

# Draft Report

## A Forecast Model of Long-Term PCB Fate in San Francisco Bay

John J. Oram and Jay A. Davis  
San Francisco Estuary Institute, Oakland, CA

January 2008

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## Executive Summary

PCBs are currently a high regulatory priority in San Francisco Bay and the subject of a TMDL. In work funded by the Regional Monitoring Program for Water Quality in San Francisco Estuary (RMP), a multi-box mass budget model was developed to improve understanding of the long-term fate of PCBs in San Francisco Bay. The model builds upon a previously developed one-box model of PCB fate and USGS salinity and sediment transport models. The Bay is represented in the horizontal by 50 boxes, each with two vertical layers representing the shallow Bay margins and the deep channels. The PCB model accounts in a spatially explicit manner for external inputs of PCBs from the various major pathways: runoff from the Central valley via the Sacramento-San Joaquin River Delta, runoff from local watersheds, atmospheric deposition, and municipal wastewater effluent. A detailed description of model development, including relevant equations and summary of calibration efforts, can be found in Oram *et al.* (2008).

In this study, the multi-box model was configured to estimate plausible future trajectories of PCB impairment over the next 100 years under various loading scenarios that conceptually span the range of conditions from no action to management actions that reduce PCB loading from specific pathways. Significant variation in predicted PCB concentrations was observed among Bay segments for all forecast scenarios.

Under the no action forecast scenario, half-lives of PCB concentrations in surface sediments ranged from ~40 years in Suisun Bay to ~85 years in San Pablo Bay and Central Bay. South Bay and Lower South Bay exhibited half-lives of approximately 45 to 50 years. Half-lives were found to be controlled by a combination of external loads, sedimentation, the vertical profile of PCBs in sediment, and exchange from neighboring segments. The relative importance of these processes varied by segment.

Reduction of PCB loads from local watersheds caused notable differences in the recovery of the Bay. Reducing loads from 20 kg/yr to 10 kg/yr decreased the half-life of San Pablo Bay to ~65 years. South Bay and Lower South Bay half-lives were reduced to

~35 years. Completely stopping all PCB loads from local watersheds reduced the half-life of San Pablo Bay to ~55 years and the half-life of Lower South Bay to ~15 years. Reduction of PCB loads from the Delta caused only minor differences in the recovery of the Bay, with effects limited to the northern Estuary (Suisun Bay and San Pablo Bay). Reduction of PCB loads from wastewater effluent caused no notable change in PCB recovery.

Sensitivity analysis indicated that model predictions were highly sensitive to the vertical profile of PCBs in sediment, the initial concentration of PCBs in sediment, sedimentation, load attenuation, in-Bay degradation, and partitioning. Considerable uncertainties are associated with estimating each of these input parameters.

Predicted effects of management actions on forecast PCB concentrations in the Bay were highly dependent on the vertical profile of PCBs in sediment. Profiles with considerable subsurface PCB mass exhibited less distinct decreases in recovery half-lives due to load reductions than profiles with less subsurface mass. Similarly, decreases in recovery half-lives due to management actions were less pronounced when the model was initialized with higher PCB concentrations in surface sediments.

## 1. Introduction

The development of Total Maximum Daily Loads (TMDLs) for priority contaminants is presently the focus of water quality management activities in San Francisco Bay (Mumley and Looker, 2004). A TMDL is currently being developed to accelerate the recovery of the Bay from PCB contamination (SFRWQCB, 2007). At present, PCB concentrations in some Bay sport fish are more than an order of magnitude above the threshold of concern for human health (Davis *et al.*, 2006). These PCB concentrations were one of the primary causes, along with mercury, of an advisory for sport fish consumption in the Bay. Reducing PCB concentrations in sport fish so that the advisory is no longer necessary is the principal goal of the PCB TMDL.

The Regional Monitoring Program for Water Quality in San Francisco Estuary (RMP) was established to provide the scientific information needed to support water quality management. The information needs of managers are articulated in the objectives and management questions that guide the RMP. One objective of the RMP is to project future contaminant status and trends based on current understanding of ecosystem processes and human activities. This report describes a significant step in development of a tool to address this objective as it relates to PCBs in San Francisco Bay: a multi-box forecast model.

## 2. Methods

### ***Model Overview***

A multi-box PCB model for San Francisco Bay (Figure 1) was initially developed by Leatherbarrow *et al.* (2005; Version 1.0). Estimates of historic PCB trends and preliminary forecasts of future trends were made. A number of iterations of the multi-box model have since been developed, with each iteration aimed at improving the dynamics of both sediment and PCB transport.

The latest iteration (Version 2.1) was documented by Oram *et al.* (2008) and focused on improving description of historic (1940-2002) PCB trends in the Bay. After initial development, the PCB model was calibrated to observed PCB concentrations in water and sediment. Despite uncertainties in historical PCB load estimates and influential parameters, the model was found to reasonably simulate current patterns of PCBs in the Bay. Extensive uncertainty analyses indicated the certainty of model predictions was approximately  $\pm 100\%$ . Detailed descriptions of model equations and input parameters, calibration and validation efforts, and uncertainty analyses are included in Oram *et al.* (2008).

### ***Forecasts of Key Input Parameters***

The ultimate goal in developing the multi-box model is to forecast PCB concentrations in water and sediment over the next 100 years. Forecast predictions require estimates of future trends in processes that affect PCB transport, fate, and storage within the sediments. For several important processes, especially future PCB loading, the data needed for accurate estimation of trends are not available.

#### *Estimation of Future Physical Forcings*

Forecasting runoff to the Bay for the next 100 years is a considerable challenge (Peterson *et al.*, 1995), especially as the Bay and its watershed (encompassing 40% of the surface area of California) are subject to the regional effects of global climate change (Knowles and Cayan, 2002), the future trends of which are uncertain and highly debated. Furthermore, the Bay is heavily influenced by freshwater diversions for agricultural, municipal, industrial, and environmental demands that are likely to change over the next century. It is therefore necessary to model the Estuary as a component of the global climate system (Peterson *et al.*, 1995). A recent study by Knowles and Cayan (2002) implemented this holistic approach and examined the potential effects of global warming on the Bay and its watershed. Projected temperature anomalies from a global climate model were incorporated into a Bay-Delta watershed model to estimate future changes in



total watershed outflow from the Delta into the Bay (Delta outflow). The resulting Delta outflow hydrographs for water years 2002 and 2090 illustrate the increase in pre-April runoff and decreased snowmelt-driven runoff in later months in 2090 compared to 2002 (Figure 2). These forecast outflow data were ultimately used by Knowles and Cayan (2002) to drive the same model of Bay salinity used in this study to investigate potential changes in salinity patterns.

In this study, inclusion of the potential effects of global climate change on the long-term fate of PCBs in the Bay was achieved by forcing the model with the Delta outflow results of Knowles and Cayan (2002). Peterson *et al.* (1995) found that Delta outflow explains 86% of the observed variability in Estuary salinity. It is therefore assumed that by including predicted Delta outflow, the model captures roughly the same percent of the variability in predicted salinity fields. A comparison of predicted salinity fields computed by this version of the model correlate well with the salinity predictions obtained by Knowles and Cayan (2002) (not shown).

Other physical forcings (wind, precipitation, evaporation, local tributary flows, and ocean salinity) were based on a subset of the time series used to force the hindcast model (see Oram and Davis, 2007 for detailed description of these forcings). Data from 1970 to 2000 were recycled to create a 100-year time series of input data to force the forecast model. The major assumption in using recycled time series is that the next 100 years will be similar to the last 30 years in terms of wind, precipitation, evaporation, local tributary flows, and ocean salinity. Tidal elevation at the mouth of San Francisco Bay was estimated using the Xtide tidal prediction package (Flater, 1998). Sea level rise was assumed to continue into the future at a rate of 3 mm/yr, consistent with the rate used for the hindcast model (Oram *et al.*, 2008). Likewise, net sedimentation was assumed to continue into the future at rates similar to those of the hindcast model (Figure 3).

*Estimation of Future PCB Loads*

Predicted daily PCB loads over the next 100 years were developed with several assumptions: (1) Loads from wastewater treatment plants were assumed to remain constant at their water year 2000 values. (2) Loads from all other sources (atmospheric deposition, local tributaries, Delta outflow) were assumed to attenuate from initial values. (3) The rating curves developed to relate SSC to tributary flow were assumed to be applicable to forecast scenarios.

In this study, attenuation is applied as a first-order decay process (default half-life=56 yrs) to PCB loads from all terrestrial source pathways entering the Bay. Attenuation serves as a parameterization of watershed processes that reduce the transport of PCBs to the Bay. Even with no further management action in our watersheds, loads can be expected to attenuate (decline) due to several factors, including:

- degradation and volatilization of PCBs in watershed soils and sediments;
- reduced emissions due to existing management efforts (e.g., controls on PCB release, hotspot cleanup action);
- erosion and transport of less highly contaminated material (the most highly contaminated soil and sediment deposits were likely eroded and transported closer to the era of peak emissions to the environment).

Very little information on PCB load attenuation is available. A few authors have made attempts to estimate attenuation rates of persistent organic contaminants in the terrestrial environment using a mass balance approach (e.g. Wania, 1999; Sweetman and Jones, 2000; Sinkkonen and Paasivirta, 2000; Ockenden *et al.*, 2003), with best estimates of half-lives for PCBs ranging from years to tens of years and even hundreds of years. Ockenden *et al.* (2003) found the bulk of the PCB soil inventory is still close to source locations, either in urban areas (within a few km of their site of use) or in rural areas (within tens to hundreds of km of their source site). Ockenden *et al.* (2003) further estimated that the bulk of PCBs manufactured and used (perhaps > 70%) are still

associated with diffusive source material that has not yet entered the environmental pool. Similarly, Sweetman and Jones (2000) suggest that the air and soil in the U.K. are close to steady-state conditions, indicating that soil inventories will remain high.

In the hindcast application of the multi-box model, estimates of historic emissions trends by Breivik *et al.* (2002) were used to estimate historic PCB loads to the Bay. It could be argued that an attenuation rate consistent with the sharp decline in the estimated emissions of Breivik *et al.* (2002) after 1990 (half-life of approximately 5-10 years) should be applied to future loads. However, the emissions estimates of Breivik *et al.* (2002), and hence the historic loads to the Bay, are primarily due to the manufacture and use of PCBs whereas the future loads are a result of PCBs in environmental pools, mostly soil-associated PCBs which Sweetman and Jones (2000) and Hung *et al.* (2001) suggest will remain high in source and remote regions. Furthermore, Breivik *et al.* (2002) used natural degradation (similar to what is termed attenuation here) half-lives of PCBs in soils ranging from 2.3-23 years in their emissions model. These time-scales were applied to the top 0.5 cm of dry soils where photolysis and oxidation are significant factors. Harner *et al.* (2001) found that burial a few millimeters below the surface could effectively occlude persistent organic pollutants from soil-air exchange (photolysis and oxidation also decrease with depth). Such barriers to mass transfer and degradation would have the effect of decreasing the attenuation of buried contaminants. While the emission estimates of Breivik *et al.* (2002) appear to be a good index of loads during the period of high use and emissions, the rapid decline in emissions to the air they predict for the 1990s is probably not a good predictor of the rate of decline in transport of particle-associated PCBs out of the Bay watersheds for either the 1990s or for the next 100 years.

### ***Sensitivity Analysis***

The sensitivity of model results to variations in individual model input parameters was tested to identify key parameters governing future PCB fate and to build confidence in model estimates (i.e., test internal mechanics of the model). The sensitivity (S) of each model parameter was determined as:

$$S = \frac{(O - O_o)}{O_o} \div \frac{(P - P_o)}{P_o}, \quad (\text{Equation 1})$$

where O is the perturbed model outcome (result),  $O_o$  is the original or ‘baseline’ model outcome, P is the perturbed model input parameter, and  $P_o$  is the best estimate of the given input parameter. Expressing model sensitivity in this way (i.e., percent change in model outcome normalized to percent change in model input parameter) allows the individual input parameters to be ranked relative to one another.

A number of model results were used to assess model sensitivity: SSC and net sedimentation were used to determine the sensitivity of the sediment model; PCB concentrations in the water column and in surface sediments and the fluxes of PCBs in the various loss pathways were used to determine the sensitivity of the PCB model. The range over which each model parameter was varied was a function of the natural variability and/or uncertainty of that individual parameter. Attempts were made to use realistic ranges for each parameter based on available information. A complete list of the model parameters tested and their respective ranges is presented in Table 1. The average model result for model year 100 was used for all sensitivity calculations.

### **3. Results and Discussion**

#### ***Confidence in the Model***

A number of findings indicate that the multi-box model reasonably captures the key processes governing PCB fate in the Bay. These findings, detailed below, help bolster confidence in model predictions.

### *Validation*

Oram *et al.* (2008) presented a detailed validation of the hindcast model. Model predicted salinity and SSC were found to be in close agreement with observations. The fact that the model was able to reproduce SSC was particularly encouraging given that the sediment model was calibrated by Lionberger and Schoellhamer (2007) to long-term net sedimentation, leaving SSC as a free model parameter. The SSC comparison was thus a true, independent, validation of model performance.

