San Francisco Estuary Regional Monitoring Program for Trace Substances

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

Model Formulation, Calibration, and Uncertainty Analysis

Version 2.1

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I. Model Overview

The multi-box model of polychlorinated biphenyls (PCBs) builds upon a tidally-averaged hydrodynamic model developed by Uncles and Peterson (1995, 1996) to interpret daily to decadal variability in salinity concentrations in San Francisco Bay. The salinity model employs a box-model approach, defining the Bay as 50 laterally-averaged segments divided into two layers for a total of 100 boxes (Figure 1). In each segment, an upper box, encompassing the shallows, overlies a bottom box that extends to the deepest part of the channel in each segment (Figure 2). The boxes are assumed to be uniformly mixed. The salinity model has been used in a number of studies of San Francisco Bay (e.g. Knowles, 1996; Knowles and Cayan, 2002).

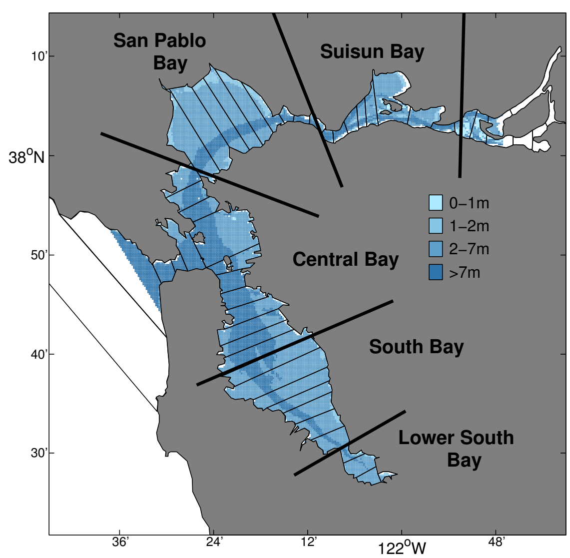

Figure 1: Plan view of model boxes.

A subsequent effort by Lionberger (2003) built on the Uncles and Peterson salinity model to develop a sediment transport model with a daily time step that simulates variability in suspended sediment concentrations (SSC) and decadal changes in sediment erosion and deposition in the

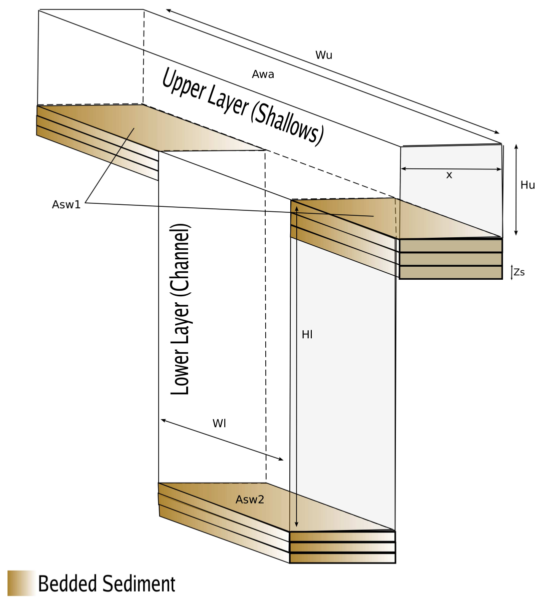

Figure 2: Model cross-section.

Bay. Erosion-deposition algorithms were developed, calibrated, and coupled to a sediment bed model. The sediment transport component has been further refined since the original formulation (Lionberger and Schoellhamer, 2007) and these refinements are included in this version of the multi-box model (v2.1). Major refinements include:

- Dynamic box volumes. The depth of each box is allowed to change over time as a function of past erosion and deposition. This allows for feedback between sedimentation history and shear stress at the bed.
- Improved calibration. The sediment model is further calibrated to net sedimentation for the four South Bay subregions defined by Foxgrover *et al.* (2004).
- Improved parameterization of tributary sediment loads. Contributions from bed load were removed and loads were distributed throughout the model in a way that is more representative of true geographic distributions.
- Improved sediment mass conservation. Delta and Lower South Bay boundary conditions account for residual mass transport.
- Explicit treatment of sea level rise ($\approx 3mm/yr$)

- Subsidence in Lower South Bay. Bathymetric change accounts for subsidence due to changes in ground water levels.
- Re-configuration of box geometry based on USGS field data. Box water-depths are updated to better represent known depths.

