	4294	14095	2664	1375	363	27744
	POTWs	11.6	2.56	0.205	2532	0.00	413	543	425	0.00	126	4053
	Direct Groundwater	34.3	271	456	130	0.00	794	188	27.1	8.17	142	2051
Lead	Atmospheric Deposition	51.3	16.0	28.2	93.7	27.7	117	97.2	38.3	42.2	12.9	524
	Surface Runoff	39	44.5	289	376	0.00	598	1762	374	227	62.1	3772
	POTWs	0.496	0.110	0.00878	108	0.00	17.7	23.3	18.2	0.00	5.42	174
	Direct Groundwater	12.7	134	125	118	0.00	364	80.3	21.5	4.53	110	970
Zinc	Atmospheric Deposition	1024	244	428	1268	230	1363	1549	318	350	166	6942
	Surface Runoff	1001	1122	7897	7846	0.00	14799	47823	9405	5369	1326	96588
	POTWs	50.8	11.2	0.898	11094	0.00	1809	2380	1861	0.00	554	17761
	Direct Groundwater	158	1263	2091	729	0.00	3704	872	126	32.0	685	9659
Total PCBs	Atmospheric Deposition	0.0465	0.0121	0.0212	0.111	0.00851	0.0995	0.0899	0.0117	0.0129	0.0131	0.426
	Surface Runoff	0.0415	0.0485	0.353	0.321	0.00	0.625	2.09	0.405	0.231	0.0541	4.17
	POTWs	0.000917	0.000203	0.0000162	0.200	0.00	0.0327	0.0430	0.0336	0.00	0.0100	0.321
	Direct Groundwater	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
Total PBDEs	Atmospheric Deposition	0.425	0.134	0.236	0.943	0.101	0.590	0.641	0.140	0.154	0.127	3.49
	Surface Runoff	0.0432	0.0524	0.386	0.368	0.00	0.674	2.26	0.447	0.274	0.0597	4.56
	POTWs	0.0283	0.00626	0.000501	6.19	0.00	1.01	1.33	1.04	0.00	0.309	9.91
	Direct Groundwater	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
Total PAHs	Atmospheric Deposition	4.72	1.64	2.88	16.2	3.50	5.49	6.86	4.83	5.32	2.60	54.0
	Surface Runoff	3.35	4.11	30.3	25.8	0.00	51.4	176	33.7	18.8	4.38	348
	POTWs	0.0496	0.0110	0.000878	10.8	0.00	1.77	2.33	1.82	0.00	0.542	17.4
	Direct Groundwater	1.39	33.3	15.2	13.0	0.00	40.3	17.2	135	4.63	11.5	272

NC: Not calculated.
POTWs: Publicly-owned treatment works.

POTWs, and direct groundwater pathways and was assumed to be distributed over time proportional to river flows. The median regional atmospheric deposition loads were set as model inputs for the atmospheric loading pathway. If a pathway loading estimate was not available for a given contaminant, the model input for that pathway load was assumed to be zero.

Although the regenerated Phase 3 loads are the current best estimates, those loads have inherent biases imparted by the study-specific assumptions, sampling design, and data rules (substitution rules for non-detects, summation rules for "total" contaminants). Except in the case of atmospheric deposition loads, there was no attempt to "normalize" the data handling methods employed by the Phase 3 studies to a common set of preferred rules. The uncertainties and known or suspected biases of the published Phase 3 loads and those regenerated for this study are described in Appendix A and summarized in Table A-10. These limitations should be considered when using the estimates as model inputs and when interpreting model predictions. In general, the regenerated loads should be considered *minimum* loading estimates (with the exception of direct groundwater discharge loads, which were *maximum* estimates).

Sediment Properties

Sediments in the fate model are divided conceptually into an active sediment layer and buried sediment. The active sediment is the upper layer of sediment that is actively exchanging contaminants with the water column via solids settling, resuspension, and diffusive exchange of dissolved contaminants. The buried layer consists of sediment that is too deep to exchange contaminants with the active sediment layer and water column.

Regional contaminant concentrations in the active sediment layer define the mass of COCs in regional marine sediments. For the Phase 2 modeling study, Pelletier and Mohamedali (2009) obtained sediment PCB data from Ecology's Environmental Information Management (EIM) database and from EPA's Environmental Monitoring and Assessment (EMAP) databases. For the present study, the search for information on COC concentrations in Puget Sound sediments was expanded to include the following data sources and sampling programs:

- Ecology's EIM database.
- Washington Coastal EMAP databases.
- Puget Sound Ecosystem Monitoring Program (PSEMP).
- King County Department of Natural Resources and Parks (KCDNRP).
- NOAA National Status and Trends Program.
- EPA *OSV Bold* Survey database.

Queries were developed to obtain sediment data collected in ocean, estuary, subtidal, and intertidal areas of Puget Sound. The thickness of the active sediment layer was defined as 10 cm, following Pelletier and Mohamedali (2009) and Boudreau (1994); thus, only concentrations measured in the 0-10 cm sediment strata were targeted by the queries. In addition to the contaminant concentration data, sediment Total Organic Carbon (TOC, %) and sample-specific moisture content data were also queried to allow for OC-normalization and conversion between wet- and dry-weight basis measurements.

Once acquired, acceptance criteria and constraints were applied to omit data that were not appropriate for the purposes of the model. The screening steps and assumptions employed when compiling the sediment data were as follows:

- Overlaps between data sets were identified and remedied. For example, the EIM data set was found to contain large subsets of the EMAP and KCDNRP data; the overlapping records were removed from the EIM data set to avoid double-counting those results.

- Sample results older than 2000 were omitted so that the data would be representative of recent or current conditions.

- Samples for which the sediment collection depth was unspecified or greater than 10 cm were removed[9].

- Samples collected prior to a known or suspected cleanup (e.g., dredging or capping) at a specific location were removed.

- Data qualifiers were translated to be consistent with those commonly used by the Manchester Environmental Laboratory (e.g., "U", "UJ", "J"); when multiple qualifiers were given, the most constraining qualifier was assigned.

- Sample results that were qualified as rejected (e.g., "REJ" qualified) were removed.

- Sample results that were qualified due to blank contamination concerns were removed.

- Sample results that were qualified as estimates (e.g., "J" qualified) were used without modification.

- All sample concentrations, detection limits (DLs), and reporting limits (RLs) were converted to common units for each contaminant.

- Sample concentrations, DLs, and RLs reported on a wet-weight basis were converted to dry-weight basis using the sample's Percent Solids, when available; otherwise, those samples were removed.

- Pairs or groups of replicate samples were averaged.

- Pairs or groups of duplicate samples were averaged.

- Samples were referenced to model regions in ArcGIS using a spatial join; samples collected outside the model regions were removed.

Methods for handling data that were reported as non-detects (NDs) and for calculating sum "totals" of contaminant groups (e.g., Total PCBs, Total PAHs) were required before statistical summaries of the sediment data could be computed. Following Pelletier and Mohamedali (2009), different rules were evaluated using cumulative frequency distribution (CFD) plots to explore the relative biases of the methods. The rules adopted for the sediment data were as follows:

- *Substitution rules for "individual" contaminants (i.e., copper, lead, zinc, and individual PAH compounds)*
    - Detected samples were used without modification.
    - ND samples were assigned 1/2 the sample DL. If no DL was available, the record was assigned 1/2 the sample RL; if no RL was available, the record was omitted.

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[9] Sediment samples collected by the *OSV Bold* Survey were from the sediment surface to a depth of 14 cm; these data were nonetheless deemed usable for the present study.

- *Substitution and summation rules for "total" contaminants (i.e., Total PCBs, Total PBDEs, Total PAHs, Total LPAHs, Total HPAHs, and Total cPAHs)*
  - For samples consisting of all detected constituents or a mix of detected and non-detected constituents, the ND constituents were assigned zero and the sample "total" was the sum of the detected constituents.
  - For samples consisting of all ND constituents, the sample "total" was assigned 1/2 the maximum DL of the constituents in the sample; if no DLs were available, the "total" was assigned 1/2 the maximum RL of the constituents in the sample; if no DLs or RLs were available, the sample was omitted.

Non-detects comprised a significant portion of the sediment data set for Total PCBs (35% of the samples) and some individual PAH compounds (e.g., 50% of the Acenaphthene samples). As a result, the substituted values may exert a relatively large influence on the estimated sediment concentrations for these organic contaminants.

The sediment data set for PCBs included both congener and Aroclor results. The sum "total" of the Aroclors in a sample was translated to an equivalent congener sum (i.e., Total PCBs) using the regression equation developed by Pelletier and Mohamedali (2009) from paired samples where congeners and Aroclors had been detected: *sum of congeners* (ug/kg) = 0.4437 x *sum of Aroclors* (ug/kg). The final sediment data set consisted of 1590 samples where Aroclor sums were converted in this manner; in contrast, only 364 samples had been analyzed for congeners and did not require conversion. Statistical summaries of Total PCB concentrations in the sediments of most regions (with the exception of Admiralty Inlet and Hood Canal South) were therefore strongly influenced by the conversion of Aroclor sums to congener sums. Pelletier and Mohamedali (2009) recognized this as a significant but relatively small uncertainty relative to other key model input data.

The final data sets from the various data sources were combined into a single aggregate data set of sediment concentrations for each contaminant (Appendix P). The collection locations of the sediment data for each contaminant are shown on the maps in Appendix B. Summary statistics for contaminant concentrations in the active sediment layer of each model region are presented in Tables B-1 through B-10.

Model inputs for the initial contaminant concentration in the active sediment layer of each region were set to the median values given in the summary statistics tables. When regional sediment data were scarce ($n \leq 2$ samples), substitution rules were employed to ensure that each region had a model input value that was based on at least three samples from a similar area of Puget Sound. For this purpose, statistical data summaries were computed for sediment data from all "basins" (Admiralty Inlet, Hood Canal North, Hood Canal South, Main Basin, The Narrows, South Sound, and Whidbey Basin), all "urban bays" (Commencement Bay, Elliott Bay, and Sinclair-Dyes Inlet), and from all 10 regions of Puget Sound. The "basins" and "urban bays" statistics were substituted as appropriate unless the number of samples comprising those data sets was also less than or equal to two, in which case the statistics derived for all 10 regions were substituted.

Given that the sediment data sets included samples collected by a variety of studies, many of which focused on characterizing concentrations near known or suspected contaminant sources, it is likely that the model inputs are biased high. In addition, inconsistent sets of PCB congeners, PBDE congeners, and PAH compounds were analyzed by the various data sources due to study-specific analytical methods and objectives. Limiting the data sets for Total PCBs, Total PBDEs, and PAH groups to only include samples with common subsets of congeners or compounds would have resulted in prohibitively low numbers of samples for the development of regional concentrations. As such, variable subsets were used and may be a source of uncertainty in the model analysis, potentially contributing to disagreements between model predictions and observed concentrations. Figure B-11 in Appendix B shows the fraction of Total PCBs represented by each of the twenty most commonly measured congeners using the sediment data from all Puget Sound regions. Figure B-12 similarly shows the relative contribution of PBDE congeners, and Figure B-13 shows the same for PAH compounds.

Water Properties

Marine waters in each region of the fate model are divided into surface and deep water column layers. The thickness of the surface layer varies by region and is determined by the depth of no motion, where the tidally averaged velocity crosses zero between the seaward-flowing surface layer and the landward-flowing deep layer (Babson et al., 2006). The depth at which each region is divided into surface and deep layers is presented in Table 1.

For Phase 2 modeling, the initial PCB concentrations in regional water layers were based on data obtained from Ecology's EIM database and EPA's EMAP databases (Pelletier and Mohamedali, 2009). Additional data were included for the present study, with data on modeled COC concentrations obtained from the following resources and sampling programs:

- Ecology's EIM database.
- King County Department of Natural Resources and Parks (KCDNRP).
- Washington Coastal EMAP databases.
- Literature (e.g., Dangerfield et al., 2007).

Queries were developed to obtain data on the concentrations of the following contaminants in the marine, estuarine, intertidal, and subtidal waters of Puget Sound: total and dissolved copper, lead, and zinc; PCB congeners[10]; PBDE congeners; and the 16 modeled PAH compounds. Total suspended solids (TSS) and dissolved and particulate organic carbon (DOC and POC, respectively) measurements were also queried.

As with the sediment data, acceptance criteria and constraints were applied to the marine water data sets to omit data that were not appropriate for the purposes of the model. The screening steps and assumptions employed when compiling the water data were as follows:

- Overlaps between data sets were identified and remedied to avoid double-counting results.

- Sample results older than 2000 were omitted so that the data would be representative of recent or current conditions.

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[10] All available PCB Aroclor samples were non-detects. With no detected results there was no way to relate Aroclor sums to equivalent sums of congeners (i.e., Total PCBs); thus, Aroclor data were not included in the water data set.

- Samples for which the collection depth was unspecified or unclear were removed.

- Samples collected prior to a known or suspected cleanup at a specific location were removed.

- Data qualifiers were translated to be consistent with those commonly used by the Manchester Environmental Laboratory (e.g., "U", "UJ", and "J"); when multiple qualifiers were given, the most constraining qualifier was assigned.

- Sample results that were qualified as rejected (e.g., "REJ" qualified) were removed.

- Sample results that were qualified due to blank contamination concerns were removed.

- Sample results that were qualified as estimates (e.g., "J" qualified) were used without modification.

- All sample concentrations, detection limits (DLs), and reporting limits (RLs) were converted to common units for each contaminant.

- Pairs or groups of replicate samples were averaged.

- Pairs or groups of duplicate samples were averaged.

- Samples were referenced to model regions in ArcGIS using a spatial join; samples collected outside the model regions were removed.

- Samples were referenced to water column layers (i.e., surface or deep) using the regional layer depths given in Table 1.

Methods for handling data reported as non-detects and for calculating sum "totals" of contaminant groups were identical to those detailed in the Sediment Properties section.

All of the samples in the copper, zinc, and Total PCB congener data sets had detected results. However, the data sets for most organic contaminants contained a combination of detected and non-detected results. Non-detects comprised a significant portion of the data sets for Total PBDEs (75% of the samples), individual PAH compounds (all of which had between 84% and 100% non-detect samples), and all PAH group "totals" (76% NDs for Total PAHs, 79% NDs for Total LPAHs, 87% NDs for Total HPAHs, and 98% NDs for Total cPAHs samples). As a result, the substituted values exert a large influence on the estimated water concentrations for these organic contaminants.

The final marine water data sets from the various data sources were combined into a single aggregate data set for each contaminant (Appendix P). The sample locations for the modeled contaminants, TSS, and organic carbon forms are shown on the maps in Appendix C. Summary statistics for contaminant concentrations in the surface and deep water column layers of each model region are presented in Tables C-1 through C-29.

Model inputs for the initial contaminant concentrations in the water column layers of each region were set to the median values given in the summary statistics tables. When data were scarce ($n \leq 2$ samples) for a given layer and region, substitution rules were employed to ensure that the model input value was based on at least three samples from a similar area of Puget Sound. For this purpose, statistical data summaries were computed for water data from the surface layer, the deep layer, and the entire water column of the "basins," "urban bays," and all 10 regions of the Sound.

Substitutions procedures were as follows when n ≤ 2 for a region and layer: (1) substituted the region's full water column statistics if that n > 2; otherwise, (2) substituted the appropriate "basins" or "urban bays" statistics for the layer if n > 2; otherwise, (3) substituted the "basins" or "urban bays" statistics for the full water column if n > 2; otherwise, (4) substituted the "all 10 regions" statistics for that layer if n > 2; otherwise, (5) substituted the "all 10 regions" statistics for the full water column if n > 2; otherwise, (6) no statistics were available for substitution.

Important considerations for the use of regional water data statistics as model inputs include:

- The COC concentration data sets included samples collected by studies that targeted known or suspected contaminant sources. Those samples may have imparted an upward bias to the statistical summaries of regional concentrations. However, any such biases were likely weak relative to similar biases in the sediment data set because the proportion of water samples collected by "ambient" monitoring studies was large.

- The data set for PBDEs was small (n = 24) and, as noted above, 75% of the samples were non-detects for which the Total PBDE result was set to the value of 1/2 the maximum congener DL. The DLs of higher brominated congeners were high for all samples such that the values assigned as Total PBDE results (125 pg/L) were 5-9 times higher than PBDE concentrations measured in the Rosario Strait by Dangerfield et al. (2007). The detected results in the PBDE data set were also suspect due to the small sample volume (1-2 L) and the susceptibility of the sampling method to contamination (i.e., due to the ubiquity of PBDEs on the sampling platform and equipment at concentrations several orders of magnitude higher than in ambient waters) (Gries and Osterberg, 2009). In contrast, Dangerfield et al. (2007) used more rigorous ultra-clean techniques and collected 250 L per sample. For these reasons, the Dangerfield[11] estimates of PBDE concentrations in the surface and deep water column layers were used as model inputs for the initial concentrations in all regional waters.

- A paucity of data was available on organic carbon (dissolved and particulate forms) in Puget Sound marine waters. Samples collected and processed using the methods of Stutes and Bos (2007) were excluded due to contamination concerns, and the remaining data were limited to six areas of the Sound. Model inputs for regions with no data required the use of regional substitutions (described above), which is a source of uncertainty that is explored later in the Sensitivity and Uncertainty section.

Finally, the water data included samples that did not necessarily share a common set of congeners or compounds. Such variations are a potential source of uncertainty for the data sets of Total PCBs, Total PBDEs, and PAH groups and may influence comparisons between model predictions and observed concentrations.

Physical-Chemical Parameters

Physical parameters describe the size and characteristics of the model domain and boundaries and define a number of important properties of the waters, suspended particulates, and sediments that affect transport and partitioning processes. For the present work, physical parameters were

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[11] The work of Dangerfield et al. (2007) was later published, with minor changes to the reported PCB and PBDE concentrations, in Frouin et al. (2013). The latter paper was not yet available when model inputs were being set.

left unchanged from the "best-estimate" values used by Pelletier and Mohamedali (2009). These parameters included regional surface areas and layer depths, water temperature, density of organic carbon, density of solids in suspended particulates, solids settling rate, sediment burial and resuspension velocities, and concentrations and densities of solids in the sediment layers. Model inputs for daily wind speeds were updated with monthly averages from regional weather stations (Appendix E). River flows were set to use a repeating long-term average hydrograph of flows and as such did not have inter-annual variations. Salinity at the ocean boundary was derived in the model using an idealized composite forcing function (i.e., a repeating 365-day cycle) for each year of the simulation following Pelletier and Mohamedali (2009).

Chemical parameters used in fate process calculations include contaminant characteristics (such as molar mass, boiling point, and LeBas molar volume), partitioning coefficients, and rate constants. A literature review was conducted to obtain values for parameters specific to newly modeled contaminants and to update the parameters used by Pelletier and Mohamedali (2009) for PCBs. Congener-specific parameters were compiled for PCBs to provide information about the ranges of possible values and to provide the capability to simulate Total PCBs using different congener parameter sets. As noted earlier, congener-specific parameters were not available for PBDEs, but homolog parameters found in the literature provided options for the simulation of Total PBDEs using a "representative" homolog. For PAHs, chemical parameters were acquired for all sixteen modeled compounds to facilitate the simulation of individual compounds as well as Total PAHs (or other groups, using parameter suites of various "representative" compounds). Metals partitioning coefficients were derived using the data compilations of TSS, DOC, and total and dissolved metals concentrations in Puget Sound; the empirical values fell within the ranges given in the literature (Allison and Allison, 2005).

The physical-chemical parameters that were used as regional model inputs for each contaminant are presented in Appendix F. While these values represent "best estimates" based on the available information from published sources and local data, some parameters had important uncertainties that should be taken into consideration when interpreting model results, including the following:

- Literature values for partition coefficients and energies of phase transfer can be quite variable for a given HOC, and in some cases they have generated considerable disagreement (e.g., Goss et al., 2004 and Baker et al., 2004). "Internally consistent" values were sought for partitioning properties in the model (i.e., values that conform to thermodynamic constraints).

- Contaminant degradation rates were intended to account for all degradation pathways (i.e., photolysis, hydrolysis, and microbial degradation). These rates are extremely difficult to accurately measure or estimate for a given ecosystem (Davis, 2004), and so potentially large uncertainties may be associated with the best-estimate values obtained from the literature. In addition, literature degradation rates vary considerably among PCB congeners (depending on the degree of chlorination) and PBDE homologs (depending on the degree of bromination), and PAH compounds may span as much as 3-4 orders of magnitude for the modeled compounds (Greenfield and Davis, 2004). Thus, the selection of a representative congener, homolog, or compound for the simulation of chemical class "totals" can strongly affect long-term fate predictions. These uncertainties are discussed further in the Sensitivity and Uncertainty Analyses section.

- The potential transformation of high molecular weight PBDE congeners to lighter, more toxic forms – a process known as debromination[12] – was not incorporated into the model. For the purposes of the model it was assumed that the concentrations of Total PBDEs in the sediments and waters of the system would be unchanged by such transformations.

- Proportionality constants for POC and DOC phase partitioning (describing the similarity in phase partitioning of POC and DOC, respectively, in relation to that of octanol) can vary substantially among different types of organic carbon (Arnot and Gobas, 2004). The selected values each have an uncertainty of approximately plus or minus a factor of 2.5 (Seth et al., 1999; Burkhard, 2000).

- The density of organic carbon (OC) was set to 0.9 kg/L following Pelletier and Mohamedali (2009). This is slightly different than the value of 1.0 kg/L used by DeGasperi et al. (2014) and Gobas et al. (1995). The influence of this parameter is explored in the Sensitivity and Uncertainty Analyses section.

Simulation Periods

The fate and transport model uses a time-varying solution approach with a user-defined time step to calculate the change in contaminant concentrations in the water and sediment layers through time. Different simulation periods were examined for different types of runs (i.e., sensitivity and uncertainty analysis, model testing, and hindcast exercises – all described in later sections), as shown in Table 4. Runs generally included a one-year period of circulation "spin-up" prior to chemical introduction in the system and a one-year "spin-down" period at the end of the simulation. Any chemical fate predictions for those periods were not used for analyses. As described earlier, the sediment and water data sets included recent data from 2000-2012, with median sample collection dates around 2006; long-term runs therefore used 2006 as the first year of contaminant fate and transport simulation.

Table 4. Simulation periods for different types of model run.

	Sensitivity/ Uncertainty	Model Testing	Hindcast Exercises
Simulation start date	1/1/2006	1/1/1999	1/1/2005
Circulation spin-up (days)	45	365	365
Contaminant integration start date	2/15/2006	1/1/2000	1/1/2006
Fate and transport modeling period (days)	20044	4749	36524
Contaminant integration end date	1/1/2061	1/1/2013	1/1/2106
Spin-down after contaminant end date	351	365	730
Simulation end date	12/18/2061	1/1/2014	1/1/2108
Total simulation period (days)	20440	5479	37619
Time step (days)	0.005	0.005	0.005

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[12] Debromination can occur via photolysis and microbial processes and on exposure to zero-valent iron (Eriksson et al., 2004; He et al., 2006; Keum and Li, 2005). The rates, reaction products, and extent of occurrence of debromination in the environment are not well established (de Wit, 2002).

Sensitivity and Uncertainty Analyses

Sensitivity and uncertainty analyses were conducted to provide insight into the parameters and data uncertainties that most strongly influence model predictions of contaminant transport and fate. The methodologies employed were consistent with standard practices for similar modeling studies (EPA, 2009a) and those used by Pelletier and Mohamedali (2009).

Sensitivity

Model *sensitivity* describes the degree to which results are affected by changes in a selected input. Sensitivity analyses help improve understanding of the relative importance of model parameters, identifying parameters that have a strong influence on model predictions and those that do not significantly affect the results. In this way, sensitivity analyses provide an indication of which inputs must be most accurately characterized to improve confidence in the model predictions.

For sensitivity evaluations, a 55-year model run was executed with all inputs set to default best-estimate values. In successive runs, specific parameters were varied individually to +/-10% of their best-estimate value, and the long-term predicted total mass of contaminants in Puget Sound sediments and waters was compared to the default run. This standard variation (+/-10%) allowed for determination of the relative influence of each parameter on model predictions. Additional runs were performed for some parameters to explore the sensitivity over a wider range of inputs (e.g., values used by similar studies or plausible parameter ranges from the literature).

The parameters that were tested are listed below. Unless stated otherwise, sensitivity analyses were conducted for the following contaminants: copper, lead, zinc, Total PCBs (simulated using the parameters of congener PCB-118), Total PBDEs (simulated with the parameters of the Tetra-BDE homolog), Total PAHs (simulated as Fluoranthene), and seven individual PAH compounds.

- Initial salinity in the water column of the model boundary.
- Concentration of dry solids in the active sediments.
- Density of organic carbon.
- Water-sediment diffusion coefficient for the active sediments.
- Solids resuspension velocity of the active sediments.
- Proportionality constant for POC phase partitioning (organics only).
- Proportionality constant for DOC phase partitioning (organics only).
- TSS-water partition coefficient (metals only).
- Sediment-water partition coefficient (metals only).
- DOC-water partition coefficient (metals only).
- Setchenow proportionality constant (organics only).
- Henry's law constant (organics only).
- Enthalpy of air-water phase change (organics only).
- Octanol-water partition coefficient (organics only).
- Enthalpy of octanol-water phase change (organics only).
- Degradation rate in the water column (organics only).

- Degradation rate in the active sediments (organics only).
- Degradation rate in the water column *and* active sediments (organics only).
- Daily wind speed at 10 m (organics only).
- Representative congener, homolog, or compound ("total" organics only).

In the default run for each contaminant, the model predicted a declining trend in total mass over the 55-year simulation period. The total mass in the Sound was predicted to approach a steady state condition, where losses approximately equaled inputs and the resulting total mass in the system remained constant. While the predicted mass after 55 years was in all cases lower than the initial mass, the relative magnitude of the reduction and how quickly the steady state condition was reached varied by contaminant (Figure 6).

The effect of each tested parameter on the predicted mass after 25 and 55 years relative to the default best-estimate run is described in Appendix G and presented in Tables G-1 through G-13. The remainder of this section provides an overview of the most notable sensitivity results.

Long-term predictions of copper, lead, and zinc masses in Puget Sound were only influenced by a few of the tested parameters. The TSS-water partition coefficient had the greatest influence, causing the long-term predicted total mass to differ from the default run by as much as 6% for copper, 14% for lead, and 51% for zinc. Varying the concentration of dry solids in the active sediments had a smaller impact, producing initial total mass differences of approximately 10% from the default runs. However, those differences decreased through time, and the long-term predictions were only slightly different from the default run (<10% difference in total masses). The model is considered to be insensitive to small (+/-10%) variations in all other tested inputs for metals simulations.
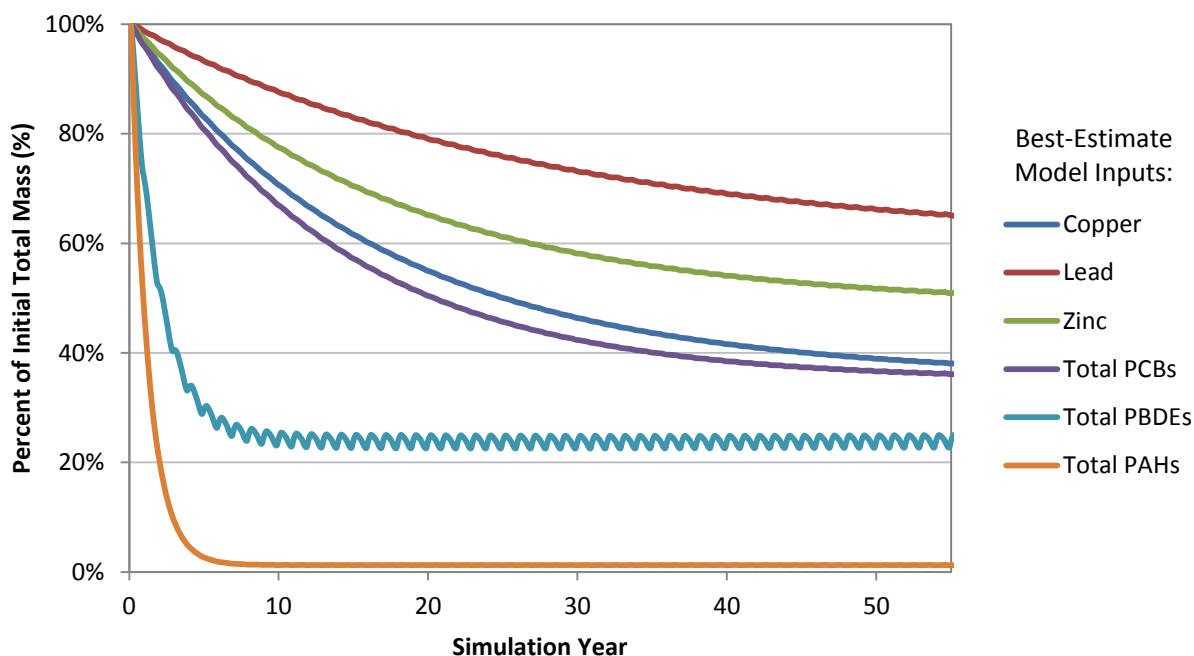
Figure 6. Total mass losses from Puget Sound predicted by the default "best-estimate" model inputs for each contaminant, presented as percent lost from the original starting mass.
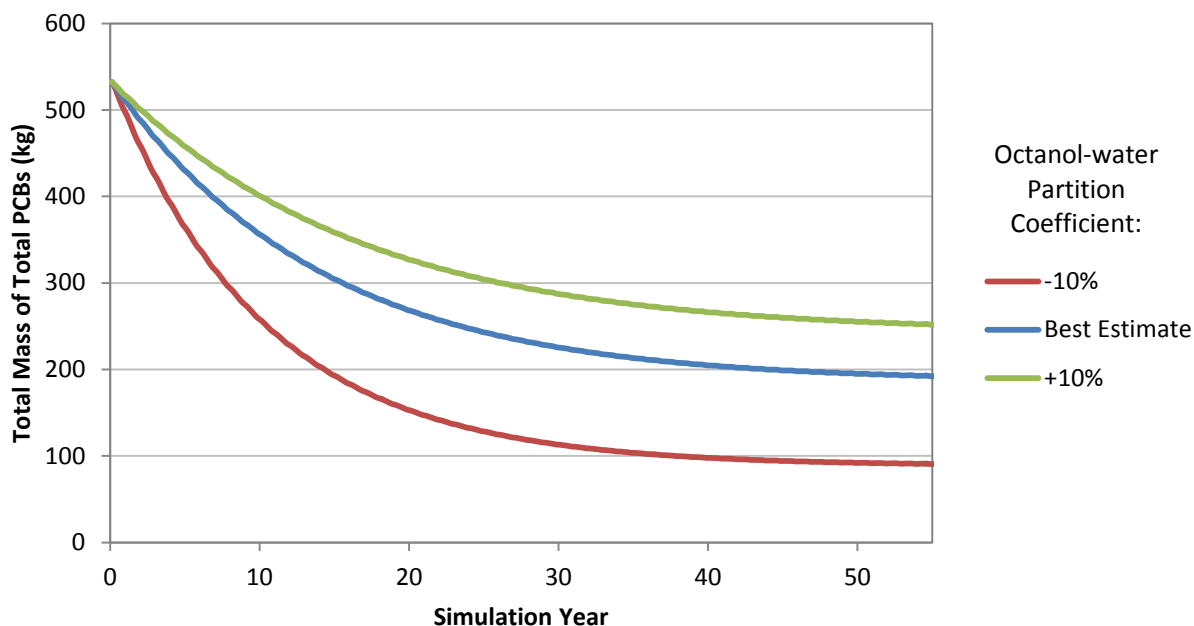
Figure 7. Total mass of Total PCBs in Puget Sound predicted using octanol-water partition coefficient (log K_{ow}) values 10% higher and lower than the best estimate.