The reproduction of the current PCB concentrations in surface sediments did not serve as a true validation of the model, as these data were used during model calibration. Thus, the comparison of the vertical profile of PCBs in San Pablo Bay sediments to observations served as the only independent validation of the PCB model. Oram *et al.* (2008) found the vertical profile to be in close agreement with observations, which suggested that the parameterizations of PCB loads and internal processes were reasonable.

### *Sensitivity to Variations in Input Parameters*

The sensitivity of model results to variations in individual model input parameters was tested to identify key parameters governing future PCB fate and to build confidence in model estimates. Table 2 summarizes the most sensitive model parameters as determined by changes in surface sediment PCB concentrations; sensitivity results for all model parameters and model results (e.g., PCBs in water, SSC, net sedimentation) are included in the Appendix. It must be noted that due to the non-linear nature of many modeled processes and the complex interactions of the various processes, the sensitivities determined here only apply to the ranges over which they were calculated. For example, from Table 2 it might be assumed that a 100% increase in water temperature would cause a roughly five-fold decrease in PCB concentrations of surface sediments in Lower South Bay ( $S=-4.76$ ). Such an assumption would be a misinterpretation of the sensitivity analyses. The correct interpretation is that a 1% increase in water temperature (from 288

deg K to 291 deg K) elicited a 4.76% decrease in the PCB concentration of surface sediments in Lower South Bay.

### Water Temperature

Surprisingly, water temperature was the most sensitive input parameter. Water temperature affects the rate at which PCBs volatilize to the atmosphere (Equations 9-15 in Oram *et al.*, 2008) and thus affects the final concentration of PCBs in both water and sediment. PCB concentrations in surface sediment were negatively correlated with water temperature, indicating that an increase in water temperature resulted in a decrease in PCB concentrations in sediments. This negative, or inverse, correlation was expected; warmer waters exhibit increased PCB volatilization rates and thus less PCB mass in water and sediment. Model results were slightly more sensitive to a decrease in water temperature than to an increase, highlighting the non-linear relationship between water temperature and volatilization. Fortunately, the temperature of the Bay is well-characterized; temperature is monitored at locations throughout the Bay at both continuous and discrete intervals. Seasonally averaged Bay water temperatures generally range from 11 to 19 degrees Celsius with a long-term mean of 15.4 degrees Celsius (Figure 4). The abundance of temperature observations and the cyclical nature of Bay water temperature minimize any associated model uncertainties.

### Initial PCB Concentration

Model results were also particularly sensitive to the initial concentration of PCBs in water and sediment. Modeled PCB concentrations in surface sediment (and water) exhibited a positive relationship to PCB concentrations at the time of model initialization (Table 2). Sensitivities were the same for increased initial concentrations as they were for decreased initial concentrations. Initial concentrations were varied  $\pm 50\%$  based on the variability in estimates of average PCB concentrations in sediment determined by RMP and NOAA-EMAP (see Figure 15 in Oram *et al.*, 2008). Model results were obviously sensitive to the initial concentration of PCBs in water and sediment. However,

the effects of this sensitivity on model forecasts are relatively minor. The multi-box model was developed to represent segment-averaged PCB concentrations, values that are well-quantified by ongoing monitoring efforts. In particular, the random sampling design employed by the RMP since 2002 is specifically designed to quantify average contaminant concentrations on a segment basis. Accurate and reliable estimates of current PCB concentrations in water and sediment are thus available, and were used to validate the hindcast model and initialize the forecast model.

It should be noted that the same scaling ( $\pm 50\%$ ) was applied to buried PCBs without altering the shape of the vertical profile. The true vertical profile of PCBs buried in Bay sediments is currently not well known. Effects of the vertical profile on forecast estimates are discussed below.

#### Erosivity, Wind-Current Shear, and Particle Settling

PCBs are highly particle-associated. Their fate in aquatic systems is therefore largely controlled by sediment transport processes. Three parameters in the sediment module of the multi-box model govern the major sediment transport processes:

- 1) erosivity describes the erosion potential of bed sediment (a high erosivity indicates an easily erodible sediment bed),
- 2) a wind-current shear parameter describes the relative effectiveness of wind and current shears to erode bed sediment, and
- 3) the particle settling velocity dictates the rate at which suspended sediments are deposited onto the sediment bed.

Not surprisingly, modeled PCB concentrations in water and sediment are sensitive to these three parameters. In general, an increase in erosion, whether by increasing erosivity or increasing wind-current shear, caused a decrease in predicted PCB concentrations in surface sediments ( $S < 0$ ; Table 2). These results were expected given that the vertical profiles of PCBs in erosional segments (all Bay segments except Lower

South Bay) were assumed to decrease with depth. Increased erosion thus exposes less-contaminated sediments. Similarly, increased deposition via increased particle settling caused a decrease in predicted PCB concentrations in surface sediments ( $S < 0$ ). These results were likewise expected given that, due to attenuation of watershed loads, less-contaminated sediments are deposited onto the bed surface. A few cases deviate from these explanations (e.g., Suisun Bay in the case of wind-current shear and Suisun and Central Bays in the case of particle settling). These cases have unique combinations of sedimentation and vertical profiles causing them to deviate from the other segments. In Central Bay, for example, an increase in particle settling prevents erosion into cleaner sediments and thus increases PCB concentrations in surface sediments (the sensitivity of particle settling in Central Bay is therefore positive;  $S > 0$ ).

The processes controlled by these three parameters are difficult to measure in the field and the applicability of lab studies is questionable. Thus, the values of each of these parameters were obtained through calibration of the sediment transport model (Lionberger and Schoellhamer, 2007). It is therefore prudent to specifically determine the sensitivity of the sediment model to changes in these parameters. Results are provided in Table 3. Briefly, the sediment model is slightly more sensitive to changes in erosivity, wind-current shear, and particle settling than is the PCB model. More importantly, the sediment model responds to parameter changes as one would expect – increased erosivity causes increased erosion and increased particle settling causes increased deposition. These observations lend confidence in the internal mechanics of the sediment, and hence the PCB, model.

### Attenuation and Degradation

Attenuation and degradation are critical parameters governing PCB fate in the Bay. Forecast results are sensitive to these parameters individually and in combination (Table 2). An increase (or decrease) in the half-life of either parameter resulted in a increase (or decrease) in PCB concentration in water and sediment.



The Lower South Bay segment was most sensitive to changes in attenuation. This segment is the only depositional Bay segment, and as such, PCB concentrations in surface sediments are more dependent on inputs from adjacent watersheds. Suisun Bay was also relatively sensitive to attenuation. Suisun is the eastern-most Bay segment and directly receives flows from the Sacramento and San Joaquin Rivers (via the Delta). Though generally erosional, Suisun Bay receives episodic inputs of PCBs from the Delta. Attenuation directly affects the magnitude of these loads, so it follows that the receiving body (Suisun) would exhibit sensitivity to attenuation. San Pablo Bay and Central Bay were the most sensitive to changes in degradation, likely a function of their slow erosion rates relative to other Bay segments. All Bay segments were more sensitive to combined changes in attenuation and degradation than they were to changes in each parameter individually. This is an expected result given that attenuation and degradation essentially control the same processes related to the breakdown of PCBs. Their only difference is that attenuation acts to decrease the watershed PCB inventory and transport to the Bay and degradation acts to decrease the Bay PCB inventory.

As mentioned earlier, little information is available regarding attenuation of PCBs, and degradation half-lives reported in the literature span many orders of magnitude. Given the sensitivity of model results to these parameters it would prudent to investigate potential field and/or lab methods to improve estimates of these parameters.

#### Koc

The partitioning of PCBs between water and sediment was a moderately influential process. Model predictions for surface sediment PCB concentrations were positively correlated to Koc, indicating that an increase (or decrease) in Koc caused an increase (or decrease) in PCB concentrations in surface sediments. From the perspective of total PCBs in the water column (i.e., sum of dissolved and particulate fractions), Koc was not a very sensitive input parameter. This is because Koc exerts its influence on the water column by affecting the competing processes of particle settling and volatilization as mechanisms for removal of PCBs. An increase in Koc increases the efficiency of

particle settling as the key process for PCB removal from the water column; a decrease in  $K_{oc}$  increases the efficiency of volatilization as the key processes (volatilization was negatively related to  $K_{oc}$ ; not shown). As a result total water column PCB concentrations were generally unaffected by changes to  $K_{oc}$ .

Partitioning of PCBs is dependent on the quantity and quality of organic carbon in bed and suspended sediment. Given that these parameters are not spatially uniform (Oros and Ross, 2004), the multi-box model allows for regionally explicit PCB partitioning. Region specific  $K_{oc}$  values were determined during model calibration (see Oram *et al.*, 2008). The sensitivity of region-specific model results to changes in regionally-specific  $K_{oc}$  was assessed as a measure of the regional interdependence of model boxes. Results indicate that model sensitivity to  $K_{oc}$  was generally limited to the region in which the  $K_{oc}$  value was altered. Lower South Bay was the only exception, showing sensitivity to changes in South Bay partitioning.

#### Organic Carbon (OC) Content of Suspended Sediment

Similar to  $K_{oc}$ , this model parameter affects the degree to which PCBs partition between water and sediment and thus affects the relative rates of PCB removal from the water column by the competing processes of volatilization and particle settling. As one would expect, PCB settling and volatilization were sensitive to changes in the OC content of suspended sediments (not shown). An increase in the OC content of suspended sediment effectively increased the efficiency of particle settling as the major process removing PCBs from the water column. As a result, the PCB concentration of surface sediments was increased.

This version of the multi-box model uses a single value (0.03) for the OC content of suspended sediment. Oros and Ross (2004) documented the spatial patterns of OC content of bed sediment. It is reasonable to believe that the OC content of suspended sediment is likewise spatially variable. Future modeling efforts may consider

implementing a spatially explicit parameterization for the OC content of suspended sediment.

### Henry's Law Constant

South and Lower South Bays were the only segments that showed sensitivity to Henry's Law Constant (HLC). HLC is a key parameter in determining the rate of PCB volatilization from the water column (see Equations 9-15 in Oram and Davis, 2007). South and Lower South Bays were also highly sensitive to changes in water temperature, another key parameter in determining the rate of PCB volatilization. It seems that the geometry (surface area and depth) and the suspended sediment concentrations (the other key factors governing volatilization) in South and Lower South Bays are such that these Bay segments are sensitive to changes in any parameter affecting PCB volatilization.

### Magnitude and Spatial Distribution of PCB Loads

The multi-box model was generally insensitive to the magnitude of PCB loads from the Delta and moderately sensitive to the magnitude and spatial distribution of PCB loads from local watersheds. Sensitivity to the spatial distribution of PCB loads from local watersheds was assessed by randomly<sup>1</sup> creating four different loading scenarios. Figure 5 indicates the percent change in PCB loads on a Bay segment basis relative to the default model setup. The southern reach of the Bay (Central, South and Lower South Bays) was the most sensitive to changes in the spatial distribution of loads (Table 2). Central Bay was sensitive to an increase in local loads (scenario four) but not to decreases, indicating exchange from other Bay segments dominates Central Bay PCB concentrations. Lower South Bay was the most sensitive to changes in both the magnitude and spatial distribution of PCB loads. The sensitivity of Lower South Bay is

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<sup>1</sup> A random number generator was used to re-distribute loads between local watersheds. However, as Figure 5 indicates, the resulting re-distributed loads were not all that random.

due to either (or both) limited exchange with other segments or its depositional regime, which makes this segment more tightly correlated to recent inputs.

One caveat to consider when analyzing these results is that the sensitivity analyses were run in forecast mode. A considerable mass of PCBs is assumed to be present below the surface sediment layer. This assumption, combined with the notion that the Bay is largely erosional (only Lower South Bay is depositional) essentially decouples the forecast model from ongoing PCB inputs. Erosion exposes buried sediments, which are assumed to contain legacy PCBs, and limits the incorporation of ongoing PCB loads into the active sediment layer. Surface sediment PCBs, and in turn water column PCBs, are therefore controlled by the subsurface inventory. This finding is tested and discussed in more detail below.

### *Response to Different Extreme Scenarios*

#### Extreme Change in Delta Outflow

Ongoing conflicts over water in California make future freshwater flows from the Delta uncertain. In light of this uncertainty it was deemed prudent to assess how changes in Delta outflow might affect the recovery of the Bay from PCB impairment. For this assessment, model runs using three times (3x) and one-third (1/3x) Delta outflow were compared to the base forecast. For these scenarios only the magnitude of Delta flows was changed, not the temporal variability. Rating curves relating Delta outflow to SSC and SSC to PCBs remained the same (see Oram *et al.*, 2008 for rating curves).

Results indicated that effects of changes in Delta outflow on PCB concentrations in surface sediments were limited to the northern Estuary (Figure 6). It has previously been demonstrated that freshwater flows from the Delta exert significant controls on the salinity distribution of South San Francisco Bay (Imberger *et al.*, 1977; Conomos, 1979). The results presented here suggest that freshwater flows from the northern Estuary are

less significant in determining the sediment transport patterns, and hence contaminant transport patterns, in South Bay.