The PCB model builds on the salinity and sediment transport models to describe long-term trends in total PCB concentrations in the water column and bed sediment and to estimate timescales of recovery with respect to water quality impairment by PCBs. Total PCBs refers to the sum of 40 individual congeners measured by the RMP[1]. The PCB model includes a post-depositional sediment-mixing model that creates storage in the sediment for accumulation and mixing of PCBs. The PCB model also accounts in a spatially explicit manner for external inputs of PCBs to the Bay from the various major transport pathways: runoff from the Central Valley via the Sacramento-San Joaquin River Delta ('Delta'), runoff from local Bay Area tributaries, atmospheric deposition (wet and dry), and municipal wastewater effluent. Along with physical processes that determine PCB transport, the model incorporates the influence of chemical specific traits of PCBs that govern partitioning between particulate and dissolved fractions, degradation in water and sediment, and volatilization into the atmosphere.

Version 1.0 of the PCB model was developed and a progress report was issued by Leatherbarrow *et al.* (2005). Significant changes have been made to the PCB model (as well as the sediment model) as a result of peer review. This document describes parameterizations and formulae used in version 2.1 of the model.

Since the hydrodynamic and sediment transport models have previously been calibrated, this study validates salinity and SSC data using recently collected data to ensure consistency between

[1]**PCB congeners measured by the RMP (IUPAC numbers) -** 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 118, 128, 132, 141, 149, 151, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, 203

studies. A decadal-scale hindcast was applied to help constrain sediment-related parameters that influence long-term trends in PCB contamination. The lack of accurate information on actual magnitudes of historic PCB loads and concentrations in the Bay precludes exact calibration of the PCB model. Consequently, the goal of the hindcast was to obtain general agreement between model results and known historic patterns and trends in loading and concentrations.

II. Model Formulation

A. Hydrodynamics (Salinity Transport)

Uncles and Peterson (1995, 1996) developed the original formulation of the model to simulate salinity transport through advection and dispersion in the longitudinal (x) direction between segments and in the vertical (z) direction between water column layers. These processes are described by the following equation:

$$\frac{\partial}{\partial t}(WS) = -\frac{\partial}{\partial x}(WUS) - \frac{\partial}{\partial z}(W\omega S) + \frac{\partial}{\partial x}(WD\frac{\partial S}{\partial x}) + \frac{\partial}{\partial z}(WK\frac{\partial S}{\partial z}) \quad (1)$$

where S = salt content; W = Estuary width; U = laterally- and tidally-averaged longitudinal current velocity; ω = laterally- and tidally-averaged vertical current velocity; K = vertical eddy diffusivity; D = longitudinal dispersion coefficient. Equation 1 is implicitly solved on a daily time step using a matrix inversion routine.

Derivations of input parameters and essential equations are discussed in detail in Uncles and Peterson (1995, 1996) and Lionberger (2003); Lionberger and Schoellhamer (2007). Daily input data used to derive parameters in Equation 1 and calibrate the model include root-mean squared coastal sea-level elevations, streamflow via the Delta and selected local tributaries (Guadalupe River, Coyote

Creek, Alameda Creek, and Napa River), wastewater effluent discharge, precipitation, and evaporation.

B. Sediment Transport

As with salinity, sediment transport between layers and segments is determined through Equation 1 with S representing daily SSC. The sediment transport model incorporates daily inputs of suspended sediment (L_{ssc}) associated with runoff entering the Bay via the Delta and the local tributaries included in the hydrodynamic model (Lionberger, 2003; Lionberger and Schoellhamer, 2007). Complete documentation of the sediment transport model is currently being developed by Lionberger and Schoellhamer (2007). Modeled SSC in the water column also changes as a result of deposition of suspended sediment and erosion of bed sediment. Following Equation 1, the overall governing equation for sediment transport is

$$\begin{aligned}\frac{\partial}{\partial t}(WS) &= -\frac{\partial}{\partial x}(WUS) - \frac{\partial}{\partial z}(W\omega S) + \frac{\partial}{\partial x}(WD\frac{\partial S}{\partial x}) + \cdots \\ & \frac{\partial}{\partial z}(WK\frac{\partial S}{\partial z}) + R_E - R_D + L_{SSC} \qquad (2)\end{aligned}$$

where S = SSC = suspended sediment concentration, R_E = time-dependent erosion flux, R_D = time-dependent deposition flux, L_{SSC} is the total external suspended sediment load per unit area.