For organic contaminants, the octanol-water partition coefficient (log K_{ow}) at 25°C was found to have a strong influence on the long-term predicted total mass. This is consistent with the findings of DeGasperi et al. (2014), Greenfield and Davis (2005), and Pelletier and Mohamedali (2009). Varying the contaminant-specific log K_{ow} values by +/-10% caused the predicted mass after 55 years to increase by up to 50% compared to the default runs for Total PCBs (Figure 7) and Total PBDEs, up to approximately 30% for Total PAHs, and as much as 80% for individual PAH compounds. Despite these substantial impacts, in all tests the model predictions showed the same declining trend of total mass through time, as typified by the default runs. These results demonstrate that the octanol-water partition coefficient is an important parameter that must be carefully estimated to achieve accurate long-term predictions of organic contaminants.

Varying the proportionality constants for POC and DOC partitioning by +/-10% had only minor effects on long-term predictions of organic contaminants, resulting in predicted total mass differences of <6% and <2.5%, respectively, compared to the default run for each contaminant. However, the literature suggests that the proportionality constants can vary among different types of organic carbon by as much as plus or minus a factor of 2.5 (Seth et al., 1999; Burkhard, 2000). Sensitivity tests at those extremes showed that the proportionality constants for POC and DOC partitioning each had a large influence on the long-term predicted total mass of organic contaminants, with the POC constant resulting in mass differences of as much as 50% compared to the default run and the DOC constant causing differences of up to 30%.

Nearly all of the other tested parameters for organic contaminants had little or no effect on the predicted steady-state mass in the system. Two notable exceptions, however, were the degradation rate and the "representative" congener, homolog, or compound that was used for modeling chemical class totals (i.e., Total PCBs, Total PBDEs, and Total PAHs, respectively). Sensitivity tests for these parameters are detailed below.

Sensitivity to Degradation Rates

Degradation rates of organic contaminants are difficult to measure or estimate for a given ecosystem. Contaminant-specific values in the literature may vary considerably, sometimes spanning 3-4 orders of magnitude (Greenfield and Davis, 2004). Rates can also be highly variable among PCB congeners, PBDE homologs, and PAH compounds based on the degree of chlorination, bromination, and molecular weight, respectively. For these reasons, additional tests were executed to characterize the model response to plausible ranges of degradation rates beyond the +/-10% variation used in standard sensitivity tests.

The best-estimate degradation rate for Total PCBs in water and in sediment (Table F-3) corresponded to a first-order half-life of 56 years. Following Davis (2004), sensitivity tests were conducted for half-lives of 0.56 years (204 days), 5.6 years, and 560 years. In the water column, the fastest tested rate (0.56-year half-life) resulted in a long-term total mass 20% lower than that predicted by the default run, while the other tested rates differed by <2.5%. In the active sediments, the faster degradation rates yielded total masses that were 90% lower (0.56-year half-life) and 60% lower (5-year half-life) than the default, while slower degradation (560-year half-life) caused only a small increase in total mass (4%). These results indicate that long-term mass predictions for Total PCBs would be substantially lower if faster degradation rates are used. While PCB congeners with a lower degree of chlorination may indeed have higher degradation rates (Davis, 2004), a more extensive review of the literature may be warranted to determine whether half-lives of less than ten years are realistic.

Best-estimate degradation rates of PBDEs (Table F-3) corresponded to half-lives of 0.4 years (150 days) in water and 1.6 years (580 days) in the active sediments. These default rates were estimated by Wania and Dugani (2003) using EPA's "Estimation Program Interface" software (EPI; www.epa.gov/oppt/exposure/pubs/episuite.htm). Lacking empirical values, sensitivity runs were conducted to test the model response to a range of slower degradation rates up to a half-life of 50 years, which is comparable to the best-estimate half-life of PCBs. Assuming equal rates for water and sediments, the tests showed that total mass predictions for Total PBDEs were strongly influenced by decreases in the degradation rates, with 50-year half-lives causing a 500% increase in the predicted total mass compared to the default run. In fact, slowing the degradation rate by an order of magnitude to a half-life of just over 10 years caused the predicted total mass to *increase* through time, approaching a steady-state mass *higher* than the initial mass (Figure 8). If plausible, slower degradation rates would therefore have major implications for long-term predictions of Total PBDE mass in the system.

Degradation rates given in Greenfield and Davis (2005) for PAH compounds corresponded to half-lives ranging from 23 days to 6.3 years, with a best-estimate value of approximately 1 year based on the selected "representative" compound, Fluoranthene. Varying the water column degradation rate within this range caused the long-term total mass of Total PAHs to decrease by 70% (compared to the default run) for the fastest degradation and increase by 20% for the slowest rate. In the active sediments, the fastest degradation rate yielded a total mass that was 20% lower than the default, while slower degradation caused nearly a 60% increase in the predicted total mass. These tests indicate that long-term predictions of Total PAHs are very sensitive to the degradation rates within the range of plausible values. Greenfield and Davis (2005) tested an even wider range of degradation rates from the literature, which resulted in

predicted losses after 5 years ranging from 0% to 100% of the initial mass for San Francisco Bay. The overwhelming influence exerted by this parameter was such that Greenfield and Davis proposed that the current understanding of degradation rates for PAHs is not sufficiently accurate to predict long-term fate with confidence.

Overall, degradation rates appear to be one of the most important parameters influencing long-term predictions for organic contaminants; unfortunately, they are also one of the most difficult parameters to accurately characterize. Due to the broad ranges of degradation rates given in the literature for many organics, a deeper evaluation of available rates may be warranted for future modeling to ensure that the most appropriate values are selected for Puget Sound. For some organic contaminants, such as PAHs, estimates of degradation rates from the literature may be so uncertain as to preclude long-term predictions (Greenfield and Davis, 2005). If modeled, long-term fate predictions for such contaminants should include bounds based on the plausible range of degradation rates, and uncertainties in degradation rates should be considered when interpreting results. For PAHs, it may also be useful for future modeling to focus on the simulation of individual compounds instead of groups of compounds (e.g., Total PAHs), as compound-specific degradation rate estimates may have less variation than rates for all of the compounds in the group.
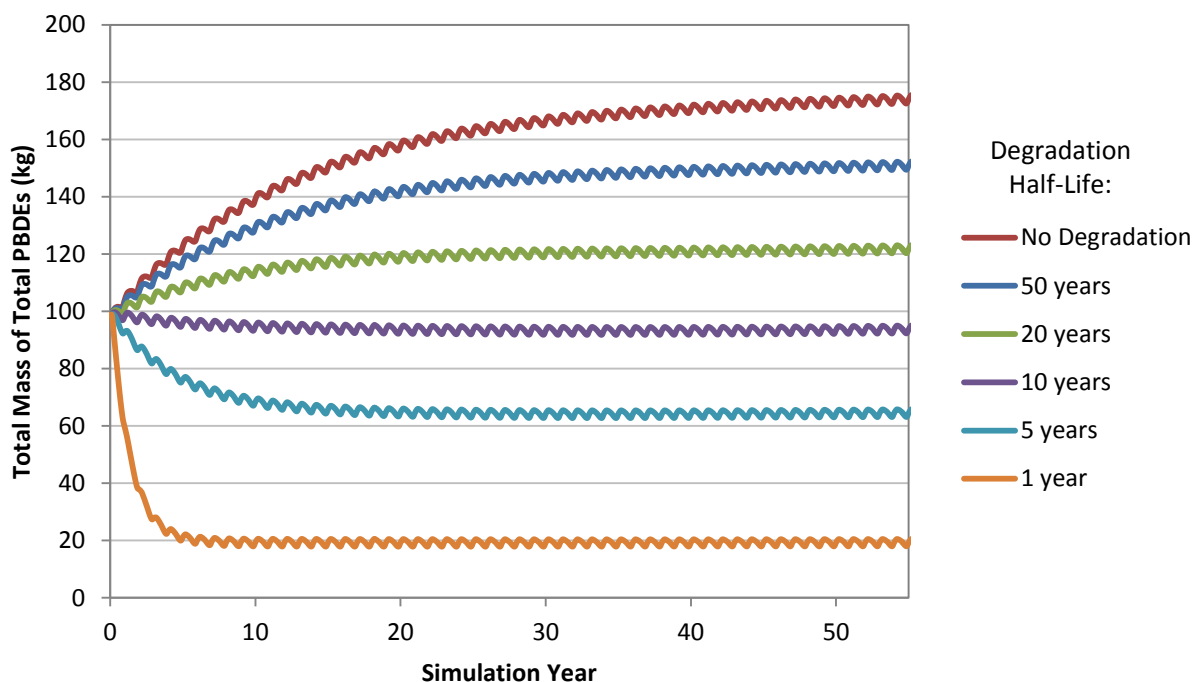
Figure 8. Total mass of Total PBDEs in Puget Sound predicted using degradation rates in water and sediment corresponding to first-order half-lives of 1 year, 5 years, 10 years, 20 years, 50 years, and no degradation.

Sensitivity to "Representative" Congener, Homolog, or Compound

As described previously, the parameter suite from an intermediate "representative" congener, homolog, and compound was used to simulate contaminant class "totals" for PCBs, PBDEs, and PAHs, respectively. Since many chemical properties vary considerably within each class, it was of interest to test the sensitivity of the model not only to the ranges of individual parameters but also to a range of chemical-specific parameter suites. Using the attributes of all possible PCB congeners, PBDE homologs, and PAH compounds to bound the model sensitivity was not reasonable. Testing therefore focused on a subset from each class based on known prevalence in Puget Sound (Figures B-11, B-12, and B-13) and spanning a reasonably wide range for individual parameters (Tables F-1 and F-2).

For Total PCBs, the default run used the parameter values specific to congener PCB-118. Five additional parameter suites were tested based on the properties of congeners 061, 101, 105, 138, and 153. The long-term predicted total masses (Figure 9) ranged from 41% lower to 27% higher than that predicted by the default run, bracketing the results for PCB-118 and affirming that congener's selection for modeling. Total PBDEs were simulated using the parameter suite of homolog Tetra-BDE for the default run and as Di-, Tri-, Penta-, Hexa-, and Deca-BDE in sensitivity tests. The predicted steady-state mass of Total PBDEs was as much as 62% lower (Di-BDE) and 62% higher (Deca-BDE) than the default run, indicating that Tetra-BDE is a good choice for representing intermediate chemical properties within the range of tested homologs. Finally, the default run for Total PAHs used the parameters of Fluoranthene, and parameter suites based on the properties of eleven different PAH compounds were tested. The resulting long-term predictions spanned a wide range, with the Naphthalene simulation predicting a total mass that was 80% lower than the default run and Benzo(g,h,i)perylene parameters predicting a
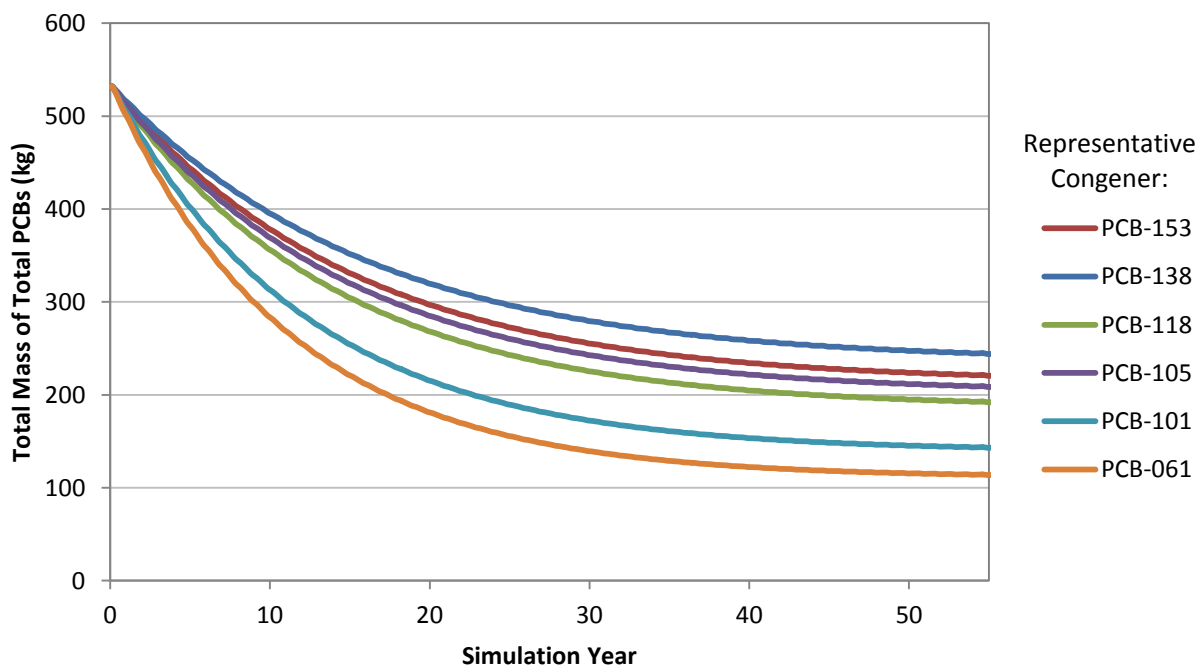
Figure 9. Total mass of Total PCBs in Puget Sound predicted using the parameter suites of various "representative" congeners.

total mass that was over 1200% higher. The results indicate that Fluoranthene is a good choice as an intermediate compound for 2-, 3-, and 4-ring PAHs, but may under-predict the long-term mass for 5- and 6-ring compounds. Nonetheless, 2-, 3-, and 4-ring compounds make up nearly 75% of the PAH mass in Puget Sound sediments (Figure B-13), and so the selection of Fluoranthene as a representative PAH compound is reasonable for the purposes of this study.

Results of the above-mentioned tests indicate that long-term model predictions are highly sensitive to the compound- and homolog-specific parameter suites selected for the simulation of Total PAHs and Total PBDEs, respectively. Long-term predictions for Total PCBs are slightly less sensitive to – though still strongly influenced by – the congener-specific parameter suite selected to represent the class. While all tests predicted decreasing total mass through time approaching a steady-state condition, it is possible that other plausible model inputs (e.g., higher loads) could create a situation where simulation using the parameters of one compound might predict an increase in total mass over time and simulation as a different compound might predict a decrease. As such, care must be taken when selecting the "representative" parameter suite, with the representative compound ideally having high prevalence in the system and parameter values that are intermediate for the class. In any case, the range of predictions resulting from plausible parameter suites should be considered when interpreting long-term model predictions.

Uncertainty

The term *uncertainty* is used to describe incomplete or imperfect knowledge about parameters, data, and assumptions. Uncertainty can arise from many sources, including measurement and analytical errors for model input data and imprecise estimates of parameters. Analyses of uncertainty are used to investigate how the model results are affected by this lack of knowledge about the true values of certain model inputs.

To evaluate the uncertainty of a specific input, the model was executed using the low and then the high values from the inter-quartile range of estimated values (i.e., 25th and 75th percentiles, respectively) while all other model inputs were held at their default best-estimate values. Results from the low and high estimates yielded a range of possible outcomes that help reveal whether uncertainty in the true value of that parameter has a significant effect on model predictions.

Key model inputs were selected for each of the modeled contaminants to evaluate the effect of their uncertainty on the predicted total mass in the active sediment layer and water column of Puget Sound. The model inputs tested included the following chemical-specific parameters, physical characteristics, loads and initial concentrations, and boundary conditions.

- Initial contaminant concentration in the water column of the model boundary.
- Initial contaminant concentration in the water column of each region.
- Initial contaminant concentration in the active sediments.
- External load to the surface water column layer.
- Concentration of TSS in the water column.
- TOC fraction in the active sediments.
- Sediment burial velocity from the active sediments.
- Concentration of POC in the water column.
- Concentration of DOC in the water column.

The effect of each tested model input on the predicted mass after 55 years relative to the default best-estimate run is described in Appendix G and presented in Tables G-1 through G-13. The remainder of this section highlights the key results of the uncertainty analyses.

Tests of the 25th and 75th percentile contaminant concentrations in the boundary waters revealed that uncertainties had a moderate to strong influence on the predicted total mass for all contaminants. The importance of this model input was expected because (1) concentrations in the deep layer of the boundary water column determine contaminant loads via inflow at the ocean boundary, and (2) ocean loads for all contaminants were much larger than those from watershed sources (surface runoff, POTWs, and groundwater) and atmospheric deposition. For metals, uncertainty runs predicted total masses after 55 years that were as much as 26% lower and 33% higher than the best-estimate run predictions. Tests for Total PCBs had similarly large deviations from the default run (20% lower and 13% higher). For Total PBDEs, boundary water concentrations were from Dangerfield et al. (2007) and summary statistics for the data were not available at the time of analysis; uncertainty tests were therefore not performed for Total PBDEs. All Total PAH samples from the deep boundary waters were non-detects, and so the 25th and 75th percentile concentrations were based on detection limits of the analyses. Nonetheless, these uncertainty tests showed that relatively small variations in the boundary water concentration of Total PAHs had considerable effects on the long-term predicted total mass in Puget Sound.

In comparison, watershed and atmospheric deposition loads had a smaller influence on the predicted total mass for metals, Total PAHs, and individual PAH compounds. For Total PCBs and Total PBDEs, however, loading estimates had a relatively high degree of uncertainty (i.e., the range between 25th and 75th percentile loads was broad; see Table A-9), which resulted in large deviations in the predicted total mass compared to the best-estimate run. The mass of Total PCBs was predicted to be 11% lower and 45% higher than the default run using the 25th and 75th percentile external loads, respectively; likewise, Total PBDEs were 19% lower and 58% higher. The median estimate of Total PCB external loading used for the Phase 2 modeling study (Pelletier and Mohamedali, 2009) was also tested to estimate the steady-state mass that would result from the much higher previous best estimate of external loading. The resulting total mass was predicted to *increase* over time and after 55 years was 470% higher than that predicted by the current best-estimate load (Figure 10). Clearly, minimization of the uncertainties associated with external loading estimates is important for model predictions of long-term trends.

Model predictions were not affected by uncertainties in the initial contaminant concentrations in the water column or the active sediments. For all of the modeled contaminants, the mass contained in the active sediments far exceeded the contaminant mass in the water column; the magnitude of initial water column concentrations were therefore of little consequence to total mass predictions. Since the contaminant concentration in the active sediments defines the mass of contaminant in the sediments, varying the concentration between the 25th and 75th percentile estimates resulted in large differences in the initial total mass in the system (Figure 11). However, over time (and under constant annual loading) the predicted total mass converged on approximately the same steady-state mass regardless of the initial concentration in the active sediments. These findings are consistent with similar results by Pelletier and Mohamedali (2009) and Davis (2004).
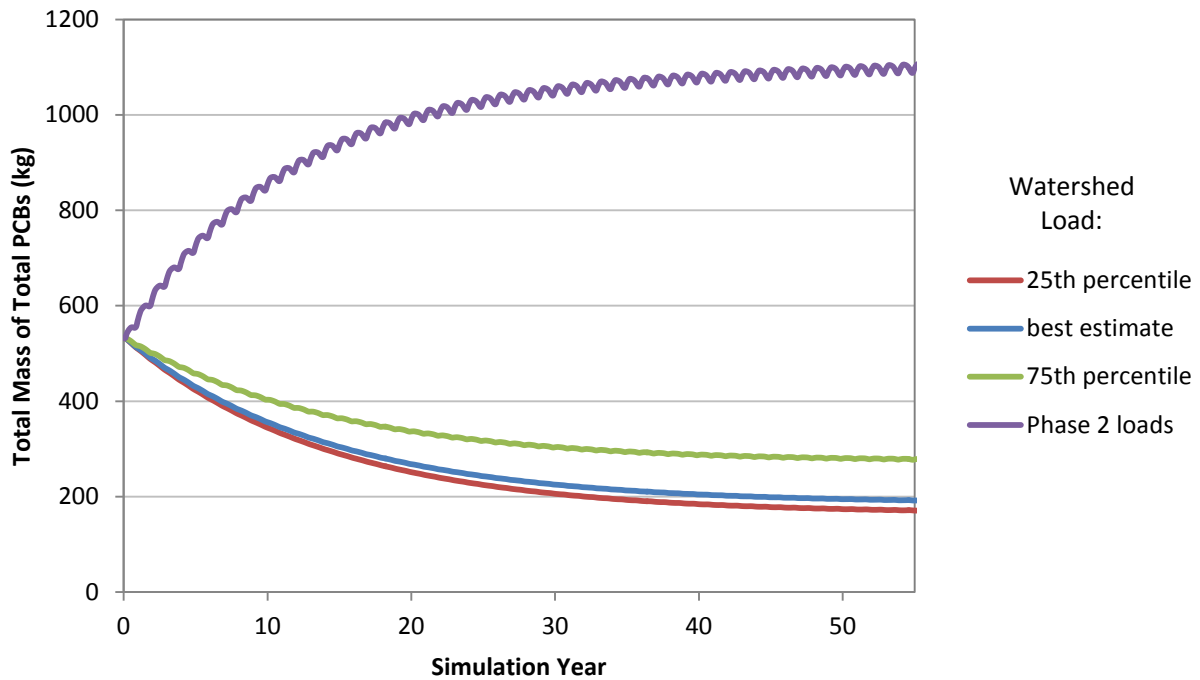
Figure 10. Predicted total mass of Total PCBs in Puget Sound resulting from uncertainties in the watershed loading estimates, with comparison to the total mass predicted using the same Phase 2 watershed loads used by Pelletier and Mohamedali (2009).
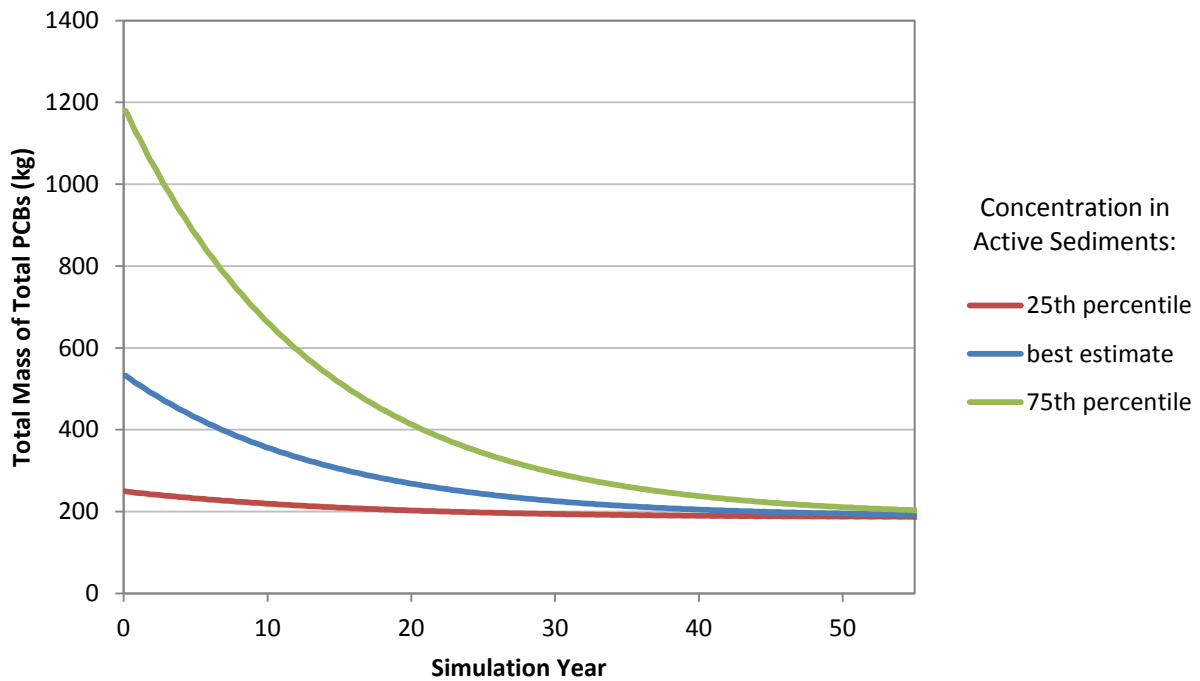
Figure 11. Predicted total mass of Total PCBs in Puget Sound resulting from uncertainties in the initial concentration in the active sediments.

Uncertainties in the model inputs relating to organic carbon (i.e., TOC fraction in the active sediments and concentrations of POC and DOC in the water column) were found to have negligible or no effects on long-term predictions for metals. Organic contaminants were likewise unaffected by the TOC fraction in the active sediments and only minimally influenced by the uncertainties in the water column concentration of DOC (<5% difference from default best-estimate runs). Uncertainty tests for POC concentrations in the water column, however, yielded wide ranges of predictions for organic contaminants. The 25th percentile concentrations resulted in long-term predicted masses that were 5-20% lower than the best-estimate runs, and 75th percentile runs predicted total masses in excess of 30% higher than the default predictions.

The primary reason for these strong effects is the influence of POC on the contaminant mass available for the various loss processes. Suspended particles with low organic carbon content have a reduced capacity for adsorbing organic contaminants, and so a higher mass is dissolved and available for advective transport (with subsequent export at the model boundary) and volatilization. At the same time, loss processes that affect particle-sorbed contaminants such as settling and burial are markedly reduced. The uncertainty runs underscore the importance of the water column POC concentration for long-term model predictions, indicating that it is an input that must be estimated carefully.

As with the POC concentration, TSS in the water column affects the mass of contaminants adsorbed to particulates and therefore can have a strong influence on which loss processes dominate. Long-term predictions of the total mass of metals in the system were only slightly influenced by the TSS concentration, with predictions differing by +/-3 to 6% from the default best-estimate runs. However, for organic contaminants that sorb strongly to particulates, the concentration of TSS in the water column had a much greater impact (Figure 12).
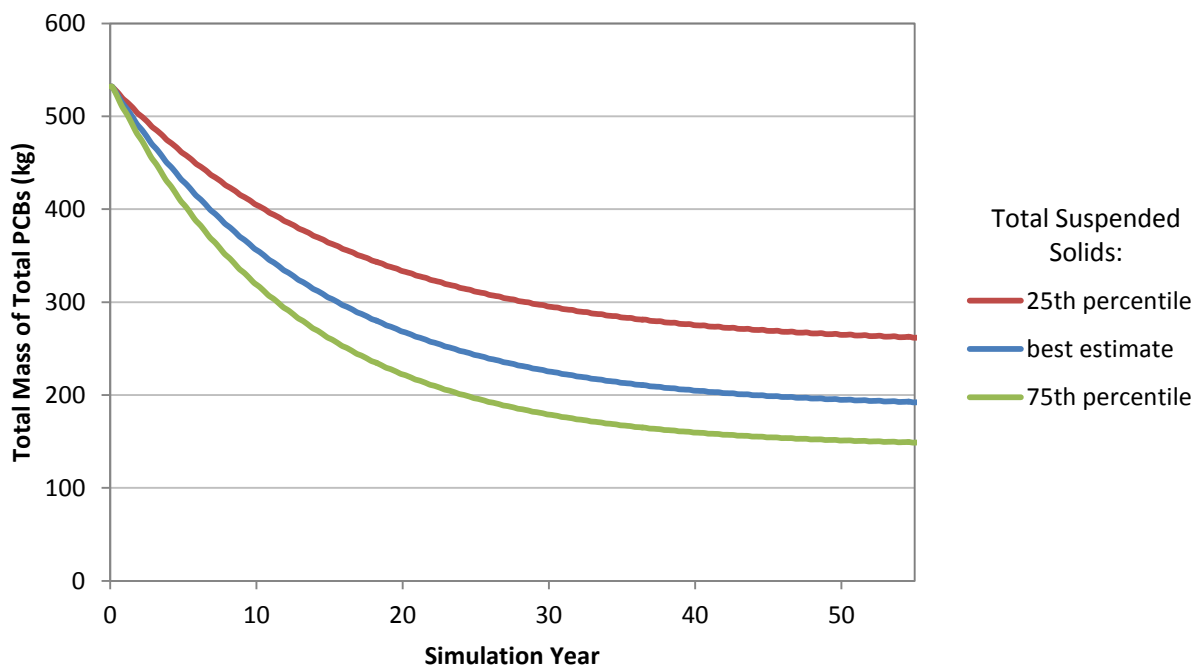
Figure 12. Predicted total mass of Total PCBs in Puget Sound resulting from uncertainties in the water column concentration of total suspended solids (TSS).

Elevated concentrations of TSS at the 75th percentile resulted in substantially lower total mass predictions compared to the default runs because a greater fraction of the contaminants remained in the water column (adsorbed to suspended particles) where they were subject to advection and eventual loss from the system via export at the boundary. Conversely, reduced concentrations of TSS at the 25th percentile predicted much higher total masses of organic contaminants, with less mass exported at the boundary and more mass lost to burial. The total mass predictions for the 25th and 75th percentile runs differed from the default runs of the modeled organic contaminants in direct proportion to the contaminants' octanol-water partition coefficient (log K_{ow}). Total PCBs had a high log K_{ow}, which resulted in predicted total masses that were 36% higher (25th percentile TSS) and 23% lower (75th percentile TSS) than the default run prediction. Total PBDEs was simulated using a slightly lower log K_{ow} value, but the influence of the TSS was similarly strong (30% higher total mass from the 25th percentile TSS; 18% lower from the 75th percentile TSS). Total PAHs were simulated with a relatively low log K_{ow} value, which resulted in a more muted response (13% higher and 5% lower predicted total mass from the 25th and 75th percentile TSS estimates, respectively).

