

FOOD WEB BIOACCUMULATION MODEL FOR POLYCHLORINATED BIPHENYLS  
IN SAN FRANCISCO BAY, CALIFORNIA, USA

FRANK A.P.C. GOBAS\* and JON A. ARNOT

School of Resource and Environmental Management, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A 1S6, Canada

(Submitted 28 April 2009; Returned for Revision 20 October 2009; Accepted 1 February 2010)

**Abstract**—We document the development and application of a food web bioaccumulation model for polychlorinated biphenyls (PCBs) in San Francisco Bay, California, USA. The model calculates spatial distributions of PCB concentrations in a range of invertebrate, fish, avian, and mammalian organisms, including harbor seals, double-crested cormorants, and Forster's terns. The performance of the model is evaluated against independent empirical PCB concentrations and shows a mean deviation between observed and model-calculated concentrations of 36% for female harbor seals and 5% for benthic invertebrates and jack smelt. The model was applied to produce bay-wide PCB concentration distributions in fish and wildlife species, which were compared with threshold effect concentrations to determine ecological risks and human health risks of fish consumption. Because of their high trophic position in the food web, harbor seals exhibited the highest concentrations of  $\sum$ PCBs, which exceeded threshold concentrations for potential adverse effects. The model was also applied to derive bay-wide target sediment concentrations for remediation as part of an ongoing total maximum daily loading characterization. The model calculated bay-wide geometric mean concentrations of  $\sum$ PCB in sediments of 1.6 to 73  $\mu\text{g}/\text{kg}$  dry weight to meet several ecological and human health risk objectives. The bay-wide geometric  $\sum$ PCB concentration in the sediments at the time of the study was 11.6  $\mu\text{g}/\text{kg}$  dry weight. The model was developed for assessing the behavior and risks of bioaccumulative substances on an ecosystem level. Environ. Toxicol. Chem. 2010;29:1385–1395. © 2010 SETAC

**Keywords**—Polychlorinated biphenyls    Bioaccumulation    Model    Risk assessment    Ecosystem management

## INTRODUCTION

San Francisco Bay is the largest estuary on the Pacific Coast of America. It includes productive wetlands and supports diverse wildlife communities alongside a densely populated urban area. As a result of runoff from contaminated streams and urban areas [1,2], effluent discharges [3,4], and atmospheric deposition [5], polychlorinated biphenyls (PCBs) are found in water and sediments throughout the estuary [6]. Concentrations of PCBs in San Francisco Bay have exceeded water quality guidelines at the majority of sampling stations throughout the bay for the entire duration that samples have been collected. Tissue concentrations of PCBs in San Francisco bay sport fish became an issue of public concern when a fish tissue monitoring study in the early 1990s resulted in a fish consumption advisory issued by California's Office of Environmental Health Hazard Assessment. The U.S. Environmental Protection Agency, as a result of the advisory, placed San Francisco Bay on the 303(d) impaired water body list for PCBs and other contaminants [6]. The Regional Water Quality Control Board initiated a total maximum daily loading (TMDL) study of the bay, as required by the Clean Water Act, to understand better the relationships between sources and PCB concentrations in water, sediments, and wildlife throughout the bay and to facilitate and support management decisions protective of wildlife and humans. An abiotic mass balance model was developed as part of the TMDL study, in order to describe the relationship between PCB inputs into the bay and resulting PCB concentrations in water and

sediments [7]. The second phase of the TMDL study is the development of a food web bioaccumulation model to investigate the relationship between PCB concentrations in water and sediments and resulting PCB concentrations in organisms of the San Francisco Bay food web. The main purpose of the model is to identify what PCB concentrations in the sediments and water of the bay must be achieved before PCB concentrations in biota of the bay will meet acceptable levels. The abiotic and biotic models can be used to determine what reductions in PCB loadings must be accomplished to ensure that wildlife are no longer at risk of PCB contamination and that people can safely consume fish caught in San Francisco Bay. The model is based on Arnot and Gobas [8] but also includes new model equations for fish-eating birds and marine mammals and is being applied to a marine system.

The objective of the present study is to develop and evaluate a food web bioaccumulation model for PCBs in San Francisco Bay. We further discuss the application of the model for deriving sediment remediation targets and the development of sediment quality criteria that are protective of the health of humans and wildlife consuming San Francisco Bay fish and shellfish. Because this effort involves a risk assessment, which is subject to judgment and interpretation, we have presented the PCB food web bioaccumulation model in a format that allows various scenarios regarding human health and ecological risks to be evaluated.

## THEORY: MODEL DEVELOPMENT

*Model objective*

The goal of this model is to characterize the relationship between bay-wide concentrations of PCBs in sediment and key biological species in the bay selected for their role as a vector

All Supplemental Data may be found in the online version of this article.

\* To whom correspondence may be addressed

(gobas@sfu.ca).

Published online 1 March 2010 in Wiley InterScience  
(www.interscience.wiley.com).

for human exposure and ecological significance. This relationship between the PCB concentrations in biota ( $C_B$  in g PCB/kg wet wt organism) and the sediment ( $C_S$  in g PCB/kg dry wt sediment), developed for each species,  $i$ , is represented by the biota–sediment accumulation factor (BSAF in kg dry wt/kg wet wt).

$$\text{BSAF}_i = C_{B,i}/C_S \quad (1)$$

The BSAF is the main output of the model and provides a method for calculating, in a forward manner, the chemical concentration in selected biological species from the chemical concentration in the sediments as  $C_B = \text{BSAF} \cdot C_S$ . The BSAF can also be used in a backward calculation, to derive a chemical concentration in the sediment that is expected to cause a particular concentration,  $C_B$  as  $C_S = C_B/\text{BSAF}$ .

#### Polychlorinated biphenyls

Model calculations were performed on a PCB congener-specific basis, because PCB congeners differ in partitioning properties and toxicity. The Regional Monitoring Program (RMP) for the bay analyzes approximately 40 PCB congeners, i.e., PCBs 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 118, 128, 132, 138, 141, 149, 151, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, and 203. These congeners, referred as the RMP40, were therefore included in the model calculations. The majority of these congeners are non-coplanar. Toxic equivalency factor (TEF) values are available for only three of the 40 PCB congeners (i.e., PCBs 101, 118, and 156). However, the TEFs of these congeners are low compared with those of coplanar PCBs such as PCBs 77, 126, and 169. As a result, PCB concentrations were expressed not in terms of toxic equivalents but as the total PCB ( $\sum \text{PCB}$ ) concentration, i.e., the sum of the concentrations of the RMP40.

#### Food web

The food web structure of San Francisco Bay is complex. The food web includes many different species with a variety of habitats. Species composition varies between locations in the bay and at different times of the year. Feeding relationships also vary between species, life stages of species, abundance of the various species, location, time of the year, and other factors. It is not possible, or necessary, to include all species in the San Francisco Bay food web in the model or to represent all possible trophic interactions. In the development of a food web structure for modeling the bioaccumulation of PCBs in SFB, we selected to include species with the following characteristics.

Species of primary management interest, i.e., the double-crested cormorant (*Phalacrocorax auritus*), Forster's tern (*Sterna forsteri*), harbor seal (*Phoca vitulina richardsi*), shiner surfperch (*Cymatogaster aggregata*), jack smelt (*Atherinopsis californiensis*), and white croaker (*Genyonemus lineatus*). The harbor seal, Forster's tern, and double-crested cormorant were included in the model because they represent species of higher trophic levels in the food web and contain the highest concentrations of PCBs. The white croaker, shiner surfperch, and jack smelt were included in the model because they are caught and consumed by local fishermen.

Species that are considered to be year-round residents of San Francisco Bay or, forage predominantly in San Francisco Bay, and are expected to be affected by remediation.

Species representing trophic guilds that are of key relevance to the food web transfer and accumulation of PCBs in the species

of interest. Relevant trophic guilds include phytoplankton and algae; zooplankton; filter-feeding invertebrates; benthic detritivores; juvenile and adult fish; male and female fish-eating birds; and male, female, and juvenile marine mammals. Species for which empirical concentration data are available. This provides the opportunity to test and ground-verify the model's calculations. Concentration data were available for Pacific oysters (*Crassostrea gigas*), California mussels (*Mytilus californianus*), shiner surfperch (*Cymatogaster aggregata*), jack smelt (*Atherinopsis californiensis*), white croaker (*Genyonemus lineatus*), double-crested cormorant (*Phalacrocorax auritus*), and harbor seal (*Phoca vitulina richardsi*).