For the northern reach of the Estuary (Suisun and San Pablo Bays), increased Delta outflow accelerated the recovery of PCBs in surface sediments (Figure 6). Conversely, decreased Delta outflow prolonged the recovery of surface sediments. These findings are consistent with the parameterizations of inputs from the Delta, which express sediment loads from the Delta as a logarithmic function of Delta outflow and PCB loads from the Delta as a logarithmic function of sediment loads (see Oram *et al.*, 2008). So while loads of sediments and PCBs are affected by changes in Delta outflow, they are relatively less affected than freshwater flows themselves. Ultimately, increased (or decreased) freshwater flows increase (or decrease) the hydraulic flushing of Suisun and San Pablo Bays, thereby accelerating (or slowing) the recovery of PCBs in surface sediments.

#### Barrel Spill – Instantaneous PCB Input

One question that arises when considering future scenarios is how the Bay would respond to an episodic input of a large quantity of PCBs. For example, how might the Bay be affected if an earthquake or some other incident caused PCBs stored in electrical equipment or building materials to be released into the environment? Examining the response of the model to this type of scenario also provides another means of evaluating the validity of the model. Model scenarios incorporating instantaneous inputs of PCBs from various watersheds were executed. Figure 7 illustrates the results of four such scenarios. For these scenarios, PCB mass (either 100 or 200 kg) was introduced into the Bay via either Alameda Creek (South Bay) or Napa River (San Pablo Bay). The release of PCB mass was started on January 1, 2010 (year 10 in Figure 7) and continued for 30 days. Results indicate that PCB concentrations in surface sediments return to near background levels within 10 years. The generally erosional nature of the Bay effectively prevented the PCB mass from mixing into sediments, thereby preventing any longer-term

impact. However, one must consider how risks to human and wildlife health might be affected by these relatively short-term elevated PCB concentrations.

A rough calculation was performed to evaluate these estimates, using the scenario that introduced 200 kg of PCBs into South Bay (via Alameda Creek) as an example. The multi-box model estimates there are  $2.3 \times 10^{13}$  kg of sediment in the upper 10 cm of South Bay. If all 200 kg of PCBs were distributed equally over South Bay and incorporated into the top 10 cm of sediment, the resulting increase in PCB concentration would be 8.8 ng/g. This is consistent with the spike observed in South Bay in Figure 7. The agreement between these first-order calculations and model estimates helps bolster confidence that the model is capturing the key physical and chemical processes controlling PCB fate.

#### *The Aggregate Uncertainty of Model Predictions*

Extensive analyses were performed by Oram *et al.* (2008) to assess the aggregate uncertainty of model predictions resulting from uncertainties and variability in model input parameters. The uncertainty and/or variability of sediment- and PCB-related input parameters were represented by statistical distributions that express how each individual parameter may vary due to geographical location, time of year, PCB congener, sediment type, and other factors. The distributions were randomly sampled and the sampled values were used by the hindcast model to produce a distribution of model results. Analysis of the set of model simulations (10,000 simulations were made) revealed that the uncertainty of model predicted PCB concentrations in surface sediments was generally  $\pm 100\%$ . Other model outputs (e.g., PCBs concentrations in water, mass of sediment eroded) exhibited similar uncertainties. For this report, the uncertainty determined on the hindcast model is assumed to apply to the forecast model.

#### *Uncertainty of Important Input Parameters*

Sensitivity analysis indicated that model predictions were highly sensitive to the vertical profile of PCBs in sediment, the initial concentration of PCBs in sediment,

sedimentation, load attenuation, in-Bay degradation, and partitioning. Considerable uncertainties are associated with estimating each of these input parameters. Of these, the initial concentration of PCBs in surface sediments and the vertical profile of PCBs in sediment elicited the most considerable changes in model predictions and therefore merit special discussion.

#### PCB Concentrations in Surface Sediment

Forecast model results are known to be highly sensitive to the initial PCB concentration in sediment. However, as noted earlier, the ambient PCB concentration in Bay surface sediments is being well-characterized by ongoing RMP monitoring efforts. Thus, in terms of surface sediment PCB concentrations, the initial conditions of the forecast model are being defined with a high degree of confidence. Continued RMP monitoring will further refine estimates of this important parameter for each Bay segment.

Oram *et al.* (2008) used a combination of NOAA-EMAP and RMP field data to calibrate and validate the hindcast model to observed PCB concentrations in surface sediment. They acknowledged that the two data sets yielded different estimates of average PCB concentrations in surface sediments and gave plausible explanations for the differences. Higher concentrations from the NOAA-EMAP monitoring efforts were attributed to a greater number of samples being taken from more highly contaminated shallow Bay margins. The RMP data included a large number of samples from the deep Bay channels.

More recent RMP data suggest that current PCB concentrations in surface sediments are even lower than those reported by Oram *et al.* (2008) (SFEI, 2007). These more recent RMP data were used to initialize the forecast model. Given the sensitivity of model predictions to the initial PCB concentration, initializing the model with the most up-to-date estimates was thought to minimize the effects of that sensitivity and yield more accurate representations of Bay recovery.

### Vertical Profile of PCB Concentrations in Sediment

The vertical profile of PCBs in Bay sediment is not well-characterized. Furthermore, given the erosional nature of the Bay, it is conceivable that future conditions will be controlled by buried PCBs. In order to evaluate the influence of this parameter, the forecast model was initialized with five different vertical profiles (Figure 8). The vertical profile scenarios tested included:

- 1) the profile estimated by the hindcast model, which represents the base forecast scenario,
- 2) a profile in which subsurface concentrations decrease linearly from the surface,
- 3) a profile in which subsurface concentrations increase linearly from the surface,
- 4) a triangular profile in which subsurface concentrations increase to a depth of 50 cm and then decrease again, and
- 5) a uniform profile in which subsurface concentrations are equal to those at the surface.

For each scenario, the initial surface concentration remained unchanged.

The sensitivity of model results to changes in the vertical profile of PCBs in sediment was determined by analyzing the percent change in PCB concentrations of surface sediments at the end of each model run relative to the ending concentration predicted by the base forecast. Results indicate that each Bay segment is sensitive to changes in the vertical profile (Table 4), with the degree of sensitivity controlled by the shape of the vertical profile and the net change in bed elevation (i.e., the region of the profile exposed by erosion). The greatest change (93%) was observed in Suisun Bay under the ‘increasing profile’ scenario. In Suisun Bay the ‘base forecast’ and ‘increasing profile’ scenarios were considerably different (Figure 8). The smallest change was observed in Lower South Bay, which is the only depositional Bay segment.

Predicted PCB concentrations in surface sediment were more dependent on external loads than on the vertical profile of PCBs in sediment. Due to the strong



influence of the vertical profile on forecast predictions, and the large uncertainty surrounding this parameter, the sensitivity of model results to changes in external loads (from local watersheds and the Delta) was determined for each vertical profile scenario. This was done by analyzing the percent change in PCB concentrations of surface sediments at the end of each model run relative to the ending concentrations predicted by the default loading scenario. Results indicate that as the subsurface PCB inventory increases, the sensitivity to external load reductions decreases (Table 5). For example, the ‘increasing’ and ‘triangular’ profiles generally increase the subsurface inventory of PCBs at the time of model initialization relative to the base forecast (Figure 8). The percent changes in PCB concentrations of surface sediments resulting from load reductions are less for these two scenarios than they are for the base forecast (Table 5).

Due to the multidimensional nature of the vertical PCB profile in sediment, it was necessary to perform the above analyses using percent change as opposed to applying the sensitivity equation used to evaluate other model parameters (Equation 1). Consequently, it is not possible to directly rank the sensitivity of model results to changes in the vertical PCB profile relative to the sensitivities of other model parameters. However, a pseudo-ranking can be achieved by comparing the results in Table 4 to those for the initial concentration in surface sediments in Table 2. Sensitivity analysis revealed that the initial concentration of PCBs was a sensitive parameter for the forecast model. The sensitivity to initial PCB concentrations was determined by varying the initial PCB concentrations by  $\pm 50\%$ . Using Equation 1 to back-calculate the percent change in surface sediments, the results of Table 2 translate to percent changes of 20% for Suisun Bay, 29% for San Pablo Bay, 38% for Central Bay, 26% for South Bay, and 18% for Lower South Bay. Comparing these results to Table 4 indicates that vertical profiles that result in an increase in the subsurface PCB inventory (e.g., ‘increasing’ and ‘triangular’ profiles) cause a greater change in model predictions than do changes in the initial PCB concentration. Through this reasoning, the vertical profile of PCBs in sediment becomes the most influential input parameter for the forecast model. Compounding the importance of this conclusion is the fact that the actual vertical profile of PCBs in sediment is not well-characterized.

### *Summary of Confidence in the Model Predictions*

Results presented so far yielded valuable information regarding the internal workings of the multi-box model: Validation of the hindcast model by Oram *et al.* (2008), in terms of salinity, SSC, and PCBs was sound; the behavior of the forecast model in response to changes in input parameters was acceptable (model predictions responded as they conceptually should); the aggregate uncertainty of the model is known; and major uncertainties associated with the vertical profile of PCBs in sediment were acknowledged and evaluated. Each of these items lends confidence in model predictions and allows for forecast predictions to be evaluated with a measurable degree of certainty.

### ***Recovery Forecasts Under Different Management Scenarios***

#### *Base Forecast – No Action*

The base forecast scenario is intended to simulate the long-term fate of PCBs in the Bay given no reductions in PCB loads other than those due to natural attenuation. This scenario began with PCB loads from all pathways equal to their water year 2000 value, initial concentrations in water and sediment equal to 2006 RMP estimates, and vertical profiles of PCBs in sediment determined by the results of the hindcast simulation. External loads were assumed to attenuate with a half-life of 56 years, the current best estimate.

Segment-averaged PCB concentrations in surface sediments were estimated to decrease over the next century with half-lives ranging from ~40 years in Suisun Bay to ~85 years in San Pablo Bay and Central Bay (Figure 9). South Bay and Lower South Bay exhibited half-lives of approximately 45 to 50 years.

Half-lives were found to be controlled by a combination of external loads, sedimentation, the vertical profile of PCBs in sediment, and exchange from neighboring segments. The relative importance of these processes varied by segment. For example, the Lower South Bay is approximately three times as contaminated as Suisun Bay, yet they exhibited very similar recovery half-lives. PCB concentrations in surface sediments in the depositional Lower South Bay were controlled by load attenuation while surface concentrations in the erosional Suisun Bay were controlled by exposure of subsurface PCBs.

The longest half-life was estimated in Central Bay. Central Bay is the only Bay segment with a direct connection to the Pacific Ocean and is therefore the segment through which all PCB mass must pass before exiting the Bay. The recovery of Central Bay was therefore controlled not only by local processes but also by processes at play in other Bay segments. The cumulative effect results in a relatively long recovery half-life for Central Bay.

Predicted PCB concentrations in subsurface sediments yield insight into the processes governing PCB concentrations in surface sediments. Figure 10 shows PCB concentrations in 100 cm of sediment as predicted by the base forecast. Erosion was clearly responsible for exposing subsurface PCBs in all Bay segments except for the Lower South Bay. Fortunately, the considerable subsurface PCB inventory in the Lower South Bay was not exposed by erosion. Degradation dominated the reduction of subsurface PCB concentrations in Lower South Bay.

Given that the vertical profile of PCBs in sediment was found to be a highly sensitive model parameter it was necessary to evaluate how changes in the vertical profile might affect the natural recovery of the Bay. This was achieved by initializing the forecast model with different vertical profiles while keeping initial surface sediment PCB concentrations and external loads (and their attenuation) consistent with the base forecast.

Predicted PCB concentrations in surface sediments resulting from the various vertical profiles were considerably different from those of the base forecast (Figure 9). Recovery half-lives were most different in the erosional Bay segments when the vertical profile increased the subsurface PCB mass (e.g., ‘increasing’ and ‘triangular’ profiles). In these scenarios, recovery half-lives were generally greater than 100 years. The depositional Lower South Bay did not exhibit such a pronounced change in half-life - as indicated earlier, the Lower South Bay is predominantly controlled by attenuation of external loads.

The initial concentration of PCBs in surface sediments was likewise found to be an important model parameter. Thus, it was necessary to determine how changes in the initial surface concentrations affected Bay recovery. This analysis was achieved by initializing the forecast model with various initial concentrations while keeping the vertical profiles and external loads consistent with the base forecast.

In general, recovery half-lives were unaffected by changes in the initial concentrations of PCBs in surface sediments (Figure 11), consistent with a first-order kinetics model. The main, and somewhat obvious, finding is that higher initial concentrations take longer to recover to water quality objectives.

#### *Local Watershed (Urban Runoff) Load Reductions*

Reduction of PCB loads from local watersheds caused notable differences in the recovery of the Bay (Figure 12). Reducing loads from 20 kg/yr (base forecast) to 10 kg/yr, for example, decreased the half-life of San Pablo Bay from ~85 years to ~65 years. South Bay and Lower South Bay half-lives were reduced from ~45-50 years to ~35 years. Completely stopping all PCB loads from local watersheds reduced the half-life of San Pablo Bay to ~55 years. The recovery of half-life of Lower South Bay under this scenario was reduced to ~15 years.

Much less pronounced differences were forecast for Central Bay, if any at all. As discussed earlier, Central Bay is the Bay segment through which all PCB mass must pass before exiting the Bay to the ocean. Reduction of external loads therefore elicits a much smaller change in Central Bay surface sediment concentrations than it does other Bay segments.