Uncertainty in the sediment burial velocity had a negligible effect on the predicted total mass in the system early on, but mid- and long-term predictions (i.e., after 25 and 55 years) for all modeled contaminants were strongly affected by this model input. Burial is an important loss process for metals, since they are not subject to degradation or volatilization losses. The 25th and 75th percentile burial velocity estimates resulted in long-term total mass predictions for copper and zinc that were approximately 30% higher and lower, respectively, than that predicted by the best-estimate runs. Lead was even more strongly impacted, with the faster 75th percentile velocity resulting in a 50% decrease in total mass after 55 years and the slower 25th percentile velocity predicting an *increasing* trend of total mass and a long-term increase of over 60% compared to the best-estimate prediction (Figure 13b).

For Total PCBs, increasing the burial velocity to the 75th percentile caused the dominant loss process to shift from export at the model boundary to burial, with a 22% lower predicted total mass; conversely, a slower burial velocity at the 25th percentile resulted in an 11% increase in the total mass in the system (Figure 13a). Interestingly, the pattern by which faster burial velocities yielded lower steady-state masses did not hold for organic contaminants with rapid degradation rates. For example, the 25th (slow) and 75th percentile (fast) burial velocities predicted long-term masses of Total PBDEs that were 30% *lower* and 23% *higher*, respectively, than the default run. The predicted mass of Total PAHs in the system also decreased using the slower burial velocity (9% lower than the default run) and increased with the faster burial (12% higher predicted total mass). In sum, these tests indicate that the sediment burial velocity is an important model input that has a considerable influence on model results. Future work should strive to minimize uncertainties in regional burial velocity estimates to improve confidence in long-term predictions.
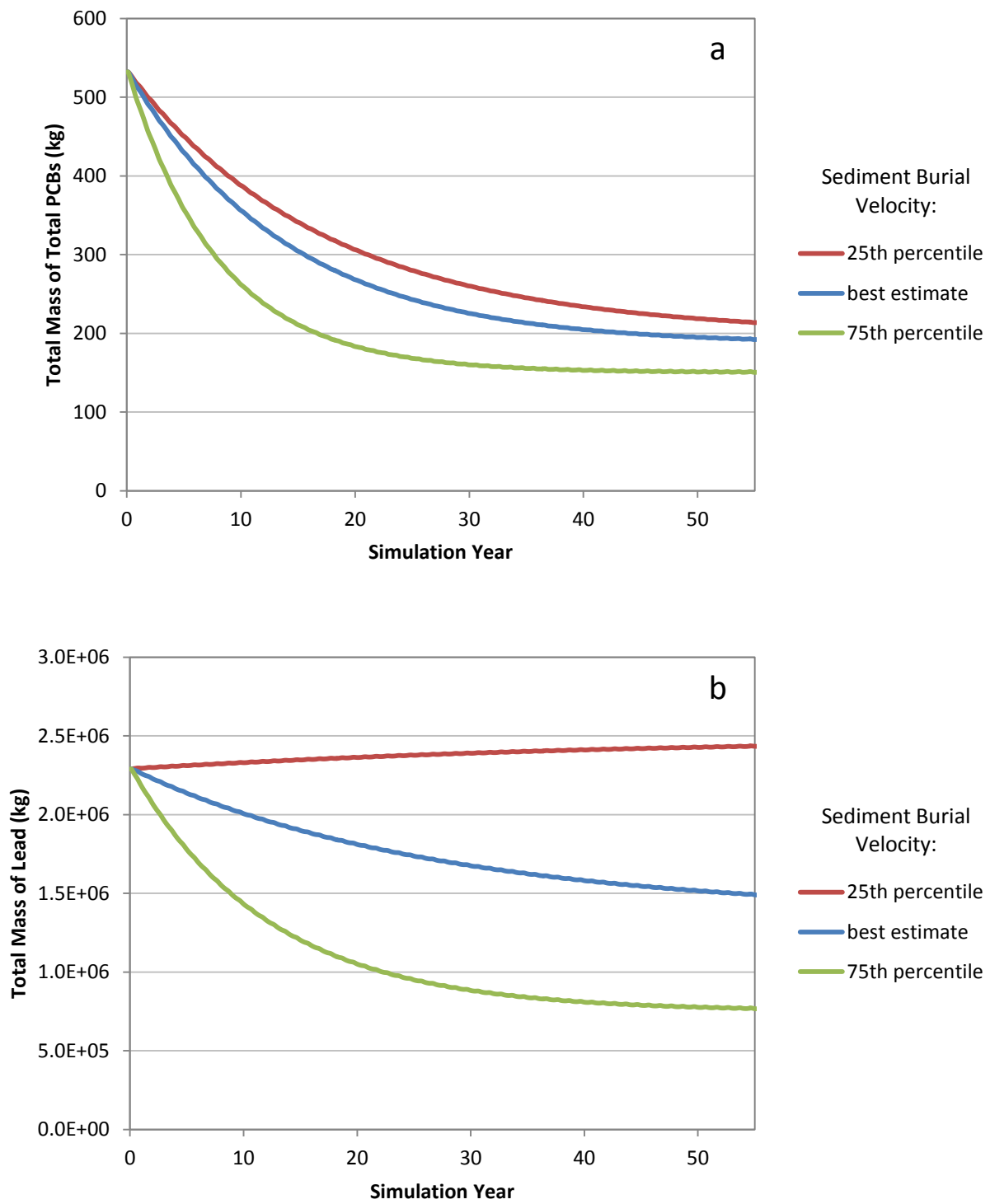
Figure 13. Predicted total mass of (a) Total PCBs and (b) lead in Puget Sound resulting from uncertainties in the sediment burial velocity.

Model Testing

To test the accuracy and determine potential biases of the fate and transport model results, the predicted concentrations in regional waters and sediments were compared to Puget Sound data. *Accuracy* refers to the closeness of model predictions to the measured values, which are assumed to represent true values. *Bias* describes the systematic deviation between model predictions and true values. In addition to providing an indication of the model skill for reproducing actual observations, these comparisons also offer insights into potential problems.

A 12-year model run was executed for each of the contaminants of concern using the best-estimate values for all model inputs. As described previously, initial concentrations of COCs in regional water layers and active sediments were set to median values from the recent (2000-2012) data compilations that were conducted for this study (summary tables given in Appendices B and C). The nominal starting date of each model run was January 1, 2000. Model-predicted concentrations in the water layers and sediments over the twelve-year simulation were plotted against the observed data from 2000 to 2012 for each model region, and the root mean square error (RMSE) of paired predicted-observed values was calculated to provide a measure of bias[13].

Timeseries plots of observed COC concentrations in the surface and deep water column and the active sediments did not show significant upward or downward trends since 2000 for any of the model regions. In contrast, best-estimate runs for all modeled contaminants predicted losses of total mass in the system throughout the twelve-year simulation (recall Figure 6), with rapid concentration declines in both the water layers and sediments. Such declining trends were not supported by the observed data. For example, Figure 14 shows the predicted concentration of Total PCBs in the active sediments of Elliott Bay along with measured concentrations from 2000 to 2012; the observed data clearly do not corroborate the predicted concentration reductions.

The cause of the disagreement between observed and predicted concentrations is not immediately clear. The lack of strong trends in the twelve years of observed data tends to support the hypothesis that contaminant concentrations in the sediments are in equilibrium with the present loads to and losses from the system. If equilibrium conditions are assumed, the model can be used to explore possible explanations for the differences in observed and predicted trends. Two approaches were considered:

- **"Hindcast" estimation of local external contaminant loads.** Hindcasting is a method used to estimate plausible inputs to the model when the inputs are not known. The possibility was considered that the current best estimates of contaminant loading from watershed sources (i.e., surface runoff, wastewater treatment plants, and groundwater) may not be representative of actual loading. Watershed loading was therefore considered to be an unknown quantity. If all model inputs other than the watershed load are reasonable, the model can be used to estimate the contaminant load from local external sources by iteratively testing various assumed loads until the predicted steady-state mass of contaminant in the sediment matches

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[13] The 12-year timeseries comparisons are more rigorous than the model testing process used previously by Pelletier and Mohamedali (2009), which involved predicted-versus-observed comparisons for only two measurements of Total PCBs in the water column of a single region (Elliott Bay) due to an extremely limited observed data set. Pelletier and Mohamedali (2009) also did not compare predicted and observed concentrations in regional sediments.

the observed mass from monitoring data. A plausible range of watershed loads can be estimated in this way by finding the range of loading that explains the variability in the observed mass of contaminant. This hindcasting approach has been used in a number of similar modeling studies; for example, Oram et al. (2008) found that hindcast estimates of PBDE loads to San Francisco Bay were substantially higher than direct estimates that were reported prior to hindcasting.

- **"Hindcast" estimation of contaminant concentrations in the boundary waters.** The possibility was considered that the direct estimates of contaminant concentrations in the water column at the ocean boundary (i.e., in the Straits of Juan de Fuca and Georgia) may not be representative of actual conditions. If all other model inputs are left at their best estimated default values and boundary concentrations are considered to be an unknown quantity, the model can be used to estimate a plausible range of boundary concentrations that explains the variability in the observed contaminant masses in Puget Sound sediments.

The following sections present the results of using the model as a hindcast tool to assess potential problems with model inputs for watershed loads and boundary water concentrations.

"Hindcast" Estimation of Watershed Loading

As was demonstrated in the uncertainty analyses, external loading has considerable influence on the long-term future mass of contaminants in Puget Sound. The model was used in "hindcast" mode to estimate a plausible range of external loading for each contaminant that would result in a buildup of mass in the active sediment layer that is consistent with the observed inter-quartile
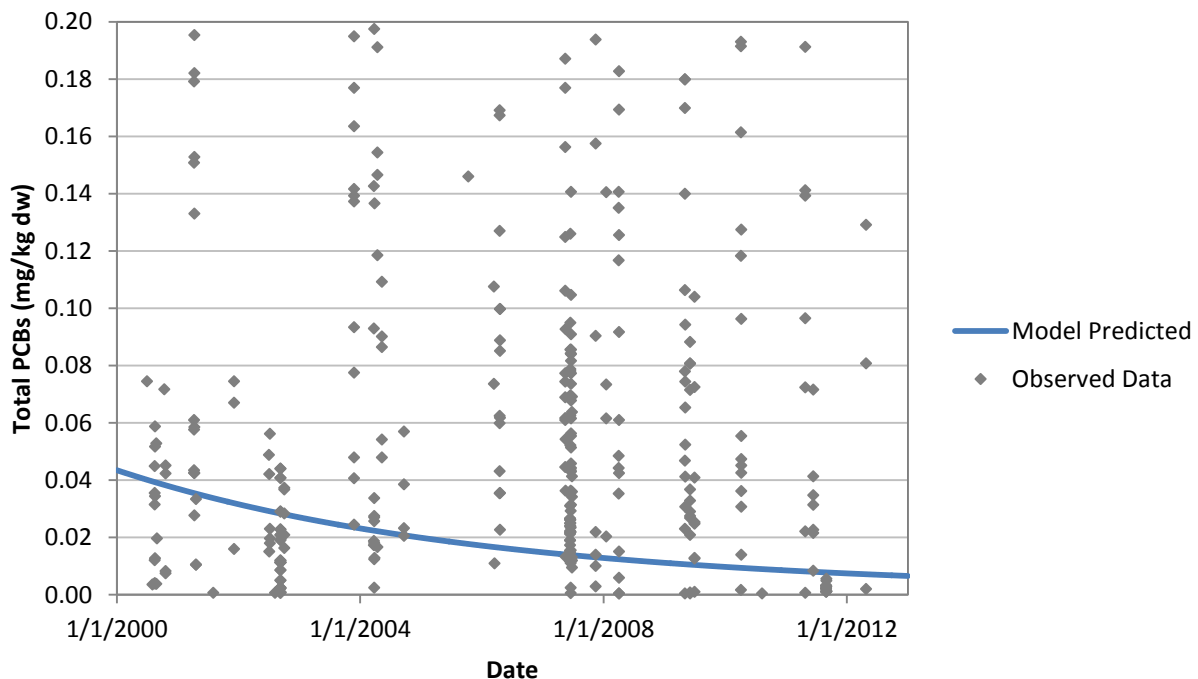
Figure 14. Comparison of model-predicted and observed Total PCB concentrations in the active sediments of Elliott Bay for the period 2000 to 2012.

range of sediment concentrations in Puget Sound. This approach has been employed by similar studies as an independent test of how well loading estimates are able to predict the observed data (e.g., DeGasperi et al., 2014; Pelletier and Mohamedali, 2009; Oram et al., 2008; Greenfield and Davis, 2005).

Hindcast runs were initialized with contaminant concentrations in the water column and active sediments set to zero. Contaminant concentrations at the ocean boundary and loading from atmospheric deposition were assumed to occur at the median best estimates described previously. The model was run for 100 years under continuous watershed loading, which resulted in the accumulation of contaminant mass in the system until a steady-state mass was achieved (with approximately equal mass losses and gains). By comparing the steady-state mass in the active sediments predicted by various watershed loads to the empirical mass in Puget Sound sediments estimated from observed concentrations, hindcast runs were used to establish bounds on the range of plausible loads.

Results from the hindcast runs for copper, lead, zinc, Total PCBs, Total PBDEs, Total PAHs, and eight PAH compounds are given in Tables H-1 and H-2. Table H-1 presents the mass buildup of each contaminant in Puget Sound sediments predicted by the best-estimate watershed loads and by zero watershed loading. Table H-2 summarizes the estimated loads required to accumulate the observed 25th percentile, median, and 75th percentile contaminant masses in Puget Sound sediments. Figures 15 and 16 illustrate the predicted accumulation of contaminant mass in the active sediments through time as a result of these various loads. The shaded regions in each timeseries plot indicate the inter-quartile range of the current inventory of contaminant mass in Puget Sound sediments (estimated from the observed concentration data).

Hindcast runs with external loading from watershed sources set to zero (Table H-1) provided estimates of contaminant mass accumulation in the system due to loading from the ocean and atmospheric deposition. Such buildup represents the mass that would be sustained regardless of reductions to contaminant sources that contribute to watershed loads. In the absence of watershed loads, the steady-state masses of copper, lead, and zinc in Puget Sound sediments were predicted to be 1500, 1200, and 4200 t (metric tons), respectively. The long-term mass buildup of Total PCBs, Total PBDEs and Total PAHs upon elimination of watershed loading approached 145, 8.1, and 148 kg, respectively. For all contaminants, the sediment mass buildup in these runs was overwhelmingly due to loading from the ocean, and as such the mass estimates are subject to uncertainties in contaminant concentrations in the boundary waters (which are explored in the following section).

Hindcast runs using the current best-estimate watershed load for each contaminant resulted in steady-state masses in the active sediment layer that were consistently below empirical inventories (Figure 15, Table H-1). Of the modeled contaminants, only lead had a best-estimate watershed load capable of building up a mass that was just within the inter-quartile range of the observed sediment mass. In fact, besides lead, only Total PCBs had a 75th percentile load that predicted a steady-state sediment mass within the inter-quartile range of observed masses. Those two cases were exceptions, however, to the characteristic under-prediction of contaminant mass in sediment by the loading estimates developed in Phase 3 of the PSTLA.

The bounds of the plausible range of watershed loads for each contaminant were delimited by those loads that were predicted to accumulate a mass of contaminant corresponding to the 25th and 75th percentile masses in Puget Sound sediments estimated from measured concentrations (Figure 16, Table H-2). For example, under a continuous watershed loading of 13.5 kg/yr, the model predicted a buildup of Total PCBs in the sediments (242 kg) that was equivalent to the 25th percentile empirical mass. Likewise, a continuous load of approximately 126 kg/yr yielded a sediment mass of Total PCBs (1173 kg) that was equivalent to the 75th percentile mass. These results suggest that the watershed load for Total PCBs would have to be between 13.5 and 126 kg/yr in order to accumulate a mass in sediments that is within the range of uncertainty of the sediment concentration data. This range of Total PCB watershed loads overlaps the lower end of the inter-quartile loading estimates of 15 to 225 kg/yr reported by Pelletier and Mohamedali (2009) and 23 to 436 kg/yr reported by Herrera (2010). Plausible ranges of watershed loads for the other modeled contaminants are given in Table H-2. Watershed loads that were predicted to yield a mass buildup in the sediments comparable to the 50th percentile (median) empirical mass inventories were as follows: 355 t/yr copper, 49 t/yr lead, 620 t/yr zinc, 47 kg/yr Total PCBs, 116 kg/yr Total PBDEs, and 1022 t/yr Total PAHs.

The hindcast exercises indicate that considerable increases in the current best-estimate watershed loads are needed to keep model results in agreement with empirical sediment inventory estimates (Table H-2). Zinc and Total PBDEs required watershed loads that were 5 and 8 times higher, respectively, than the Phase 3 best-estimate loads in order to match the median observed masses in Puget Sound sediments. Similarly, best-estimate loads for copper, lead, and Total PCBs each had to be increased by a factor of approximately 10 to achieve the median observed masses. In marked contrast, the best-estimate loads for Total PAHs and many individual PAH compounds had to be increased by several orders of magnitude to build up steady-state masses in the sediments comparable to empirical inventories. The results are consistent with Greenfield and Davis (2005), who found that extremely large PAH loads far in excess of literature values were required to overcome rapid degradation losses in their model of San Francisco Bay. While there is high uncertainty associated with PAH degradation rates (Appendix G), hindcast runs for PAH compounds with the slowest degradation rates (e.g., benzo[a]pyrene and benzo[b]fluoranthene) nonetheless predicted that loads around 10 to 20 times higher than the best estimates would be required to accumulate the median observed masses in Puget Sound sediments. These results suggest that the Phase 3 PAH loads may be underestimates regardless of the uncertainties associated with PAH degradation rates.

The current mass of each modeled contaminant in Puget Sound sediments appears to be at equilibrium with watershed loadings that far exceed the Phase 3 loading estimates, which suggests one of the following possibilities:

- **External loading from the watershed may be underestimated.** The actual watershed loads to Puget Sound may be approximately 5 to 10 times higher than the median Phase 3 loads. Several lines of evidence support the hypothesis that the Phase 3 loads may be low. First, the Phase 3 estimates for loadings via surface runoff and POTWs were reported as *minimum estimates* due to the study data rules (i.e., substitution rules for non-detects and summation rules for chemical class "totals"; see Appendix A). The unit area load methods employed in the Phase 3 surface runoff study may have imparted an additional downward bias compared to other methods by dampening the load signal from forested areas, which

represent over 80% of the Puget Sound watershed (Ecology, 2011). In the Phase 3 surface runoff report, Herrera (2011) also cautioned that, owing to the sampling strategy, the surface runoff loading estimates may not adequately represent stormwater in areas adjacent to Puget Sound where conveyance systems discharge to marine waters. Indeed, Hobbs et al. (2015) summarized recent (2007-2013) data collected by NPDES Phase I Municipal Stormwater permittees and found that contaminant concentrations measured in stormwater were typically higher than those estimated by Herrera (2011). Stormwater may therefore contribute a substantial additional load to model regions bordered by highly developed areas.

- **Contaminant masses in the sediments may be overestimated.** Data on contaminant concentrations in Puget Sound sediments may have an upward bias due to non-random sampling. Sediment data included samples collected by a variety of studies, many of which focused on characterizing concentrations near suspected contaminant sources, and so it is possible that the median regional values from the observed data set were overestimates of "ambient" regional conditions. If so, the total mass of each contaminant in Puget Sound sediments (calculated from the median observed concentration in each region) and the hindcast-estimated load needed to accumulate that mass would also be biased high. Such bias could explain some of the disparity between the Phase 3 loads and the hindcast-estimated loads. However, if the 25th percentile observed sediment concentrations were assumed to be representative of ambient conditions, Figure 16 and Table H-2 show that it would nonetheless require watershed loads 3 to 4 times higher than the best-estimate Phase 3 loads to build up the 25th percentile mass of most contaminants. These results suggest that the Phase 3 loads are underestimates despite potential upward biases in the sediment data.

- **External loading from the watershed may be decreasing.** External loading may be changing over time and may have recently decreased. The watershed loads that were predicted to be in equilibrium with measured sediment concentrations (from 2000 to 2012 data) were much higher than the Phase 3 loading estimates. If the Phase 3 loads are correct, they would suggest that dramatic declines in contaminant loads have occurred in recent years and that the sediment concentrations are in the process of adjusting to these changes (i.e., sediment concentrations are not yet in equilibrium with the current loads). Contaminants with high degradation rates such as PBDEs and PAHs are predicted to achieve steady-state masses in the active sediments in relatively short periods of time (<10 years; see Figure 6), and so the watershed load decreases would need to have occurred very recently for the sediments to be out of equilibrium with the current loads. In contrast, loading reductions for PCBs and metals might take around 40 years for the mass in sediments to reach steady-state, and so active sediment concentrations may still be in the process of adjusting to historic declines in watershed loading. Even so, there is currently no evidence in the sediment and water data to suggest these large magnitude declines in watershed loads.

It is difficult to determine which of these hypotheses explains the discrepancy between empirical watershed loading estimates from the Phase 3 PSTLA studies and the substantially higher loads predicted by the hindcast exercises. In actuality, a combination of these hypotheses may be involved. Continued monitoring efforts to characterize ambient contaminant concentrations in Puget Sound sediments may yield a more accurate mass budget to help resolve this discrepancy.
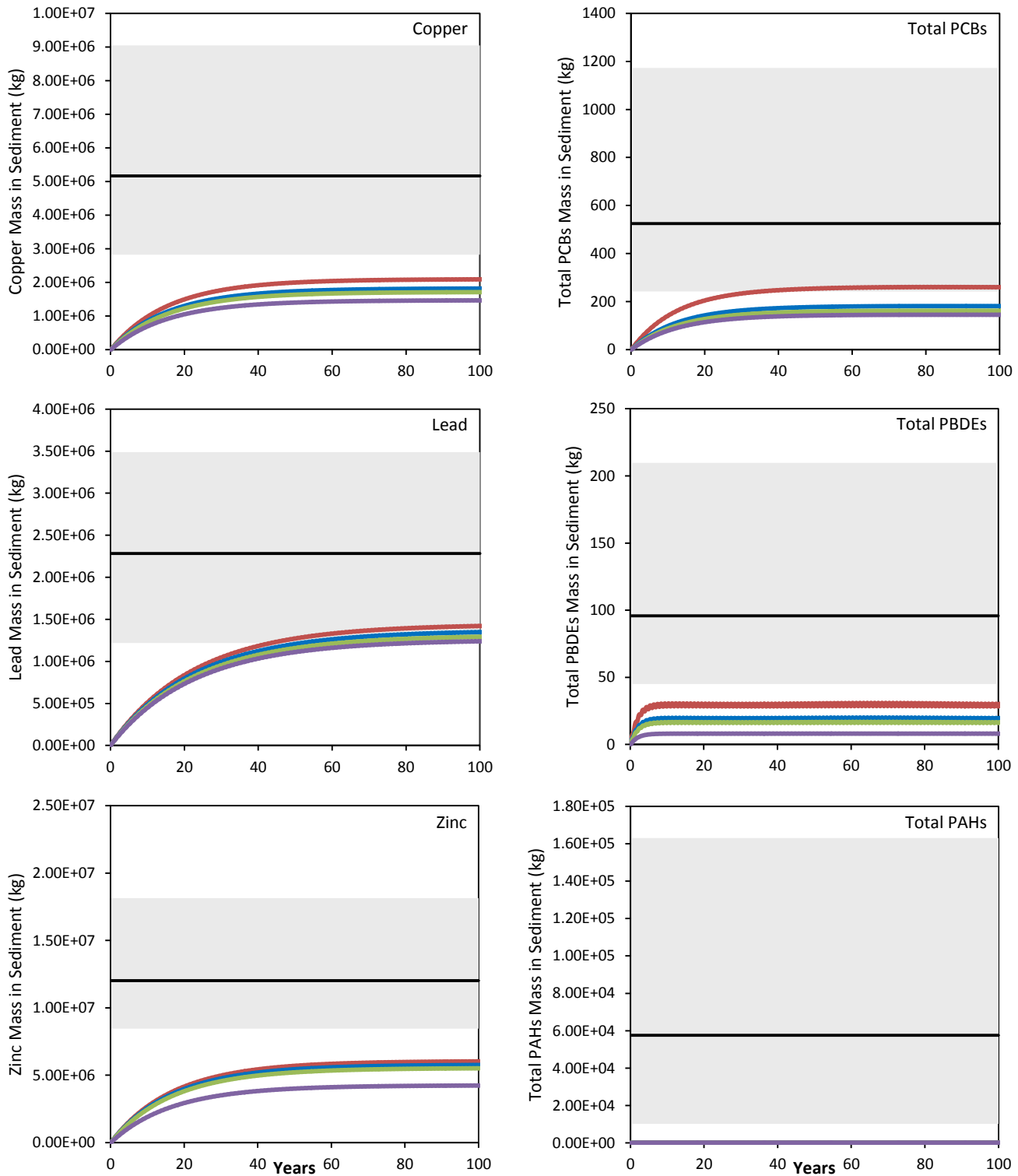
Figure 15. Hindcast predictions of contaminant mass accumulation in Puget Sound active sediments resulting from the following watershed loads: zero (purple line), 25th percentile (green line), median (blue line), and 75th percentile (red line).

The shaded region is the inter-quartile range of observed mass in the active sediments; the horizontal black line is the median observed mass.
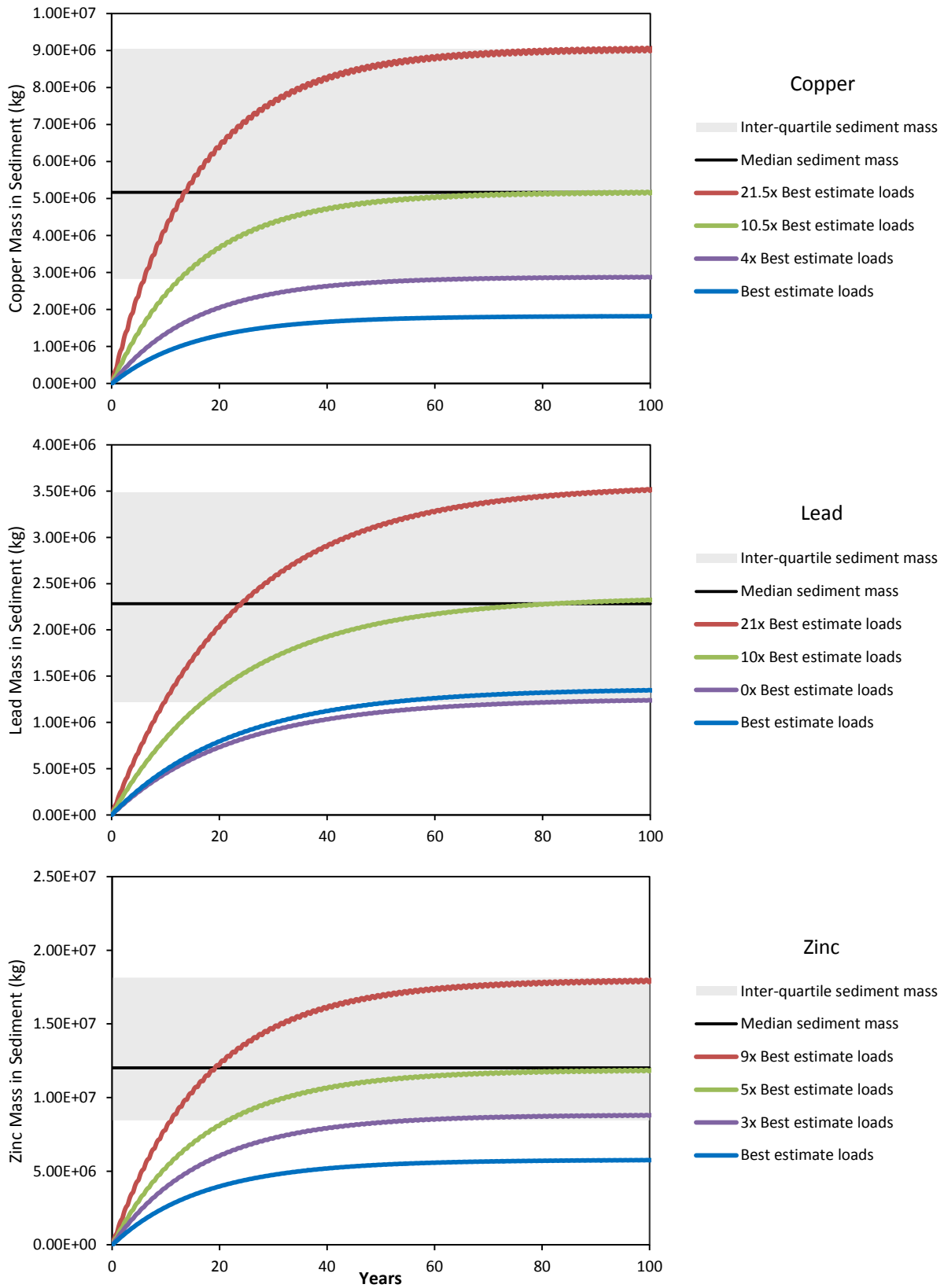
Figure 16. Hindcast results for the predicted loads needed to accumulate observed contaminant masses in Puget Sound active sediments.
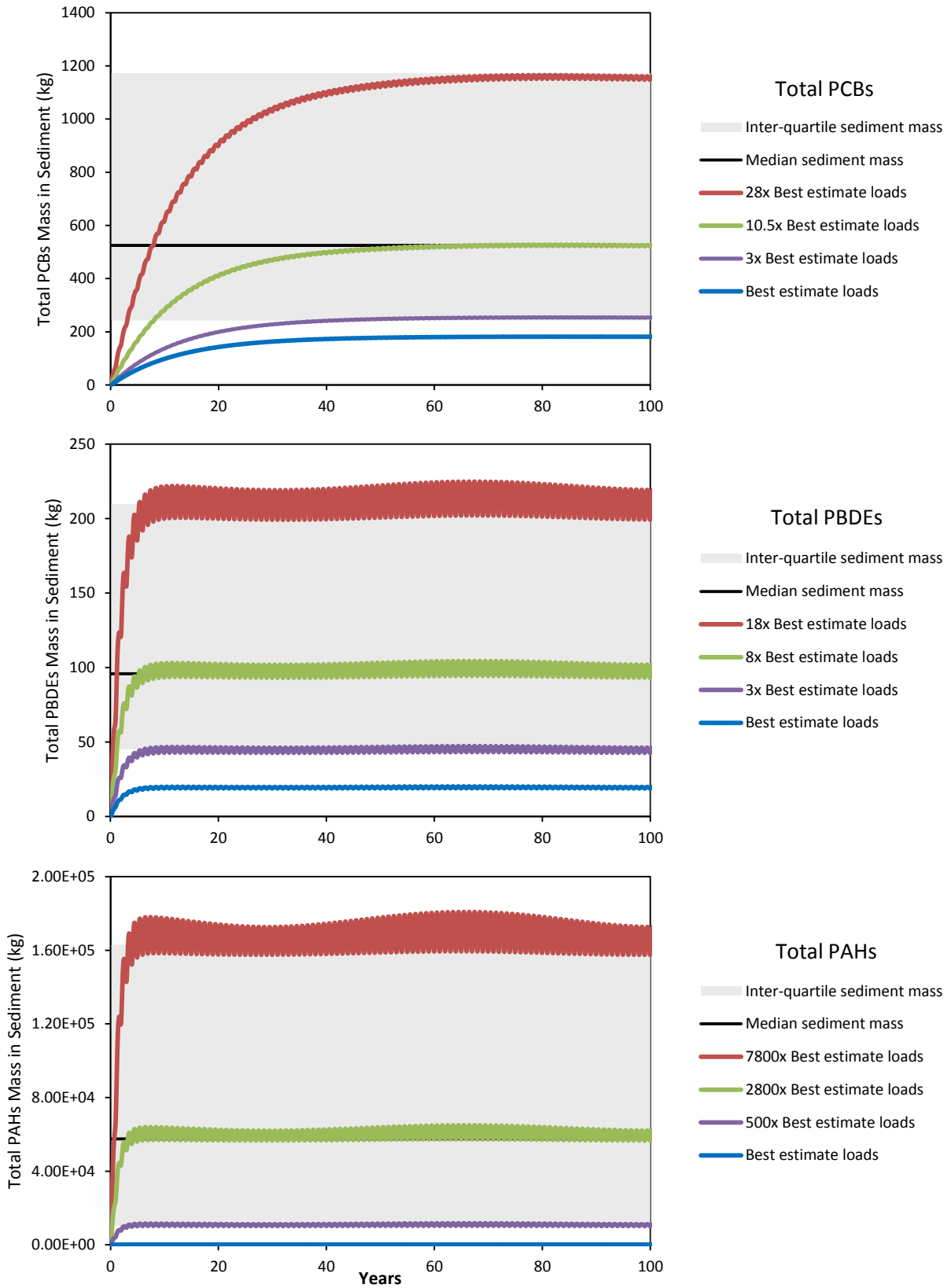
Figure 16 (continued). Hindcast results for the predicted loads needed to accumulate observed contaminant masses in Puget Sound active sediments.