Derivations of input parameters in Equation 2 are discussed in detail in Lionberger (2003) and Lionberger and Schoellhamer (2007). Briefly, simple empirical algorithms are used to calculate R_E and R_D. R_E is calculated as a function of shear stress applied to bed sediment by current and wind wave orbital velocities. Input data incorporated into the model for shear stress calculations include daily wind velocity data collected from locations in Suisun Bay and San Francisco International Airport. R_D is calculated as a function of particle settling velocity and SSC. The algorithms that determine rates of erosion (R_E) are coupled with a sediment bed model that accounts for the increased compaction and strength of bed sediment with increased depth and the corresponding reduction in erosion potential. The bed sediment model is comprised of an erodibility profile that describes differential R_E in three layers. The top 2-cm sediment layer of unconsolidated sediment erodes at constant R_E based on current and wind wave orbital velocities. From 2-cm to 6-cm depth, R_E decreases exponentially to 25% of the surface R_E. Below the 6-cm depth, R_E remains constant at 25% of the surface R_E.

One key finding of Lionberger (2003) was that the model could simulate SSC or bathymetric change quite well, but could not do both simultaneously. The sediment transport model was then formulated on a decadal time scale (1/1/1940 to 9/30/2002) to simulate bathymetric change, leaving SSC as a free parameter, with net erosion and deposition calibrated to long-term bathymetric changes in the Bay (e.g., Jaffe *et al.*, 1998; United States Geological Survey, 2004; Foxgrover *et al.*, 2004). This hindcast required estimation of suspended-sediment inputs from tributaries over that time period. Daily SSC inputs via the Delta were derived using a rating curve that computes suspended-sediment flux downstream of the Delta (at Mallard Island) as a function of Delta outflow (calculated by DAYFLOW program developed by the California Department of Water Resources (DWR)) and SSC measured at Sacramento River at Freeport (USGS Station 11447650). Prior to 1957, the first year of SSC data collection at Freeport, SSC at Mallard Island was estimated based on Delta outflow. The sediment transport model corrects for the tidal dispersion of suspended sediment flux entering the Bay from the Delta using methods outlined in McKee *et al.* (2005b). Local tributary suspended-sediment inputs were estimated based on rating curves relating estimated

SSC to daily tributary flows using USGS daily streamflow data and sediment observations for Guadalupe River (11169000), San Francisquito Creek (11164500), Alameda Creek (11179000), Walnut Creek (11183500), and Napa River (11458000) (Schoellhamer and Lionberger, 2004). Additionally, the sediment model accounts for longer-term changes associated with sea-level rise and subsidence. Sea level rise is assumend to have a constant rate of 3 mm/yr. Subsidance is accounted for in Lower South Bay only and is based on actually observations from 1930 to 1982.

C. PCB Transport

The PCB model builds on the previously developed hydrodynamic and sediment transport models to describe PCB transport and PCB interaction between water and sediment in the Bay. Accordingly, PCBs are physically mixed and advected in the water column according to Equation 1, with S replaced by total PCBs in the water column (C_t). PCBs associated with suspended sediment (particulate PCBs (C_p)) in the water column interact with bed sediment PCBs according to the sediment erosion-deposition algorithms and mass-balance approach of Equation 2. Additional components of the PCB model include (1) the influence of physical and chemical properties that govern PCB partitioning, degradation, and volatilization into the atmosphere, (2) external PCB loads to the Bay from various transport pathways, and (3) a depth-dependent sediment mixing model that accounts for post-depositional storage and mixing of PCBs in bed sediment. A conceptual diagram of a daily time-step of the PCB model is seen in Figure 3. Each sub-time-step is outlined below and described in detail in the following sections.

1. **External Loads:** PCB loading from local tributaries, the Delta, atmospheric deposition, and wastewater effluent occurs at the beginning of each daily time step.

2. **Mixing and Advection:** Total PCBs in the water column undergo longitudinal and vertical advection and dispersion.

3. **Partitioning, Volatilization, and Degradation:** PCBs in the water column partition between dissolved and particulate fractions. Dissolved PCBs volatilize into the atmosphere. PCBs in water and sediment are degraded.

4. **Sediment-Water Exchange:** Particulate PCBs in the water column interact with underlying bed sediment through erosion or deposition. Dissolved PCBs in the water column interact with dissolved PCBs in sediment pore water by diffusion.

5. **Sediment Mixing:** PCBs in bed sediment are mixed vertically.