We further minimized the number of species in the model to keep the model simple and make the model calculations more transparent. This approach produced a food web model that included one category for phytoplankton; one category for zooplankton; eight invertebrate species (including detritivores and filter feeders); two bird species (including male and female birds as well as eggs for each avian species); and male, female, juvenile, and newborn harbor seals. The species that were included in the model and their feeding relationships are listed Supplemental Data Tables S1, S2, and S3 and are illustrated in Figure 1. The Supplemental Data include additional rationale for species selection.

#### Spatial distribution

The  $\sum \text{PCB}$  concentrations in sediments range from virtually nondetectable levels to concentrations as high as 9 mg/kg (dry sediment) [7], and concentrations in water range from approximately 77 pg/L to approximately 3,700 pg/L [9]. This spatial variability in the total PCB concentrations causes significant variation in exposure to PCBs among biota of the bay. Organisms with limited mobility (e.g., certain invertebrates such as mussels and polychaetes) are likely to reflect the PCB concentrations in their immediate environment. Hence, if they reside in a hot spot, PCB concentrations are likely to be greater than concentrations in organisms that inhabit less PCB-polluted sections of the bay. However, seals, cormorants, terns, and several of the fish species investigated in the present study have foraging areas that include large sections of the bay and are therefore exposed to a wider range of PCB concentrations in the sediments. The PCB concentrations in these organisms are expected to reflect a spatial average of the concentrations to which they are exposed. Also, species that are widely distributed in the bay will exhibit bay-wide spatially averaged concentrations depending on the areas within the bay where they reside and forage. If information on the spatial distribution of wildlife and associated PCB concentrations in sediments in the bay is available, it is possible to calculate PCB concentrations in wildlife based on their foraging behavior. However, this information is not currently available. To calculate the PCB concentrations in wildlife species that are widely distributed in the bay, we assumed that the available PCB sediment concentration data collected by monitoring programs in the bay represent the distribution of PCB concentrations to which the wildlife populations in the bay are exposed. This assumption is reasonable for several reasons. First, PCB sediment concentration-monitoring programs have included a large number of stations throughout the bay (Supplemental Data Fig. S1). Large numbers of independent sediment PCB concentration measurements (~1,284) have been collected from these stations and can

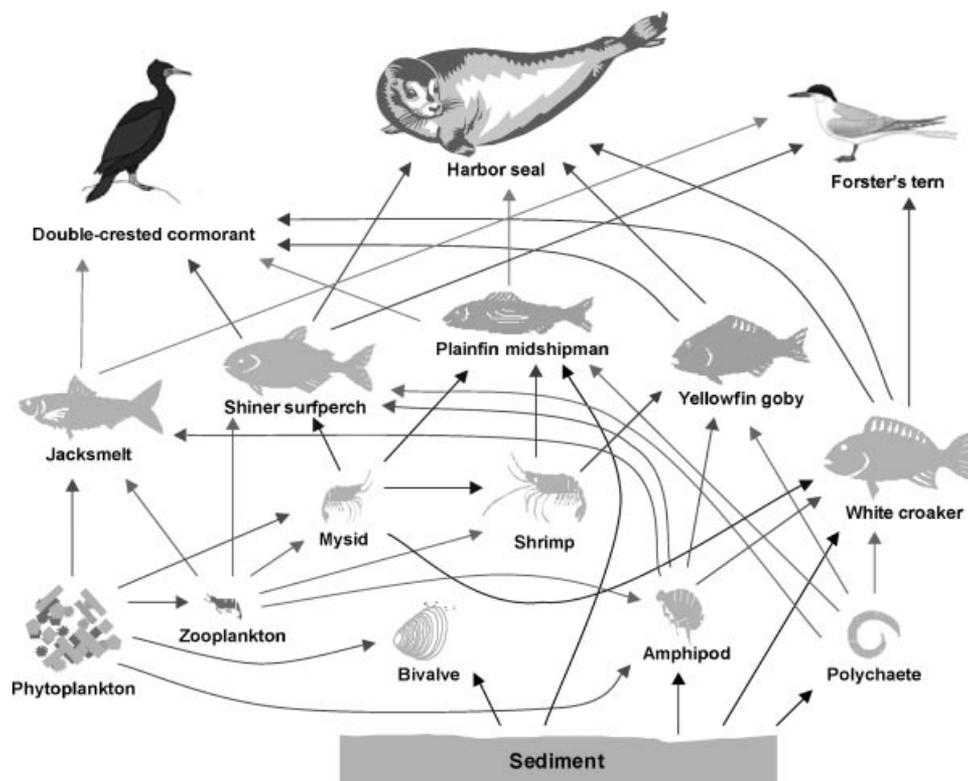


Fig. 1. Conceptual diagram illustrating organisms included in the model and their trophic interactions.

provide a reasonable representation of the spatial distribution of the PCB concentrations in the bay. Second, the wildlife species included in the model are distributed over large areas of the bay area and are year-round residents of the bay.

#### Time

The San Francisco Bay food web bioaccumulation model applies a steady-state approach to estimate the PCB concentrations in biota from PCB concentrations in the sediments. This approach is based on the assumption that, under the conditions of interest, PCB concentrations have had sufficient time to exchange between water, sediments, and the organisms of the food web to achieve a steady state or pseudosteady state. An important implication of the selection of the steady-state approach is that PCB concentrations in biota are directly proportional to the PCB concentrations in the bay sediment. This means that temporal changes in the PCB concentrations in the biota of the bay will match those in the sediments. We believe that this assumption is justified, because the time response of the PCB concentrations in the sediment to changes in loadings and external conditions is quite slow compared to the time response of PCB concentrations in biota. Davis [7] estimated that the half-life of PCBs in San Francisco Bay is approximately 20 years. A comparable half-life of PCBs calculated in adult white croaker is approximately 100 d. This implies that the temporal response of the PCB concentration in most organisms is controlled by the time response of the sediments, which acts as the slowest compartment, and that the rate-controlling step of PCB concentration changes over time.

#### Model description for phytoplankton, zooplankton, benthic invertebrates, and fish

The algorithms used for phytoplankton, zooplankton, benthic invertebrates and fish are essentially those reported

by Arnot and Gobas [8]. This model is based on the presumption that the exchange of PCB congeners between the organism and its ambient environment (Supplemental Data Fig. S2) can be described by a single equation for a number of aquatic organisms.

$$C_B = [k_1 \cdot (m_O \cdot \phi \cdot C_{WT,O} + m_P \cdot C_{WD,S}) + k_D \cdot \sum P_i \cdot C_{D,i}] / (k_2 + k_E + k_G + k_M) \quad (2)$$

where  $C_B$  is the wet weight concentration (g/kg wet wt) of the PCB congener in the organism,  $k_1$  is the clearance rate constant ([L/kg wet wt]/d) for uptake via the respiratory area (i.e., gills and skin),  $m_O$  is the fraction of the respiratory ventilation that involves overlying water,  $m_P$  is the fraction of the respiratory ventilation that involves sediment associated pore water,  $\phi$  (unitless) is the fraction of the total chemical concentration in the overlying water that is freely dissolved and can be absorbed via membrane diffusion,  $C_{WT,O}$  is the total concentration of the PCB congener in the water column above the sediments (g/L),  $C_{WD,S}$  is the freely dissolved PCB congener concentration in the sediment associated pore (or interstitial) water (g/L),  $k_D$  is the clearance rate constant ([kg/kg wet wt]/d) for chemical uptake via ingestion of food and water,  $P_i$  is the fraction of the diet consisting of prey item  $i$ ,  $C_{D,i}$  is the concentration of PCB congener (g/kg) in prey item  $i$ ,  $k_2$  is the rate constant (1/d) for elimination of PCBs via the respiratory area (i.e., gills and skin),  $k_E$  is the rate constant (1/d) for the elimination of the PCB congener via excretion into egested feces,  $k_G$  is the growth rate constant expressed as fixed annual proportional increases in the organism's wet weight  $W_B$  (kg) over time  $t$ , i.e.,  $dW_B/(W_B \cdot dt)$ , and  $k_M$  is the rate constant (1/d) for metabolic biotransformation of the PCB congener. The

methods for derivation of the model state variables can be found in the Supplemental Data.