"Hindcast" Estimation of COC Concentrations in the Boundary Waters

Concentrations in the deep layer of the boundary water column determine contaminant loads via inflow at the ocean boundary. Uncertainties in this concentration (henceforth referred to as the "boundary water concentration" for simplicity) were found to have a strong influence on model predictions (see Appendix G). In fact, relative to watershed loading uncertainties, uncertainties in the boundary water concentration was a more important driver of the long-term contaminant mass in the system. This is due to the magnitude of contaminant loads at the boundary, which are much larger than those from watershed sources (surface runoff, POTWs, and groundwater) and atmospheric deposition.

The "hindcast" approach was employed to estimate the range of boundary water concentrations for each contaminant that would result in a buildup of mass in the active sediment layer that is consistent with the inter-quartile range of recent sediment concentrations measured in Puget Sound. For all hindcast runs, contaminant concentrations in the water column and active sediments of each model region were initially set to zero. Watershed loads (via surface runoff, POTWs, and groundwater) and atmospheric deposition were assumed to occur at the median best estimates described previously. With all other model inputs fixed, runs were executed using various boundary water concentrations to predict the steady-state mass in Puget Sound sediments that would accumulate due to contaminant loading at the ocean boundary. Bounds on the range of plausible boundary water concentrations were established by those concentrations that produced a mass buildup in the sediments comparable to current inventories of contaminant mass estimated from sediment concentration data.

The hindcast results for copper, lead, zinc, Total PCBs, Total PBDEs, Total PAHs, and eight PAH compounds are summarized in Tables H-3 and H-4. Table H-3 presents the sediment mass buildup predicted by the best-estimate boundary water concentrations and by zero ocean loading (i.e., mass accumulation due solely to watershed loading and atmospheric deposition). The boundary water concentrations that yielded mass accumulations equivalent to the observed 25th percentile, median, and 75th percentile contaminant masses in Puget Sound sediments are given in Table H-4. Figures 17 and 18 show the predicted accumulation of contaminant mass over the 100-year simulation period resulting from these various boundary concentrations. The shaded region in each plot indicates the inter-quartile range of the current contaminant mass in Puget Sound sediments.

With a boundary water concentration of zero, the predicted steady-state mass (Table H-3) represents the contaminant buildup due to loadings from surface runoff, wastewater treatment facilities, direct groundwater discharge, and atmospheric deposition. In the absence of contaminant inflow at the ocean boundary, the steady-state masses of copper, lead, and zinc in the active sediment layer were predicted to be 365, 120, and 1606 t (metric tons), respectively. Likewise, the long-term mass buildup of Total PCBs, Total PBDEs, and Total PAHs in the sediments approached 40, 14, and 25 kg, respectively. For PBDEs, the mass accumulation due to watershed sources exceeded that due to ocean loading (14 kg from watershed sources and the atmosphere versus 8.1 kg from ocean loading and atmospheric deposition). However, for all other contaminants, loading from the ocean was the dominant source of the mass buildup in the sediments.

Hindcast runs using 25th percentile, median, and 75th percentile concentrations in the boundary waters consistently under-predicted empirical sediment mass inventories (Figure 17, Table H-4). The only exception was lead, for which the median and 75th percentile boundary concentrations resulted in steady-state masses that were within the inter-quartile range of the observed sediment mass. No other contaminant even had a 75th percentile boundary water concentration sufficient to cause a mass buildup greater than or equal to the observed 25th percentile sediment mass.

The boundary water concentrations that were predicted to yield a mass buildup in the sediments comparable to the 50th percentile (median) empirical mass inventories were as follows: 0.91 ug/L copper, 0.19 ug/L lead, 1.70 ug/L zinc, 113 pg/L Total PCBs, 191 pg/L Total PBDEs, and 1.70 ug/L Total PAHs. Generally, boundary water concentrations approximately 2 to 4 times higher than the best estimates were required to accumulate the median observed sediment mass of each contaminant (Figure 18). The necessary Total PBDE concentration, however, was just over 15 times higher than the best-estimate boundary concentration. As was the case in the hindcast loading exercises, the results for PAHs were highly anomalous, with a factor of 400 increase of the best-estimate boundary concentration needed to match the median observed sediment mass in the system. The substantial increase in the ocean load of PAHs was apparently required to overcome rapid degradation losses. It should also be noted that all Total PAH samples from the boundary waters were non-detects, and so the best-estimate concentration was determined by the sample detection limits (i.e., each ND sample was assigned the value of 1/2 the detection limit; see Model Inputs section) which may have imparted an upward or downward bias (i.e., actual concentrations may be higher or lower).

The plausible range of boundary water concentrations for each contaminant was determined by those concentrations that were predicted to result in a sediment mass buildup corresponding to the 25th and 75th percentile empirical masses (Figure 18, Table H-4). Estimated plausible ranges of metals concentrations in the boundary waters were as follows: 0.5 to 1.7 ug/L copper, 0.1 to 0.3 ug/L lead, and 1.2 to 2.7 ug/L zinc. Total PCBs and Total PBDEs had plausible ranges of approximately 48 to 260 pg/L and 74 to 456 pg/L, respectively. Finally, the estimated plausible range for the concentration of Total PAHs in the boundary waters was 0.3 to 4.8 ug/L, although uncertainties in PAH degradation rates may limit the utility of these estimates.

The current mass of each modeled contaminant in Puget Sound sediments appears to be at equilibrium with contaminant concentrations in the ocean boundary waters that are considerably higher than the current best-estimate concentrations. These discrepancies may be attributable to one or several causes, including the possible over-estimation of sediment masses, uncertainties in key model inputs (e.g., degradation rates), and under-estimation of watershed loads, all of which were described previously in the Hindcast Loading section. It is also possible that contaminant concentrations in the boundary waters may in fact be underestimated. Actual boundary water concentrations of copper, lead, zinc, and Total PCBs may be around 2 to 4 times higher than median estimates from the recent data (2000-2012) compilation. While non-detects were not an issue for boundary water samples of these contaminants, the data sets may not fully represent deep boundary water concentrations due to limited temporal coverage and small sample size (n = 8 or 9 for each contaminant; see Tables C-1 through C-4).

For Total PBDEs, it is not clear why the boundary concentrations measured by Frouin et al. (2013) were a factor of 15 lower than those estimated by the hindcast runs, especially considering their large sample volumes (200 L) and clean sampling methods. Again, a small number of samples and seasonal coverage may have contributed to the discrepancy in observed and hindcast-predicted boundary concentrations, but another possible cause was the influence uncertainties of PBDE degradation rates and underestimated watershed loads on hindcast results.

Finally, boundary water samples for Total PAHs may have underestimated actual concentrations due to sampling issues (i.e., small number of samples and insufficient sample volume) and due to the substitution and summation rules used for non-detects. These potential downward biases may have accounted for some of the 400-fold difference between the best-estimate boundary water concentration and the hindcast-predicted concentration needed to build up the observed sediment mass, but the influence of fast, highly uncertain PAH degradation rates on long-term model predictions likely had a much larger role in the hindcast results for PAHs.

A combination of the above-mentioned factors may have contributed to discrepancies between the current best estimates of contaminant concentrations in the ocean boundary waters and the substantially higher concentrations predicted by the hindcast exercises. Sampling efforts to refine estimates of contaminant concentrations in the deep waters of the Strait of Juan de Fuca just outside the sill at Admiralty Inlet would improve confidence in ocean loading estimates. Since ocean loads were found to be large relative to watershed and atmospheric loads for most contaminants, reducing uncertainties in the boundary concentration inputs may provide more accurate model predictions of long-term contaminant fate.
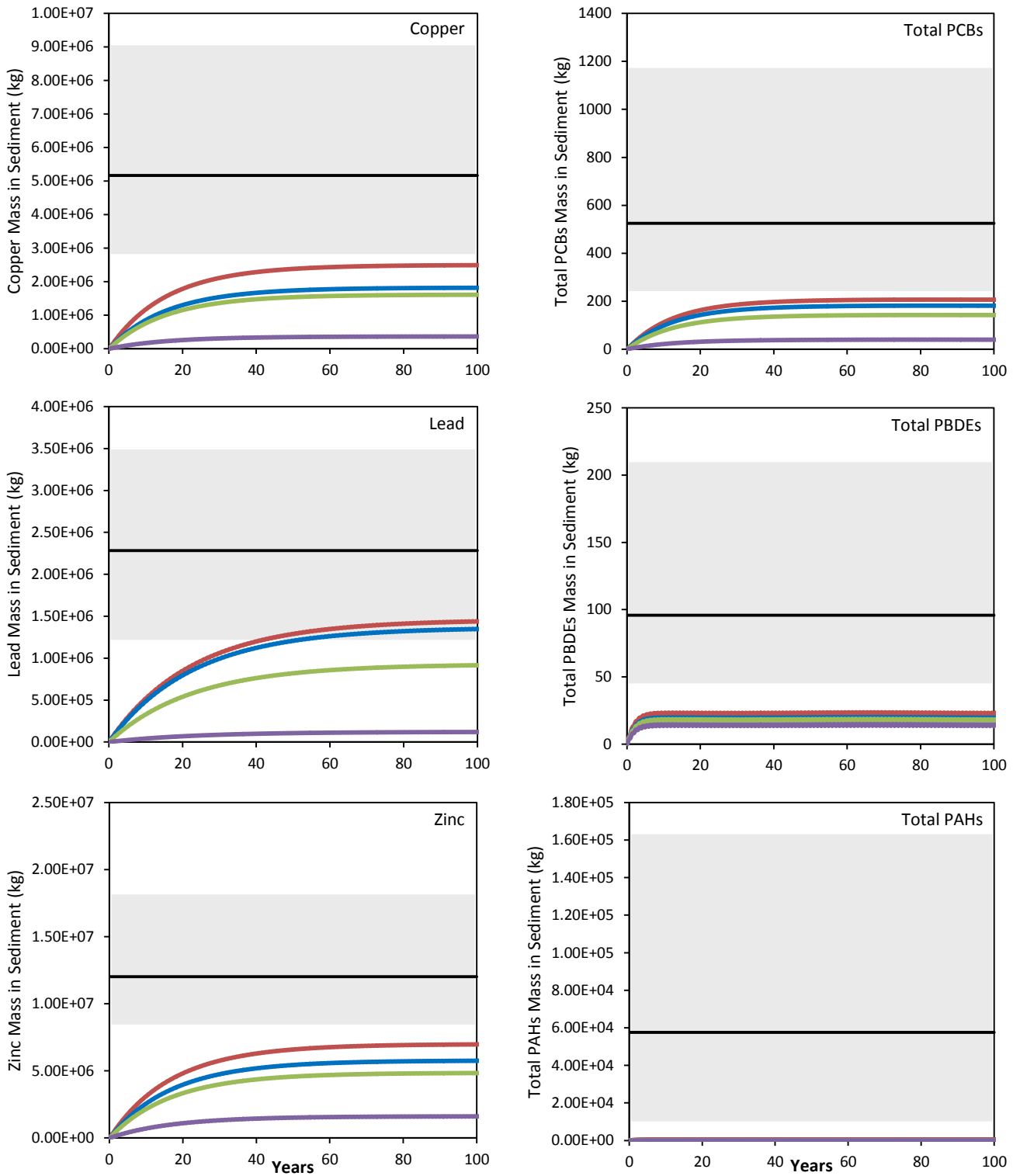
Figure 17. Hindcast predictions of contaminant mass accumulation in Puget Sound active sediments resulting from the following concentrations in the deep boundary waters: zero (purple line), 25th percentile (green line), median (blue line), and 75th percentile (red line).

The shaded region indicates the inter-quartile range of observed contaminant mass in the active sediments; the horizontal black line is the median observed mass.
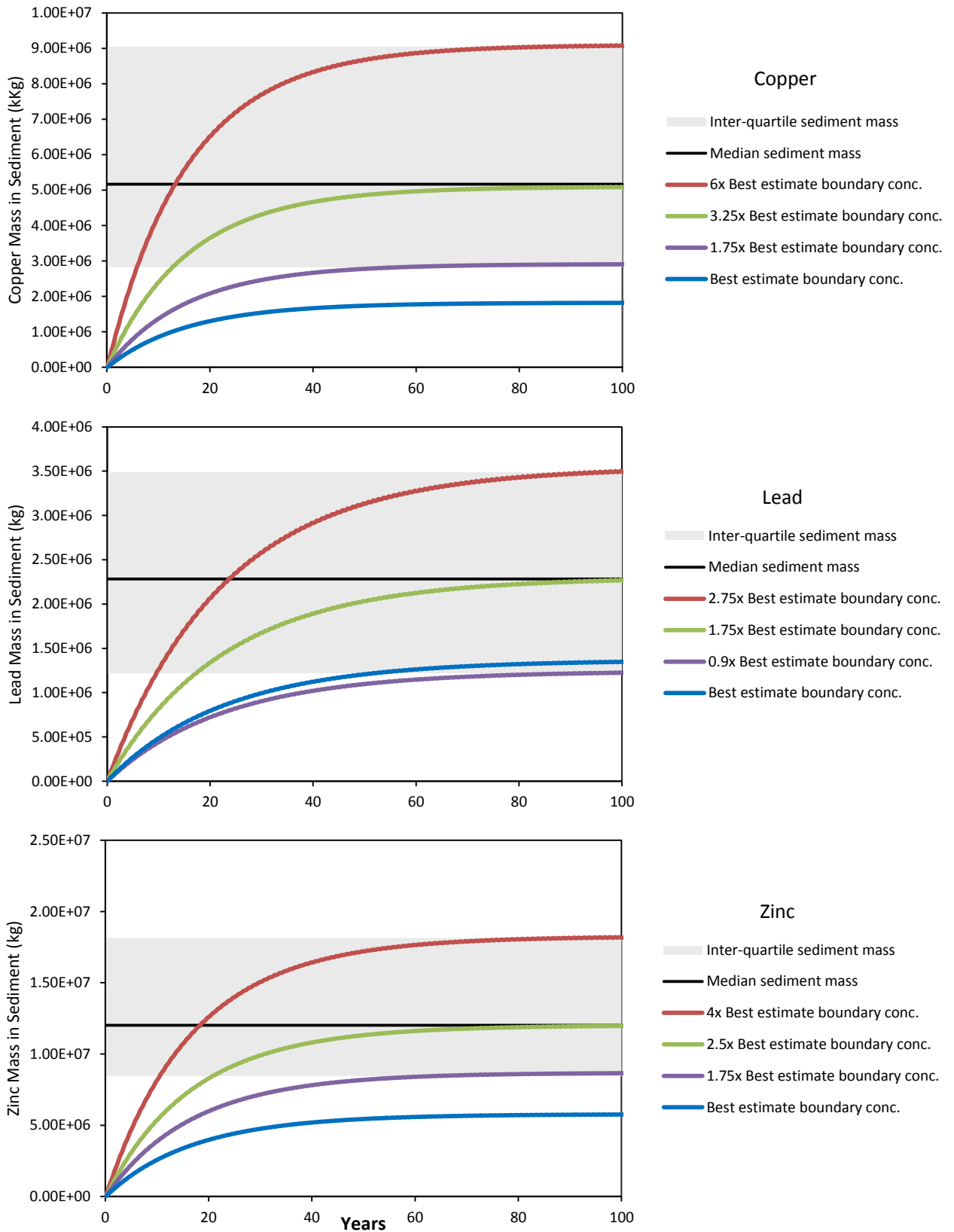
Figure 18. Hindcast results for the predicted deep boundary water concentrations needed to accumulate observed contaminant masses in Puget Sound active sediments.
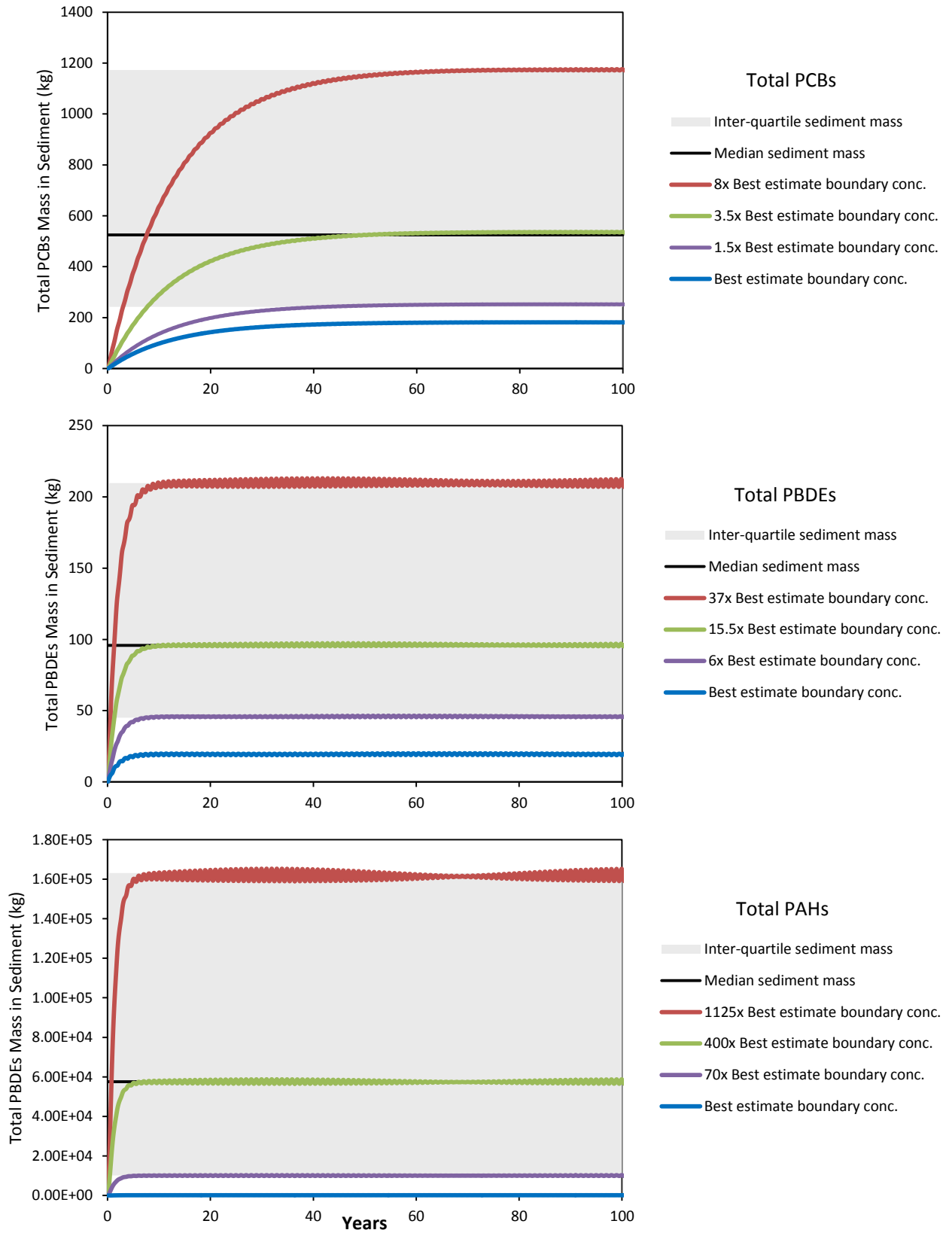
Figure 18 (continued). Hindcast results for the predicted deep boundary water concentrations needed to accumulate observed contaminant masses in Puget Sound active sediments.

Results and Findings

"Best-Estimate" Runs

When the model was implemented using the best-estimate values of all model inputs, the total mass of each contaminant in Puget Sound was predicted to decline through time and approach a steady-state condition with approximately constant mass in the system (Figure 6). The predicted steady-state masses were roughly as follows: 2000 t (metric tons) copper, 1500 t lead, 6200 t zinc, 190 kg Total PCBs, 24 kg Total PBDEs, and 750 kg Total PAHs. These forecasts assume that loads from watershed sources (i.e., surface runoff, POTW discharges, and groundwater) and atmospheric deposition remain constant at the rates estimated by the Phase 3 PSTLA studies.

The amount of time required for half of the initial mass to be lost varied by contaminant (Table 5). The loss of metals from the system was predicted to take longer than the time needed for comparable reductions of organic contaminants, in part due to the more limited loss processes available to metals (i.e., metals do not volatilize or degrade). For organic contaminants, mass losses of PAHs and PBDEs were predicted to be considerably more rapid than PCBs, with half the original mass achieved in 1.0 years, 2.2 years, and 20 years, respectively. The twenty- and ten-fold faster mass losses for PAHs and PBDEs suggest that, in comparison to PCBs, Puget Sound would respond more quickly to loading reductions for these contaminants. The estimated time to reach half the initial mass of individual PAH compounds (Table G-3) generally increased with PAH size and was inversely related to the compound-specific degradation rate in sediments.

Table 5. Cumulative contaminant mass loads and losses (kg) predicted over a 55-year simulation period with all model inputs set to their best-estimate values.

	Copper	Lead	Zinc	Total PCBs [a]	Total PBDEs [b]	Total PAHs [c]
Starting mass	5,240,000	2,290,000	12,100,000	532	98.8	59,500
Inflow at the ocean boundary	8,830,000	3,400,000	21,400,000	1,020	468	134,000
Watershed loading	1,820,000	265,000	6,670,000	242	778	19,600
Atmospheric deposition	70,000	28,200	374,000	23.0	188	2,910
Total mass loading	10,700,000	3,700,000	28,500,000	1,280	1,430	157,000
Outflow at the ocean boundary	8,030,000	812,000	18,100,000	848	601	126,000
Burial	5,920,000	3,680,000	16,300,000	540	49.3	2,850
Degradation	0	0	0	183	832	79,000
Volatilization	0	0	0	52.6	26.4	7,180
Total mass losses	14,000,000	4,490,000	34,400,000	1,620	1,510	215,000
Total mass in year 55	2,000,000	1,490,000	6,190,000	193	23.7	754
% of initial mass lost	61.8%	34.8%	49.0%	63.8%	76.0%	98.7%
Time to 50% of initial mass	25 yr	>55 yr	>55 yr	20 yr	2.2 yr	1.0 yr

[a] Total PCBs were simulated using the parameters of congener PCB-118.

[b] Total PBDEs were simulated using the parameters of homolog Tetra-BDE with initial concentrations in the boundary waters and regional water column layers set to median values from the Strait of Georgia and Rosario Strait reported in Frouin et al. (2013).

[c] Total PAHs were simulated using the parameters of Fluoranthene; direct groundwater loading estimates were excluded from watershed loads due to high uncertainties.

For example, Naphthalene (a 2-ring LPAH) had the fastest degradation rate and was predicted to decline to half its initial mass in a matter of weeks, while Benzo(b)fluoranthene (a 5-ring HPAH) was more resistant to degradation and took just over four years to lose half its original mass. These findings are consistent with the modeling work of Greenfield and Davis (2005) who estimated similarly fast losses for PAH compounds in San Francisco Bay.

The relative importance of the various loading pathways and loss processes to the long-term predicted contaminant mass also differed by contaminant. Figures 19 and 20 illustrate the cumulative contribution of the various source and loss pathways for the best-estimate runs. At the end of the 55-year simulation when the mass in the system was at or near steady-state, the model predicted that the dominant loss pathway for most contaminants was export at the ocean boundary, which generally accounted for around half of the cumulative loss from the system (Table G-2). For metals the only other loss process was burial, which was responsible for 80% of the removal of lead and just under half of the copper and zinc losses. Burial was also an important loss pathway for PCBs, accounting for about a third of the removal, but for the other organic contaminants (including individual PAH compounds) burial was insignificant and rarely contributed to more than 3% of the long-term total losses. Degradation was a key loss process for organic contaminants, causing 55% of the cumulative PBDE mass reduction and between 25 and 70% of the mass losses for PAHs. However, the much slower degradation rate for PCBs (half-life of 56 years compared to approximately 1 year for PBDEs and from several weeks to several years for PAH compounds) resulted in degradation accounting for only 11% of the cumulative loss of PCBs from the system. Finally, volatilization played a small role in the removal of organic contaminants (generally <5% of the total loss), with those contaminants that sorb more strongly to solids (e.g., HPAHs versus LPAHs) having lower losses because only dissolved-phase organics are available for volatilization.

Model Performance and Utility

The fate and transport model predicted a decreasing trend for the total mass of each contaminant in Puget Sound using the best-estimate values of all model inputs. However, when region-specific predictions of contaminant concentrations in water and sediment were compared to recent data collected from 2000 to 2012, the rapid declines forecast by the model were not supported by the data (e.g., Elliott Bay, Figure 14). In general, the measured contaminant concentrations in the surface and deep water column and the active sediments did not show a clear upward or downward trend since 2000 for any of the model regions. This disagreement between predicted and observed concentrations indicates that the present best estimates of total contaminant loads are insufficient to maintain the levels observed in the environment.