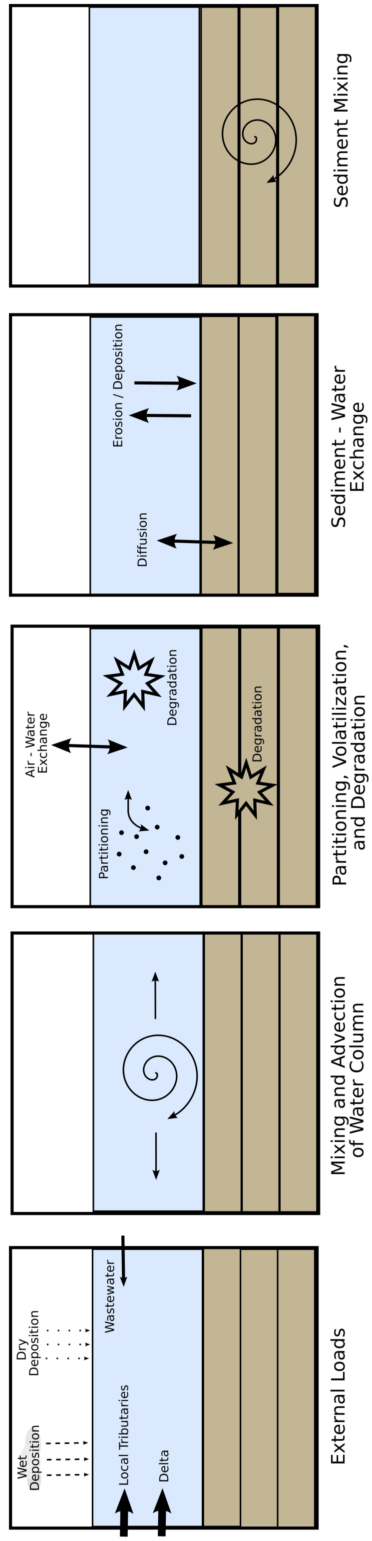

Figure 3: Conceptual diagram of a daily time-step of the PCB model.

In addition to the transport equation governing total PCBs in the water column (Equation 1), three equations are required to model the various physical and chemical processes controlling PCBs in water and sediment; one for PCBs in the water column (Equation 3); one for PCBs in the surface sediment layer (Equation 4); and one for vertical mixing of PCBs in buried sediment layers (Equation 5).

Total PCBs in the water column:

$$\frac{\partial C_t}{\partial t} = -K_v C_t - K_{dw} C_t + \frac{K_{sw} C_{s_1} \rho_s Z_s}{H} - K_{ws} C_t + \psi_{sw} + L_{PCB} \tag{3}$$

PCBs in surface sediment layer $(i = 1)$*:*

$$\frac{\partial C_{s_1}}{\partial t} = \psi_{ws} - K_{ds_1} C_{s_1} - K_{sw} C_{s_1} + \frac{K_{ws} H C_t}{Z_s \rho_s} - D_{b_1} \left(\frac{C_{s_1} - C_{s_2}}{Z_s} \right) \tag{4}$$

PCBs in buried sediment layers $(i = 1 \rightarrow N)$*:*

$$\frac{\partial C_{s_i}}{\partial t} = \frac{\partial}{\partial z} \left(D_{b_i} \frac{\partial C_{s_i}}{\partial z} \right) - K_{ds_i} C_{s_i} \tag{5}$$

Detailed descriptions of each model parameter are given in the following sections. A complete table of model parameters is included in Table 1.

Table 1: Table of key model parameters.