The sensitivity of forecast PCB concentrations in surface sediments to changes in local watershed loads was not as distinct when the model was initialized with different vertical profiles (Table 5). Profiles with considerable subsurface PCB mass (e.g., ‘increasing’ or ‘triangular’ profiles) exhibited less distinct decreases in recovery half-lives due to reductions in local watershed loads than profiles with less subsurface mass (e.g., ‘declining’ or ‘uniform’ profiles). Similarly, decreases in recovery half-lives were less pronounced when the model was initialized with higher PCB concentrations in surface sediments (not shown).

#### *Delta Load Reductions*

Reduction of PCB loads from the Delta caused only minor differences in the recovery of the Bay (Figure 13). As was the case for changes in Delta outflow (i.e., freshwater flows), effects of reduced PCB loads from the Delta were limited to the northern Estuary (Suisun Bay and San Pablo Bay). The degree to which reduced PCB loads from the Delta affected forecast PCB concentrations in surface sediments was even less pronounced for vertical profiles with significant subsurface mass (e.g., ‘increasing’ and ‘triangular’ profiles) and for elevated initial PCB concentrations (not shown).

#### *Wastewater Effluent Load Reductions*

Reduction of PCB loads from wastewater effluents caused no detectable change in forecast PCB concentrations in surface sediments (Figure 14).

## ***Source and Loss Pathways***

A Bay-wide mass budget was constructed to account for the various pathways contributing to overall PCB inputs and losses in the forecast model (Table 6). Local watersheds were identified as delivering the vast majority (74%) of PCB mass to the Bay. Wastewater effluent and the Delta contributed only 13% and 10% of total PCBs loads respectively. Atmospheric deposition was a minor contributor to total PCB inputs (2%).

The notion of local watersheds delivering the majority of PCB loads to San Francisco Bay is not unexpected; Bay Area local watersheds are largely urban and/or industrial, land uses that are generally associated with elevated PCBs. Wastewater PCB loads of a similar magnitude to loads from the Delta, however, was more surprising. It must be noted, though, that modeled PCB loads from the Delta were subject to attenuation. Wastewater loads were not attenuated, under the assumption that wastewater treatment is unlikely to decrease effluent concentrations below current levels<sup>2</sup>. So while Delta loads were initially greater than wastewater loads, after 100 years attenuation decreased them to a point where the cumulative (100-year) PCB load from wastewater exceeded that from the Delta. While wastewater constituted a greater cumulative load, that load is relatively diffuse (distributed throughout the Bay) compared to the load from the Delta. Delta PCB loads therefore exerted greater control on PCB concentrations in the Bay than did wastewater loads (see Figure 13 and Figure 14 and previous discussion).

PCB losses were quantified for the base forecast and the four vertical profile scenarios. Outflow through the Golden Gate was the major loss pathway for all scenarios, accounting for 42-50% of total PCB losses (Table 6). Burial of PCBs below 100 cm of sediment (14-30%) and volatilization of PCBs to the atmosphere (19-25%) were the next most important loss pathways, the relative contribution of each being determined by the subsurface PCB mass. Burial was more important for scenarios with significant

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<sup>2</sup> Wastewater loads are likely to attenuate as residual PCBs in the sewage collection system and in the food supply dissipate. However, no conclusive information exists regarding the relative rate at which this load attenuation might occur.

subsurface PCB mass (e.g., ‘base forecast’, ‘increasing’, and ‘triangular’ profiles), while volatilization was more important for the ‘decreasing’ profile scenario. In-Bay degradation was a minor contributor to total PCB losses (9-10%).

### *Erosion of Buried PCBs*

A question that arises when assessing plausible future scenarios of PCB impairment is “What is the mass input of PCBs into surface sediments and the water column from erosion of buried sediment?” Or more appropriately, “How much subsurface PCBs will be exposed due to erosion into legacy deposits?” The answer depends on the degree of erosion and the subsurface PCB inventory.

Assuming, as observations and the sediment transport model suggest, that the Bay will continue to be net erosional into the future, the key driver becomes the subsurface PCB inventory. Table 7 presents forecast PCB fluxes to the surface sediments (top 5 cm) from buried sediments under the various vertical profiles used in previous analyses. Results are presented on a Bay-segment basis in order to help identify those segments with the potential to expose significant PCB mass.

PCB mass inputs due to erosion were smallest in Suisun Bay and Lower South Bay. Suisun Bay was forecast as erosional while Lower South Bay was forecast as depositional (Figure 3). Yet fluxes of PCBs from buried sediments were quite similar for the two segments of the Bay. PCB concentrations in Suisun Bay are quite low (~1 ng/g at the surface), resulting in small PCB fluxes. Lower South Bay, on the other hand, has the highest surface concentrations (~6 ng/g) but is net depositional. PCB fluxes due to erosion of buried sediments were limited to infrequent, short-term (i.e., episodic) erosion.

Central Bay exhibited the greatest input of PCBs due to erosion of buried sediments. Erosion over the large Central Bay (surface area ~396 km<sup>2</sup>) combined with relatively high PCB concentrations (~5 ng/g at the surface) resulted in large inputs of PCBs from buried sediments. South Bay had the second largest fluxes from buried sediments. While

concentrations and erosion rates in South Bay are similar to those in Central Bay, South Bay is smaller overall (~185 km<sup>2</sup>) and therefore a smaller mass of PCBs is mobilized from erosion of buried sediments.



## 4. Literature Cited

- Breivik, K., Sweetman, A., Pacyna, J. M., and Jones, K. C. (2002). Towards a global historical emissions inventory for select PCB congeners – a mass balance approach. *Science of the Total Environment*, 290, 199-224.
- Conomos, T.J., (1979). *Properties and Circulation of San Francisco Bay Waters*. Pages 47-84 in T.J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division of the American Association for the Advancement of Science, San Francisco, California.
- Davis, J. A., Hetzel, F., Oram, J. J., and McKee, L. (2007). Polychlorinated biphenyls (PCBs) in San Francisco Bay. *Environmental Research*, 105(1).
- Flater, D. (1998). Xide: Harmonic tide clock and tide predictor. <http://www.flaterco.com>.
- Harner, T., Bidleman, T. F., Jantunen, L. M. M., and Mackay, D. (2001). Soil-air exchange model of persistent pesticides in the United States cotton belt. *Environmental Toxicology and Chemistry*, 20, 1612-1621.
- Hung, H., Halsall, C. J., Blanchard, P., and P Fellin, H. H., Stern, G., and Rosenberg, B. (2001). Are PCBs in the Canadian Arctic atmosphere declining? Evidence from 5 years of monitoring. *Environmental Science and Technology*, 35, 1303-1311.
- Imberger, J, Kirkland, WB, and Fischer, HB. (1977). *The effect of delta outflow on the density stratification in San Francisco Bay*: Report to Assoc. of Bay Area Governments. Rep. HBF-77/02. Berkeley, CA. 109pp.
- Knowles, N. and Cayan, D. (2002). Potential effects of global warming on the Sacramento-San Joaquin watersheds and the San Francisco estuary. *Geophysical Research Letters*, 29(18), 38-1,38-4.
- Leatherbarrow, J. E., Oram, J. J., and Davis, J. A. (2005). Draft report: A model of long-term PCB fate and transport in San Francisco Bay, CA. SFEI Contribution 388. San Francisco Estuary Institute, Oakland, CA.
- Lionberger, M. A., and Schoellhamer, D. (2007). A tidally-averaged sediment transport model of San Francisco Bay, California. Technical report, USGS. In preparation.
- Mumley, T. E. and Looker, R. (2004). Adaptive implementation of TMDLs – The mercury example. In *The Pulse of the Estuary*. San Francisco Estuary Institute, Oakland, CA.

- Ockenden, W. A., Breivik, K., Meijer, S. N., Steinnes, E., Sweetman, A., and Jones, K. C. (2003). The global re-cycling of persistent organic pollutants is strongly retarded by soils. *Environmental Pollution*, 121, 75-80.
- Oram, J. J., Davis, J. A., and Leatherbarrow, J. E. (2008). A model of long-term PCB fate in San Francisco Bay: Model formulation, calibration, and uncertainty analysis (v2.1). SFEI Contribution ##. San Francisco Estuary Institute, Oakland, CA.
- Oros, D. R., and Ross, J. R. M. (2004). Polycyclic aromatic hydrocarbons in San Francisco Estuary sediments. *Marine Chemistry*, 86, 169-184.
- Peterson, D., Cayan, D., DiLeo, J., Noble, M., and Dettinger, M. (1995). The role of climate in estuarine variability. *American Scientist*, 83, 58-67.
- SFRWQCB (2007). Draft Basin Plan Amendment and TMDL Implementation Plan. San Francisco Regional Water Quality Control Board.
- SFEI (2007). The Pulse of the Estuary: Monitoring and Managing Water Quality in the San Francisco Estuary. SFEI Contribution 532. San Francisco Estuary Institute, Oakland, CA.
- Sinkkonen, S. and Paasivirta, J. (2000). Degradation half-lives of PCDDs, PCDFs, and PCBs for environmental fate modeling. *Chemosphere*, 40, 943-949.
- Sweetman, A. and Jones, K. C. (2000). Declining PCB concentrations in the U.K. atmosphere: evidence and possible causes. *Environmental Science and Technology*, 34, 863-869.
- Wania, F. (1999). Global modeling of polychlorinated biphenyls. WECC Report 1/99, WECC Wania Environmental Chemists Corp., Toronto, Ontario, Canada.

Table 1 - Model input parameters tested during sensitivity analysis.

Parameter	Region	Best Estimate*	Alternate Values Tested	Units
Koc	Baywide	Region Specific	x10, /10	
Koc	LSB	8.00E+05	x10, /10	
Koc	SB	8.00E+05	x10, /10	
Koc	CB	7.50E+06	x10, /10	
Koc	SPB	4.00E+06	x10, /10	
Koc	CAR	5.00E+05	x10, /10	
Koc	SU	8.00E+05	x10, /10	
Henry's Law Constant	Baywide	3.94	25.4, 1.01	
PCBs in Rain	Baywide	1000	13000, 50	pg/L
Dry Atmospheric PCB Deposition Rate	Baywide	1000	2100, 390	pg/m <sup>2</sup> /d
Water Temperature	Baywide	288	291, 286	Kelvin
OC of Susp. Sed.	Baywide	0.03	0.05, 0.01	
Sed. Vertical Mixing Rate	Baywide	71	170, 12	cm <sup>2</sup> /yr
Sed. Vertical Mixing Extinction Coef.	Baywide	9	15, 5	cm
Degradation Half-Life	Baywide	56	224, 112, 28	years
Attenuation Half-Life	Baywide	56	224, 112, 28	years
Attenuation & Degradation (Combined)	Baywide	56	224, 112, 28	years
Water-Sediment Mass Transfer Coef.	Baywide	0.0024	0.0036, 0.0012	m/d
Conc. Solids in Sediment	Baywide	0.5	0.75, 0.25	kg/L
OC of Bed Sediment	Baywide	Region Specific	+/- 20%	
Erosivity	Baywide	Region Specific	+/- 20%	
Wind-Current Shear	Baywide	Region Specific	+/- 20%	
Particle Settling	Baywide	Region Specific	+/- 20%	
Initial PCB Concentration in Water and Sediment	Baywide	Region Specific; See Figure XX	+/- 50%	
Spatial Distribution of Tributary PCB Loads		See Figure XX		
Magnitude of Tributary PCB Loads	Baywide	20	40, 0	kg/yr
Magnitude of Delta PCB Loads	Baywide	Calculated online	-100%	kg/yr

\* Refers to either best estimate from literature or from results of model calibration.