The lack of evidence for trends in the sediment data over approximately the last decade suggests that contaminant concentrations in the sediments may be in equilibrium with the present loads to and losses from the system (i.e., sediment conditions are steady-state). Assuming equilibrium conditions, the model was used in "hindcast" mode to determine (1) the external load from watershed sources (e.g., surface runoff, POTW discharges, and groundwater) that would be necessary to build up the observed contaminant masses in sediments, and (2) the contaminant concentrations in the deep boundary waters that would result in ocean loads sufficient to build up the observed contaminant masses in Puget Sound sediments.
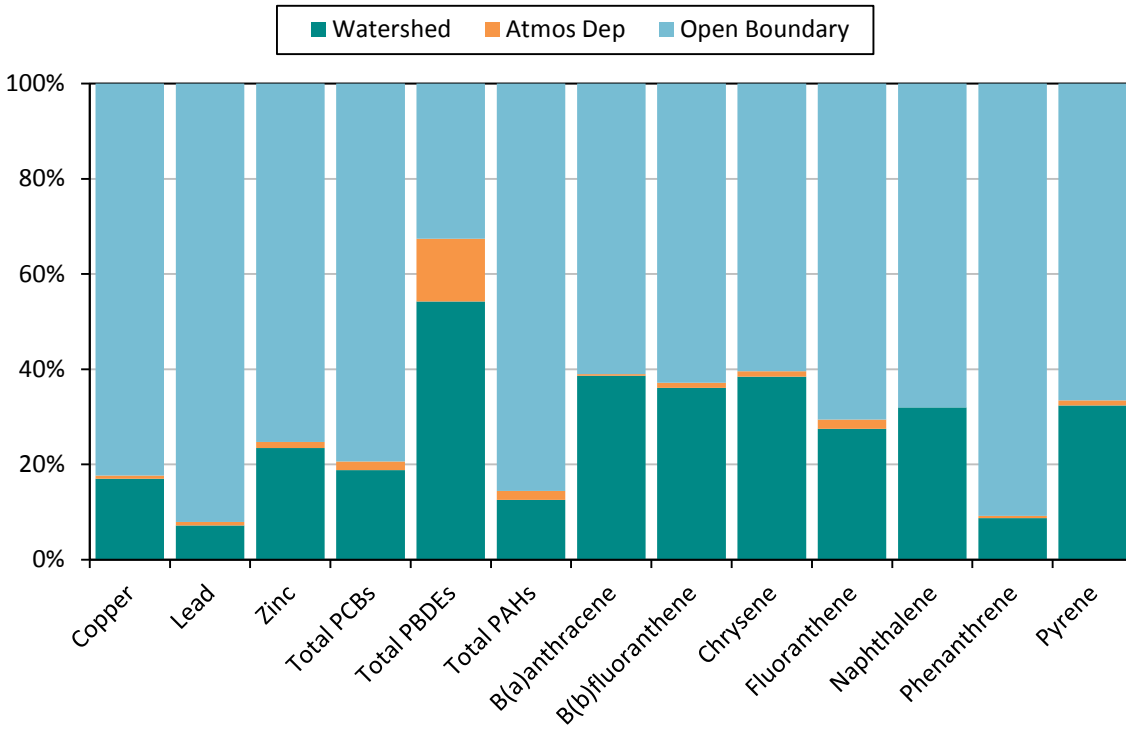
Figure 19. Model-predicted cumulative contribution of contaminant mass loading pathways to Puget Sound over 55 years.
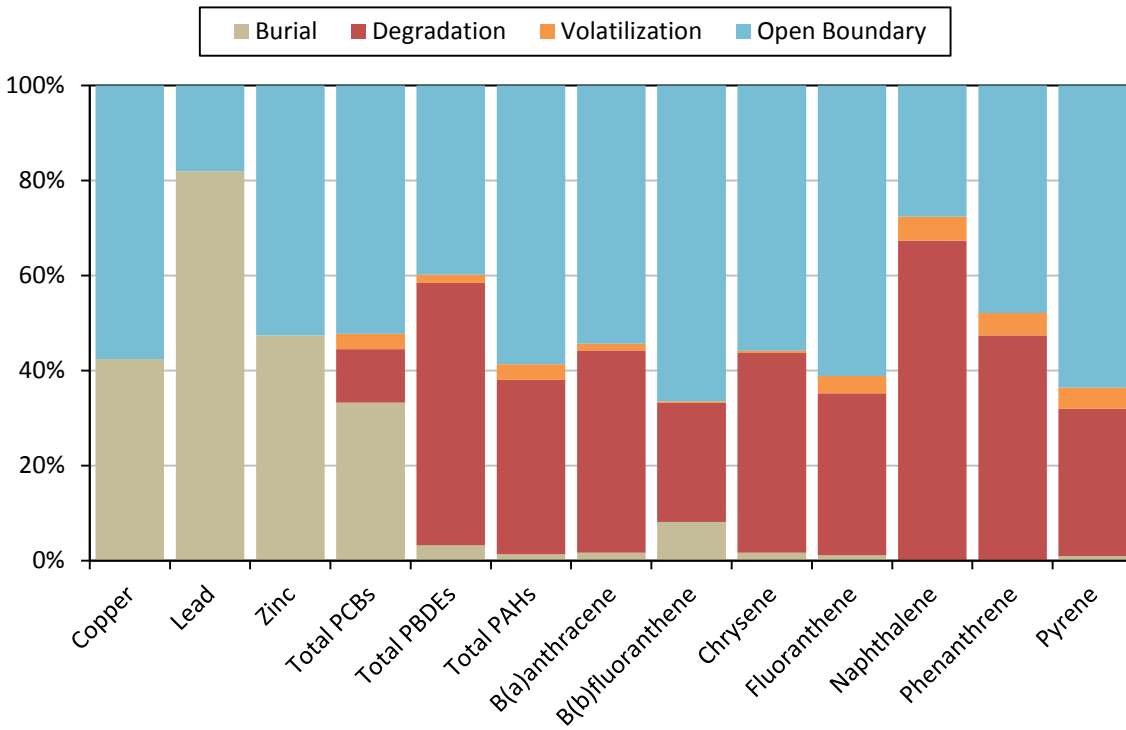
Figure 20. Model-predicted cumulative contribution of contaminant mass loss processes to Puget Sound over 55 years.

Key findings of the hindcast exercises were as follows:

- Considerable increases in the current best-estimate watershed loads were needed to keep model results in agreement with empirical sediment mass inventory estimates. For copper, lead, zinc, Total PCBs, and Total PBDEs, watershed loads 5 to 10 times higher than the Phase 3 best-estimate loads were required in order to match the observed masses in Puget Sound sediments. Watershed loads that were predicted to yield a mass buildup in the sediments comparable to the 50th percentile (median) empirical mass inventories were as follows: 355 t/yr copper, 49 t/yr lead, 620 t/yr zinc, 47 kg/yr Total PCBs, and 116 kg/yr Total PBDEs.

- Boundary water concentrations approximately 2 to 4 times higher than the best estimates were required to accumulate the observed sediment mass of copper, lead, zinc, and Total PCBs. The best-estimate concentration of Total PBDEs in the boundary waters had to be increased by a factor of 15 to build up a steady-state mass in the sediments comparable to the observed mass. The boundary water concentrations that were predicted to yield a mass buildup in the sediments equivalent to the median empirical mass inventories were as follows: 0.91 ug/L copper, 0.19 ug/L lead, 1.70 ug/L zinc, 113 pg/L Total PCBs, and 191 pg/L Total PBDEs.

- The results for Total PAHs in both hindcast exercises were anomalous and appeared to be overwhelmed by uncertainties in PAH degradation rates. Indeed, the current understanding of degradation rates for PAHs may not be sufficiently accurate to predict long-term fate with confidence (Greenfield and Davis, 2005).

The hindcast analyses suggest that the current best estimates of watershed loading, contaminant concentrations in the deep boundary waters, or both, may be underestimated. Although not explored in the present study, another possibility is that the rates governing loss processes in the model may be incorrect and slower losses (e.g., degradation) could potentially sustain the observed contaminant masses in the system[14]. At present it is difficult to determine which of these hypotheses explains the discrepancies between model predictions and the observed data. Continued monitoring efforts to characterize ambient contaminant concentrations in Puget Sound sediments and sampling to refine estimates of concentrations in the deep waters of the Strait of Juan de Fuca (just outside the sill at Admiralty Inlet) may yield a more accurate mass budget to help resolve these differences.

Given that the observed concentration data do not corroborate the rapid declines predicted by the model, the fate and transport component of the PSRTM is not presently considered to be usable for forecast scenarios. Several of the intended analyses outlined in the project QAPP (Osterberg and Pelletier, 2012) were therefore not performed. These included the planned use of the updated model in a hypothetical management capacity to (1) estimate reductions in contaminant loadings needed to meet sediment and water quality standards, and (2) estimate the time required to achieve those endpoints under various loading reductions. Despite the limited utility of the fate and transport model, the hindcast exercises and the preliminary forecast efforts described in

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[14] Except in a few rare cases, the sensitivity and uncertainty analyses did not find any rate parameters for which adjustments within the plausible range were sufficient to overcome the trend of rapid declines in total mass that were predicted by the model. This suggests that loading deficits are more likely responsible for the inability to maintain contaminant masses at observed levels.

this report nonetheless demonstrate the value of the model for exploring the interplay of processes controlling the dynamics of each contaminant in Puget Sound.

Another outcome of the fate and transport modeling was a better understanding of the parameters that must be more accurately characterized to improve confidence in the model results, which will aid in setting priorities for future research. According to the sensitivity and uncertainty analyses, refined estimates of the following contaminant-specific model inputs could improve model predictions of long-term contaminant fate: degradation rate, octanol-water partition coefficient, concentration in the deep waters of the ocean boundary, and external loads from watershed sources. Other important inputs included the proportionality constant for POC partitioning, POC concentration and TSS in regional waters, and regional sediment burial and resuspension velocities. Because model results were strongly influenced by these inputs, obtaining realistic estimates of these parameters will be an important challenge in further developing the fate and transport component of the PSRTM.

Food Web Bioaccumulation Model

Model Setup

The food web bioaccumulation component of the PSRTM developed by Pelletier and Mohamedali (2009) predicted the steady-state concentration of Total PCBs that would accumulate in each of the principal organisms of the Puget Sound marine food web due to long-term exposure to user-specified PCB concentrations in the active sediments and water column. In the bioaccumulation model, individual species (or representative classes) are sub-models that simulate the fluxes of PCBs into and out of the organism. These sub-models are linked together through feeding interactions to represent the food web. Unlike the fate and transport model in which model regions interact and the entire Puget Sound ecosystem is simulated at once, the bioaccumulation model must be executed separately for each region, with region-specific values of sediment and water PCB concentrations defined in the model inputs.

Pelletier and Mohamedali (2009) configured the PSRTM based on the work of Condon (2007) and Gobas and Arnot (2005) to simulate the bioaccumulation of individual PCB congeners in the modeled organisms. The predicted congener concentrations are summed in the model to provide an estimate of Total PCB concentration in each organism. In this configuration, the subset of modeled congeners is selected by the user; for example, Condon (2007) simulated 57 different PCB congeners and Pelletier and Mohamedali (2009) selected 22 congeners based on their known occurrence in sediment and biota. For the present study, a suite of 20 congeners was selected for PCBs and 17 congeners were selected for the expansion of the model to simulate PBDEs. The modeled congeners were chosen because of their prevalence in sediment and biota data (i.e., high frequency of analysis and detection) and because those congeners comprised a majority of the Total PCB and Total PBDE mass in Puget Sound sediments (see Figures B-11 and B-12). They were therefore considered to be reasonably representative of the behavior of the entire class of PCBs and PBDEs.

The following sections describe modifications that were made to the bioaccumulation component of the PSRTM to facilitate simulation of PCBs and PBDEs, and the development of model inputs to prepare the model for calibration and scenario exercises.

Model Code Updates

As with the fate and transport component of the PSRTM, the computer code used to execute the calculations for the food web bioaccumulation component was written in Microsoft Excel's Visual Basic for Applications (VBA) programming language. Excel worksheets serve as the user interface for entering model inputs and viewing output results.

Although the bioaccumulation model was originally developed for the simulation of PCBs, the framework and modeled processes were designed to be applicable to other hydrophobic organic contaminants (HOCs). As such, adaptation of the model to simulate PBDEs did not require modification of the VBA code, but simply involved the entry of PBDE-specific inputs (e.g., concentrations in the sediments and water column, chemical characteristics for modeled

PBDE congeners) in place of the existing inputs for PCBs. The development of model inputs for PBDEs and the revision of PCB inputs are discussed in the Model Inputs section.

One change was made to the bioaccumulation model code to address a problem identified since the work of Pelletier and Mohamedali (2009). The problem involved a function that calculated the fugacity of lipids for poikilotherms (cold-blooded organisms) using the octanol-air partition coefficient at the body temperature of *homeotherms* (warm-blooded organisms). This function was corrected to instead use the ambient water temperature. The user interface of the model was also modified to enhance efficiency as follows: (1) added lookup tables containing summary data statistics of observed PCB and PBDE concentrations in the sediments, waters, and biota of each region, and (2) provided dropdown menus to facilitate automatic population of all model inputs for a user-specified region and contaminant.

No attempt was made to account for the potential metabolic debromination of PBDEs by organisms in the food web model. Debromination involves the transformation of high molecular weight PBDE congeners to lighter forms. For marine organisms, metabolic debromination may lead to the preferential buildup of lighter, more toxic congeners. As such, it may be an important aspect of the elimination and accumulation of PBDEs, influencing the levels and congener patterns throughout the food web. For the purposes of the present study, it was assumed that the bioaccumulation of *Total* PBDEs in modeled organisms would be unchanged by such transformations. Future work should consider making debromination explicit in the PSRTM.

Model Inputs

Inputs for the bioaccumulation model are used to define environmental conditions, contaminant concentrations in sediments and waters to which organisms are exposed, chemical properties of modeled contaminants, food web structure and feeding relationships between the modeled organisms, and species-specific biological parameters. Generally, inputs for PCBs were updated from those used by Pelletier and Mohamedali (2009) whenever possible and new inputs were developed for the simulation of PBDEs. The following sub-sections describe the sources of data and parameters and the development of the final model inputs.

Regional Environmental Conditions and Contaminant Concentrations

A number of variables representing environmental conditions were established by Pelletier and Mohamedali (2009) using empirical data from Puget Sound. These variables included the mean annual water and air temperatures; dissolved oxygen concentration; organic carbon content of the sediments in each region; and regional concentrations of total suspended solids (TSS), dissolved organic carbon (DOC), and particulate organic carbon (POC) in the water column. Where applicable, Pelletier and Mohamedali (2009) used the same values for these inputs as those employed in the fate and transport model. For the present study, the following inputs were updated with median regional values from the recent (2000-2012) data compilations: sediment organic carbon, TSS in the water column, and concentrations of DOC and POC in the water column. These are the same values that were used as inputs to the fate and transport model for organic carbon content of the sediments (Table B-4), but for water column variables, the median of the recent observed data from both the surface and deep water column layers was used.

Current concentrations of sediment PCBs and PBDEs were estimated based on the median of observed data for each region, as discussed earlier in the "Sediment Properties" section of this report and summarized in Table B-2. Likewise, water column concentrations of PCBs were updated based on recently compiled data, as described in the "Water Properties" section, with regional concentrations assigned the median value from the combined surface and deep layer data set for that region. For PBDE concentrations in regional waters, however, the observed data set was small and included a high frequency of non-detects and a number of suspect values. Median concentrations measured by Frouin et al. (2013) in the Rosario Strait were therefore used as the water column PBDE concentration in each region.

Because the model simulates the bioaccumulation of individual congeners separately, the Total PCB and Total PBDE concentrations in the sediments and waters of each region had to be allocated among the modeled congeners. Since the majority of the mass for these contaminants in Puget Sound is found in the sediments, allocation sought to reflect the fraction of each congener in the observed sediment data[15]. The first step was to determine the average percent contribution[16] of each modeled congener to the total measured concentration (represented by the sum of the 20 and 17 modeled congeners for PCBs and PBDEs, respectively). Congener-specific percent contributions were then multiplied by the regional median concentration in the sediment and in the water column to obtain environmental concentrations of each modeled congener. As previously stated, the model simulates the bioaccumulation of each congener using the allocated concentration and according to congener-specific chemical parameters.

The environmental conditions, final regional contaminant concentrations, and allocated congener-specific concentrations that were used as inputs to the bioaccumulation model are tabulated in Appendix I.

Food Web Structure and Dietary Assumptions

The bioaccumulation model developed by Condon (2007) for PCBs in the Strait of Georgia was adapted to Puget Sound by Pelletier and Mohamedali (2009) with only minor changes to the modeled species and trophic linkages defined in the original. For the present study, the Puget Sound food web established by Pelletier and Mohamedali (2009) was used. Additional species were not incorporated into the food web for this study, but feeding relationships were modified slightly during model calibration (described later in the "Model Calibration" section). The same food web was used for all regions and for simulation of both PCBs and PBDEs.

Modeled Organisms

The PSRTM food web includes important species and major taxonomic groups such as phytoplankton and macrophytes, various herbivorous and predatory zooplankton, detritivores, benthic invertebrates, shellfish, crabs, amphipods, krill, forage fish (herbivorous and omnivorous), and piscivorous fish (demersal and pelagic). The top predators in the model food web include harbor seals, double-crested cormorants, and great blue herons. Condon (2007)

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[15] Sediment data pooled from all regions were used for the determination of the relative contribution of each congener. For model inputs, the congener proportions were assumed to be the same across all regions.

[16] The contribution of each congener to the "total" concentration was normalized to the congener-specific number of results to remove any biases that would be caused by differences in the frequency of analysis among the congeners.

originally focused on these top predators because (1) they are subject to potentially high contaminant doses as a result of their trophic position, (2) they are resident and consume local organisms, and (3) empirical values for biological parameters were readily available for these organisms. Orcas were not used as top predators in the model, but fish-eating harbor seals occupy the same trophic position and have a diet similar to that of orcas. In addition, harbor seals have a much smaller feeding range, which makes them more amenable to region-specific prediction of bioaccumulation.

Feeding Relationships

The feeding relationships linking the top predators in the model to their prey and ultimately to regional sediments and waters are illustrated in Figure 5. The diet matrix for the food web, which tabulates the dietary preferences of each of the modeled species, is presented in Table J-1. Condon (2007) provides references to diet studies in the literature that were used to create the original diet matrix for the Strait of Georgia food web. As stated previously, Pelletier and Mohamedali (2009) did not significantly alter diet fractions from those developed by Condon (2007) when the model was adapted to Puget Sound. During calibration of the bioaccumulation model for the present study, adjustments were made to the dietary preferences for some species based on information from other Puget Sound modeling studies that included these organisms. Extensive re-structuring of the food web, however, was beyond the scope of this project.

Contaminant Concentrations in Biota

Data describing observed concentrations of PCBs and PBDEs in Puget Sound biota were necessary for evaluation of the model skill for predicting bioaccumulation in each modeled organism. For PCBs, the data compiled by Pelletier and Mohamedali (2009) were used as a starting data set and was updated with recent data. Existing compilations of observed data on PBDE concentrations in Puget Sound biota were not available, and so data sets were developed from scratch. Sources of data for both contaminants included the following resources and sampling programs:

- Studies conducted for Phase 3 of the PSTLA[17].
- Washington Department of Fish and Wildlife (WDFW).
- Puget Sound Ecosystem Monitoring Program (PSEMP).
- NOAA National Status and Trends (NS&T) Mussel Watch (MW) Program database[18].
- Project ENVironmental InVESTment (ENVVEST) database.
- Washington Coastal EMAP databases.
- Ecology's EIM database.
- King County Department of Natural Resources and Parks (KCDNRP).
- Data summaries in the peer-reviewed literature.

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[17] Several studies were conducted during Phase 3 of the PSTLA to fill data gaps and improve estimates of contaminants in specific organisms in Puget Sound, including phytoplankton and krill (West et al., 2011a), pelagic fishes (Pacific hake and walleye pollock; West et al., 2011b), and harbor seal pups (Noel et al., 2011).
[18] The NS&T data portal can be accessed at http://ccma.nos.noaa.gov/about/coast/nsandt/download.aspx.

Species-specific concentration data were compiled from the various sources, along with metadata on sampling methods, relevant characteristics of the collected organisms (such as wet weight, length, age, lipid content), analytical methods, and data rules employed, if known. Once compiled, acceptance criteria were applied to omit data that were not appropriate for the purposes of the model. The screening steps used were as follows:

- Overlaps between data sets were identified and remedied to avoid double-counting results.
- Sample results older than 2000 were omitted so that the data would be representative of recent or current conditions.
- Sample results that were qualified as rejected (e.g., "REJ" qualified) were removed.
- Sample results that were qualified due to blank contamination concerns were removed.
- Sample results that were qualified as estimates (e.g., "J" qualified) were used without modification.
- All sample concentrations, detection limits (DLs), and reporting limits (RLs) were converted to common units for each contaminant. With the exception of harbor seal results, data reported on a lipid-weight basis were converted to wet-weight using the sample-specific lipid content, if available; otherwise, a typical lipid fraction for comparable organisms was obtained from other data sets or publications.
- Samples for which the collection location was unspecified or unclear (i.e., those that could not be associated with a particular model region) were removed. Samples were referenced to model regions in ArcGIS using a spatial join, and samples collected outside the model regions were removed.

In addition, tissue samples that were not classified as "whole body" could not be used to evaluate the model results (i.e., observed-versus-predicted comparisons) and were removed from the data set. Use of fish fillet data, for example, would have required the development of regression equations based on empirical fillet and whole-body contaminant concentrations to facilitate conversion to whole-body estimates. These types of data were not readily available and such calculations were beyond the scope of the present study. Omitting non-whole-body data caused considerable loss of information on PCB and PBDE concentrations in Puget Sound biota, such as the recently reported concentrations in Dungeness crab (*Metacarcinus magister*) and spot prawns (*Pandalus platyceros*) from eight different regions of the Sound (Carey et al., 2014).

Due to the overall scarcity of data on PCB and PBDE concentrations in Puget Sound biota, the compilation of observed data for this study sought to retain as much data as possible for use in model testing and calibration. In some cases, there were multiple data sources for a particular organism in a specific region. Analytical methods also varied between and sometimes within studies. Following the precedent of Pelletier and Mohamedali (2009), "like" data that shared a common source and analytical method were combined into regional data sub-sets, or "pools." The mean and standard deviation (where applicable) of the separate pools of data in each region were determined and tabulated for comparison with the model-predicted concentration for that specific organism and region. When there were multiple pools of data for a species in a region, the same model prediction was compared to each pool's mean observed concentration during model calibration.

Appendix K summarizes the biota data compiled for this project, with observed concentrations of PCBs in Puget Sound biota given in Table K-1 and PBDE concentrations presented in Table K-2.

Several species in the model food web were known to be migratory, including chum salmon, coho salmon, Chinook salmon, and some Pacific herring. These species begin their lives in Puget Sound, spend the majority of their adult lives feeding and growing in the ocean, and return to the Sound and its rivers to spawn. Since these organisms feed primarily outside the model domain and are only present as outmigrant juveniles and when passing through to reach spawning areas, the PCB and PBDE concentrations in their bodies as adults are not reflective of exposure in Puget Sound or specific regions therein. In the model these species were classified as "immigrants" (as opposed to "residents" that reside year-round), and empirical values were used to define their whole-body concentrations when estimating exposure from these fish to their predators. The immigrant species data used in the model are described below and summarized in Tables K-3 and K-4.

- Data for all immigrant species was collected by WDFW under the auspices of PSEMP and provided by James E. West (WDFW, personal communication, 2013 and 2009).
- Both resident and immigrant varieties of Pacific herring were included in the model food web. Regional concentrations of PCBs and PBDEs in resident herring were predicted by the bioaccumulation model based on the feeding preferences specified in Table J-1 and regional contaminant levels in the sediments and water column. Contaminant concentrations in immigrant herring were constants specified in the model inputs (Tables K-3 and K-4) based on WDFW data from three locations in Puget Sound. Pacific herring prey for all predators were assumed to be resident.
- Model inputs for PCB and PBDE concentrations in immigrant chum and coho salmon were set to mean observed values from the available Puget Sound data. The same values were used for all model regions.
- When possible, region-specific values of contaminant concentrations in immigrant Chinook salmon were developed using data from regional rivers (South Sound regional concentrations were based on data from the Deschutes and Nisqually Rivers; Elliott Bay values were based on Duwamish River data). The remaining model regions used mean concentrations of PCBs and PBDEs in Chinook salmon from all Puget Sound sampling sites.
- In addition to immigrant Chinook salmon, resident blackmouth salmon were defined in the model food web. Regional contaminant concentrations in blackmouth salmon were predicted by the model based on the feeding preferences given in Table J-1.
- The model inputs for Total PCB and Total PBDE concentrations in the various immigrant fish were allocated to the modeled congeners according to the average percent contribution of each congener in the observed data for each species.

Chemical and Biological Parameters

Tables L-1 and L-2 present the congener-specific inputs used for various chemical parameters in the bioaccumulation model. These inputs include chemical properties that control the physical-chemical partitioning of each congener (e.g., between the organism and water, between air and the organism, and between the gastrointestinal tract and the organism). For PCBs, the congener-specific values for partitioning coefficients and enthalpies of phase change that were used by

Pelletier and Mohamedali (2009) were retained for the present work. PBDE congener parameters were developed from Palm et al. (2004). Other chemical parameters required by the model included the Setschenow proportionality constant, proportionality constants for POC and DOC phase partitioning, and disequilibrium factors for POC and DOC partitioning in the water column. These inputs were assigned the same values that were used for fate and transport model inputs (see Table F-2).

Values for biological parameters used in the model are presented in Tables L-3 through L-10. These parameters describe characteristics of each species represented in the model food web, including body weight, water fraction, lipid content, and non-lipid organic matter (NLOM) content. Other biological parameters had application to multiple modeled species, such as the NLOM-octanol proportionality constant, the particle scavenging efficiency of filter-feeders, growth rate factors, fractions of respiration involving pore water, dietary assimilation efficiencies (i.e., digestion efficiencies), dietary chemical transfer efficiencies, diffusive transfer efficiency at respiratory surfaces, and metabolic transformation rates.

Values for these biological parameters were unchanged from those used by Pelletier and Mohamedali (2009) for initial model inputs, but were adjusted during calibration based on parameters compiled from the modeling literature, with preference for values estimated from Puget Sound empirical data (see Table M-1). With the exception of metabolic transformation rates, biological parameter values were the same for PCB and PBDE simulations. Congener-specific metabolic rates for PCBs (Table L-11) in cormorants, heron, and adult harbor seals were obtained from Condon (2007); PCB congeners not modeled by Condon were assigned the average metabolic rate of those congeners given in Condon (2007) for each species. For PBDEs (Table L-12), all congeners were assigned the same metabolic rate, which was optimized during model calibration.

Model Calibration

Once the food web model setup was completed, with all inputs set to the default values used by Pelletier and Mohamedali (2009) or updated based on recent data (2000-2012) as described in previous sections, model calibration was performed. The term *calibration* describes the process of adjusting model parameters within physically defensible ranges until the resulting predictions give the best possible match with observed data (EPA, 2009a). Model calibration for the food web component of the PSRTM was an iterative procedure involving a combination of quantitative goodness-of-fit statistics and best professional judgment to achieve the most accurate and least biased results.

Calibration Process

Calibration was first conducted for PCBs due to the availability of data on concentrations in a wide variety of Puget Sound biota (i.e., compared to the relative scarcity of PBDE data). After executing initial runs for each region, the predicted PCB concentrations in regional biota were compared to observed data and evaluated for obvious patterns, such as consistent over- or under-prediction in a specific region or for a particular organism. In successive runs, one or several parameters were adjusted in an effort to improve first the model skill for predicting PCB

concentrations in lower trophic level organisms, then progressively working through the middle and upper trophic levels. Parameter adjustments were based on literature values from similar modeling studies[19] and the observed data for Puget Sound (e.g., typical wet weights of specific organisms) and were guided by preliminary sensitivity and uncertainty analyses that identified the most important parameters influencing organism-specific predicted concentrations. Several apparent regional biases led to the examination of region-specific model inputs to find and correct possible issues. For example, the median TSS measured in the North Hood Canal region was much higher than that of South Hood Canal, and sampling locations in the North suggested that the TSS may be biased high due to nearshore influences. Adopting the median South Hood Canal TSS value (which was perhaps more representative of ambient regional TSS) in the North was found to considerably improve the model predictions. Organism-specific diets were also modified as needed and as supported by the literature[20] to improve the calibration.

Calibration of the food web model for PBDEs followed a similar process. For the initial PBDE runs, all parameter changes that were made during calibration of the PCB model (with the exception of contaminant-specific inputs) were applied to the PBDE model to avoid inconsistencies. Due to the prevalence of non-detects and high variability of the regional data on PBDE concentrations in the water column, concentrations measured by Frouin et al. (2013) in the Rosario Strait were initially assigned to each region. As calibration runs were executed, if model predictions for the organisms in a given region were consistently low or high compared to the observed data, the regional water column concentration of PBDEs was adjusted away from the Frouin value in an attempt to correct those biases. Harbor seal metabolic rates for PBDEs were not found in the literature, and so the congener-specific PCB rates from Condon (2007) were tested; all PBDE congeners were assigned the same rate, which was varied from the minimum (zero) to the maximum PCB metabolic rate until the best agreement between predicted and observed biota concentrations in all regions was achieved. Any further adjustments to parameters and feeding relationships were made in both the PCB and PBDE models, and if the calibrations were not improved in both models, those changes were discarded. A complete record of the specific changes made during calibration of the food web model can be found in Table M-1 of Appendix M.

Calibration Results

Tables M-2 and M-3 present comparisons of observed Total PCB concentrations in Puget Sound biota with those predicted by the calibrated food web model. Tables M-4 and M-5 compare predicted and observed concentrations for the Total PBDE model.

Model bias was measured by the ratio of predicted to observed tissue concentrations, with ratios below 1.0 indicating under-prediction and ratios above 1.0 indicating over-prediction. For example, a ratio of 0.5 indicates that the model prediction is half of the observed concentration, and a ratio of 2.0 indicates that the model prediction is twice the observed value. This approach

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[19] Adjustments to biological parameters were based on values used by DeGasperi et al. (2014), Alava et al. (2012), Lachmuth et al. (2010), Windward (2010), Townes-Witzel (2007), Condon (2007), and Gobas and Arnot (2005), and were also informed by the references cited in those studies.

[20] Adjustments to organism diets were guided by DeGasperi et al. (2014), Preikshot et al. (2013), Alava et al. (2012), Li (2012), Harvey et al. (2010), Lachmuth et al. (2010), and Windward (2010). Such modifications were typically small; extensive re-structuring of the feeding relationships in the PSRTM was beyond the scope of this project.

has been used by similar studies to evaluate model performance (DeGasperi et al., 2014; Alava et al., 2012; Pelletier and Mohamedali, 2009). Model bias between 0.5 and 2.0 is considered good performance and comparable to that achieved by other applications of this bioaccumulation model (e.g., DeGasperi et al., 2014; Pelletier and Mohamedali, 2009; Condon, 2007).

The overall model bias for each contaminant was calculated as the geometric mean of individual predicted-observed ratios across all species and at all locations. For PCBs the bioaccumulation model had an overall bias of 0.97, indicating excellent agreement with the available biota data. The PBDE model had a bias of 0.59, which indicates that on average the model predictions were about 40% lower than the observed values. While the PBDE model was not able to predict the observed concentrations as well as the PCB model, the overall bias was nonetheless within the acceptable range and is considered reasonable for the purposes of this project.

The model skill for predicting tissue concentrations of PCBs and PBDEs was not uniform across all species or all regions. Tables 6 and 7 summarize the bias of model predictions for individual taxa (across all regions) and the bias of model predictions within each specific region (including all species for which predicted-observed comparisons were possible). Figures 21 and 22 present this information graphically and show that the bias varied considerably among species and between regions. Model predictions on a species-specific or regional basis were generally within a factor of two compared to observed values, with the following exceptions:

- The model under-predicted concentrations of both Total PCBs and Total PBDEs in shellfish, which were simulated using the biological parameters of mussels and compared to data from the Mussel Watch program and ENVVEST project. For PCBs, the geometric mean of the predicted-observed ratios from all regions of Puget Sound was essentially at the low end of the reasonable bias range (0.48), but the bias of PBDE predictions for mussels was well below the acceptable range (0.21). Tables M-2 and M-4 show that the model successfully predicted the observed concentrations of both PCBs and PBDEs at some locations while substantially under-predicting at others. These results suggest that mussels in some areas may be exposed to elevated levels of contaminants in excess of the region-wide "ambient" concentrations that were used as model inputs. Such localized contamination "hot spots" could be due to the proximity of some sampling sites to both point and non-point sources in the nearshore environment. The model would not be expected to accurately predict contaminant accumulation by mussels in areas where local concentrations in the sediments and/or water column differ greatly from the simulated conditions (i.e., median regional concentrations). Since the model was able to predict observed concentrations in some areas, the calibration for mussels was deemed acceptable for the purposes of this project.