Parameter	Symbol	Units	Best Estimate	Comments
Width of upper layer	W_u	m		
Width of lower layer	W_l	m		
Water depth of upper layer	H_u	m		
Water depth of lower layer	H_l	m		
Longitudinal box length	X	m		
Depth into sediment layer	z	cm		
Thickness of sediment layers	Z_s	cm	5	
Number of sediment layers	N	unitless	20	
Area of water-air interface	A_{wa}	m^2		
Area of sediment-water interface	A_{sw}	m^2		
Longitudinal current veolcity	U	m/d		Calculated in sediment transport module
Vertical current velocity	ω	m/d		Calculated in sediment transport module
Longitudinal Dispersion coefficient	D	m^2/d		Calculated in sediment transport module
Vertical eddy diffusivity	K	m^2/d		Calculated in sediment transport module
Salinity	S	mg/l		
Suspended sediment concentration	SSC	mg/l		
Total PCB concentration in water	Ct	pg/l		
Dissolved PCB concentration in water	Cd	pg/l		
Particulate PCB concentration in water	Cp	pg/l		
Fraction PCB dissolved in water	ϕ_{DW}	unitless		Calculated in PCB transport module
PCB concentration in i^{th} sediment layer	Cs_i	ng/g		Sediment associated (ie., particulate)
Fraction PCB dissolved in sediment pore water	ϕ_{DS}	unitless		Calculated in PCB transport module
Sediment mixing coefficient	Db	cm^2/yr		Fuller et al. 1999
Depth dependent mixing parameter	γ	cm		Fuller et al. 1999
Degradation rate in water	K_{dw}	1/d	3.3e-5	Davis, 2004 (56 yr half-life)
Degradation rate in sediment	K_{ds}	1/d	3.3e-5	Davis, 2004 (56 yr half-life)
Sediment-to-water diffusion rate	K_{sw}	1/d		Calculated in PCB transport module
Water-to-sediment diffusion rate	K_{ws}	1/d		Calculated in PCB transport module
Volatilization rate	K_v	1/d		Calculated in PCB transport module
Net PCB mass transfer from sediment to water due to sedimentation	Ψ_{sw}	pg/L/d		Calculated in PCB transport module
Net PCB mass transfer from water to sediment due to sedimentation	Ψ_{ws}	ng/g/d		Calculated in PCB transport module
Erosion flux	R_E	$g/m^2/d$		Calculated in sediment transport module
Depositon flux	R_D	$g/m^2/d$		Calculated in sediment transport module
Bulk PCB concentration in burried sediment	Cb	ng/g	0	
Total external SSC load	L_{SSC}	$kg/m^2/d$		Calculated in sediment transport module
Total external PCB load	L_{PCB}	$kg/m^2/d$		Calculated in PCB transport module
Organic carbon content of suspended particles	OC	unitless	0.03	Daivs, 2004
Organic carbon content of sediment	OC_{sed}	unitless	0.006-0.014	Region specific; Oros and Ross, 2004
Sediment density	ρ_s	g/m^3	6.7e5 - 9.9e5	Region specific; Lionberger, 2003
Concentration of solids in sediment	Css	kg/l	0.5	Daivs, 2004
Organic carbon-water partitioning coefficient	Koc	unitless	8.0e5 - 7.5e6	Region Specific; Determined during model calibration
Water temperature	Tw	deg C	15	Daivs, 2004
Volatilization mass transfer rate	V_E	m/d		Calculated in PCB transport module
Mass transfer coefficient across air layer	V_{EA}	cm/s		Calculated in PCB transport module
Mass transfer coefficient across water layer	V_{EW}	cm/s		Calculated in PCB transport module
Temperature dependent Henry's Law constant	K_{AW}	unitless		Calculated in PCB transport module
Henry's Law constant at 298K	H_{298K}	$Pa\text{-}m^3/mol$	3.94	Daivs, 2004
Temperature dependent Henry's Law constant	H_{TW}	$Pa\text{-}m^3/mol$		Calculated in PCB transport module
Universal gas constant	R	$Pa\text{-}m^3/mol\text{-}K$	8.314	
Schmidt number for carbon dioxide	S_{CCO2}	unitless		Daivs (2004) and Hornbuckle et al. (1994), esimated in PCB module
Schmidt number for PCB	S_{CPCB}	unitless	2650	Daivs (2004) and Hornbuckle et al. (1994)
Diffusivity of PCB in air	D_{PCBA}	cm^2/s	0.051	Daivs (2004) and Hornbuckle et al. (1994)
Diffusivity of water in air	D_{WA}	cm^2/s	0.239	Daivs (2004) and Hornbuckle et al. (1994)
Water-sediment mass transfer coefficient	V_d	m/d	0.0024	Range 0.00024-0.024 (Davis, 2004)
Attenuation rate	atten	1/d	3.3e-5	56 yr half-life based on degredation in water and sediment

1. External Loads

The daily time step of the model requires daily input data on PCB loadings. It is important to recognize the inherent complexities in characterizing daily variability in loading of trace contaminants to the Bay from major transport pathways. In particular, storm events are responsible for runoff-driven contaminant loads of relatively large magnitude that occur on the duration of hours to days (Leatherbarrow *et al.*, 2004; McKee *et al.*, 2005b). This degree of temporal and spatial variability is difficult to capture in the Bay Area. As a result, contaminant loads associated with rainfall and runoff are poorly understood. For lack of either hydrologic models that describe processes of contaminant transport in Bay watersheds or methods of extrapolating existing information, the approach used in this study to estimate daily PCB loads is intended solely to provide the model with short-term episodic (days to weeks) pulses of PCBs associated with realistic durations and magnitudes of runoff from storm events.