#### Model description for harbor seals

Supplemental Data Figure S3 provides a conceptual overview of major routes of PCB uptake and elimination in harbor seals. PCB uptake is due predominantly to dietary uptake and inhalation of air. Elimination of PCBs from the seals is due to exhalation of air and excretion in fecal matter and urine. In addition, certain PCB congeners can be metabolized in harbor seals [10,11]. Female seals can also transfer PCBs to their offspring by giving birth to pups and by lactation. Molting and growth periods can also affect PCB concentrations. Harbor seals are known to fast and molt at particular times of the year, and female animals give birth and nurse their pups for a period of approximately four weeks. To represent these processes in a relatively simple model, it is important to consider some key characteristics of PCBs. First, PCBs are lipophilic chemicals that build up high concentrations in the lipids of organisms. Seals contain large amounts of fat in their blubber. The whole-body-weight lipid content of healthy harbor seals in the bay varies between 36 and 50%. This means that the great majority of PCBs are found in the lipid tissues. Second, PCBs show a natural tendency to establish a chemical equilibrium. This means that, within an organism such as a seal, PCBs distribute themselves between various parts of the organism in a way that the concentrations in lipids of any part of the organism approach equality. This behavior of PCBs is particularly relevant to transfer of PCBs from female seals to their pups. If it can be assumed that PCBs in mother and pup achieve an internal equilibrium, then the lipid-normalized concentration in female seals will not change upon parturition. In essence, the reduction in the mass of PCBs in the mother upon parturition (due to transfer to the pup) is associated with a proportional drop in lipid mass, causing the lipid-normalized concentration to remain the same. The same principle is at work during lactation. Assuming that PCBs are equally distributed among fats in the nursing female, transfer of PCB in milk does not cause a change in concentration as proportional declines in PCB mass and lipid mass occur during lactation. The same philosophy applies to molting. Although production of offspring, lactation, and molting are not expected to have an immediate effect on the lipid-normalized concentration in the seal, they do have a long-term concentration effect in seals because of the growth dilution effect that takes place during fetal development, milk production, and skin formation. Seals have to grow body mass to accommodate these processes in addition to any net (year-to-year) increases in body weight. This process of growth takes place more gradually over the seal's life cycle and can be represented as a continuous process. Naturally, the growth-induced decline of the PCB concentration in seals is compensated by intake of PCB with the diet that makes growth possible. The steady-state solution of the mass balance equation (Supplemental Data Eqn. S25) in the harbor seals is

$$C_{HS,I} = (k_A C_{AG} + k_D \cdot \sum [P_i \cdot C_{D,i}]) / (k_O + k_E + k_U + k_G + k_P + k_L + k_M) \quad (3)$$

where  $C_{HS,I}$  is the lipid-normalized concentration of the PCB congener in the seal,  $C_{AG}$  is the gaseous aerial concentration (g/L),  $k_A$  is the inhalation rate constant ([L/kg lipid]/d),  $k_D$  is the clearance rate constant ([kg/kg lipid]/d) for PCB uptake via

ingestion of food and water,  $P_i$  is the fraction of the diet consisting of prey item  $i$ ,  $C_{D,i}$  is the concentration of the PCB congener (g/kg lipid) in prey item  $i$ ,  $k_O$  is the rate constant (1/d) for exhalation of PCB via the lungs,  $k_E$  is the rate constant (1/d) for the elimination of the PCB congener via excretion into egested feces,  $k_U$  is the rate constant for urinary excretion of PCBs,  $k_G$  is the rate constant for growth dilution (accounting for year-to-year increases in the net growth of the animals),  $k_P$  is the rate constant for transfer of PCBs into the pups (representing the increase in lipid mass [equivalent to the postparturition lipid mass of the pup] over the duration of the gestation period),  $k_L$  is the rate constant for transfer of PCBs to the pups as a result of lactation (portraying the growth of lipid mass of the female seals over the year that is transferred to the pup during lactation), and  $k_G$ ,  $k_P$ , and  $k_L$  are expressed as fixed annual-proportional increases in body lipid weight over time  $t$ , i.e.,  $dW_{S,I}/(W_{S,I} \cdot dt)$ , where  $W_{S,I}$  is the weight of the lipids in the seal and has units of  $d^{-1} \cdot k_M$ , the rate constant for metabolic transformation of the PCB congener. A whole-organism wet-weight-based concentration in the seal,  $C_{HS}$ , can be calculated from the lipid-normalized concentration as  $C_{HS} = L_{HS} \cdot C_{HS,I}$ , where  $L_{HS}$  is the lipid content of the harbor seal. The whole-organism lipid content undergoes significant changes throughout the year. Therefore, the wet weight concentration in the seal can be expected to undergo changes of similar magnitude. These changes can be represented in the model by varying  $L_{HS}$ . The lipid content in seals is high; hence, the contribution of nonlipid organic matter as a storage compartment for PCBs is relatively insignificant. Further description of the model for harbor seals is included in the Supplemental Data.

#### Model description for cormorants and terns

The uptake of PCBs in birds is due to dietary uptake and inhalation of air. Polychlorinated biphenyls are eliminated in exhaled air, fecal matter, and urine and by metabolic biotransformation (Supplemental Data Fig. S4). During periods of growth, PCB concentrations can be affected by growth dilution, which is not a real elimination process but reduces PCB concentrations in the animals.

Female birds can also transfer PCBs into eggs. In the model, the effect of the deposition of PCBs in eggs on the maternal PCB body burden is comparable to the transfer of PCBs to offspring and milk in harbor seals. This assumes that PCBs are well distributed among the lipid tissues in the bird. Hence, a reduction in the mass of PCBs in the mother as a result of transfer of PCBs in the eggs is associated with a proportional drop in lipid mass, causing the lipid-normalized concentration to remain approximately the same. The main impact of producing eggs on the maternal PCB body burden is the result of the increase in body mass required to produce the eggs. Growth causes a decline of the PCB concentration in the female birds. This is compensated by intake of PCB with the diet that makes growth possible. The PCB concentration in the bird is the result of the balance between uptake and elimination rates, which at steady state can be represented by

$$C_{C,I} = (k_A C_{AG} + k_D \cdot \sum [P_i \cdot C_{D,i}]) / (k_O + k_E + k_G + k_C + k_M) \quad (4)$$

where  $C_{C,I}$  is the lipid-normalized concentration of the PCB congener in either the cormorant or the tern,  $C_{AG}$  is the gaseous aerial concentration (g/L),  $k_A$  is the inhalation rate constant ([L/kg lipid]/d),  $k_D$  is the clearance rate constant ([kg/kg lipid]/d) for PCB uptake via ingestion of food and water,  $P_i$  is the fraction of

the diet consisting of prey item  $i$ ,  $C_{D,i}$  is the concentration of the PCB congener (g/kg) in prey item  $i$ ,  $k_O$  is the rate constant (1/d) for exhalation of PCB via the lungs of the birds,  $k_E$  is the rate constant (1/d) for the elimination of the PCB congener via excretion into egested feces,  $k_G$  is the rate constant for growth dilution resulting from year-to-year increases in the net body mass of the birds,  $k_C$  is the rate constant for transfer of PCBs into eggs in female birds (representing the increase in lipid mass resulting from egg production), and  $k_M$  is the rate constant for biotransformation of the PCB congener in the bird. The whole-organism wet-weight-based concentration,  $C_C$ , can be calculated from  $C_{C,i}$  as  $C_C = L_C \cdot C_{C,i}$ , where  $L_C$  is the lipid content of the cormorants or the terns. A detailed description of the model is given in the Supplemental Data.

## MATERIALS AND METHODS

### Model parameterization

Model parameterization involves the selection of state variables to ensure that the model is representative of conditions in the bay. The octanol–water ( $K_{OW}$ ) and octanol–air ( $K_{OA}$ ) partition coefficients of the PCB congeners that were used in the model calculations are summarized in Supplemental Data Table S4, which lists the freshwater-based  $K_{OW}$  values at the mean ambient water temperature of the bay (14.9°C) and their saltwater equivalents derived following Xie et al. [12]. The saltwater-based  $K_{OW}$  values were used in the calculations for fish. The freshwater-based  $K_{OW}$  values at 37.5°C were used to represent partitioning between lipids and aqueous media (e.g., urine) in warm-blooded mammals and birds. Supplemental Data Table S4 also includes the  $K_{OA}$  values at 37.5°C, which are used to estimate the exchange of PCBs between warm-blooded animals and the air via the lungs. The input variables used to characterize the environmental conditions in the bay are included in Supplemental Data Table S5. The body weight and lipid content of the species represented in the San Francisco Bay food web model are listed in Supplemental Data Table S1. They include 23 species, several age classes, male and female animals, and their offspring and eggs. Supplemental Data Table S6 details the selection of biological parameters for each organism in the food web model. Supplemental Data Table S7 includes the metabolic biotransformation rate constants used in the model. Supplemental Data Tables S2 and S3 list the feeding preferences of the various species represented in the model.