**Table 2 - Sensitivities of various model input parameters as determined by Equation 1. Shading indicates sensitivities greater than 0.25 or less than -0.25. Values in parentheses indicate either the degree of change or the alternate value tested for each parameter.**

Model Parameter	PCBs in Surface Sediments					
	Region					
	SU	SPB	CB	SB	LSB	BAY
Koc (All x 10)	0.09	0.03	0.02	0.12	0.10	0.06
Koc (All / 10)	0.74	0.57	0.37	0.81	0.79	0.64
Koc (LSB x 10)	0.00	0.00	0.00	0.00	0.04	0.00
Koc (LSB / 10)	0.00	0.00	0.01	0.09	0.72	0.06
Koc (SB x 10)	0.00	0.00	0.01	0.11	0.04	0.04
Koc (SB / 10)	0.01	0.03	0.06	0.80	0.30	0.32
Koc (CB x 10)	0.00	0.00	0.01	0.00	0.00	0.00
Koc (CB / 10)	0.01	0.01	0.33	0.02	0.01	0.16
Koc (SPB x 10)	0.00	0.02	0.00	0.00	0.00	0.01
Koc (SPB / 10)	0.02	0.55	0.02	0.00	0.00	0.16
Koc (CAR x 10)	0.00	0.00	0.00	0.00	0.00	0.00
Koc (CAR / 10)	0.01	0.00	0.00	0.00	0.00	0.00
Koc (SU x 10)	0.08	0.00	0.00	0.00	0.00	0.00
Koc (SU / 10)	0.73	0.02	0.01	0.00	0.00	0.01
Henry's Law Constant (25.4)	-0.03	-0.03	-0.02	-0.07	-0.06	-0.04
Henry's Law Constant (1.01)	-0.20	-0.16	-0.13	-0.62	-0.51	-0.33
Water Temperature (286)	-2.10	-1.73	-1.31	-5.73	-4.76	-3.12
Water Temperature (291)	-1.91	-1.58	-1.18	-5.02	-4.18	-2.75
OC of Susp. Sed. (0.01)	0.55	0.37	0.23	0.70	0.66	0.47
OC of Susp. Sed. (0.05)	0.31	0.15	0.09	0.43	0.37	0.24
Degradation (28 yrs)	0.16	0.21	0.19	0.14	0.08	0.20
Degradation (112 yrs)	0.20	0.27	0.25	0.16	0.10	0.26
Degradation (224 yrs)	0.20	0.28	0.26	0.17	0.10	0.27
Attenuation (28 yrs)	0.29	0.19	0.09	0.23	0.35	0.18
Attenuation (112 yrs)	0.58	0.36	0.17	0.45	0.75	0.36
Attenuation (224 yrs)	0.67	0.41	0.20	0.52	0.86	0.41
Attenuation & Degradation (28 yrs)	0.42	0.37	0.27	0.34	0.42	0.37
Attenuation & Degradation (112 yrs)	0.81	0.66	0.43	0.64	0.86	0.64
Attenuation & Degradation (224 yrs)	0.92	0.73	0.47	0.72	1.00	0.71
Erosivity (+20%)	-0.58	-0.28	-0.83	-0.40	-0.33	-0.37
Erosivity (-20%)	-0.53	-0.32	-0.98	-0.43	-0.32	-0.39
Wind-Current Shear (+20%)	0.06	-0.47	-0.08	-0.35	-0.26	-0.38
Wind-Current Shear (-20%)	0.06	-0.51	-0.05	-0.26	-0.25	-0.33
Particle Settling (+20%)	0.44	-0.58	0.10	-0.39	-0.20	-0.43
Particle Settling (-20%)	1.73	-0.73	0.37	0.36	0.01	-0.18
Initial PCB Conc (+/-50%)	0.41	0.58	0.76	0.53	0.36	0.59
Spatial Distribution of PCB Loads (1)	0.04	0.09	-0.06	0.27	0.47	
Spatial Distribution of PCB Loads (2)	0.11	0.08	-0.18	0.19	0.56	
Spatial Distribution of PCB Loads (3)	0.14	0.07	-0.13	0.20	0.52	
Spatial Distribution of PCB Loads (4)	-0.09	0.09	1.21	0.36	0.56	
Magnitude of Tributary PCB Loads (+/-100%)	0.38	0.29	0.16	0.41	0.60	0.33
Magnitude of Delta PCB Loads (-100%)	0.15	0.07	0.02	0.00	0.00	0.02

**Table 3 - Sensitivities of sediment model input parameters as determined by Equation 1. Shading indicates sensitivities greater than 0.25 or less than -0.25.**

Model Parameter	Suspended Sediment Concentration						Net Sedimentation					
	Region						Region					
	SU	SPB	CB	SB	LSB	BAY	SU	SPB	CB	SB	LSB	BAY
Erosivity + 20%	0.50	0.81	0.82	0.79	0.74	0.78	-1.47	-2.32	-1.56	-1.32	-4.14	-1.67
Erosivity - 20%	0.57	0.86	0.86	0.84	0.80	0.83	-1.62	-2.29	-1.57	-1.36	-4.23	-1.71
Wind-Current Shear + 20%	0.04	0.11	0.08	0.24	0.30	0.16	-0.10	-1.71	0.25	-0.39	-3.79	-0.15
Wind-Current Shear - 20%	0.04	0.12	0.08	0.24	0.29	0.17	-0.11	-1.46	0.23	-0.37	-3.50	-0.13
Particle Settling + 20%	-0.45	-0.75	-0.71	-0.71	-0.62	-0.69	1.51	0.67	1.38	1.07	3.61	1.39
Particle Settling - 20%	-0.62	-1.04	-0.99	-1.03	-0.88	-0.98	1.99	1.75	1.77	1.81	5.02	1.97

1 **Table 4 – Effects of varying the vertical profile of PCBs in sediment on future PCB concentrations in**  
 2 **surface sediments. Surface sediments are defined as the top 5-cm of sediments.**

<b>Scenario</b>	<b>Bay Segment</b>	<b>Ending PCB Concentration in Surface Sediment (ng/g)</b>	<b>% Change from Base Forecast</b>
Base Forecast	Suisun Bay	0.4	--
	San Pablo Bay	1.6	--
	Central Bay	2.4	--
	South Bay	1.7	--
	Lower South Bay	1.8	--
Decreasing Profile	Suisun Bay	0.5	7%
	San Pablo Bay	1.8	9%
	Central Bay	1.7	-30%
	South Bay	1.8	4%
	Lower South Bay	1.6	-10%
Increasing Profile	Suisun Bay	0.9	93%
	San Pablo Bay	2.7	65%
	Central Bay	3.4	38%
	South Bay	3.0	75%
	Lower South Bay	2.2	18%
Triangular Profile	Suisun Bay	0.8	90%
	San Pablo Bay	3.0	81%
	Central Bay	3.4	37%
	South Bay	3.1	80%
	Lower South Bay	2.2	21%
Uniform Profile	Suisun Bay	0.6	45%
	San Pablo Bay	2.1	31%
	Central Bay	2.5	0%
	South Bay	2.2	31%
	Lower South Bay	1.8	0%

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1 **Table 5 – Effects of external PCB loads on future PCB concentrations in surface sediments (top 5-**  
 2 **cm) for the various vertical profile scenarios.**

Scenario	Bay Segment	Ending PCB Concentration in Surface Sediment (ng/g)			Percent Change from Default	
		Default Loads	No Trib Loads	No Loads	No Trib Loads	No Loads
Base Forecast	Suisun Bay	0.4	0.3	0.2	-38%	-59%
	San Pablo Bay	1.6	1.2	0.9	-29%	-42%
	Central Bay	2.4	2.1	1.9	-16%	-24%
	South Bay	1.7	1.0	0.9	-41%	-47%
	Lower South Bay	1.8	0.7	0.7	-60%	-64%
Decreasing Profile	Suisun Bay	0.5	0.3	0.2	-35%	-55%
	San Pablo Bay	1.8	1.3	1.1	-27%	-39%
	Central Bay	1.7	1.3	1.1	-23%	-34%
	South Bay	1.8	1.1	1.0	-40%	-45%
	Lower South Bay	1.6	0.5	0.5	-67%	-71%
Increasing Profile	Suisun Bay	0.9	0.7	0.6	-20%	-30%
	San Pablo Bay	2.7	2.2	2.0	-18%	-26%
	Central Bay	3.4	3.0	2.8	-12%	-17%
	South Bay	3.0	2.3	2.2	-24%	-27%
	Lower South Bay	2.2	1.1	1.0	-51%	-54%
Triangular Profile	Suisun Bay	0.8	0.7	0.6	-20%	-31%
	San Pablo Bay	3.0	2.5	2.3	-16%	-23%
	Central Bay	3.4	3.0	2.8	-12%	-17%
	South Bay	3.1	2.4	2.3	-23%	-26%
	Lower South Bay	2.2	1.1	1.0	-49%	-53%
Uniform Profile	Suisun Bay	0.6	0.5	0.4	-26%	-40%
	San Pablo Bay	2.1	1.7	1.4	-22%	-32%
	Central Bay	2.5	2.1	1.9	-16%	-24%
	South Bay	2.2	1.5	1.4	-31%	-35%
	Lower South Bay	1.8	0.7	0.7	-60%	-64%

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**Table 6 – Overall PCB mass budget for various initial vertical profiles. Values indicate the cumulative mass (kg) in each pathway after 100 year forecast.**

Pathway	Base Forecast		Decreasing Profile		Increasing Profile		Triangular Profile		Uniform Profile		
	Cumulative Mass (kg)	% of Total	Cumulative Mass (kg)	% of Total	Cumulative Mass (kg)	% of Total	Cumulative Mass (kg)	% of Total	Cumulative Mass (kg)	% of Total	
<b>Inputs</b>	Local Watersheds	1128	74.2%								
	Delta	154	10.1%								
	Atmospheric Dep.	35	2.3%								
	Wastewater	203	13.4%								
	<b>Total Inputs</b>	1520									
SAME AS BASE FORECAST											
<b>Exports</b>	Burial	903	22.9%	401	14.0%	1458	29.5%	1185	24.4%	863	22.9%
	Degradation	354	9.0%	287	10.0%	445	9.0%	482	9.9%	354	9.4%
	Outflow	1902	48.2%	1444	50.6%	2090	42.3%	2182	44.9%	1740	46.1%
	Volatilization	787	19.9%	724	25.3%	951	19.2%	1007	20.7%	816	21.6%
	<b>Total Exports</b>	3946		2856		4945		4857		3773	

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**Table 7 - PCB flux into active sediments (top 5-cm) from buried sediments under various initial vertical profiles. Values indicate the cumulative mass (kg) after 100 year forecast.**

Bay Segment	Cumulative PCB Flux to Active Sediments from Buried Sediments (kg) after 100 years				
	Base Forecast	Declining Profile	Increasing Profile	Triangular Profile	Uniform Profile
Suisun Bay	15	30	65	68	44
San Pablo Bay	90	66	132	163	91
Central Bay	750	244	832	870	526
South Bay	275	280	532	610	376
Lower South Bay	29	4	19	24	10
<b>Total</b>	1159	625	1580	1734	1047

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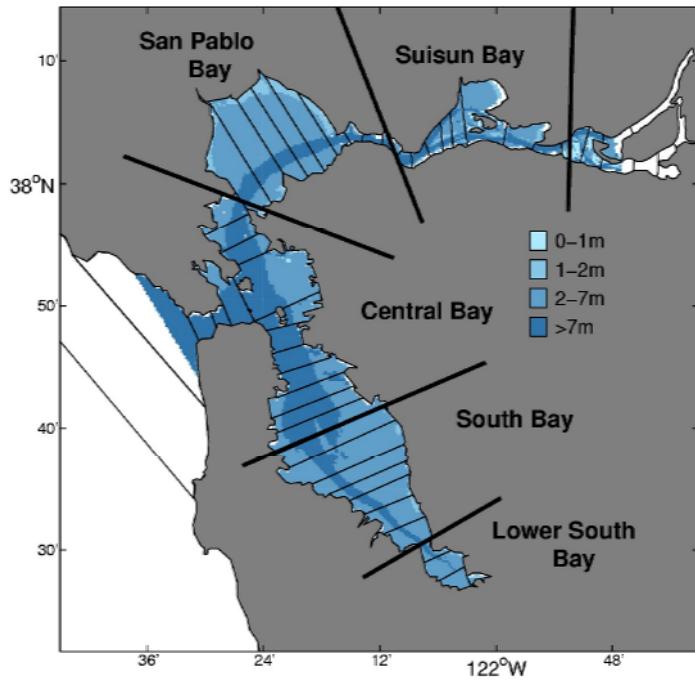


Figure 1 - Map of San Francisco Bay showing Bay segments and model boxes.



Figure 2 – Forecast Delta outflow for water years 2002 and 2090 from Knowles and Cayan (2002).

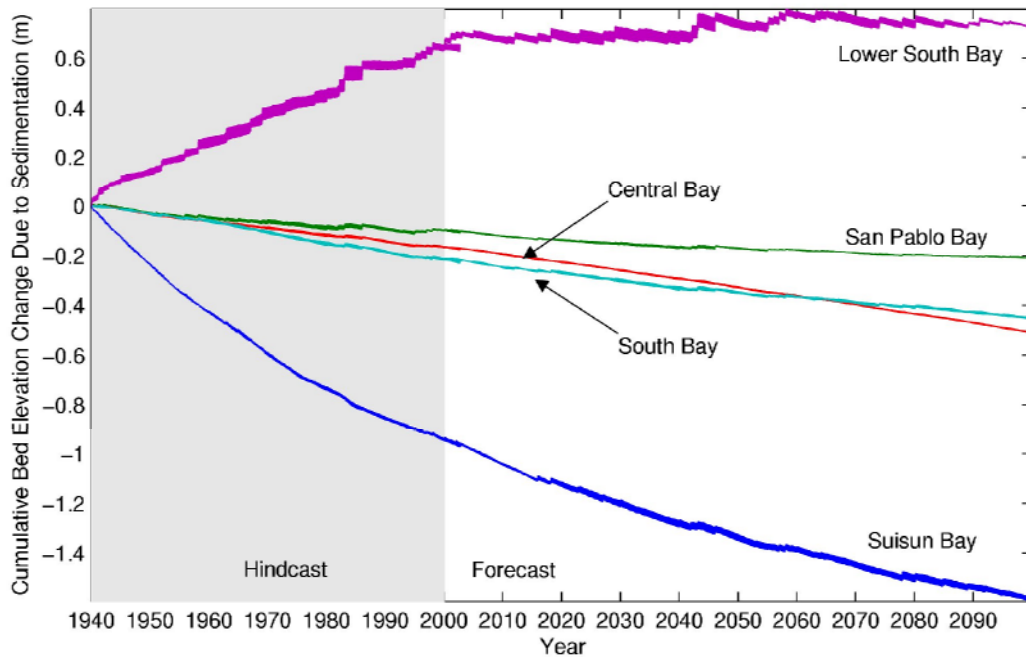


Figure 3 - Net sedimentation patterns in hindcast and forecast models.