- The concentration of Total PBDEs in the "predatory invertebrates" organism class (simulated as the large krill species *T. spinifera*) was under-predicted by the model. However, the bias (0.29) was based on a single comparison of predicted and observed concentrations, with three samples comprising the observed data set. As such, additional sampling may be warranted and closer scrutiny of the biological parameters and feeding relationships used for this class may be needed to ensure that they are representative of *T. spinifera*.

- The over-estimation of Total PCB concentrations in staghorn sculpin (bias of 2.93) may be attributed to uncertainties in the observed data, which comprised only two samples. Both

samples were non-detects, and so the observed concentration values were derived from analytical reporting limits and may not be an accurate characterization of the true values. While this is a data gap that could be fulfilled in future monitoring, the model food web developed by Condon (2007) and adapted by Pelletier and Mohamedali (2009) does not define staghorn sculpin as prey for any higher trophic level organisms. Therefore, the feeding relationships in the model may need to be reviewed and updated in the future to better incorporate sculpin and several other organisms not consumed by modeled species into the model food web.

- The ratio of predicted to observed concentrations of Total PCBs in spiny dogfish was notably high at 4.39, indicating substantial over-estimation by the model. However, the bias value was based on a single predicted-observed comparison in Admiralty Inlet, with the observed concentration equal to the average of four samples. Because dogfish in the model represent a very small fraction of the adult harbor seal diet, improving the accuracy of the prediction was not seen as critical to the overall model utility.

- The model underestimated the observed concentrations of Total PBDEs in herring (bias of 0.28). Although herring data were only available for two regions (Sinclair/Dyes Inlet and South Sound), those regions each had a robust observed data set of over 40 samples. In both regions, the predicted Total PBDE concentration in herring approximately matched the lower bound of the range of observed values. The under-prediction of herring tissue concentrations suggests that the ambient sediment and water column concentrations used as model inputs may not be representative of the areas where herring forage. Despite the downward bias of herring predictions and the importance of herring to the harbor seal diet, the model was able to predict the observed harbor seal pup concentrations reasonably well. As such, only cursory adjustments to herring parameters were made for this project.

- The predicted Total PBDEs in Pacific hake underestimated observed concentrations (bias of 0.40). The observed data set comprised over 50 samples from six different regions. In four regions, the predicted concentration in hake was less than the lowest concentration measured in that region. The consistent under-prediction of Total PBDE concentrations in hake across regions suggests that the biological parameters and/or diet fraction assumptions used in the model may require further adjustments. As with herring, it is also possible that hake obtain a significant portion of their diet in areas that are more highly contaminated relative to "ambient" regional levels. Considering the importance of Pacific hake to the diet of harbor seals in the model, an objective of future modeling should be improved prediction of PBDEs in hake.

- While model predictions of Total PCBs in biota showed good agreement with observed data in all regions, Total PBDE predictions in several regions had a downward bias (indicating under-estimation of observed concentrations) that was outside the target bias range (Table 7). South Sound, Main Basin, and Whidbey were approximately at the lower end of the bias range (0.50, 0.45, and 0.39, respectively) primarily due to strongly underestimated shellfish concentrations in those regions but also influenced by the under-prediction of Total PBDEs in herring and hake. Sinclair/Dyes Inlet had the strongest downward bias of all regions (0.18), but the only predicted-observed concentration comparisons available for that region involved shellfish and herring (both of which were discussed above). Future monitoring to determine PBDE concentrations in additional species may be needed for Sinclair/Dyes Inlet to resolve whether model predictions for other organisms are similarly biased low.

Table 6. Bias of model-predicted concentrations of Total PCBs and Total PBDEs in specific organisms (across all regions for which observed data were available).

Bias values in bold type are outside the target range (0.5 to 2.0).

Organism	Total PCBs				Total PBDEs			
	n	Bias	Positive SD	Negative SD	n	Bias	Positive SD	Negative SD
Phytoplankton	7	0.62	0.80	0.48	7	1.47	1.94	1.11
Krill (*E. pacifica*)	6	0.90	1.04	0.78	6	1.07	1.52	0.76
Shellfish (mussels)	18	**0.48**	1.32	0.17	9	**0.21**	0.64	0.07
Predatory inverts	1	1.01	-	-	1	**0.29**	-	-
Graceful crab	3	1.28	1.58	1.03	-	-	-	-
Shiner surfperch	4	1.29	1.55	1.08	-	-	-	-
Staghorn sculpin	4	**2.93**	9.75	0.88	-	-	-	-
Ratfish	6	1.04	2.17	0.50	-	-	-	-
Spiny dogfish	1	**4.39**	-	-	-	-	-	-
English sole	19	1.28	2.40	0.68	1	0.66	-	-
Herring (resident)	3	0.56	0.93	0.34	2	**0.28**	0.34	0.23
Pacific hake	6	1.00	1.67	0.60	6	**0.40**	0.64	0.25
Walleye pollock	4	1.56	2.70	0.91	4	0.84	1.47	0.48
Blackmouth salmon (resident)	1	1.28	-	-	1	0.58	-	-
Harbor seal (pup)	5	1.31	2.27	0.76	4	1.05	1.27	0.86
TOTAL	88	0.97	2.19	0.43	41	0.59	1.49	0.23

Bias: Geometric mean of all predicted-observed concentration ratios for a given species.
n: Number of predicted-observed comparisons.
SD: Standard deviation.

Table 7. Bias of model-predicted biota concentrations of Total PCBs and Total PBDEs for individual regions (including all species for which observed data were available).

Bias values in bold type are outside the target range (0.5 to 2.0).

Model Region	Total PCBs				Total PBDEs			
	n	Bias	Positive SD	Negative SD	n	Bias	Positive SD	Negative SD
Admiralty Inlet	4	0.68	3.65	0.13	1	1.26	-	-
Commencement Bay	5	1.77	3.69	0.85	1	1.53	-	-
Elliott Bay	11	0.91	1.52	0.55	6	0.94	1.42	0.62
Hood North	11	1.04	2.09	0.51	5	0.92	1.58	0.53
Hood South	6	1.33	2.35	0.75	5	0.85	1.39	0.53
Main Basin	14	0.65	1.44	0.29	9	**0.45**	1.17	0.17
Sinclair/Dyes Inlet	13	1.73	3.76	0.80	2	**0.18**	0.40	0.08
South Sound	14	0.69	1.35	0.36	6	0.50	1.45	0.17
Whidbey Basin	10	0.88	1.92	0.40	6	**0.39**	1.40	0.11
TOTAL	88	0.97	2.19	0.43	41	0.59	1.49	0.23

Bias: Geometric mean of all predicted-observed biota concentration ratios for a given region.
n: Number of predicted-observed comparisons.
SD: Standard deviation.

Figure 21. Model bias for predicted concentrations of Total PCBs (upper plot) and Total PBDEs (lower plot) in Puget Sound biota.

For each organism the geometric mean of predicted/observed ratios across all regions is shown. Error bars are standard deviations of the geometric mean for each organism. The shaded area indicates the target bias range (0.5 to 2.0). "TOTAL" includes all species and all locations. Herring and blackmouth salmon classes are resident.

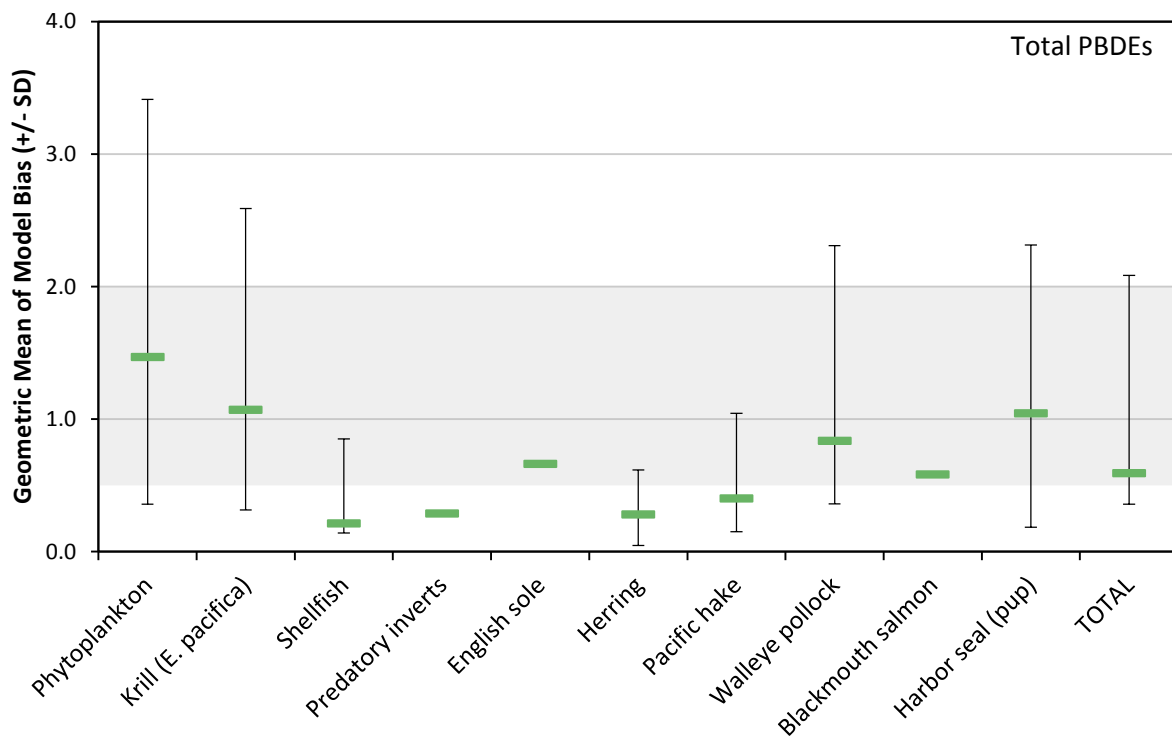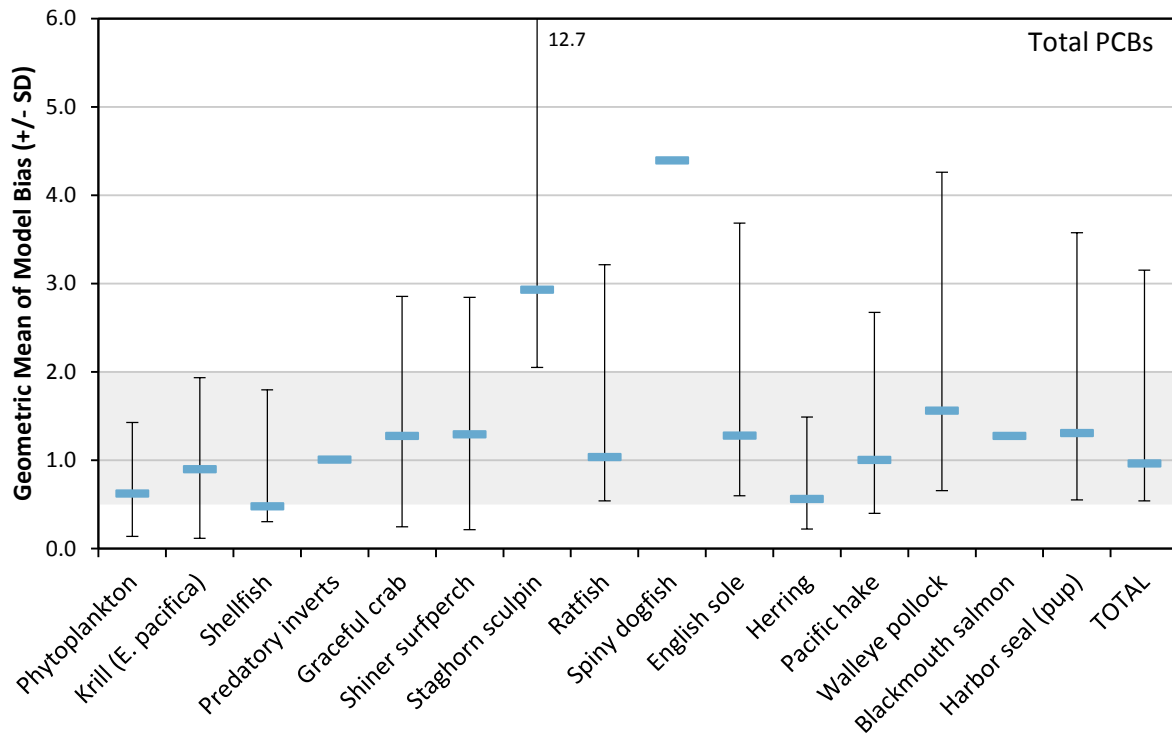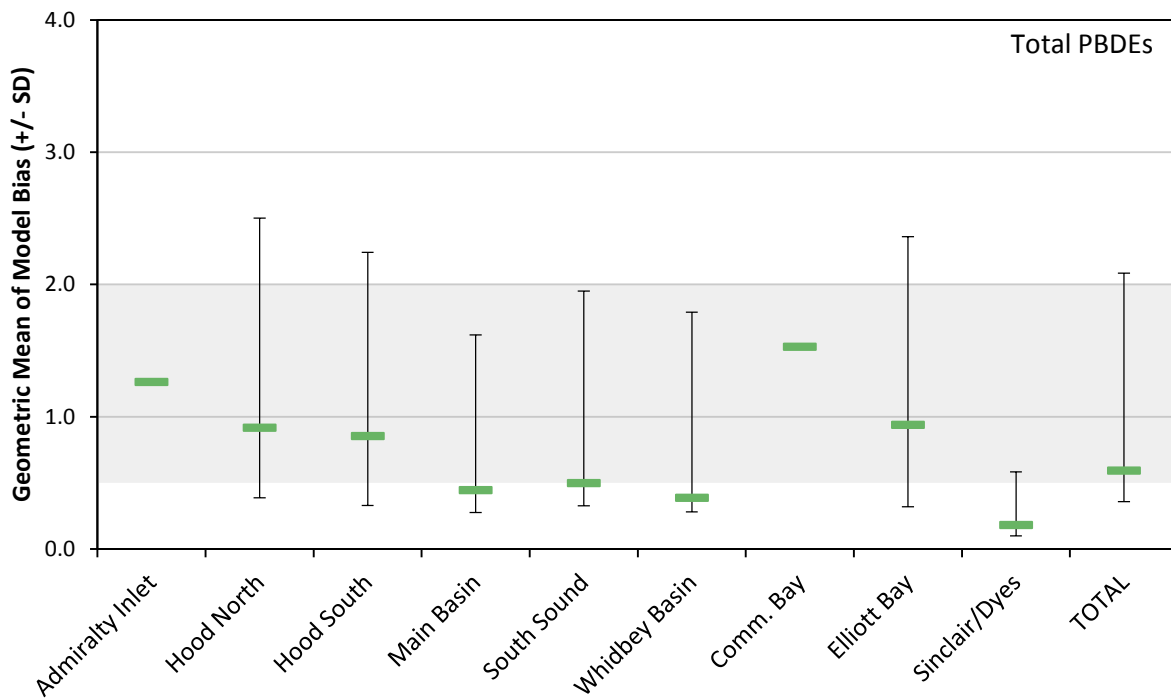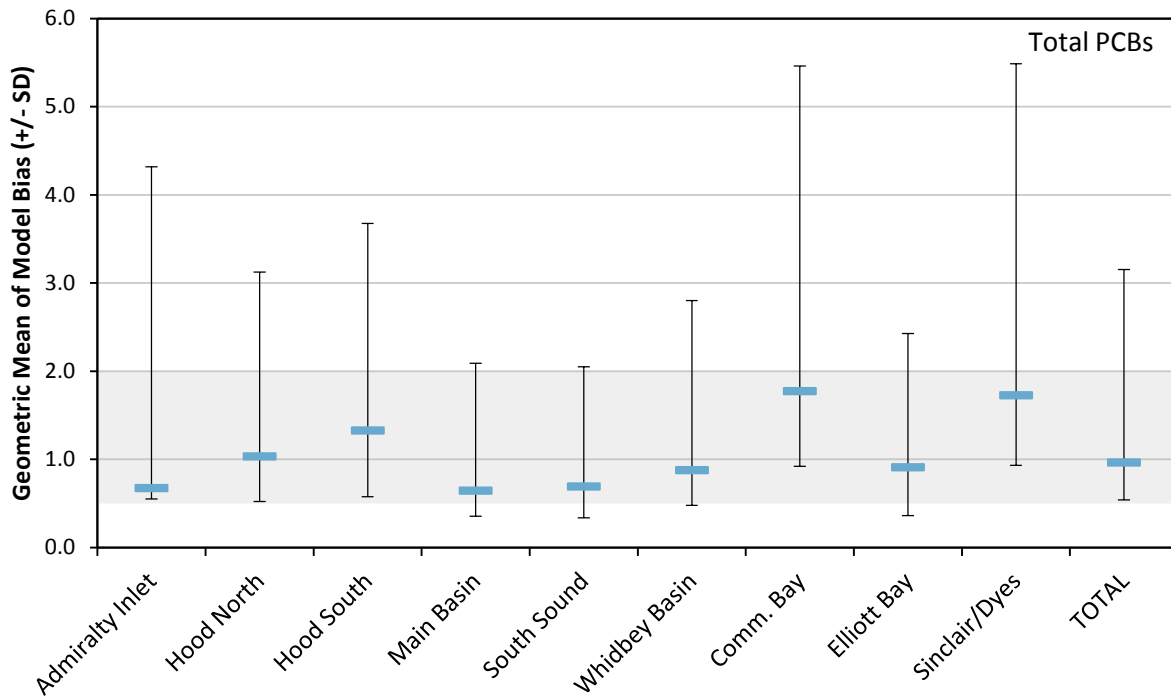Figure 22. Model bias for predicted concentrations of Total PCBs (upper plot) and Total PBDEs (lower plot) in regional biota.

For each region the geometric mean of predicted-observed ratios across all species is shown. Error bars are standard deviations of the geometric mean for each region. The shaded area indicates the target bias range (0.5 to 2.0). "TOTAL" includes all species and all locations.

Throughout the calibration process, highest priority was given to predicting contaminant concentrations in species that are important to the harbor seal food web. The aim was to describe the bulk of the observed data for these organisms; however, when data were available from multiple locations in a region for a given species, it was not expected – nor was it possible in some cases – that the model could predict the mean observed concentration at all locations within a factor of two (for example, see the predicted-observed comparisons for English sole in the Main Basin given in Table M-2). Inconsistencies in sampling methods, environmental conditions, analytical methods and endpoints, quantity of samples, temporal coverage, and data rules employed by the various studies that contributed to the observed data set may explain some of the biases that were outside the target range in the predicted-observed comparison tables (Tables M-2 to M-5).

Despite the wider biases of model predictions for some species, overall the calibrated model was shown to predict the observed concentrations in most modeled organisms with reasonable accuracy. For the top predator in the model food web, harbor seals, no data on contaminant concentrations in adults were available for comparison with model predictions. However, several recent studies have reported Total PCB and Total PBDE concentrations in the blubber of harbor seal pups from several regions of Puget Sound. Table 8 summarizes these observed data and presents the model-predicted concentrations for comparison. Agreement between predicted and observed concentrations of both PCBs and PBDEs in harbor seal pups was good for the Main Basin, South Sound, and Whidbey Basin. The predicted concentration of Total PBDEs in Hood Canal South harbor seal pups was also reliable, but the prediction for Total PCBs slightly over-estimated the observed concentrations in that region (bias of 2.61). These results indicate that the model skill for predicting contaminant concentrations in harbor seal pups is generally good for Puget Sound basins. Contaminants in seal pups residing in the urban bays of the Sound, however, is a data gap that should be addressed by future sampling to bolster confidence in the model predictions for areas with elevated contaminant concentrations.

Table 8. Predicted and observed concentrations (ng/g lw) of Total PCBs and Total PBDEs in the blubber of harbor seal pups.

Source for all results was Noel et al. (2011), except South Sound 2003 data were from Tabuchi et al. (2006). Bias values in bold type are outside the target range (0.5 to 2.0).

Sampling Location	Model Region	Collection Year	n	% lipids	Observed Concentration (Mean +/- SD)			Predicted Conc.	Bias
Total PCBs									
Dosewallips R., Quilcene Bay	Hood South	2009	8	97.5	1570	+/-	210	4104	**2.61**
Orchard Rocks, Blakely Rocks	Main Basin	2009	3	81.7	6340	+/-	1530	4474	0.71
Gertrude Island	South Sound	2009	7	95.2	4020	+/-	730	5211	1.30
Gertrude Island	South Sound	2003	7	95.2 *	6238	+/-	1008	5211	0.84
Skagit Bay	Whidbey Basin	2009	6	98.7	2590	+/-	630	4974	1.92
Total PBDEs									
Dosewallips R., Quilcene Bay	Hood South	2009	8	97.5	250	+/-	50	294	1.17
Orchard Rocks, Blakely Rocks	Main Basin	2009	3	81.7	820	+/-	140	720	0.88
Gertrude Island	South Sound	2009	7	95.2	860	+/-	130	769	0.89
Skagit Bay	Whidbey Basin	2009	6	98.7	480	+/-	100	621	1.29

* No percent lipids value was given in Tabuchi et al. (2006). The value shown is the mean lipid content of the seven Gertrude Island harbor seal pups biopsied by Noel et al. (2011) in 2009

Sensitivity Analyses

Two types of analyses were conducted to evaluate the sensitivity of the bioaccumulation model results to variations in individual parameters. The first analysis involved changing each input parameter by 5% independently and assessing the impact on predicted contaminant concentrations in organisms. The second analysis sought to clarify the relative influence of contaminant concentrations in the waters of a region versus those in the sediments.

Sensitivity to Individual Parameter Variations

Sensitivity analyses were conducted to determine the relative influence of individual parameters on model results. These analyses followed methodologies consistent with similar modeling studies (e.g., DeGasperi et al., 2014). The process for evaluating model sensitivity involved correlation analysis of Monte Carlo simulation output to determine the relative contribution of each tested parameter to variance.

First, tested parameters were assigned to lognormal distributions with a standard deviation of 5% of the mean and sampled by Monte Carlo for 1,000 simulations. Each of the 1,000 simulations had a corresponding output prediction for the randomized inputs. A Spearman rank-order correlation analysis between the randomized inputs (i.e., parameter values) and the corresponding outputs (i.e., predicted contaminant concentration in each organism) was then conducted to determine the percent contribution of each tested parameter to variance for each organism. These steps were automated in Microsoft Excel using an Add-In called YASAIw (Pelletier, 2009; Eckstein et al., 2000).

The calibrated PCB and PBDE models were used for the sensitivity analyses, with regional model inputs set to Main Basin best-estimate values[21]. Nearly all possible parameters were tested, including environmental characteristics and abiotic inputs, chemical parameters, organism-specific biological parameters, and contaminant concentrations in sediments and the water column. Testing the sensitivity of the model to food web structure (i.e., feeding relationships) and organism-specific dietary preferences, however, was beyond the project scope.

The type of bioaccumulation model used in this study (i.e., based on the model developed by Arnot and Gobas, 2004) is known to be extremely sensitive to the octanol-water partition coefficient (log K_{ow}). The log K_{ow} is integral to several partitioning algorithms used in the model and has been shown to have a much greater influence on model results than any other parameter, with more than 70% contribution to variance (EPA, 2009b). Because the influence of the log K_{ow} would "flood out" the relative variance attributed to other parameters, the log K_{ow} was excluded from the sensitivity analyses.

The results of the sensitivity analyses for PCBs and PBDEs were similar and are summarized in Tables N-1 and N-2, respectively. The tables list the parameters that contributed to more than 10% of the variance of each individual taxon's predicted concentration.

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[21] It was not practical to conduct sensitivity analyses on all model regions, so the Main Basin was selected as an example region for sensitivity testing.

For the modeled primary producers phytoplankton and kelp, passive diffusion is the only pathway for the uptake of contaminants dissolved in the water column. That uptake is offset by losses via growth and diffusion, with the rate of diffusive losses dependent on the composition of the plant in terms of water, non-lipid organic carbon (NLOC), and lipids. Sensitivity tests showed that small variations in the fractions of water, NLOC, and lipids in primary producers caused large changes (relative to other tested parameters) in the predicted contaminant concentrations of plants. While the concentration in the water column determines the amount of contaminant available for uptake, model-predicted contaminant concentrations in plants were found to be less sensitive to changes in the water concentration than to changes in the composition of the plant.

Model-predicted concentrations for filter-feeders (herbivorous zooplankton, copepods, and krill) were sensitive to variations in the water column concentration of PCBs or PBDEs and to concentrations of dissolved organic carbon (DOC) and dissolved oxygen. These parameters influence rates of dietary uptake (i.e., by affecting feeding rates and determining contaminant levels in the principal prey item, phytoplankton), respiratory uptake, and respiratory elimination by filter-feeders. These parameters also had a strong influence on predicted concentrations of organisms such as amphipods whose diet consists primarily of these filter-feeding zooplankton and krill.

For lower trophic level organisms associated with the benthos (e.g., shellfish, crabs, and grazing invertebrates), model predictions were most sensitive to the species-specific water, non-lipid organic matter (NLOM), and lipid fractions and to water and sediment concentrations of PCBs or PBDEs. A portion of respiration for such organisms involves sediment pore water, and these parameters affect the rates of contaminant uptake and loss via the respiration pathway. For more pelagic invertebrates such as spot prawns, parameters relating to the dietary uptake and elimination of contaminants were found to have a larger influence, especially the dietary absorption efficiency of lipids.

For mid- and upper-trophic level organisms such as fish, birds, and seals, the parameter for which small variations had the greatest influence on model predicted concentrations was the dietary absorption efficiency of lipids for that organism or for the primary prey item in its diet. The dietary absorption efficiency affects the balance between the rate at which contaminants are digested (i.e., absorbed from the diet via the gut) and the rate of elimination via fecal egestion. Small changes to the dietary assimilation efficiency of lipids had a strong influence on the accumulation of contaminants, with lower assimilation efficiencies resulting in increased elimination via fecal egestion and lower predicted biota concentrations. Other studies that used this model, including DeGasperi et al. (2014), Windward (2010), Condon (2007), and Gobas and Arnot (2005), also found the dietary absorption efficiency of lipids to be one of the most influential parameters.

The results of these sensitivity analyses underline the importance of accurately characterizing the following parameters:
- Dietary absorption efficiency for lipid (organism-specific).
- Fractions of water, NLOM (or NLOC for plants), and lipid (organism-specific).
- Contaminant concentration in the water column and sediments.
- DOC and dissolved oxygen concentrations in the water column.

Sensitivity to Contaminants in Water or Sediment

Additional sensitivity tests were conducted to assess the relative influence of contaminant concentrations in water versus sediment on the model-predicted concentration in each organism. For five separate regions (three basins and two urban bays), successive runs were executed holding the sediment concentration constant at its median observed value while the water concentration was varied between 0.01 and 2.0 times its median value[22]. Similar runs were then executed varying sediment concentrations while holding the water concentration constant.

Figure 23 gives an example of the output from these tests, showing the response of predicted concentrations in four organisms to variations in sediment and water concentrations. The point of intersection in each plot is the predicted biota concentration based on best-estimate values for both sediment and water concentrations. The slope of the lines reflects the degree to which changes to contaminant concentrations in either water or sediment affect biota concentrations. A steeper slope for one media compared to the other indicates that for the same relative change away from the best-estimate value of each media, the media with the steeper slope had a greater influence on the predicted organism concentration. Thus, Figure 23 shows that changes to contaminant concentrations in the water column of Elliott Bay had a stronger influence on predicted concentrations in phytoplankton and herring, while changes to sediment concentrations had a greater influence on predicted concentrations in shellfish (i.e., mussels) and English sole.

The results of these sensitivity analyses for PCBs and PBDEs are summarized in Table 9. The table presents the matrix that had the dominant influence on the predicted concentration for each organism in the tested regions. Similar patterns were seen between PCB and PBDE results. Variations in contaminant concentrations in the water column had a stronger influence (compared to the sediments) on predicted concentrations in the organisms of relatively "clean" regions where sediment concentrations were low. In fact, in the three basins tested (Admiralty Inlet, Main Basin, South Sound) changes in water concentrations were found to be more influential than sediments for all organisms in the model food web. In contrast, in regions where sediment concentrations were high, such as the urban bays tested (Elliott Bay and Commencement Bay), the influence of sediment contaminants was greater than that of water for many organisms. Other findings of the sensitivity tests included the following:

- Phytoplankton in the model were not sensitive to variations in sediment contaminants and only responded to changes in water concentrations.

- While some organisms, such as plants, were more affected by water column contaminants in every region, no organisms were found to have higher sensitivity to sediment contaminants in every region tested.

- Water had a stronger influence on organisms that have water as a major exposure pathway. For example, the feeding relationships of phytoplankton, herbivorous zooplankton, copepods, and amphipods link these organisms to the water in relatively simple and direct ways. Even in the urban bays, changes in water concentrations generally had equal or greater effects on PCB and PBDE concentrations in these organisms than did similar changes in sediments.

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[22] The relative changes applied to the sediment and water concentrations were the same for all regions (0.01x to 2.0x the median observed values). However, the *magnitude* of those changes varied by region based on the regional median observed concentrations. For example, a relative change of 1.6x for PCBs in South Sound sediments represented a shift of 0.55 ng/g dw; the same relative change (1.6x) for Elliott Bay was a shift of 26.1 ng/g dw.

- PBDEs in water had a dominant influence in Elliott Bay, while sediment PBDEs had a stronger influence in Commencement Bay. This makes sense in that the ratio of water to sediment PBDE concentrations in Elliott Bay more closely matched that of the basins (where water was the dominant matrix) and the ratio for Commencement Bay more closely resembled that of urban bays (where sediment tended to have more influence).