### Model calculations and evaluation

The model is constructed in Microsoft Excel 2000™ (<http://www.rem.sfu.ca/toxicology/models/models.htm>). In the model, the concentration in the sediments is presented in a logarithmic format as  $\log C_S$ , such that the log normal distribution of the sediment concentration can be presented as a normal distribution of  $\log C_S$ . The model outcome, i.e., the BSAF, is also presented in a logarithmic format as  $\log \text{BSAF}$ , which provides the advantage that the log normal distribution of the BSAF can be presented as a normal distribution of  $\log \text{BSAF}$ . The model can be applied in a forward manner to predict concentrations in biota based on sediment concentrations or in a backward manner to predict concentrations in sediment based on biota concentrations.

In the forward application of the model, the actual distribution of concentrations in the sediments is used to calculate the concentration distributions in various species in the bay accord-

ing to

$$\log C_B = \log \text{BSAF} + \log C_S \quad (5)$$

The frequency distribution of concentrations in the target organisms can be used to determine the risks of exceeding target or toxic threshold concentrations (Fig. 2). The effect of remediation efforts on bay-wide PCB concentrations can be explored with the current model by entering the anticipated or actual spatial concentration distribution of  $C_S$  after remediation.

In the backward application of the model (Fig. 2), the concentration in the sediment expected to meet ecological and/or human health criteria ( $C_S$ ) is calculated based on the target PCB concentration in a fish or wildlife species ( $C_B$ ) according to

$$\log C_S = \log C_B - \log \text{BSAF} \quad (6)$$

Uncertainty in the BSAF can produce a distribution of concentrations in the sediments that meets the target.

### Sensitivity analysis

The PCB food web bioaccumulation model for San Francisco Bay was evaluated by using a sensitivity analysis, a model-performance analysis, and an uncertainty analysis. The sensitivity analysis assesses the impact of variability or error in the model's state variables (e.g., organism weight, lipid content, temperature) on the model outcome (i.e., the BSAF of total PCBs in bay fish and wildlife) and is detailed in the Supplemental Data.

### Model testing and performance analysis

The model performance analysis evaluated the accuracy of the model by comparing model predicted  $\text{BSAF}_P$  to independent, observed  $\text{BSAF}_O$  of PCB congeners. It involved entering the geometric mean PCB congener concentrations in sediment and water and calculating the concentrations in biota and corresponding  $\text{BSAF}_P$ . The observed BSAF ( $\text{BSAF}_O$ ) of PCB congeners and  $\sum \text{PCBs}$  were calculated from measured concentrations in biota and sediments as  $C_B/C_S$ . Observed PCB concentrations in sediments; filter feeders *Mytilus californianus* (California mussels) and *Crassostrea gigas* (Pacific oyster); three fish species, i.e., jack smelt (*Atherinopsis californiensis*), white croaker (*Genyonemus lineatus*), and shiner surfperch (*Cymatogaster aggregate*); and eggs from a resident bird species (i.e., the double-crested cormorant, *Phalacrocorax auritus*) were collected as part of regional monitoring programs (RMPs) in 1999, 2000, and 2001. Harbor seals were sampled between 1989 and 1993 as detailed in the Supplemental Data, and eggs were collected from year-round colony residents that eat fish from San Francisco Bay [13]. No model calibration efforts were undertaken.

The mean model bias ( $MB$ ) derived on a congener-specific basis can be used as a measure of model performance for each species as

$$MB_j = 10 \left( \frac{\sum_{i=1}^n \left[ \log \left( \frac{\text{BSAF}_{P,i}}{\text{BSAF}_{O,i}} \right) \right]}{n} \right) \quad (7)$$

$MB_j$  is the geometric mean (assuming a log normal distribution of the ratio  $\text{BSAF}_{P,i}/\text{BSAF}_{O,i}$ ) of the ratio of predicted and observed BSAFs for all PCB congeners,  $i$ , in a particular species,  $j$ , included in the analysis.

To express model performance for  $\sum \text{PCBs}$  quantitatively, we used the model bias  $MB^*$ , which is derived for each species

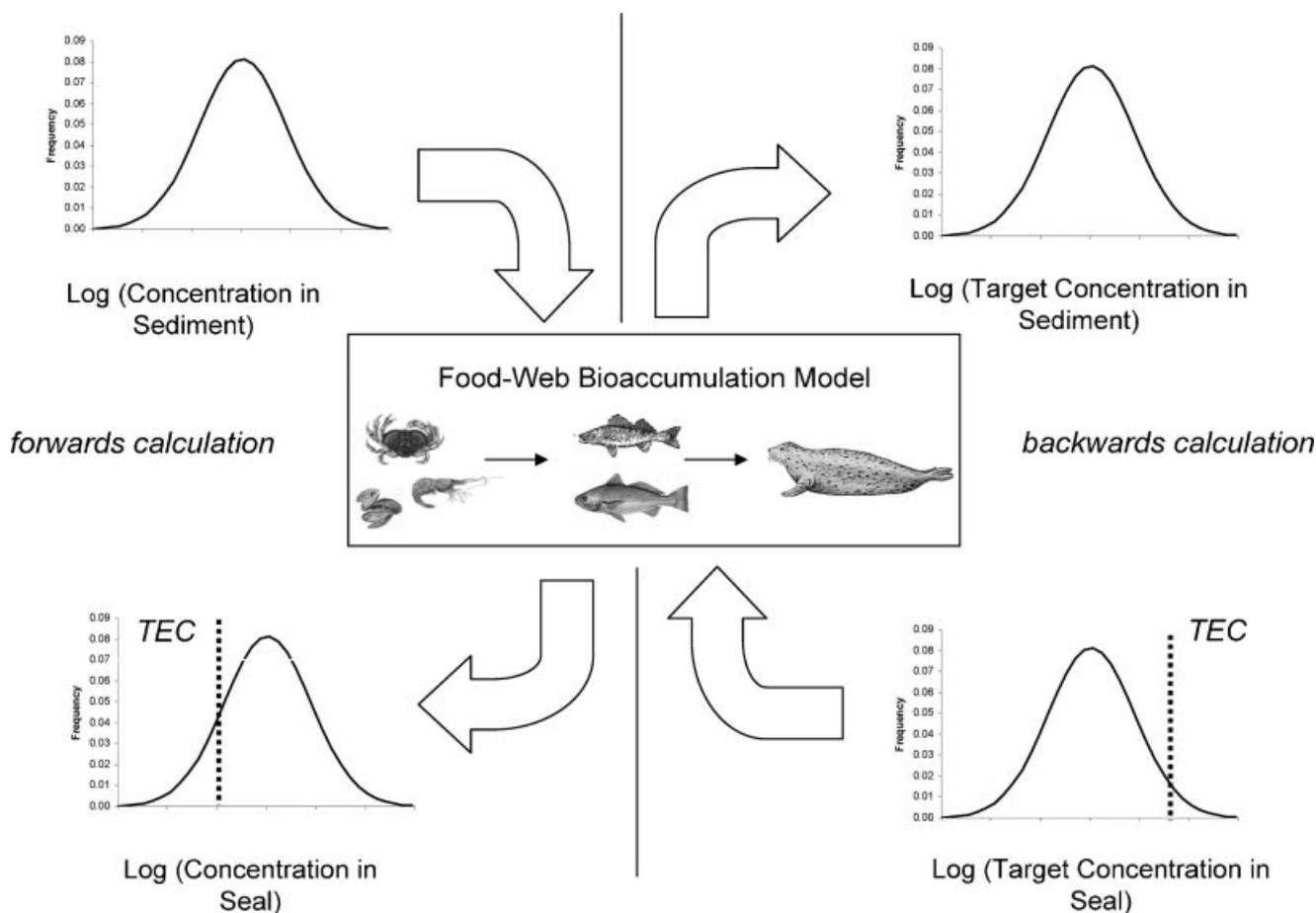


Fig. 2. Conceptual diagram illustrating the application of the model for risk assessment (i.e., calculation of the fraction of the population with concentrations exceeding the threshold effect concentration [TEC]) in the forward calculation and the derivation of target concentrations for remediation in the backward calculation.

as

$$MB_j^* = 10 \left( \frac{\sum_{i=1}^m \left[ \log \left( \frac{BSAF_{P,\Sigma PCB}}{BSAF_{O,\Sigma PCB}} \right) \right]}{m} \right) \quad (8)$$

$MB_j^*$  is the geometric mean of the ratio of the predicted BSAF of  $\Sigma PCB$  ( $BSAF_{P,\Sigma PCB}$ ) and the observed BSAF of  $\Sigma PCB$  ( $BSAF_{O,\Sigma PCB}$ ) for all observations,  $m$ , in species  $j$ .