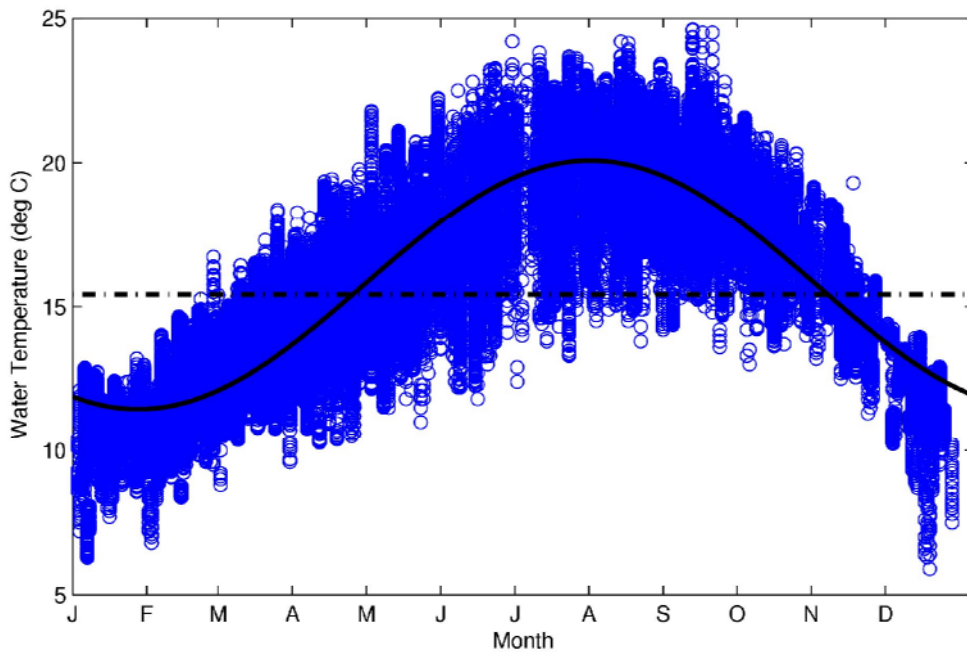


Figure 4 - Bay water temperature from 1969 to 2006. Scatter points represent discrete (approximately monthly) observations. The sinusoidal black line indicates the long-term mean seasonal trend. The horizontal dashed line indicates the long-term mean temperature of 15.4 deg C. Date are from <http://sfbay.wr.usgs.gov/access/wqdata>.

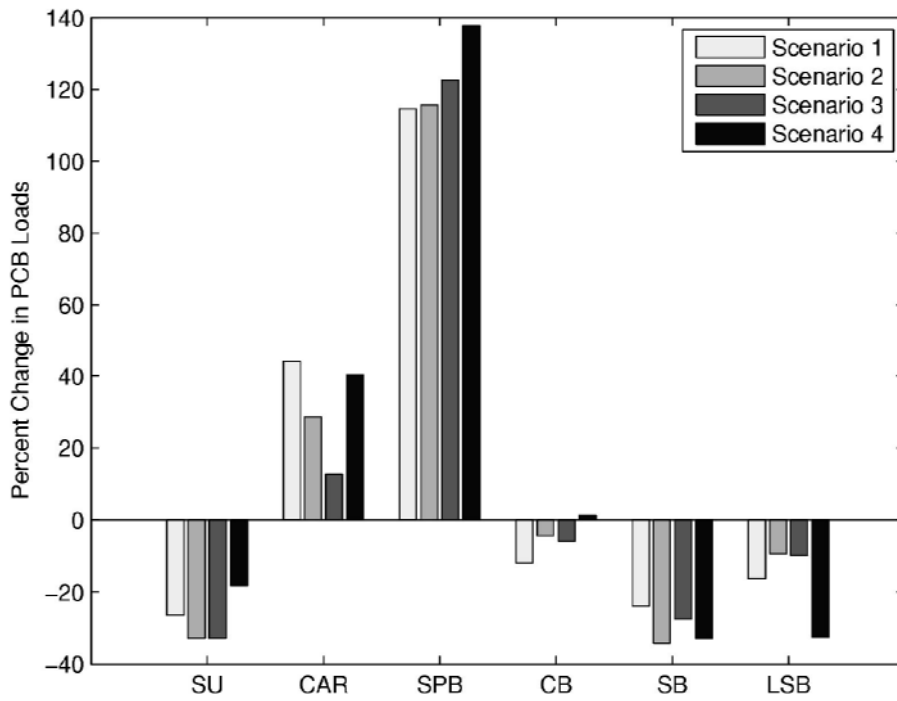


Figure 5 - Scenarios used to test the sensitivity of model results to the spatial distribution of PCB loads from local watersheds.

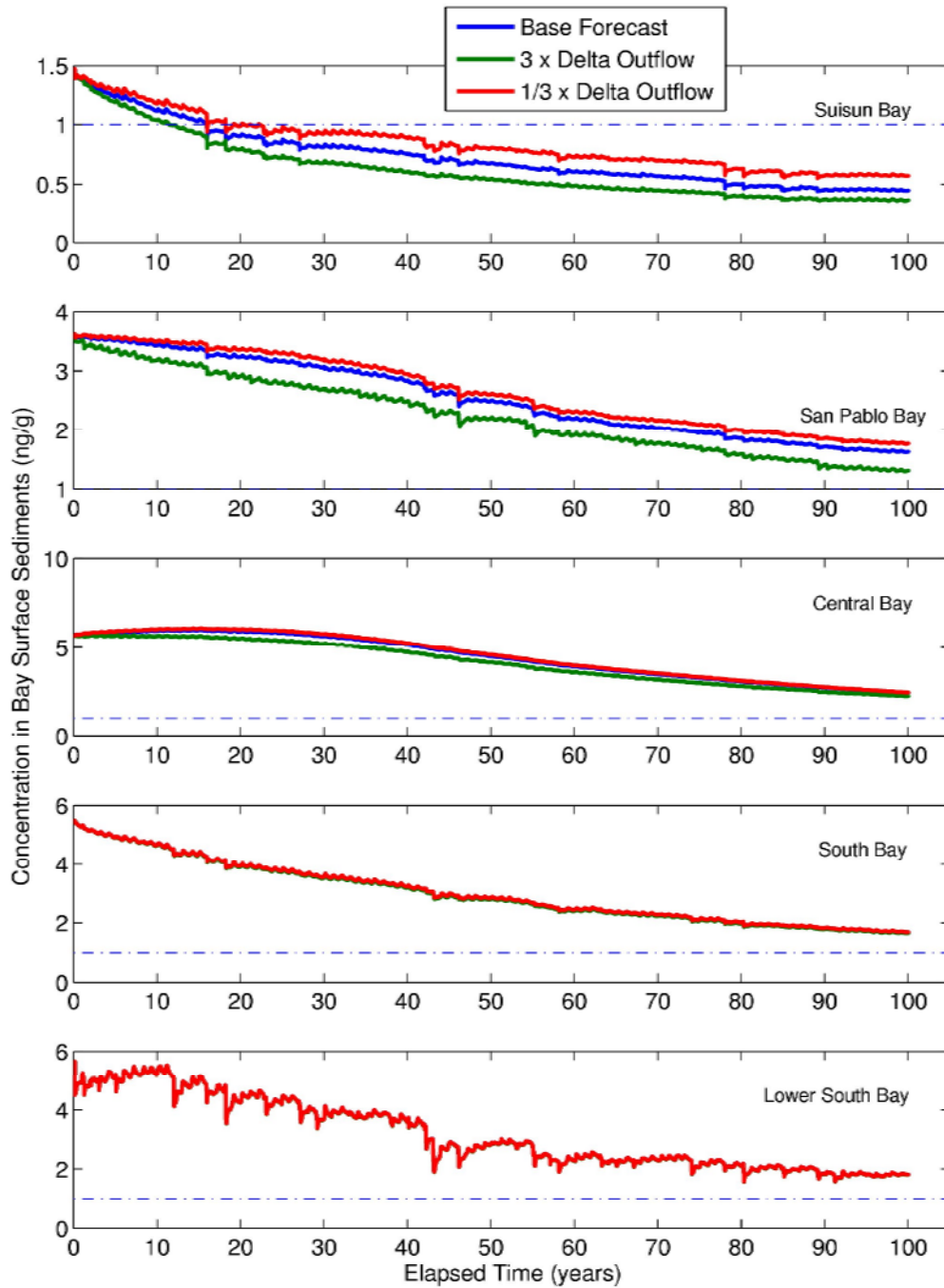


Figure 6 – PCB concentrations in surface sediments (top 5-cm) resulting from extreme changes in Delta Outflow.