In sum, the sensitivity tests showed that in relatively uncontaminated areas where contaminant concentrations in the sediments were low, predicted concentrations of contaminants in biota were more strongly influenced by changes to contaminant concentrations in the water column than by comparable changes in sediment concentrations. Although the majority of PCB and PBDE mass in the Sound is stored in the sediments, these results indicate the importance of contaminants in water as an exposure route and driver of bioaccumulation in many areas. Efforts to decrease contaminant concentrations in Puget Sound marine waters (e.g., by actions to reduce loads or prevent releases) may therefore be a critical component of strategies to achieve ecosystem health goals. Sensitivity analyses also indicated that the influence of sediments was greater in areas where sediment concentrations were elevated. These results underscore the importance of sediment cleanup activities for reducing contaminant uptake and bioaccumulation in the urban bays and at regional contaminant "hot spots."
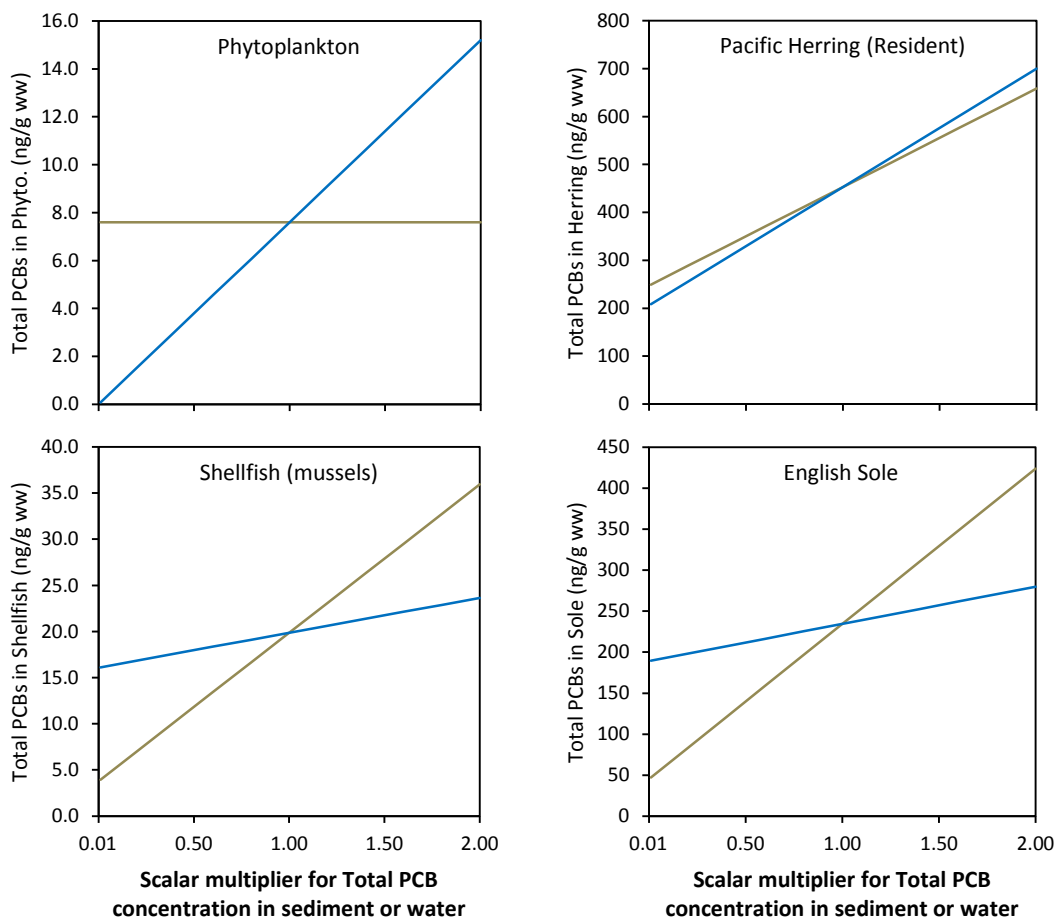

Figure 23. Sensitivity test results showing how changes to Total PCB concentrations in the sediments (brown line) or water column (blue line) of Elliott Bay influence the model-predicted concentration of four organisms.

Table 9. Results of sensitivity tests to determine whether Total PCB and Total PBDE concentrations in the active sediments or in the waters of a region had greater influence on the predicted concentration in each species.

| Organism | Polychlorinated Biphenyls (PCBs) | | | | | Polybrominated Diphenyl Ethers (PBDEs) | | | | |
| | Basins | | | Urban Bays | | Basins | | | Urban Bays | |
	Admiralty Inlet	Main Basin	South Sound	Comm. Bay	Elliott Bay	Admiralty Inlet	Main Basin	South Sound	Comm. Bay	Elliott Bay
Phytoplankton	water	water	water	water	water	water	water	water	water	water
Kelp / Seagrass	water	water	water	water	water	water	water	water	water	water
Herbivorous zooplankton	water	water	water	sediment	water	water	water	water	water	water
Large copepod (*N. plumchrus*)	water	water	water	sediment	water	water	water	water	water	water
Small copepod (*P. minutus*)	water	water	water	sediment	water	water	water	water	water	water
Shellfish (mussels)	water	water	water	sediment	sediment	water	water	water	sediment	water
Crab	water	water	water	sediment	sediment	water	water	water	sediment	sediment
Grazing invertebrates	water	water	water	sediment	sediment	water	water	water	sediment	water
Carnivorous zooplankton (amphipods)	water	water	water	sediment	water	water	water	water	water	water
Krill (*E. pacifica*)	water	water	water	sediment	sediment	water	water	water	water	water
Predatory invertebrates	water	water	water	sediment	sediment	water	water	water	sediment	water
Spot prawn	water	water	water	sediment	sediment	water	water	water	sediment	water
Graceful crab	water	water	water	sediment	sediment	water	water	water	sediment	water
Small pelagic fish (seal prey)	water	water	water	sediment	sediment	water	water	water	water	water
Small pelagic fish (bird prey)	water	water	water	sediment	sediment	water	water	water	water	water
River lamprey	water	water	water	sediment	water	water	water	water	water	water
Miscellaneous demersal fish (seal prey)	water	water	water	sediment	sediment	water	water	water	water	water
Miscellaneous demersal fish (bird prey)	water	water	water	sediment	sediment	water	water	water	sediment	water
Pacific hake	water	water	water	sediment	sediment	water	water	water	water	water
Spiny dogfish	water	water	water	sediment	sediment	water	water	water	water	water
Walleye pollock	water	water	water	sediment	sediment	water	water	water	water	water
Northern smooth-tongue	water	water	water	sediment	water	water	water	water	water	water
English sole	water	water	water	sediment	sediment	water	water	water	sediment	water
Pacific herring (resident)	water	water	water	sediment	water	water	water	water	water	water
Blackmouth salmon (resident)	water	water	water	sediment	sediment	water	water	water	water	water
Ratfish	water	water	water	sediment	sediment	water	water	water	sediment	water
Shiner surfperch	water	water	water	sediment	sediment	water	water	water	sediment	water
Staghorn sculpin	water	water	water	sediment	sediment	water	water	water	sediment	water
Double-crested cormorant (adult male)	water	water	water	sediment	sediment	water	water	water	sediment	water
Double-crested cormorant (adult female)	water	water	water	sediment	sediment	water	water	water	sediment	water
Great blue heron (adult male)	water	water	water	sediment	sediment	water	water	water	sediment	water
Great blue heron (adult female)	water	water	water	sediment	sediment	water	water	water	sediment	water
Harbor seal (adult male)	water	water	water	sediment	sediment	water	water	water	water	water
Harbor seal (adult female)	water	water	water	sediment	sediment	water	water	water	water	water
Harbor seal (1 yr old)	water	water	water	sediment	sediment	water	water	water	water	water
Harbor seal (pup)	water	water	water	sediment	sediment	water	water	water	water	water

Model Application

The calibrated bioaccumulation model predicts whole-body concentrations of Total PCBs and Total PBDEs in regional biota that would result from long-term exposure to user-specified levels of contaminants in the sediments and waters of the ecosystem. Accordingly, the model can be used as a tool to inform management concerns and explore management scenarios, such as the ecosystem response to contaminant loading reductions via specific pathways or to post-dredging reductions in sediment concentrations. The outcomes of such exercises can help managers identify and prioritize the most effective strategies to achieve ecosystem recovery goals.

Pelletier and Mohamedali (2009) applied the bioaccumulation model in a forecasting capacity. First, they used the fate and transport model to estimate future concentrations of Total PCBs in regional waters and sediments. They then assigned the predicted environmental concentrations as inputs to the bioaccumulation model to estimate the accumulation of Total PCBs that would be expected in the biota of each region. Similar exercises were planned for the present study. It was intended that the current best estimates of PCB and PBDE loads from watershed sources would be incrementally reduced in the fate and transport model until the long-term predicted concentrations in all regional sediments and waters, as well as the biota concentrations predicted therefrom, met specific environmental quality targets (e.g., Washington State sediment and water quality standards and National Toxics Rule criteria). Since the updated fate and transport model was deemed unusable for forecast scenarios (as discussed earlier in this report), it was not possible to employ the bioaccumulation model as anticipated.

To demonstrate application of the bioaccumulation model in a hypothetical management context, the model was instead used to determine the extent to which current contaminant concentrations in sediments and waters must be reduced to achieve specific target concentrations in various organisms. The biota endpoints and the results of these example scenarios are described below.

Model Scenario Threshold Concentrations (MSTCs)

Biota targets for bioaccumulation model exercises were referred to as Model Scenario Threshold Concentrations, or MSTCs. These endpoints generally describe organism-specific whole-body concentrations above which there are documented adverse health effects to organisms or to consumers of aquatic organisms. Possible MSTCs were compiled from a variety of regulatory and advisory criteria and organism-specific toxicity thresholds from the literature, including:

- Puget Sound Partnership (PSP) Ecosystem Recovery Targets.
- Washington Department of Ecology Fish Tissue Criteria.
- EPA Fish Tissue Benchmarks.
- Canadian Council of Ministers of the Environment (CCME) Tissue Residue Guidelines, Federal Fish Tissue Guidelines, and Federal Wildlife Dietary Guidelines.
- British Columbia Ministry of Environment (BCMoE) Fish and Shellfish Guidelines.
- Literature values for organism-specific Adverse-Effects Thresholds.

These criteria are tabulated in Table O-1 of Appendix O.

Table 10. Model Scenario Threshold Concentrations (MSTCs) used as target endpoints in example management scenarios for the bioaccumulation model.

Biota MSTC	Organism(s)	Criteria Type	Intended Protection	Source
Polychlorinated Biphenyls (PCBs)				
1300 ng PCB/g lw	Harbor seal pups	Adverse-effects threshold	Harbor seal pups	Mos et al. (2010)
2400 ng PCB/g lw	English sole, Pacific herring, Blackmouth salmon	Adverse-effects threshold	English sole, Pacific herring, Blackmouth salmon	PSP Ecosystem Recovery Targets (PSP, 2012)
50 ng PCB/g ww	Blackmouth salmon	Wildlife dietary threshold	Wildlife consumers	Hickie et al. (2007)
33 ng PCB/g ww	English sole, Pacific herring, Blackmouth salmon	Human dietary threshold	Human consumers at recreational rates	PSP Ecosystem Recovery Targets (PSP, 2012)
10 ng PCB/g ww	English sole, Pacific herring, Blackmouth salmon	Human dietary threshold	Human consumers at subsistence rates	PSP Ecosystem Recovery Targets (PSP, 2012)
Polybrominated Diphenyl Ethers (PBDEs)				
1300 ng PBDE/g lw	Harbor seal pups	Adverse-effects threshold	Harbor seal pups	Mos et al. (2010)
1400 ng PBDE/g lw	English sole, Pacific herring, Blackmouth salmon	Adverse-effects threshold	English sole, Pacific herring, Blackmouth salmon	PSP Ecosystem Recovery Targets (PSP, 2012)

PSP: Puget Sound Partnership.

Endpoints (i.e., MSTCs) were selected for the example management scenarios based on their application to modeled organisms and relevance to Puget Sound management interests. When multiple criteria were found for a specific protection, the selected MSTC was generally the lowest value or among the lowest available values. The selected biota MSTCs for Total PCBs and Total PBDEs are presented in Table 10.

For PCBs, the primary endpoints used in model scenarios were PSP Ecosystem Recovery Targets for whole body concentrations in English sole, Pacific herring, and resident blackmouth Chinook salmon. MSTCs for these fish included an adverse-effects threshold based on the work of Meador (2002) on salmonids, as well as dietary thresholds for the protection of human consumers of these fish at recreational and subsistence ingestion rates. The dietary thresholds were based on Washington Department of Health consumption advice for Puget Sound salmon (fillets) that used non-cancer endpoints for human health screening levels and assumed an intake of 40 g/day for recreational consumption and 140 g/day for subsistence consumers. Another MSTC was set at the dietary threshold for mammalian consumers of Chinook salmon given in Hickie et al. (2007), which was derived from the CCME Tissue Residue Guideline for the protection of fish-eating wildlife (CCME, 1999). Finally, the adverse-effects threshold for PCBs in harbor seals from Mos et al. (2010) was selected as an MSTC for harbor seal pups to protect the most sensitive life stage of these top predators (i.e., pups have a high level of sensitivity to developmental toxicity).

Fewer criteria were available for PBDE endpoints. The PSP Ecosystem Recovery Target for PBDE concentrations in English sole, Pacific herring, and resident blackmouth Chinook salmon was adopted as an MSTC for those fish. The target was based on the whole body concentration that was observed to cause increased susceptibility to disease in juvenile salmon (Arkoosh et al., 2010). CCME Federal Fish Tissue Guidelines also provided adverse-effects thresholds for fish; however, those criteria were found to be less protective[23] than the PSP target and so were not used for model scenarios. Adverse-effects thresholds for PBDEs in marine mammals were not found in the literature, but similarities in PCB and PBDE structures would suggest similar toxic effects (Ross et al., 2013) and so the MSTC for PCBs in harbor seal pups was also assumed for PBDEs.

Scenarios

Once MSTCs were established, model runs were executed to investigate (1) how the current predicted contaminant concentrations in the biota of each region compare to the various MSTCs, and (2) regional sediment and water concentration reductions that would be required in order to meet each biota endpoint. The model setup used for the scenario exercises was the final calibrated model for each contaminant (see Appendices I, J, K, and L for inputs), with initial contaminant concentrations in regional sediments and waters set to the values in Table I-1.

Comparison of Model-Predicted Biota Concentrations to MSTCs

Initial model runs were executed using the best estimates of regional sediment and water concentrations to predict contaminant concentrations in English sole, Pacific herring, resident blackmouth Chinook salmon, and harbor seal pups for current conditions. The predicted biota concentrations were multiplied by a species- and region-specific correction factor[24] to adjust for known biases in the model (based on comparisons to observed data), and the resulting biota concentrations are given in Table O-4. The adjusted predictions were then compared to the various biota MSTCs, as presented in Figures 24 through 29. If a predicted value exceeded an MSTC, the reduction needed to meet the MSTC was calculated (expressed as a percentage of the predicted concentration). These percent reductions of current biota concentrations needed to achieve the MSTCs are detailed in Table O-5 for PCBs and Table O-6 for PBDEs. Notable findings from these analyses include the following:

- Harbor seal pups were predicted to accumulate PCBs to concentrations above the adverse-effects threshold in all regions of Puget Sound. Predicted PCB concentrations for harbor seal pups in the urban bays would have to be reduced by around 90% to meet the MSTC (1300 ng/g lw). In the basins of the Sound, concentrations in harbor seal pups required

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[23] The homolog-specific CCME criteria were summed and converted to a lipid-weight basis assuming 2 to 12% lipids for comparison with the PSP target.
[24] Correction factors were defined as the inverse of the model bias for a given organism and region (Table O-2 for PCBs and Table O-3 for PBDEs). The bias of the model-predicted concentration for a particular organism in a region was the geometric mean of the available predicted-observed ratios for that organism in that region. If no such observed data were available, the bias was assigned the geometric mean of the predicted-observed ratios for that organism across all regions. Correction factors were derived using the results of the final calibration run for each contaminant, with regional sediment and water concentrations set at current best-estimate values (Table I-1).

reductions ranging from 17% to 80% to meet that threshold, with the largest reductions needed in the Main Basin and South Sound.

- Predicted PCB concentrations in English sole, Pacific herring, and blackmouth salmon were below the adverse-effects threshold of 2400 ng/g lw in all Puget Sound basins.

- The predicted PCB concentration in English sole was below the dietary threshold for recreational consumption rates (33 ng/g ww) in all basins. However, all other dietary thresholds for English sole, Pacific herring, and blackmouth salmon were exceeded in all of the basins. The most protective MSTC (i.e., that which required the largest percent reduction of the predicted biota concentration) was the dietary threshold for Pacific herring at subsistence rates (10 ng/g ww), followed very closely by the same dietary threshold for blackmouth salmon.

- All of the PCB MSTCs were exceeded in the urban bays, with the exception of the adverse-effects threshold for Pacific herring (2400 ng/g lw) in Sinclair/Dyes Inlet. Pelletier and Mohamedali (2009) suggested that the herring sampled in Sinclair Inlet may forage outside of the Inlet in the relatively cleaner areas of the Main Basin, which could explain why PCB concentrations in these herring were low relative to other urban bays.

- The predicted PBDE concentrations in harbor seal pups from Commencement Bay and Elliott Bay were above the adverse-effect threshold of 1300 ng/g lw. These predicted concentrations would need to be reduced by approximately 14% and 45%, respectively, to meet the MSTC. Harbor seal pups in the remaining urban bay (Sinclair/Dyes Inlet) and in all Puget Sound basins were predicted to accumulate PBDEs to concentrations below the adverse-effects threshold.

- Model-predicted PBDE concentrations in English sole, Pacific herring, and blackmouth salmon were below the target adverse-effects threshold (1400 ng/g lw) in all Puget Sound basins and urban bays.

In general, comparisons of the model-predicted bioaccumulation in various species to estimated adverse-effects concentrations and dietary thresholds indicated that many of the biota endpoints would be exceeded at current environmental concentrations of PCBs and PBDEs. The largest exceedances of the biota thresholds were predicted to occur in the urban bays of Puget Sound (Commencement Bay, Elliott Bay, and Sinclair/Dyes Inlet). In the basins, predicted biota concentrations were also above several of the thresholds but by much smaller magnitudes.
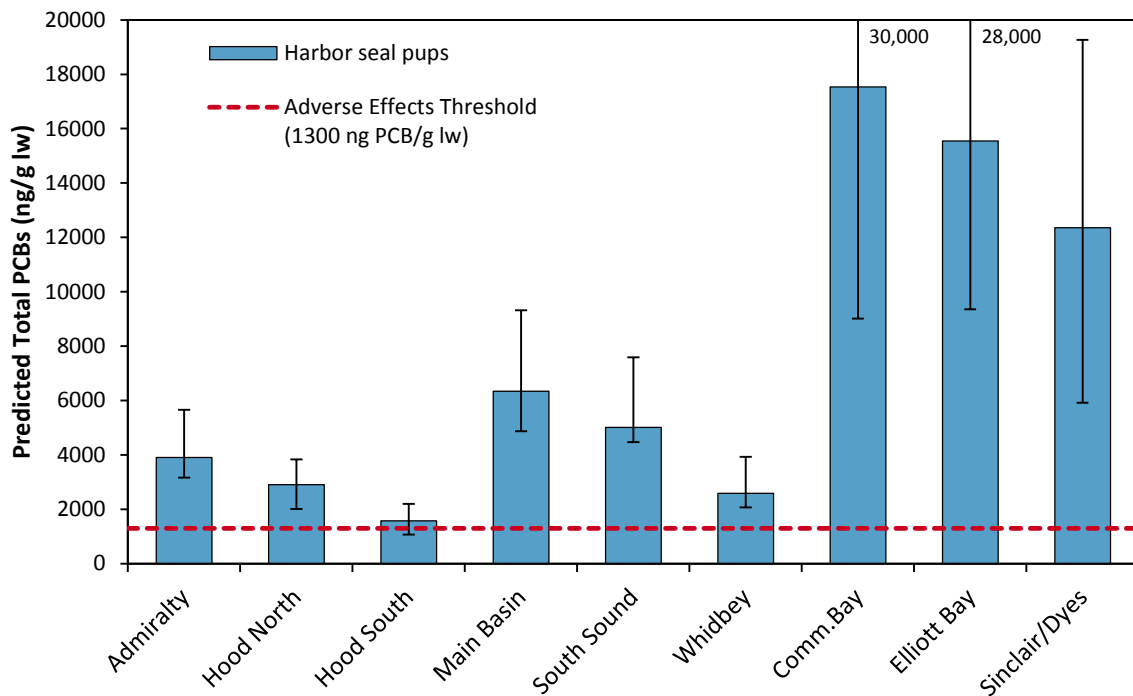
Figure 24. Predicted Total PCBs in harbor seal pups compared to an adverse-effects threshold.

Error bars show the range of predictions using 25th (lower bars) and 75th percentile (upper bars) sediment and water concentrations in each region.
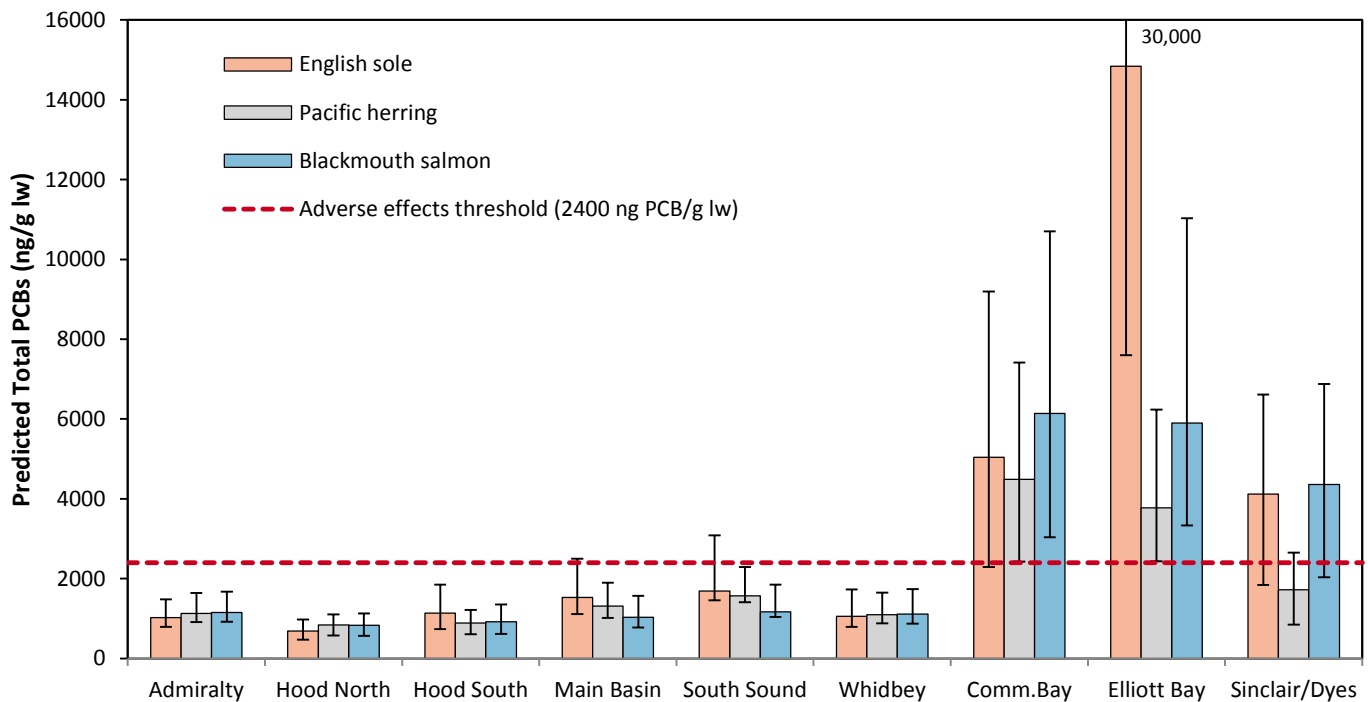
Figure 25. Predicted Total PCBs in English sole, Pacific herring, and blackmouth salmon compared to an adverse-effects threshold.

Error bars show the range of predictions using 25th (lower bars) and 75th percentile (upper bars) sediment and water concentrations in each region.

Figure 26. Predicted Total PCBs in blackmouth salmon compared to a wildlife dietary threshold.

Error bars show the range of predictions using 25th (lower bars) and 75th percentile (upper bars) sediment and water concentrations in each region.
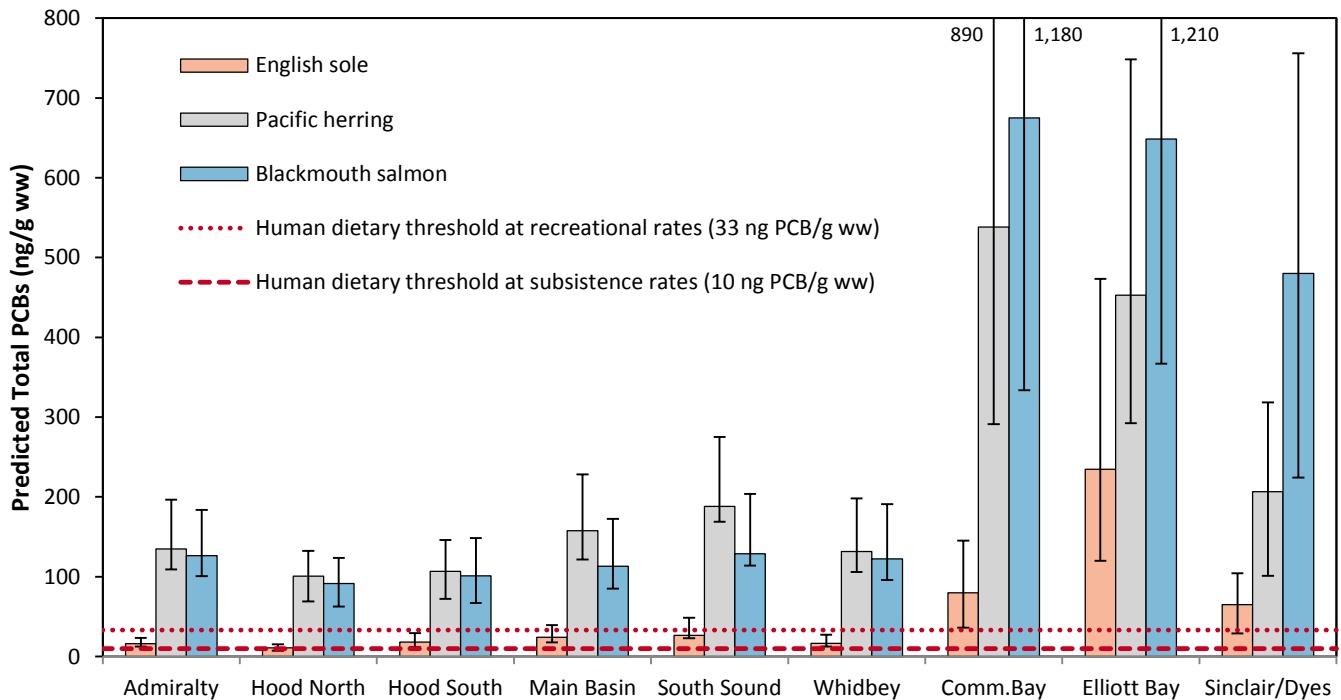
Figure 27. Predicted Total PCBs in English sole, Pacific herring, and blackmouth salmon compared to human dietary thresholds.

Error bars show the range of predictions using 25th (lower bars) and 75th percentile (upper bars) sediment and water concentrations in each region.

Figure 28. Predicted Total PBDEs in harbor seal pups compared to an adverse-effects threshold.

Error bars show the range of predictions using 25th (lower bars) and 75th percentile (upper bars) sediment and water concentrations in each region.

Figure 29. Predicted Total PBDEs in English sole, Pacific herring, and blackmouth salmon compared to an adverse-effects threshold.