The model bias ( $MB$  or  $MB^*$ ) is a measure of the systematic overprediction ( $MB > 1$ ) or underprediction ( $MB < 1$ ) of the model. In the calculation of  $MB$ , over- and underestimations of the observed BSAF values have a tendency to cancel out. Hence,  $MB$  tracks the central tendency of the ability of the model to predict PCB congener concentrations. It is a useful measure of model performance if total PCBs ( $\Sigma PCB$ ) are of primary interest. The variability of over- and underestimation of measured values is represented by the 95% confidence interval (CI) of  $MB$ , i.e., 95% CI =  $\text{antilog}(\log MB \pm [t_{v,0.05} \times \log \text{standard deviation}])$ . The 95% CI represents the range of BSAFs that includes 95% of the observed BSAFs. It is a measure of the uncertainty of the model predictions. Because of the log normal distribution of the ratio of predicted and observed BSAFs, this variability can be expressed as a factor (rather than a term) of the geometric mean. The model's performance improves when  $MB$  and  $MB^*$  approach 1.0 and their 95% CIs become smaller. Model bias and  $MB^*$  and their 95% CIs represent several

sources of error, including model parameterization errors and errors in model structure and philosophy, as well as analytical and sampling errors in the empirical data (e.g., chemical concentrations in water, sediment, and biota) and natural, spatial, and temporal variability in the empirical data used in the model-performance analysis.

#### Uncertainty analysis

Uncertainty in the model input parameters (i.e.,  $\log C_S$ ) and in the model calculations (i.e.,  $\log BSAF$ ) are propagated in the estimate of  $\log C_B$  in terms of the standard deviation,  $SD_{CB}$ , of  $\log C_B$  (i.e., the geometric mean concentration).  $SD_{CB}$  is calculated from the standard deviation of  $\log BSAF$  ( $SD_{BSAF}$ ) and the standard deviation of  $\log C_S$  ( $SD_{CS}$ ) as

$$SD_{CB} = \sqrt{(SD_{CS}^2 + SD_{BSAF}^2)} \quad (9)$$

The  $SD_{CS}$  was determined by representing  $\Sigma PCB$  concentrations in sediment samples collected from the bay in terms of a single log normal distribution with a mean  $\log C_B$ , which is the geometric mean  $\Sigma PCB$  concentration in the sediment, and a standard deviation  $SD_{CS}$ . The  $SD_{BSAF}$  was determined as the SD of the frequency distribution for  $\log (BSAF_O/BSAF_P)$ , where  $BSAF_O$  is the ratio of observed concentrations in biota,  $C_B$ , and the geometric mean concentration in the sediments,  $C_S$ , and  $BSAF_P$  is the ratio of the calculated concentrations in biota,  $C_B$ ,

and the geometric mean concentration in the sediments,  $C_S$ . For every observed concentration,  $C_B$ , there is one  $BSAF_O/BSAF_P$ . Multiple observations of  $C_B$  create a log normal distribution, and  $SD_{BSAF}$  is the SD of this distribution. One of the advantages of using empirical observations to assess uncertainty is that it includes many sources of uncertainty, whereas Monte Carlo simulation is limited to model parameterization uncertainty. Because uncertainty in observed  $\sum PCB$  concentrations in biota reflects spatial variation in  $\sum PCB$  concentrations in sediments, which is specifically considered by  $SD_{CS}$  in Equation 9, the estimated uncertainty in  $C_B$  may be somewhat overestimated by this method. However, the spatial resolution of the monitoring program for biota concentrations was quite limited and did not include the full geographic distribution of the bay. As a result, the effect of double counting uncertainty resulting from spatial distribution in sediment concentrations on the estimation of uncertainty in  $C_B$  is likely small.

Uncertainty analysis through Monte Carlo simulation was considered (supporting document) but found to be problematic because of the interdependence of state variables and lack of data to define uncertainty distributions for several state variables. The interdependence of several state variables, including feeding rates, growth rates, fecal egestion rates, and feeding preferences, caused inconsistencies in the energy and mass balance of the model. The associated error was deemed to be too large for the Monte Carlo simulations to provide meaningful estimates of model uncertainty.

#### Model application for risk assessment

To assess the risks of  $\sum PCB$  concentrations on certain target species in San Francisco Bay, we compiled  $\sum PCB$  concentrations for 1,284 sediment samples collected from the bay between 1999 and 2001 under the RMP sediment sampling program and expressed the concentrations in terms of a single log normal distribution. Equations 5 and 9 were then used to calculate log normal distributions of  $\sum PCB$  concentrations in biota species. The resulting frequency distributions were then compared with selected ecological and human health-based threshold effect concentrations (Table 1). The ecological risks of PCB concentrations in harbor seals were assessed by comparing the calculated PCB concentrations with a threshold effect concentration (TEC) for total PCBs of 11  $\mu g/g$  lipid. The TEC is the geometric mean of the no-observed-adverse-effects level (NOAEL; 5.2  $\mu g/g$  lipid) and the lowest-observed-adverse-effects level (LOAEL; 25  $\mu g/g$  lipid) as proposed by Kannan et al. [14] based on studies by Boon et al. [10] and Brouwer et al. [15]. Wet-weight-based concentrations of 3.6 to 6.8 ppm, reported and reviewed by Hoffman et al. [16], were selected to estimate ecological risks of total PCBs in double-crested cormorants. These concentrations were associated with embryonic mortality, beak deformities, and clubfoot in the field. To simplify the characterization of possible effects on double-crested cormorants, we used an LOAEL of 5,000  $\mu g/kg$  wet-weight body mass. Wet-weight-based concentrations of 6 to 26 ppm in eggs, reported and reviewed by Hoffman et al. [16] and based on data by Kubiak et al. [17], Hoffman et al. [18], and Tillit et al. [19], were used to estimate the potential for PCBs to cause toxic effects in Forster's terns. These concentrations in eggs were associated with embryonic mortality, impaired reproductive success, subcutaneous edema of head and neck, aryl hydrocarbon hydroxylase induction, and beak deformities [16]. For the characterization of the toxic effects in Forster's terns, we used an LOAEL of 6,000  $\mu g/kg$  wet weight in eggs in the model. We also calculated the  $\sum PCB$  concentration in each fish

species associated with an upper bound excess lifetime human cancer risk of  $10^{-5}$  and a human health hazard index for 1 in humans consuming fish from San Francisco Bay. This is described in the Supplemental Data.

#### Model application to derive sediment target levels

To derive geometric mean  $\sum PCB$  concentrations expected to meet particular  $\sum PCB$  concentrations in fish and wildlife associated with various human health and ecological risks (listed in Table 1), we used Equation 6. One of the consequences of the calculation of geometric means is that, at the calculated sediment concentrations, approximately half the receptor population of the bay can be expected to contain concentrations that exceed the target values, whereas the PCB concentration in the other half of the population will be less than the target concentrations. An alternative application of the model is the calculation of the geometric mean PCB concentration in the bay sediments that is expected to result in a 5% exceedence of target concentrations. To do this, we used Equation 5 and changed the geometric mean  $\sum PCB$  concentrations in the sediments (while maintaining  $SD_{CS}$ ) to produce a  $\sum PCB$  concentration frequency distribution in biota at which 5% of the expected PCB concentrations in biota are in excess of the human health and ecological target concentrations for toxicity. In essence, this involves shifting the PCB concentration distributions in the target organisms to make the upper 95% CI equal to the criterion value (e.g., TEC) rather than the geometric mean of the distribution.

## RESULTS AND DISCUSSION

#### Sensitivity analysis

Supplemental Data Tables S8 to S11 illustrate the sensitivity of the abiotic and biotic state variables of the model. Certain parameters such as organism water content and water absorption efficiency have little impact on model outputs. Other parameters such as the lipid content (and organic carbon content in phytoplankton), lipid and nonlipid organic carbon (i.e., protein and carbohydrate), and digestion efficiencies are among the most sensitive parameters in the model. These parameters control the lipid and organic matter content in the gastrointestinal tract of an organism following a feeding event and are largely responsible for the dietary biomagnification of PCBs. The growth rate (in, e.g., phytoplankton and seals) and the coefficients used to calculate the growth rate (in invertebrates and fish) are also sensitive model state variables. Organism growth (concentration dilution) is an important process con-

Table 1. Internal concentrations in San Francisco Bay, California, USA, sport fish and wildlife associated with a 1:100,000 upper bound excess human cancer risk, a human health hazard index in excess of 1, and the no-observed-adverse effect level (NOAEL), lowest-observed-adverse effect level (LOAEL), and threshold effect concentration (TEC)

Endpoint	Organism	Concentration
Human excess lifetime cancer risk ( $10^{-5}$ )	Fish	52 $\mu g/kg$ wet wt
Human health hazard (H = 1)	Fish	207 $\mu g/kg$ wet wt
LOAEL	Cormorant egg	5,000 $\mu g/kg$ wet wt
LOAEL	Tern egg	6,000 $\mu g/kg$ wet wt
TEC	Harbor seal	11,000 $\mu g/kg$ lipid
LOAEL	Harbor seal	25,000 $\mu g/kg$ lipid
NOAEL	Harbor seal	5,000 $\mu g/kg$ lipid

trolling the total body concentration for higher  $K_{OW}$  PCBs that are not effectively eliminated by other loss processes such as respiration and biotransformation.