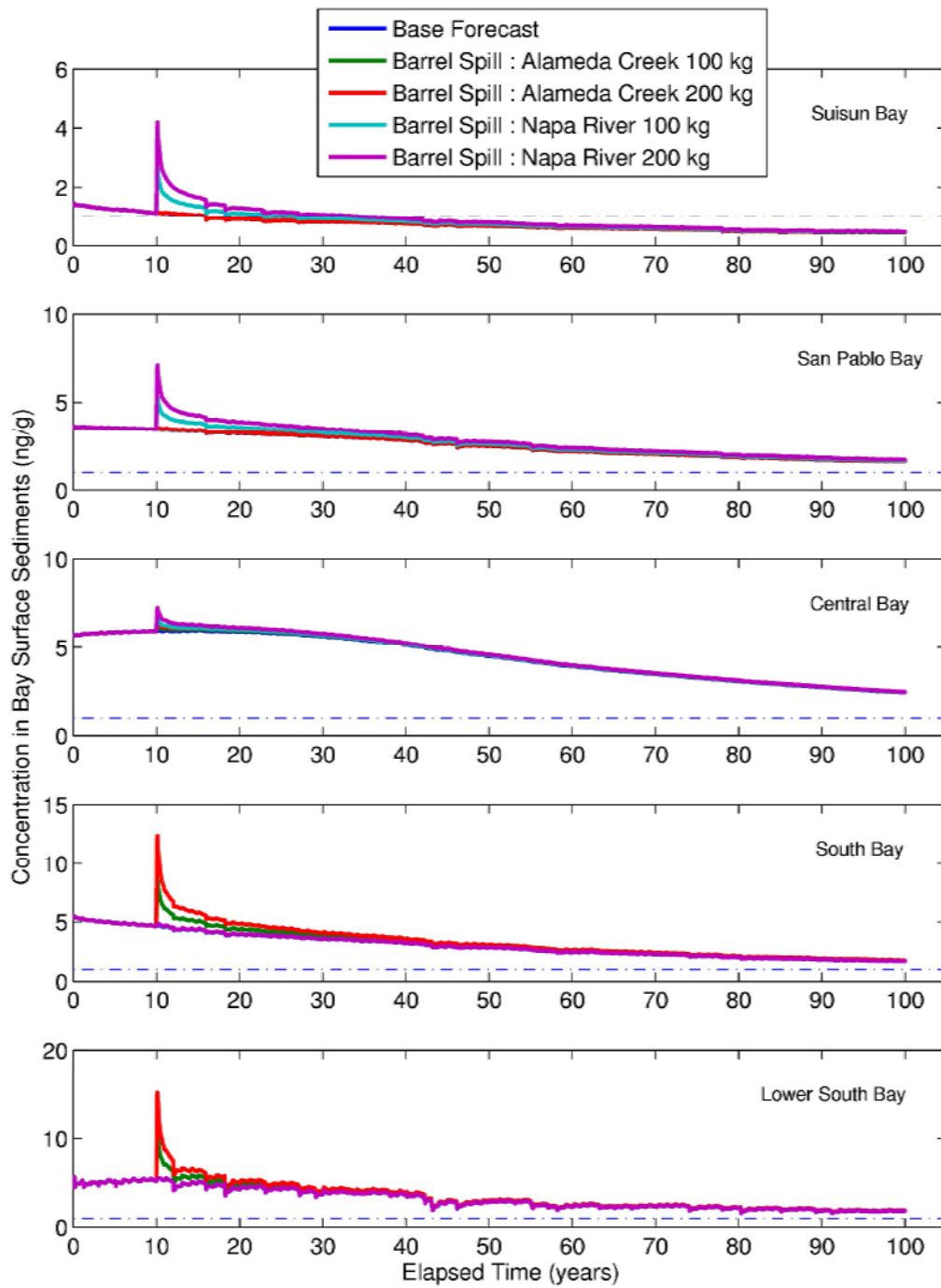
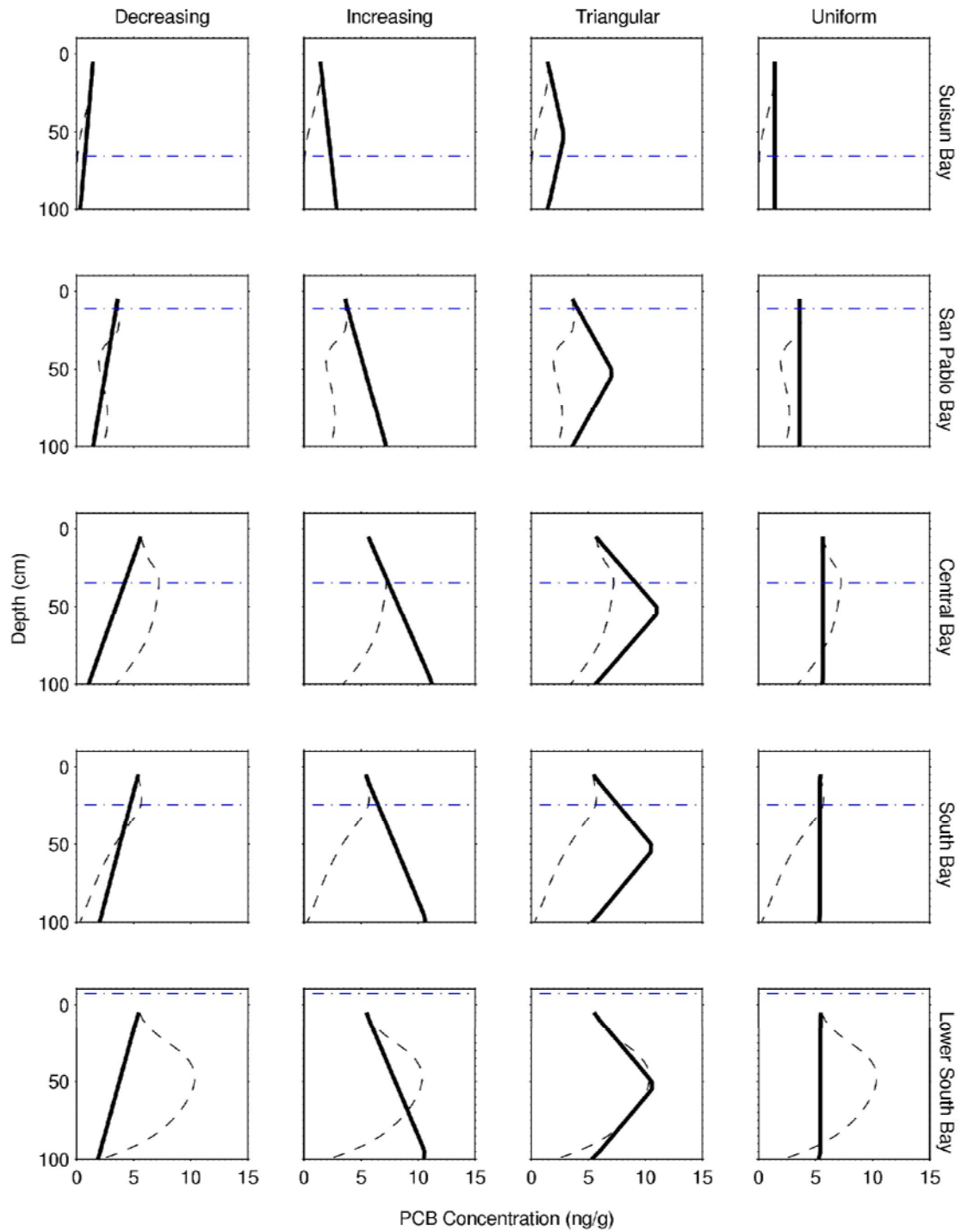
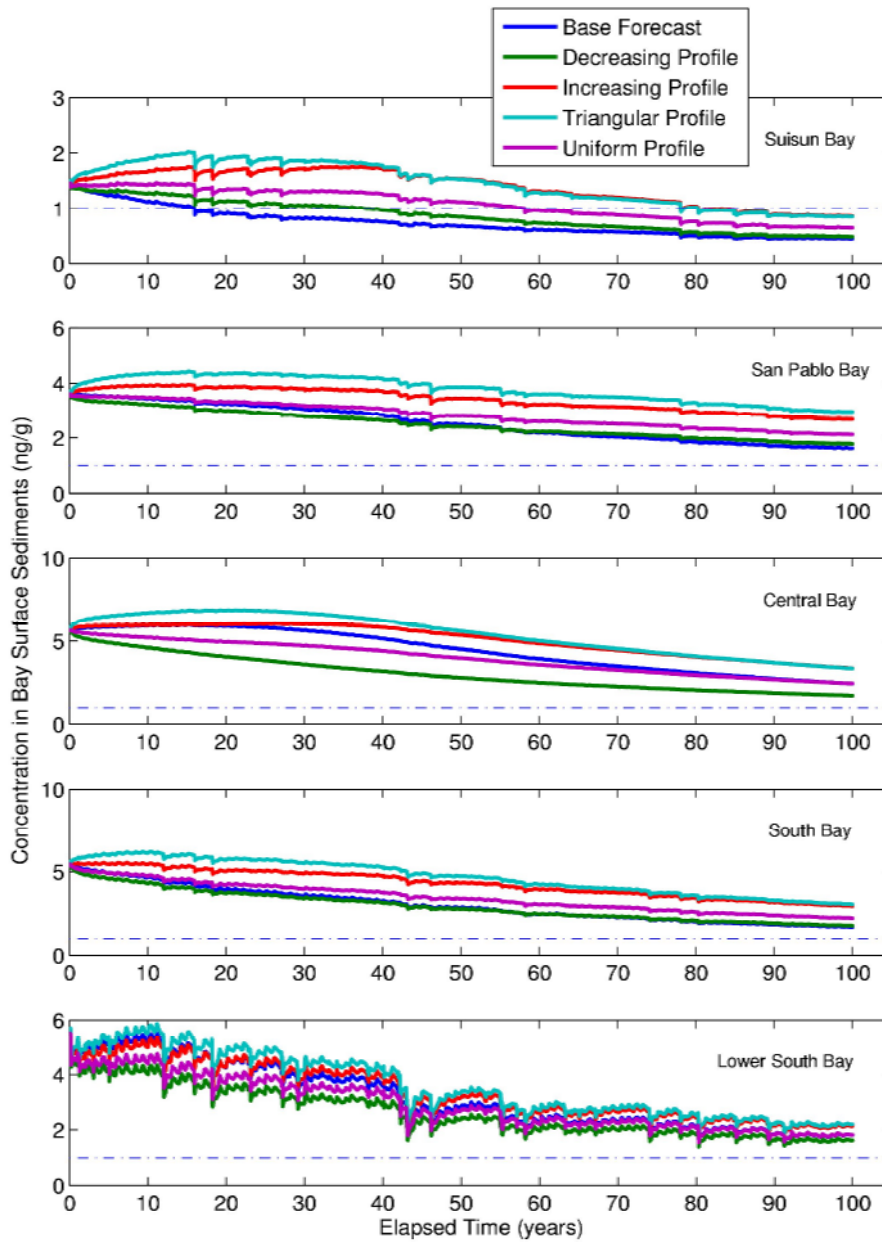


Figure 7 - PCB concentrations in surfaces sediments (top 5-cm) resulting from episodic PCB inputs (i.e., barrel spill) at year ten.



**Figure 8 - Schematic of the various vertical profiles of PCBs in sediment. The dashed line indicates the vertical profile used by the base forecast. The blue line indicates the average horizon (i.e., the region of the profile exposed by erosion) for each Bay segment.**



**Figure 9 - Recovery of surface sediments (top 5-cm) under no action scenarios (i.e., default loading) for the base forecast and vertical profile scenarios.**

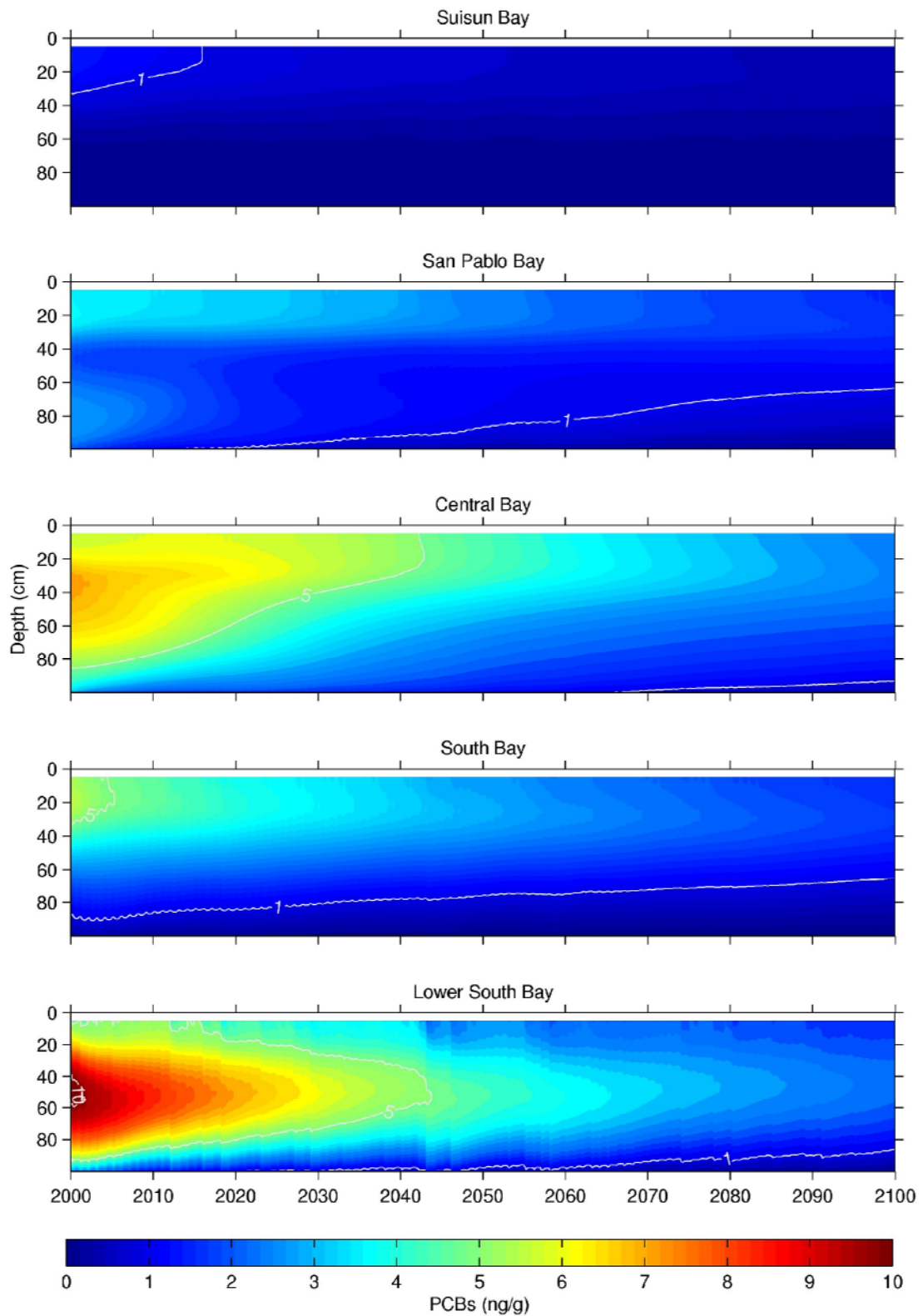


Figure 10 – Predicted PCB concentrations in 100 cm of sediment from 2000 to 2099 from the base forecast.



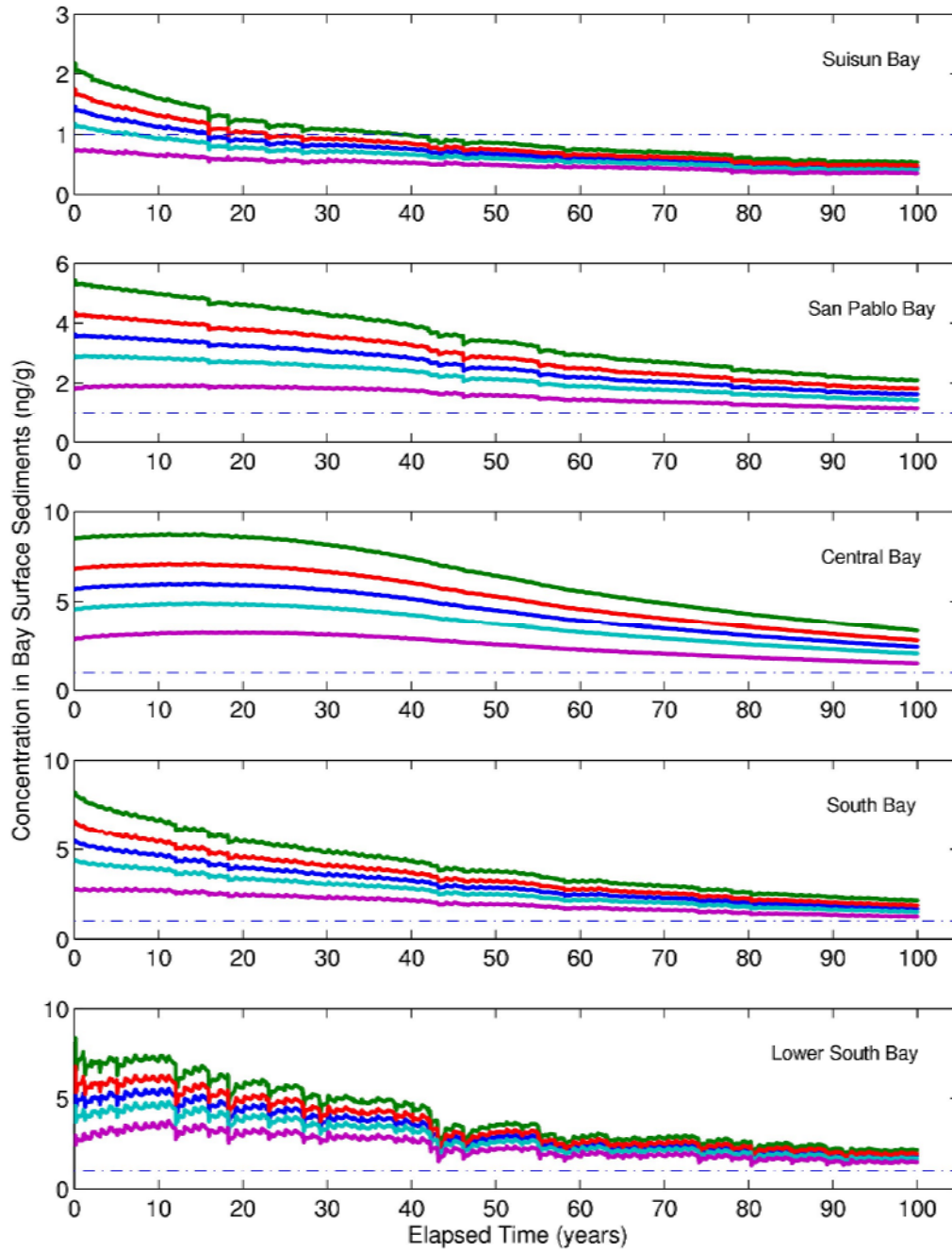


Figure 11 – Recovery of surface sediments (top 5-cm) under no action scenarios (i.e., default loading) for various initial PCB concentrations.