Error bars show the range of predictions using 25th (lower bars) and 75th percentile (upper bars) sediment and water concentrations in each region.
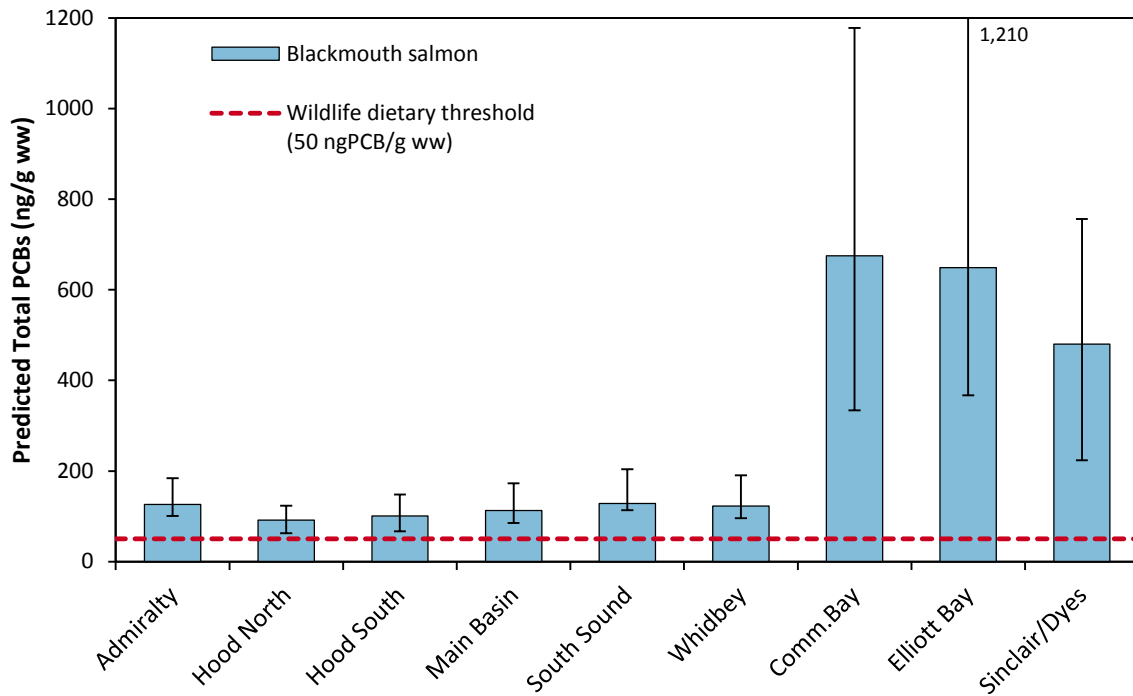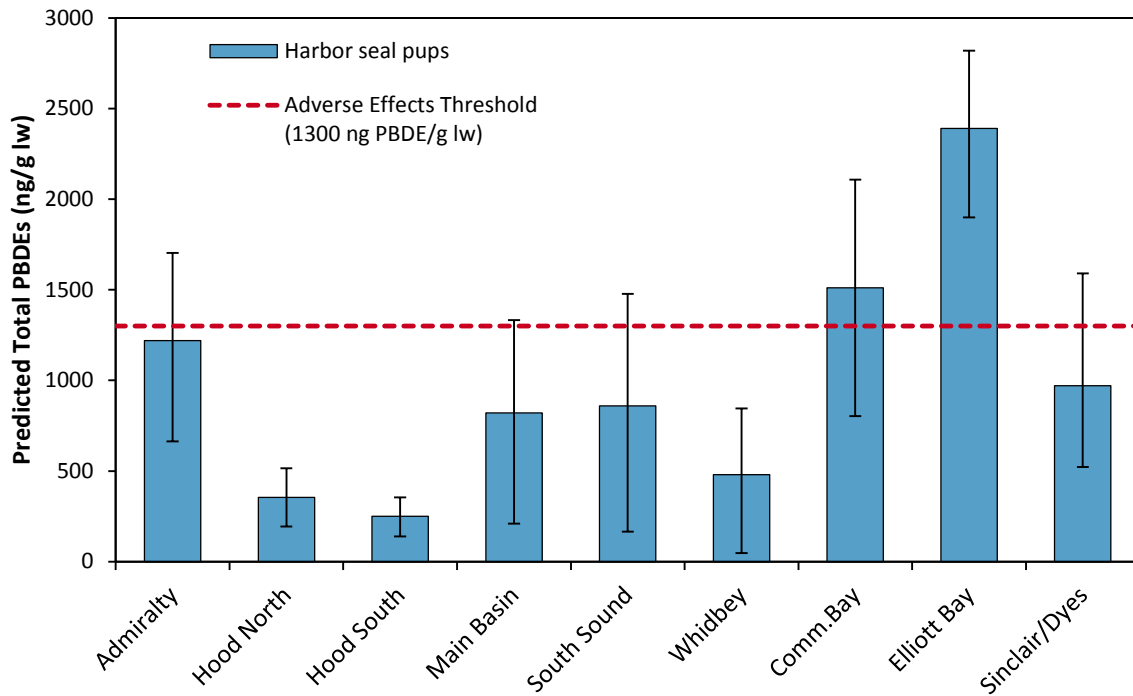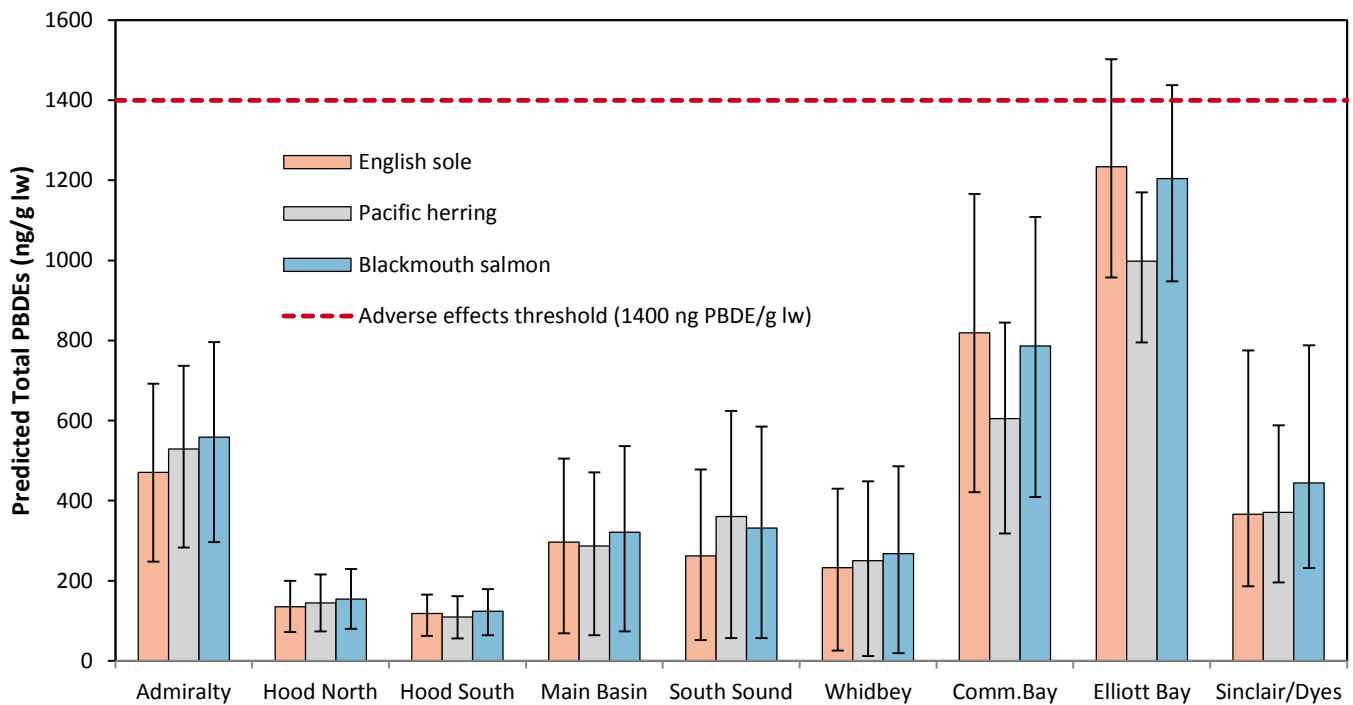
Reductions of Sediment and Water Concentrations Needed to Meet Biota MSTCs

Having identified the locations where specific biota MSTCs were exceeded, the bioaccumulation model was next used to investigate the degree to which contaminant concentrations in the environment would have to be reduced in order to meet the biota targets. In successive runs, regional sediment and water concentrations were incrementally reduced to determine the concentrations at which the biota MSTCs were achieved. As the concentrations were varied from one run to the next, the relative magnitudes of sediment and water concentrations in each region were held constant (i.e., changes were applied equally, and neither sediment nor water concentrations were preferentially reduced). The correction factors given in Tables O-3 and O-4 were again used to adjust the model-predicted biota concentrations as the sediment and water concentrations were varied away from current conditions.

Contaminant concentrations in the sediments and water column of each region that resulted in predicted biota concentrations at or below the biota MSTCs are given in Tables O-7 and O-8 for PCBs and Tables O-9 and O-10 for PBDEs, along with the current best estimates of regional environmental concentrations for comparison. The percent reductions in regional sediment and water concentrations needed to reach target concentrations (Tables O-11 and O-12) mirrored the biota reductions described above. That is, there was approximately a direct relationship between the percent reduction of the contaminant concentration in an organism needed to meet a specific target and the percent reduction of the contaminant concentration in the environment (sediment and water) needed to meet the same target. Other notable results included:

- In both the basins and urban bays of Puget Sound, the sediment PCB concentrations needed to meet the most protective biota MSTCs were just above the minimum concentrations in the observed data set for each individual region (see Table B-2). However, those minimum concentrations were all non-detect results, which suggests that PCB concentrations in marine sediments would have to be near analytical detection limits to achieve the most restrictive MSTCs (dietary thresholds for herring or salmon consumption at subsistence rates).

- To achieve the dietary thresholds for herring, salmon, and English sole consumption and the adverse-effects threshold for harbor seals, water column PCB concentrations generally had to be at or below the minimum measured concentrations in each basin (all of which were detected results; see Table C-4). Data on PCBs in the waters of the urban bays were limited but indicated that the concentrations needed to achieve almost all of the biota MSTCs would be below the minimum measured concentrations.

- Current best estimates of PBDE concentrations in Puget Sound sediments and waters were sufficiently low that adverse-effects thresholds for English sole, Pacific herring, and resident blackmouth salmon were not predicted to be exceeded in any region.

- Sediment and water concentrations of PBDEs in all basins and in Sinclair/Dyes Inlet yielded predicted concentrations below the target threshold in harbor seal pups. In Elliott Bay and Commencement Bay, however, sediments would have to be reduced approximately to their 25th percentile observed concentrations to meet the harbor seal pup MSTC.

Overall, the scenario results indicated that substantial reductions of PCB concentrations in the sediments and waters throughout Puget Sound would be needed to bring biota concentrations below adverse-effects levels and dietary thresholds for several mid- to upper-trophic level species. The magnitude of the needed reductions was much higher in the urban bays compared to the basins of the Sound. For PBDEs, biota concentrations in all basins and in Sinclair/Dyes Inlet were predicted to be below the evaluated adverse-effects thresholds, but moderate reductions of PBDEs in the sediments and waters of the other urban bays (Elliott Bay and Commencement Bay) would be needed to meet target biota concentrations. In a management context, the sediment and water concentrations derived in this exercise could be used as ecologically-relevant targets to inform remediation and pollution control strategies and provide benchmarks for effectiveness monitoring.

Summary and Conclusions

The purpose of the present study was to update and expand the Puget Sound Regional Toxics Model (PSRTM). The primary objectives were to:

- Modify the PSRTM to provide the capability to simulate contaminants beyond PCBs, including PBDEs, selected PAHs, copper, lead, and zinc.
- Incorporate new loading estimates and recent regional data to improve model inputs and reduce uncertainty in the model predictions.

To accomplish these objectives, the following tasks were completed:

- Compiled recently collected data on concentrations of PCBs, PBDEs, PAHs, copper, lead, and zinc in the sediments and waters of Puget Sound and the Strait of Juan de Fuca to define model inputs and boundary conditions. Data on PCB and PBDE concentrations in Puget Sound biota were also summarized for comparison with bioaccumulation model predictions.
- Calculated contaminant loads to each model region via atmospheric deposition and watershed pathways (i.e., surface runoff, POTWs, and groundwater) using the data and methods that were employed in the development of the Puget Sound basin-wide loading estimates published in recent Ecology reports.
- Searched the literature to obtain contaminant-specific parameters describing chemical properties, partitioning, and rates of various processes. The modeling literature was also reviewed for organism-specific parameters and feeding relationships for modeled species.
- Modified the PSRTM code to provide the capability to simulate fate and transport processes for PCBs, PBDEs, selected PAHs, copper, lead, and zinc, and the bioaccumulation of PCBs and PBDEs in the Puget Sound food web.
- Attempted to calibrate the fate and transport model to regional data for each of the modeled contaminants (including re-calibration for PCBs). The bioaccumulation model was calibrated so that predicted concentrations of PCBs and PBDEs across all species and regions gave the best possible match to observed data.
- Assessed the sensitivity of the fate and transport model to changes in individual parameters, as well as the influence of uncertainties in various model inputs on long-term model predictions. For the bioaccumulation model, the relative influence of contaminants in sediments versus water on the predicted concentration in each species was also evaluated.
- Conducted exercises to test the performance and assess the utility of the updated fate and transport model. Diagnostic exercises were also carried out to investigate inconsistencies between model results and actual conditions.
- Performed bioaccumulation model exercises to demonstrate the utility of the model for hypothetical management scenarios, including estimation of regional sediment and water concentrations needed to meet various biota endpoints. The biota endpoints (called Model Scenario Threshold Concentrations, or MSTCs) were adverse-effects concentrations from the literature or dietary thresholds based on Puget Sound Partnership targets.

The following sections highlight some of the important findings of this project.

Fate and Transport Model

The fate and transport model tended to underestimate the concentration of contaminants in Puget Sound sediments and waters compared to observed data. The model also predicted rapidly declining trends for all contaminants that were not supported by the observed data. Possible causes were explored with the model, and the results suggested that one or both of the following may explain the discrepancies between model predictions and the observed data:

- Contaminant loadings from watershed sources (including surface runoff, POTWs, and direct groundwater discharges) may have been underestimated in recently published studies. The model was used to back-calculate, or hindcast, how much higher the local sources would need to be in order to predict reasonable concentrations in Puget Sound. This analysis indicated that watershed loading sources would need to be approximately 5 to 10 times higher than current best-estimate values to match observed contaminant masses in the Sound.

- Contaminant concentrations in the waters of the Straits of Juan de Fuca and Georgia may have been underestimated in previously published studies. These waters represent the ocean boundary of the model and determine the magnitude of contaminant loading from the ocean to Puget Sound. The model was used to hindcast how much higher the boundary water concentrations would need to be in order to predict reasonable concentrations in Puget Sound. Ocean boundary water concentrations would need to be approximately 2 to 4 times higher than the current best estimates to match observed contaminant masses in the Sound.

Based on preliminary model runs with all inputs and parameters set to the best currently available values, the relative importance of loss pathways and processes to the long-term fate of contaminants in Puget Sound differed by contaminant.

- The dominant loss pathway for most contaminants was export at the ocean boundary, which generally accounted for around half of the cumulative loss from the system.

- Burial was responsible for over 80% of the removal of lead and approximately half of the long-term losses of copper and zinc. Burial was also an important loss pathway for PCBs, accounting for about a third of the removal, but for other organic contaminants burial was not an important loss process.

- Degradation was a key loss process for some organic contaminants, accounting for around half of the long-term loss of PBDEs and PAHs. However, degradation only accounted for a small fraction of the long-term loss of PCBs from the system due to their much slower degradation rates (half-life of 56 years for PCBs compared to approximately 1 year for PBDEs and from several weeks to several years for PAH compounds).

- Volatilization played only a small role in the removal of organic contaminants relative to other loss processes. The metals addressed are not affected by volatilization.

Sensitivity analyses provided an understanding of the parameters to which the model is most sensitive. For organic contaminants, the octanol-water partition coefficient (log K_{ow}) and degradation rates in water and sediment were found to have a strong influence on predictions of long-term fate. For metals, the TSS-water partition coefficient (i.e., coefficient for partitioning between suspended sediments and water) and the concentration of dry solids in the active sediments were moderately influential.

Despite the incorporation of updated loading estimates and recently collected data, uncertainties remain that limit the utility of the model as a tool for estimating loading reductions that would be needed to meet management targets for contaminants in sediment, water, or biota on a Puget Sound basin-wide scale. These uncertainties are primarily related to the following areas: watershed loads, contaminant concentrations in the ocean boundary waters, and regional concentrations of organic carbon (dissolved and particulate) and suspended solids in the water column. Obtaining realistic estimates for these influential model inputs will be an important challenge for further development of the fate and transport component of the PSRTM.

In sum, the fate and transport model for PCBs in Puget Sound was successfully updated and expanded with the capability to simulate PBDEs, PAHs, copper, lead, and zinc. However, uncertainties remain that limit the utility of the model for informing management decisions.

Food Web Bioaccumulation Model

The calibrated model for the bioaccumulation of PCBs and PBDEs in the Puget Sound food web predicted biota concentrations with accuracy comparable to similar modeling studies. For PCBs, the model had an overall bias across all species and regions of 0.97, indicating excellent agreement with the observed data (perfect agreement would be 1.00). While the PBDE model tended to underestimate observed biota concentrations, the overall bias of 0.59 was within the acceptable limits.

Scenario exercises demonstrated the utility of the bioaccumulation model for exploring hypothetical management questions.

- The model identified locations in Puget Sound where the observed PCB or PBDE concentrations in the sediments and waters were predicted to cause contaminants to bioaccumulate in organisms at concentrations exceeding adverse-effects levels or dietary thresholds. The largest exceedances of biota thresholds were predicted in the urban bays (Commencement Bay, Elliott Bay, and Sinclair/Dyes Inlet). In the basins of Puget Sound, predicted biota concentrations were also above some of the thresholds but by much smaller magnitudes than urban bay exceedances.

- The model was also used to determine how low environmental concentrations of PCBs or PBDEs would have to be in each region to ensure that biota thresholds would be met. The model predicted that sediment concentrations would generally have to be near analytical detection limits to meet the most restrictive biota thresholds, while contaminants in water would have to be at or below minimum measured concentrations. In a management context, the sediment and water concentrations derived in this exercise could inform the development of ecologically-relevant targets or benchmarks for effectiveness monitoring.

Sensitivity tests for the bioaccumulation model indicated that changes to contaminant concentrations in the water column had a greater influence on biota concentrations than did comparable changes in sediment concentrations, particularly in relatively uncontaminated regions where contaminant concentrations in the sediments were low. In contrast, the influence of sediments was greater in urban bays where sediment concentrations were typically much higher. Although the majority of PCB and PBDE mass in the Sound is stored in the sediments, these results indicate the importance of contaminants in water as an exposure route and driver of

bioaccumulation in many areas. Efforts to decrease contaminant concentrations in Puget Sound marine waters (e.g., by actions to reduce loads and prevent releases) may therefore be a critical component of strategies to achieve ecosystem health goals. For the urban bays and regional "hot spots" where contaminants in the sediments are high, these results also underscore the importance of sediment cleanup activities for reducing the uptake and bioaccumulation of contaminants in the food web.

Another outcome of the sensitivity analyses was a better understanding of the relative influence of individual parameters on the model results. The most influential parameters included the octanol-water partition coefficient, organism-specific dietary absorption efficiency for lipids, organism-specific composition (in terms of water, non-lipid organic matter, and lipid fractions), contaminant concentrations in regional waters and sediments, and dissolved organic carbon concentrations in regional waters. More accurate characterization of these important parameters would be useful for further refinement of the model calibration.

Overall, the food web bioaccumulation model was shown to be a useful tool for evaluation of the relationships between contaminant concentrations in water, sediment, and biota, and interactions among trophic levels in the Puget Sound ecosystem.

Recommendations

Fate and Transport Model

Future efforts to model contaminant fate and transport in Puget Sound should focus on smaller geographic areas, such as individual urban bays or selected watersheds. At the present Puget Sound basin-wide scale, data collection to improve characterization of watershed and ocean loads may not be feasible due to the quantity of data needed and the cost of acquiring high quality data. Focusing on finer spatial scales would help reduce uncertainties in critical model inputs (e.g., local loading) and would make it economically feasible to collect data to support the model. Examples of appropriate smaller scales for fate and transport modeling include the recent modeling work on PCBs in Lake Washington by King County (DeGasperi et al., 2014) and the ongoing multi-agency work on the Lower Duwamish Waterway for which modeling will be used in support of source control strategies.

If there is a desire to continue Puget Sound basin-wide modeling, the following data gaps and uncertainties should be addressed:

- **Monitor ocean boundary water contaminants.** Data on contaminant concentrations in the waters of the model's ocean boundary (i.e., in the Strait of Juan de Fuca just beyond the sill at Admiralty Inlet) are needed. Model predictions are especially sensitive to the concentrations in the ocean boundary waters, and additional data would help to reduce uncertainty in this important model input.

- **Monitor contaminants associated with suspended sediments in Puget Sound.** Currently there is a gap in data for contaminants sorbed to suspended sediments in the Puget Sound marine water column. The collection of such data would enable comparisons of observed and model-predicted contaminant concentrations in regional suspended sediments, thereby adding confidence to model predictions of contaminant partitioning in the environment.

- **Monitor contaminants in Puget Sound sediments and waters.** Increased monitoring of contaminant concentrations in the sediments and water column of Puget Sound are recommended to monitor status and trends of contaminants in the aquatic ecosystem, to provide data for model inputs and for comparison with model predictions, and to assess the effectiveness of source control strategies. Such monitoring should employ a probabilistic and spatially unbiased sampling strategy to avoid potential biases from non-random sampling and the targeting of contaminant "hot spots."

- **Monitor regional atmospheric deposition.** Atmospheric deposition was an important loading pathway for some contaminants (e.g., PBDEs). Because atmospheric deposition for some contaminants is correlated with development (Brandenberger et al., 2010), it is likely that loads from atmospheric deposition will increase as human population increases. Establishment of a sampling program to monitor trends in contaminant deposition at stations around Puget Sound would provide information on changes in atmospheric loading that may be occurring. This would be useful in conjunction with modeling to explain or interpret observed trends in contaminant concentrations in the waters and sediments of the Sound.

- **Check and refine estimates of contaminant loading from direct groundwater.**
  Groundwater loads in Pitz (2011) were upper-bound estimates due to limited data available
  for characterizing ambient conditions, very high frequency of non-detects in the data, and
  upward biases produced by the study data rules. In addition, there was not sufficient data
  available to develop region-scale groundwater loading estimates for PCBs or PBDEs.
  Confirmation or additional data collection to support the direct groundwater estimates would
  be helpful to increase confidence in these model inputs.

Food Web Bioaccumulation Model

The bioaccumulation component of the PSRTM was shown to perform well as a stand-alone
model that can be used to explore how PCB and PBDE concentrations in Puget Sound biota
respond to varying levels of these contaminants in the sediments and waters of the ecosystem.
The following recommendations would further enhance the utility of the bioaccumulation model:

- **Monitor water column contaminants.** Limited data were available on water column
  concentrations of PCBs and PBDEs in Puget Sound. Model sensitivity analyses showed that
  contaminant concentrations in the water column have a large influence on predicted biota
  concentrations in all regions, especially in areas where sediment concentrations are relatively
  low. New sampling to refine estimates of water column concentrations would help reduce
  uncertainties in this key model input.

- **Monitor harbor seal pups in urban bays.** No observed data were available for
  contaminant concentrations in harbor seal pups of the urban bays of Puget Sound. As a
  result, the bias of predicted pup concentrations in the urban bays could not be determined and
  was assumed to be the same as that of the basins. Since contaminant concentrations in the
  sediments and waters of the urban bays tend to be much higher than in the basins, it would be
  useful to verify that the model is capable of predicting pup concentrations in the urban bays
  as accurately as it does for pups in the basins. Data collection on contaminant levels in the
  blubber of harbor seal pups from the urban bays would clarify whether the present calibration
  is suitable or needs to be adjusted for harbor seal pups in the urban bays.

- **Improve understanding of lipid content of various species in the food web.** The lipid
  content of each modeled species is an important parameter that has a strong influence on the
  predicted contaminant concentration for a given organism. The lipid content values specified
  in the model inputs should be reviewed for key species and for organisms most directly
  involved in their food webs. If necessary, values should be updated to ensure that they are
  representative of the organism size, age, and gender class being simulated. Moreover, some
  thresholds for contaminants in biota are specified on a lipid-weight basis (for example, the
  targets for harbor seal pups), and so lipid content values must be accurately characterized to
  avoid errors when comparing predicted biota concentrations and the thresholds.

- **Improve understanding of feeding relationships and regional food webs.** Differences in
  species and feeding relationships may exist between the regions of Puget Sound. Consulting
  with regional biologists could help clarify regional distinctions. If significant regional
  differences exist, a next step in the development of the bioaccumulation model would be to
  create region-specific food webs to account for such differences.

- **Monitor contaminants in biota.** Further biota sampling should be conducted to determine contaminant concentrations in species throughout the Puget Sound food web. Ideally, biota data would be whole-body concentrations collected at multiple locations spanning the range of environmental conditions found in each region, and would also be coincident and co-located with sampling for contaminants in water and sediment. Additional biota data would provide more robust comparisons of model predictions to observed data, allowing for re-calibration of the model (if necessary) to improve the agreement of predicted and observed biota concentrations.

- **Improve understanding of partitioning parameters.** Partitioning coefficients (e.g., K_{ow}, K_{oa}) used in the bioaccumulation model were not changed from those used by Pelletier and Mohamedali (2009) and Condon (2007). Some of the congener-specific values were inconsistent with those used for the fate and transport model. Since the octanol-water partition coefficient was shown to have a far greater influence on predicted biota concentrations than any other model parameter, future modeling efforts should review and, if necessary, revise the values currently used in the bioaccumulation model.

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Glossary, Acronyms, and Abbreviations

Glossary

Accuracy: The closeness of model predictions to measured values, which are assumed to represent true values.

Acute conditions: Changes in the physical, chemical, or biological environment which are expected or demonstrated to result in injury or death to an organism as a result of short-term exposure to the substance or detrimental environmental condition.

Anthropogenic: Human-caused.

Bias: The systematic deviation between model predictions and true values.

Bioaccumulation: The process by which the chemical concentration within an organism achieves a level that exceeds that in its environment as a result of chemical uptake through all possible routes of exposure (e.g., dietary, dermal, respiratory).

Biomagnification: The process in which the chemical concentration in an organism achieves a level that exceeds that in the organism's diet, due to dietary absorption.

Carcinogen: A chemical or chemical group that has been identified as "carcinogenic to humans" or "likely to be carcinogenic to humans" by the Environmental Protection Agency, as a Group 1, 2A, or 2B carcinogen by the International Agency for Research on Cancer, or as a "known to be human carcinogen" or "reasonably anticipated to be a human carcinogen" by the National Toxicology Program.

Chemical: A naturally occurring element, mixture, or group of organic and inorganic compounds that is produced by or used in a chemical process. Chemical "groups" share a common chemical structure.

Chronic conditions: Changes in the physical, chemical, or biological environment which are expected or demonstrated to result in injury or death to an organism as a result of repeated or constant exposure over an extended period of time to a substance or detrimental environmental condition.

Degradation: The process by which organic chemicals are transformed into derivative chemicals and ultimately broken down.

Effluent: An outflowing of water from a natural body of water or from a man-made structure. For example, the treated outflow from a wastewater treatment plant.

Geometric mean: A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were

calculated. This is helpful when analyzing bacteria concentrations, because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the nth root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

Half-life: The amount of time required for a quantity to decrease to half its value as measured at the beginning of the time period.

Interquartile: A measure of the statistical dispersion of a data set, equal to the difference between the upper and lower quartiles (75th and 25th percentiles, respectively).

Media (or medium): A component of the environment (air, water, soil, or sediment) in which a contaminant is measured and from which an organism can accumulate contaminants.

Median: A statistical measure of central tendency, equal to the numerical value separating the higher half of a data set from the lower half. The median is the same as the second quartile, or 50th percentile.

Model scenario threshold concentration (MSTC): Project-specific term used to describe a chemical concentration in water, sediment, or biota above which exposed aquatic organisms and ecosystem processes may not be adequately protected from toxic effects.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Persistence: The tendency of a chemical to remain in the environment without transformation or breakdown into another chemical form. It refers to the length of time a chemical is expected to reside in the environment and be available for exposure.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural,

recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Salmonid: Fish that belong to the family *Salmonidae*. Species of salmon, trout, or char.

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Sub-lethal effects: Negative impacts that do not cause immediate or direct death.

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Total suspended solids (TSS): Dry weight measure of the portion of solids retained by a filter.

Toxicity: The degree to which a substance or mixture of substances can harm humans, plants, or wildlife.

Volatilization: The mass transfer process whereby a dissolved substance is vaporized.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

25th percentile: A statistical number obtained from a distribution of a data set, above which 75% of the data exists and below which 25% of the data exists.

75th percentile: A statistical number obtained from a distribution of a data set, above which 25% of the data exists and below which 75% of the data exists.

Acronyms and Abbreviations

COC	Contaminant of concern
cPAH	Carcinogenic PAH
DL	Detection limit
DOC	Dissolved organic carbon
e.g.	For example
EAP	Environmental Assessment Program (Ecology)
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database (Ecology)
EMAP	Environmental Monitoring and Assessment Program (EPA)
EPA	U.S. Environmental Protection Agency
et al.	And others
GIS	Geographic Information System software
HOC	Hydrophobic organic contaminant
HPAH	High molecular weight PAH
i.e.	In other words

KCDNRP	King County Department of Natural Resources and Parks
LDW	Lower Duwamish Waterway
LPAH	Low molecular weight PAH
MEL	Manchester Environmental Laboratory
MSTC	Model scenario threshold concentration (See Glossary above)
MW	Mussel Watch (NOAA)
ND	Non-detect
NOAA	National Oceanic and Atmospheric Administration
NTR	National Toxics Rule
OSV	Ocean Survey Vessel
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ether
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyl
POC	Particulate organic carbon
POTW	Publicly owned treatment works
PSEMP	Puget Sound Ecosystem Monitoring Program
PSP	Puget Sound Partnership
PSRTM	Puget Sound Regional Toxics Model
PSTLA	Puget Sound Toxics Loading Analysis
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
RL	Reporting limit
RMSE	Root mean square error
RPD	Relative percent difference
RSD	Relative standard deviation
SJF	Strait of Juan de Fuca
SOG	Strait of Georgia
TOC	Total organic carbon
TSS	Total suspended solids (See Glossary above)
UAL	Unit area load
VBA	Visual Basic for Applications (Microsoft)
WAC	Washington Administrative Code
WASP	Water Quality Analysis Simulation Program (EPA)
WDFW	Washington State Department of Fish and Wildlife
WRIA	Water Resource Inventory Area

Units of Measurement

°C	degrees centigrade
Å	angstrom, a unit of length equal to 1/10,000,000,000 of a meter
atm	standard atmosphere, a unit of pressure
cm	centimeter, a unit of length equal to 1/100 of a meter
cm/h	centimeters per hour
cm/s	centimeters per second
cm/yr	centimeters per year

cP	centipoise, a unit of dynamic viscosity
dw	dry weight basis
g	gram, a unit of mass
g/day	grams per day
g/m^3	grams per cubic meter
g/mol	grams per mole
g/yr	grams per year
J	joule, a unit of energy
K	degrees Kelvin
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
kg/L	kilograms per liter
kg/yr	kilograms per year
kJ	kilojoule, a unit of energy equal to 1,000 joules
km	kilometer, a unit of length equal to 1,000 meters
L	liter, a unit of volume
L/kg	liters per kilogram
L/s	liters per second (0.03531 cubic foot per second)
lw	lipid weight basis
m	meter, a unit of length
m/day	meters per day
mg	milligram, a unit of mass equal to 1/1,000 of a gram
mg/kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
MGY	million gallons per year
mole	an International System of Units (IS) unit of matter
mol/L	moles per liter
m/s	meters per second
ng	nanogram, a unit of mass equal to 1/1,000,000,000 of a gram
ng/g	nanograms per gram (parts per billion)
ng/L	nanograms per liter (parts per trillion)
Pa	pascal, a unit of pressure
pg	picogram, a unit of mass equal to 1/1,000,000,000,000 of a gram
pg/L	picograms per liter (parts per quadrillion)
psu	practical salinity units
t	metric ton, a unit of mass equal to 1,000 kg
t/yr	metric ton per year
TEQ	toxic equivalent
ug	microgram, a unit of mass equal to 1/1,000,000 of a gram
ug/kg	micrograms per kilogram (parts per billion)
ug/L	micrograms per liter (parts per billion)
um	micrometer, a unit of length equal to 1/1,000,000 of a meter