#### Model testing and performance analysis

Figure 3 and Supplemental Data Figure S5 to S11 illustrate model-predicted and observed BSAFs for the 40 PCB congeners included in the RMP monitoring program. The figures show that the model-predicted BSAFs are within the range of observed BSAFs. The figures further illustrate that the congener patterns of PCBs in all of the organisms are reasonably well reproduced by the model. Figure 4 illustrates model-predicted and observed BSAFs for  $\sum$ PCB. The observed log BSAF of  $\sum$ PCB contains 95% CIs ranging between approximately 0.4 (for cormorants) and 1.0 (for male harbor seals) and reflecting considerable variability among the observed BSAFs in the bay. Figure 4 illustrates that the model-predicted BSAFs of  $\sum$ PCB are well within the range of the observed values.

Table 2 illustrates that the mean MB among the 40 PCB congeners ranges between 0.96 for female harbor seals to 1.56 for male harbor seals and is close to 1 for all organisms. The mean  $MB^*$  for the BSAF of  $\sum$ PCB ranges between 0.64 for female harbor seals to 1.05 for benthic invertebrates and jack smelt and is also close to 1 for all organisms. Thus, the model produces little systematic over- or underestimation of PCB congener concentrations.

#### Uncertainty analysis

Table 2 shows that the 95% CIs of the mean MB (congeners) range between factors of 3.74 for shiner surfperch and 7.43 for male harbor seals. The 95% CIs of the mean  $MB^*$  ( $\sum$ PCBs) range between factors of 2.04 for cormorant eggs and 9.65 for male harbor seals. This illustrates that over- and underestimations of the BSAF for individual PCB congeners or for individuals of a specific species can be considerable even if the predicted mean concentration values are close to the observed

values. The CIs can be viewed as the uncertainty in the BSAF model estimates.

#### Model application for risk assessment

Table H in the Supplemental Data compiles  $\sum$ PCB concentrations from a total of 1,284 sediment samples collected from San Francisco Bay between 1999 and 2001 under the RMP sediment-sampling program. It illustrates the distribution of PCB concentrations in the bay and shows substantial variability in the  $\sum$ PCB concentrations in the sediments of the various sections of the bay (i.e., North, Central, and South). The  $\sum$ PCB concentration distributions range by approximately two orders of magnitude in the northern and southern sections of the bay and by three orders of magnitude in the central section of the bay. The  $\sum$ PCB concentrations in the northern section are somewhat lower than those in the central and southern sections of the bay. Figure 5 compiles all the data in a single bay-wide concentration distribution, which was then represented by a single log normal distribution to calculate bay-wide concentration distributions. Figure 5 shows that the log normal distribution that was used in the model to represent the current level of PCB contamination in the bay is in reasonable agreement with the measured distribution of the 1,284 sediment concentration data from the bay. The geometric mean of this distribution is  $11.6 \mu\text{g}/\text{kg}$  dry sediment. The 95% CI of the geometric mean  $\sum$ PCB concentration in the sediments is equivalent to a factor of 7.4. This indicates that fish and wildlife in the bay are exposed to PCB concentrations that vary substantially.

Figure 6 illustrates the results of the model calculations of the  $\sum$ PCB concentration in some key species of the San Francisco Bay food web. It shows predicted  $\sum$ PCB concentration distributions (calculated with Eqn. 9) that include uncertainty in the BSAF as well as the variability in the  $\sum$ PCB concentrations in the sediments. The distributions of the predicted PCB concentrations in biota are therefore not solely a reflection of model uncertainty. They also reflect the variability

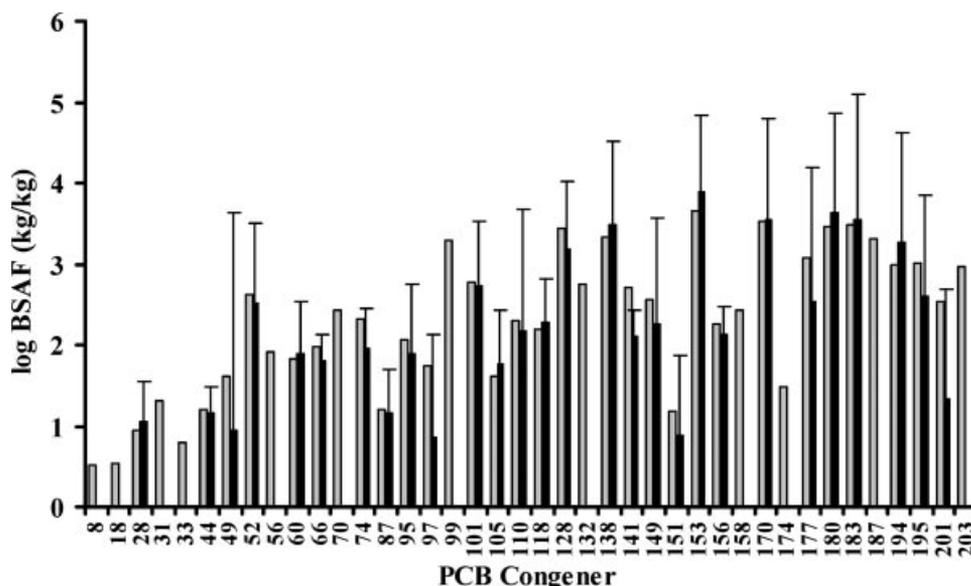


Fig. 3. Model-predicted (gray columns) and observed (black columns;  $\pm 1$  SD) biota–sediment bioaccumulation factors (BSAFs in kg dry sediment/kg wet wt organism) of approximately 40 polychlorinated biphenyl (PCB) congeners in adult male harbor seals (*Phoca vitulina richardsi*) in San Francisco Bay, California, USA.

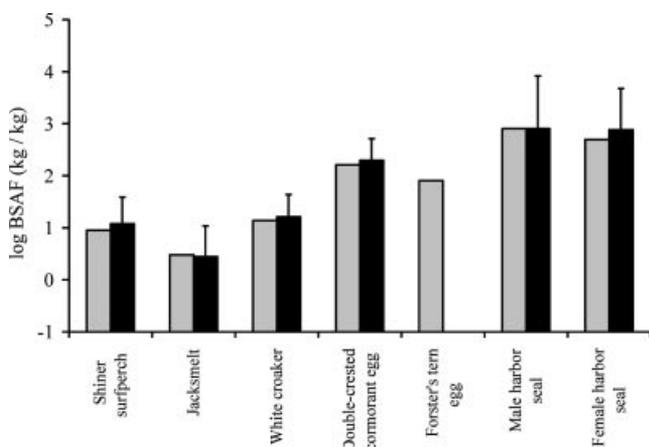


Fig. 4. Model-predicted (gray columns) and observed (black columns) mean biota-sediment bioaccumulation factors (BSAFs in kg dry sediment/kg wet wt organism) of total polychlorinated biphenyls ( $\Sigma$ PCBs) in several species in San Francisco Bay, California, USA. Error bars represent 95% confidence intervals.

in PCB concentrations in the sediments of the bay. In fact, the variability of the PCB concentrations in the bay sediments is the largest contributor to the 95% CIs of the predicted geometric mean  $\Sigma$ PCB concentrations in biota species. Figure 6 also illustrates the distributions of observed PCB concentrations, which are narrower than the predicted distribution of the PCB concentrations for the entire bay. This is because animal-sampling programs were carried out in certain areas of the bay, which causes observed concentration distributions to underrepresent the spatial distribution of PCB concentrations in biota in the entire bay.

Figure 6 shows that approximately 80% of the bay-wide male and 60% of the bay-wide female harbor seals are expected to contain  $\Sigma$ PCB concentrations in excess of the threshold effect concentration of 11 mg/kg lipid. It also shows that approximately 20% of the resident cormorant egg population in the bay is expected to exceed the LOAEL. Approximately 77% of the bay-wide white croaker population is expected to contain PCB concentrations that, based on the risk assessment scenarios used in the present study, will produce an upper bound excess cancer risk of  $1 \times 10^{-5}$  for consumers of fish. Half of the white croaker population in the bay can be expected to contain PCB concentrations that exceed the maximum acceptable daily intake (i.e.,  $H \geq 1$ ) for bay fish consumers considered in the risk assessment scenario.