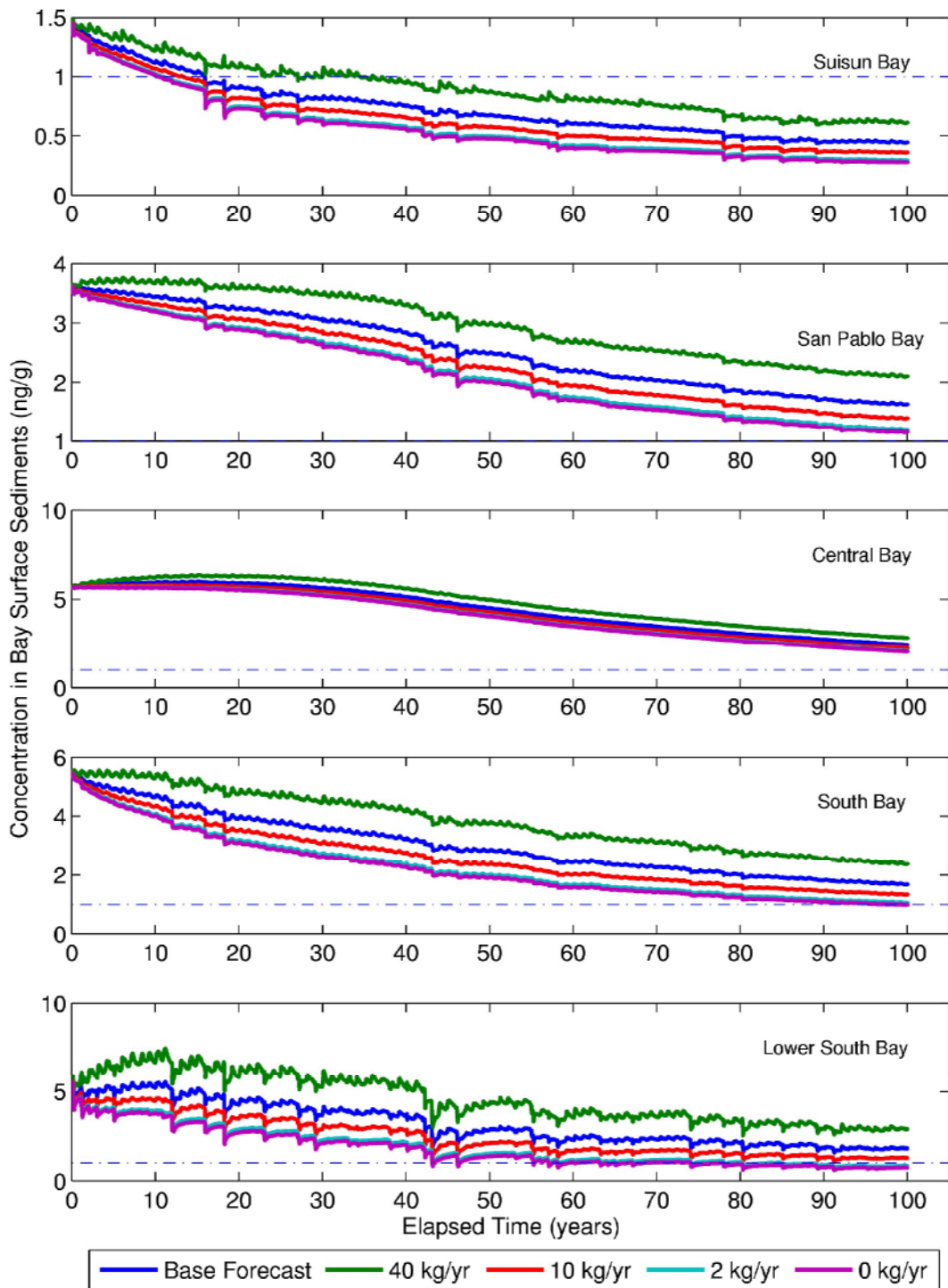


Figure 12 - Recovery of surface sediments (top 5-cm) due to changes in loads from local watersheds. The loading from local watersheds under the base forecast is 20 kg/yr.

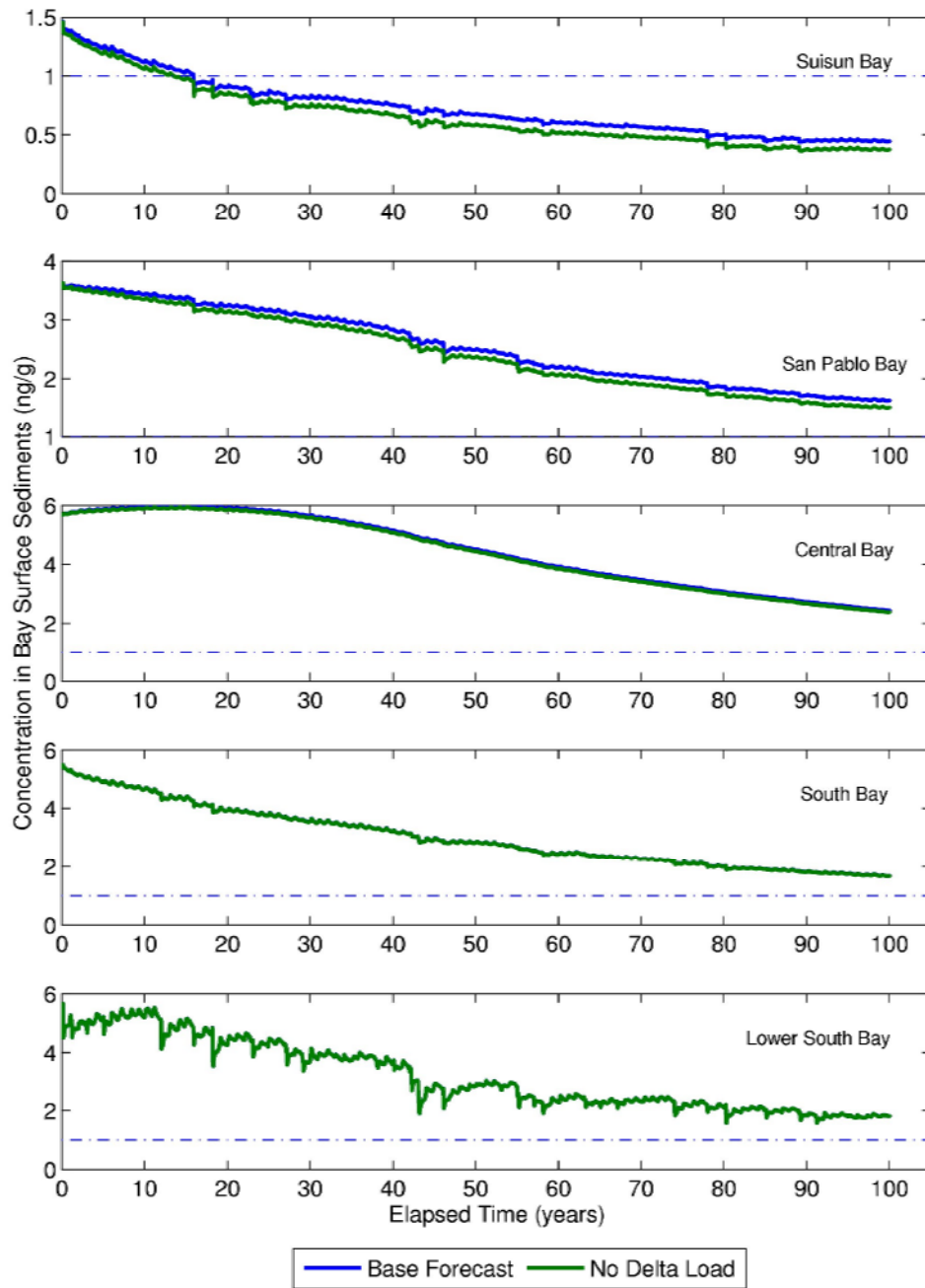


Figure 13 - Recovery of surface sediments (top 5-cm) under reduced Delta PCB loads.

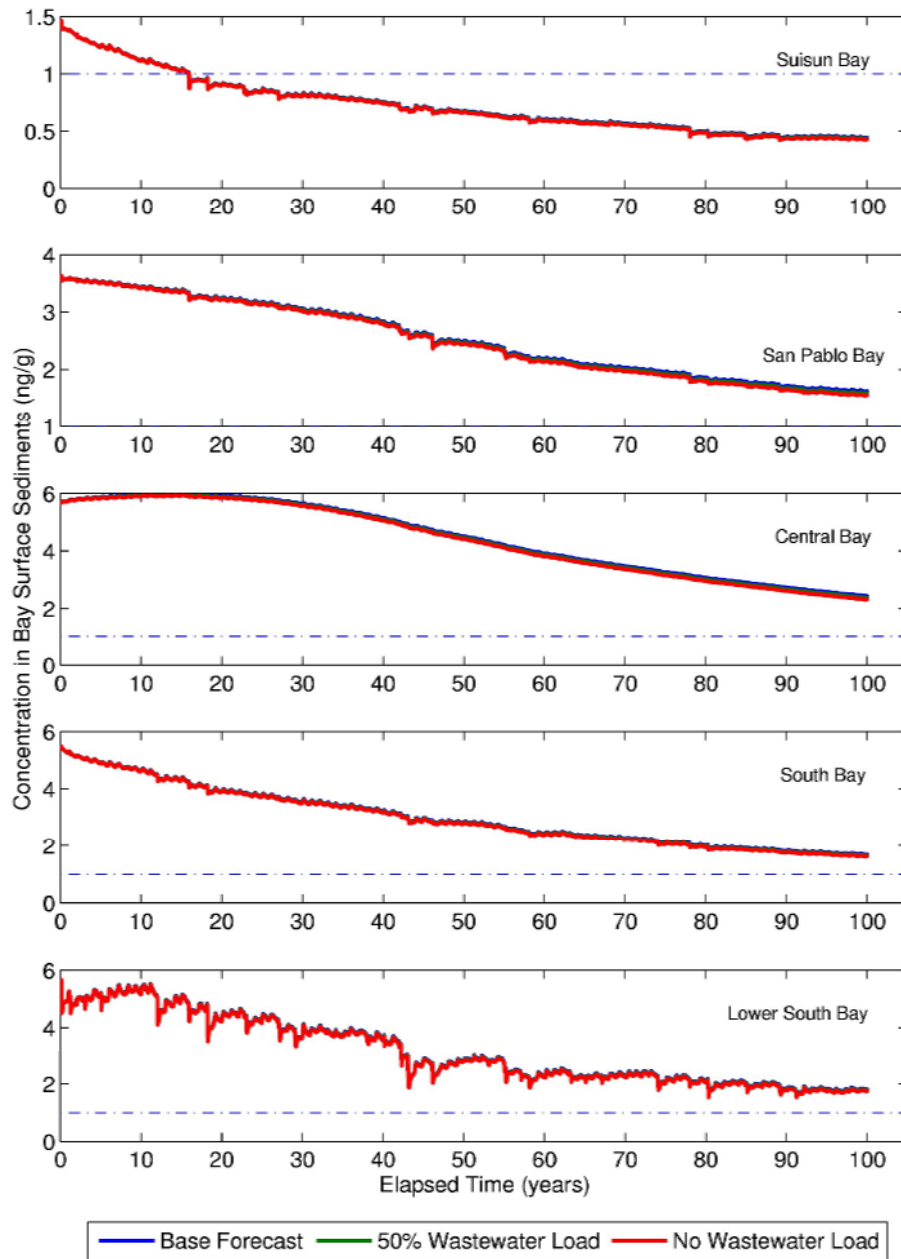


Figure 14 - Recovery of surface sediments (top 5-cm) resulting from changes in wastewater PCB loads.