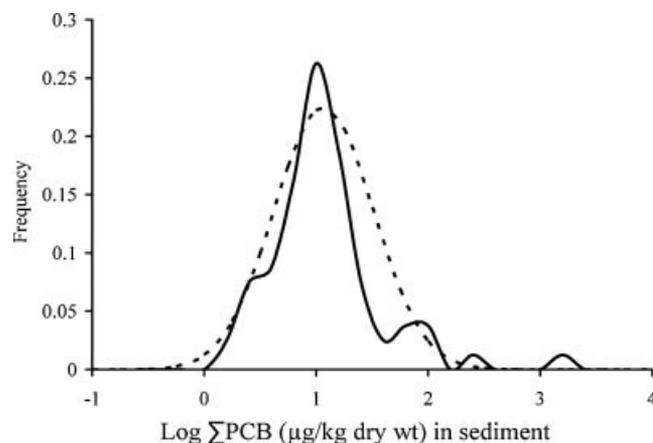


Fig. 5. Distributions of the total combined PCB congener ( $\Sigma$ PCB) concentrations in sediments of San Francisco Bay, California, USA. Solid line represents actual distribution based on 1,284 sediment concentration data collected in San Francisco Bay between 1999 and 2001. Dashed line represents the distribution used in the model application.

#### Model application to derive sediment target levels

Table 3 illustrates the results of the calculations conducted to explore possible target concentrations for PCB concentrations in the sediments that meet various human health and ecological risk criteria. The geometric mean  $\Sigma$ PCB concentration in the sediments that causes a geometric mean concentration in cormorant eggs equal to the LOAEL is approximately 31  $\mu$ g/kg dry wt, i.e., substantially greater than the current geometric mean  $\Sigma$ PCB concentration at the time of the study of 11.6  $\mu$ g/kg dry wt. However, if only 5% of the eggs are to contain concentrations equal to or below the LOAEL, a geometric mean concentration less than 12  $\mu$ g/kg dry wt is required. Bay-wide geometric mean PCB concentrations in sediments of 5.9 and 9.5  $\mu$ g/kg dry wt are expected to cause geometric mean concentrations equal to the TEC in adult male and female harbor seals, respectively. Geometric mean concentrations less than 0.58 and 1.5  $\mu$ g/kg dry wt are required to cause 95% of the male and female harbor seals in the bay to fall below the TEC. It is important to stress that, in the calculation of the 5% exceedence rate of threshold effect concentrations, we have used the expected bay-wide distributions calculated with the help of past data. Remediation can produce significant changes in bay-wide PCB concentration distributions. These changes can affect the magnitude of the

Table 2. The mean model bias for specific congeners ( $MB$ ) and for the combined total PCB congener ( $\Sigma$ PCBs) concentrations ( $MB^*$ ), 95% confidence intervals (95% CI), number of comparisons ( $n$ ), and logarithmic equivalents, i.e.,  $\log MB$  and  $\log MB^*$  and their standard deviations (SD), for several species of San Francisco Bay, California, USA

Species	Name	$MB$ ( $n$ ) 95% CI <sup>a</sup>	$\log MB$ (SD)	$MB^*$ ( $n$ ) 95% CI <sup>a</sup>	$\log MB^*$ (SD)
California mussel	<i>Mytilus californianus</i>	1.33 (32) 0.37–4.78	0.12 (0.28)	1.05 (13) 0.31–3.52	0.02 (0.25)
Pacific oyster	<i>Crassostrea gigas</i>	1.34 (32) 0.37–4.86	0.13 (0.29)	1.05 (9) 0.32–3.47	0.02 (0.23)
Shiner surfperch	<i>Cymatogaster aggregate</i>	1.00 (38) 0.27–3.74	0.00 (0.29)	0.75 (18) 0.23–2.43	-0.13 (0.24)
Jack smelt	<i>Atherinopsis californiensis</i>	1.30 (35) 0.43–3.94	0.12 (0.24)	1.05 (15) 0.27–4.07	0.02 (0.28)
White croaker	<i>Genyonemus lineatus</i>	1.31 (38) 0.33–5.18	0.12 (0.31)	0.93 (8) 0.35–2.47	-0.04 (0.21)
Cormorant egg	<i>Phalacrocorax auritus</i>	1.33 (38) 0.39–4.50	0.12 (0.27)	0.79 (8) 0.31–2.04	-0.10 (0.18)
Male harbor seal	<i>Phoca vitulina</i>	1.51 (28) 0.31–7.43	0.18 (0.35)	0.95 (4) 0.09–9.69	-0.02 (0.36)
Female harbor seal	<i>Phoca vitulina</i>	0.96 (28) 0.17–5.38	-0.02 (0.38)	0.64 (2) 0.10–4.02	-0.19 (0.19)

<sup>a</sup>95% confidence interval (CI) = antilog ( $\log MB \pm [t_{v,0.05} \times \text{standard deviation}]$ ).

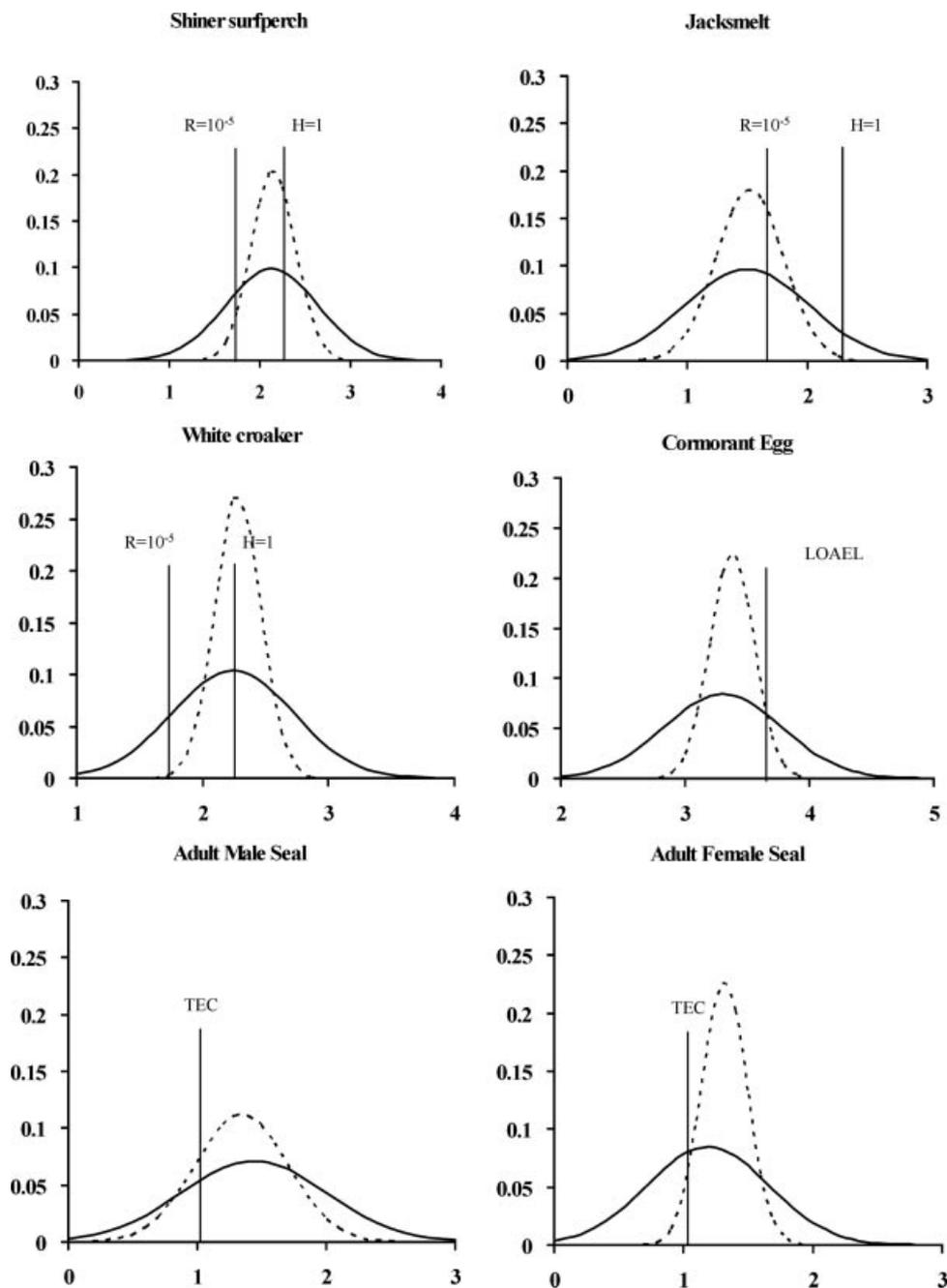


Fig. 6. Normal probability distributions for model calculated (solid line) and observed (dashed line) total combined PCB congener ( $\sum\text{PCB}$ ) concentrations in San Francisco Bay, California, USA, fish and cormorant eggs (in  $\mu\text{g}/\text{kg}$  wet wt) and in adult male and female harbor seals (in  $\text{mg}/\text{kg}$  lipid) for the period between 1999 and 2001. Human consumption cancer risk end point  $R$  of  $10^{-5}$ , human health hazard index  $H$  of 1.0, lowest-observed-adverse effect level (LOAEL) of  $5 \mu\text{g}/\text{g}$  wet wt body mass for cormorants, and threshold effect concentration (TEC) of  $11 \text{ mg}/\text{kg}$  lipid in harbor seals.

95% CIs. For example, when remediation involves PCB hot spots in the bay, the after-remediation 95% CIs of bay-wide PCB sediment concentration distributions can be expected to be somewhat narrower than the before-remediation distributions. This implies that current estimates of geometric mean concentrations associated with the 5% exceedence of threshold effect concentrations may somewhat overestimate the extent of the required concentration reduction. The scenarios used for human health risk assessment indicate that geometric mean

PCB concentrations in the sediments equal to or less than  $3.8 \mu\text{g}/\text{kg}$  dry wt are required for the consumption of white croaker at the assumed consumption rate to produce a  $10^{-5}$  upper bound for human lifetime cancer risk. The selected human health and ecological risk criteria are subjects of debate and judgment dependent on ecological and human health objectives and the state of science; therefore, we have constructed the model such that new criteria for  $C_B$  can be easily introduced in Equation 6.

Table 3. San Francisco Bay, California, USA, geometric mean target concentrations (in  $\mu\text{g}/\text{kg}$  dry wt) of combined total PCB congeners ( $\sum\text{PCBs}$ ) in sediment expected to meet various human health and ecological criteria: no-observed-adverse effect level (NOAEL), lowest-observed-adverse effect level (LOAEL), and threshold effect concentration (TEC)

Criterion	Organism	$\sum\text{PCB}$
Geometric mean upper bound excess human lifetime cancer risk of $10^{-5}$ among bay fish consumers	Shiner surfperch	4.3
Geometric mean human health hazard ( $H = 1$ )	Shiner surfperch	17
Geometric mean upper bound excess human lifetime cancer risk of $10^{-5}$ among bay fish consumers	Jack smelt	18
Geometric mean human health hazard ( $H = 1$ )	Jack smelt	73
Geometric mean upper bound excess human lifetime cancer risk of $10^{-5}$ among bay fish consumers	White croaker	3.2
Geometric mean human health hazard ( $H = 1$ )	White croaker	14
Geometric mean concentration equal to the LOAEL	Cormorant egg	24
5% of eggs exceed the LOAEL	Cormorant egg	14
Geometric mean concentration equal to the TEC (11,000 $\mu\text{g}/\text{kg}$ lipid)	Male harbor seal	4.6
5% of animals exceed the TEC (11,000 $\mu\text{g}/\text{kg}$ lipid)	Male harbor seal	1.6
Geometric mean concentration equal to the TEC (11,000 $\mu\text{g}/\text{kg}$ lipid)	Female harbor seal	6.2
5% of animals exceed the TEC (11,000 $\mu\text{g}/\text{kg}$ lipid)	Female harbor seal	3.6

### SUPPLEMENTAL DATA

Food web bioaccumulation model for polychlorinated biphenyls in San Francisco Bay, California, USA. (1,818 KB DOC)

**Acknowledgement**—The authors acknowledge the Clean Estuary Partnership (CEP) for their help and insights throughout the completion of the study as well as their financial support of the study. Many individuals were crucial to the success of the present study. They are acknowledged in the supporting information.

### REFERENCES

- Gunther AJ, Salop P, Bell D, Feng A, Wiegel J, Wood R. 2001. Initial characterization of PCB, mercury, and PAH concentration in the drainages of Western Alameda County, CA. Alameda Countywide Clean Water Program, Hayward, CA, USA, p 45.
- Kinetic Laboratories. 2002. Joint stormwater agency project to study urban sources of mercury and PCBs. Kinetic Laboratories, Santa Cruz, CA, USA.
- Yee D, Leatherbarrow J, Davis JA. 2001. South bay/fairfield-suisun trace organic contaminants in effluent study. San Francisco Estuary Institute, Oakland, CA, USA.
- Yee D, Leatherbarrow J, Davis JA. 2002. Bacwa polychlorinated biphenyls in municipal effluent wastewater study. San Francisco Estuary Institute, Oakland, CA, USA.
- Tsai P, Hoenicke R, Yee D, Bamford HA, Baker JE. 2002. Atmospheric concentrations and fluxes of organic compounds in the northern San Francisco estuary. *Environ Sci Technol* 36:4741–4747.
- State Water Resources Control Board. 2000. California 305(b) report on water quality. Prepared as required by The Federal Clean Water Act section 305(b). Sacramento, CA, USA.
- Davis JA. 2004. The long term fate of PCBs in San Francisco Bay. *Environ Toxicol Chem* 23:2396–2409.
- Arnot JA, Gobas FAPC. 2004. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ Toxicol Chem* 23: 2343–2355.
- San Francisco Estuary Institute. 1999. 1997 Annual report: San Francisco estuary regional monitoring program for trace substances. San Francisco Estuary Institute, Richmond, CA, USA.
- Boon JP, Reijnders PJH, Dols J, Wensvoort P, Hillebrand MTJ. 1987. The kinetics of individual polychlorinated biphenyl congeners in female harbor seals (*Phoca vitulina*), with evidence for structure-related metabolism. *Aquat Toxicol* 10:307–324.
- Boon JP, Van der Meer J, Allchin CR, Law RJ, Klungsoyr J, Leonards PEG, Spliid H, Storr-Hansen E, Mckenzie C, Wells DE. 1997. Concentration-dependent changes of PCB patterns in fish-eating mammals: Structural evidence for induction of cytochrome p450. *Arch Environ Contam Toxicol* 33:298–311.
- Xie WH, Shiu WY, Mackay D. 1997. A review of the effect of salts on the solubility of organic compounds in seawater. *Mar Environ Res* 44:429–444.
- Davis JA, Greenfield BK, Ross J, Crane D, Ichikawa G, Negrey J, Spautz H, Nur N. 2004. Cisnet technical report: Contaminant accumulation in eggs of double-crested cormorants and song sparrows in San Pablo Bay. Contribution 412. San Francisco Estuary Institute Oakland, CA, USA, p 21.
- Kannan K, Blankenship AL, Jones PD, Giesy JP. 2000. Toxicity reference values for the toxic effects of polychlorinated biphenyls to aquatic mammals. *Hum Ecol Risk Assess* 6:181–201.
- Brouwer A, Reijnders PJH, Koeman JH. 1989. Polychlorinated biphenyl (PCB)-contaminated fish induces vitamin a and thyroid hormone deficiency in the common seal (*Phoca vitulina richardsi*). *Aquat Toxicol* 15:99–106.
- Hoffman DJ, Rice CP, Kubiak TJ. 1996. PCBs and dioxins in birds. In Beyer WN, Heinz GH, Redmon-Norwood AW, eds, *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations*, Lewis, Boca Raton, FL, USA, pp 165–207.
- Kubiak TJ, Harris HJ, Smith LM, Schwartz TR, Stalling DL, Trick JA, Sileo L, Docherty DE, Erdman TC. 1989. Microcontaminants and reproductive impairment of the Forster's tern on Green Bay, Lake Michigan—1983. *Arch Environ Contam Toxicol* 18:706–727.
- Hoffman DJ, Rattner BA, Sileo L, Docherty D, Kubiak TJ. 1987. Embryotoxicity, teratogenicity, and aryl hydrocarbon hydroxylase activity in Forster's terns on Green Bay, Lake Michigan. *Environ Res* 42:176–184.
- Tillitt DE, Kubiak TJ, Ankley GT, Giesy JP. 1993. Dioxin-like potency in Forster's tern eggs from Green Bay, Lake Michigan, North America. *Chemosphere* 26:2079–2084.