Daily PCB inputs were modeled for four major external pathways: runoff from the Sacramento-San Joaquin Rivers (the Delta), runoff from local Bay Area tributaries, wastewater effluent, and atmospheric deposition.

The Delta

The PCB model accounts for PCB loads entering the Bay from the Central Valley (via the Delta) based on estimated concentrations of total PCBs on suspended sediment. Total PCB concentrations are comprised of the sum of dissolved and particulate fractions. During high flow events from January 10th, 2002 to January 6th, 2003, Leatherbarrow *et al.* (2004) collected 20 water samples for analysis of total PCBs and SSC from Mallard Island, located approximately 5 km downstream of the confluence of the Sacramento and San Joaquin Rivers. A nearly significant relationship existed between total PCBs and SSC (Figure 4, $p=0.055$, $\alpha=0.05$). Four samples collected in

May 2003 were not included in the analysis due to unexplained variation in measured total PCB concentrations. A daily load of total PCBs from the Delta (L_{Delta}) was established by calculating total PCB concentrations in Delta outflow from predicted SSC in Delta outflow using one of the regression equations in Figure 4 (*log regression is the default*). Resulting total PCB concentrations are multiplied by Delta outlow to determine the daily load (kg) applied at the Delta (box 38). Continued monitoring at Mallard Island will help refine the applied relationship between total PCB concentrations and SSC in the Delta region.

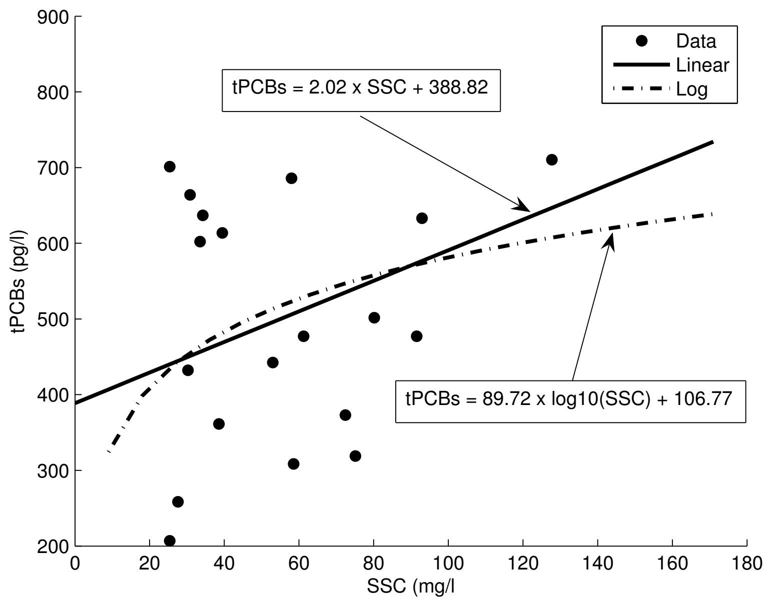

Figure 4: Total PCBs and SSC in Mallard Island water samples from WY 2001 and WY 2002 Leatherbarrow *et al.* (2004) illustrating both linear and logarithmic regressions.

Local Tributaries

Limited information is available from the few studies that have attempted to estimate PCB loads to the Bay from local tributaries. As part of a sediment survey to measure concentrations of PCBs and mercury in storm drains and creeks of Bay Area watersheds in 2000 and 2001, KLI (2002,

2005) used a model based on the Rational Method to derive an order-of-magnitude (median) PCB loading estimate of 39 kg per year from the local tributaries in an average year (range: 8.6-103.2 kg/yr). In WY 2003, McKee and Leatherbarrow (2005) conducted a loading study in Guadalupe River, which drains to Lower South San Francisco Bay. They estimated that approximately 1.2 ± 0.2 kg of PCBs were transported through Guadalupe River from November 2002 to May 2003 during a year with average hydrological conditions. A subsequent study by McKee *et al.* (2005a) estimated a PCB load of approximately 0.7 ± 0.2 kg for water years 2004 and 2005. Considering that the Guadalupe River watershed comprises approximately 8% of the combined watershed area of the nine Bay Area counties, it is reasonable to hypothesize that the combined PCB load from local tributaries in an average year is on the order of 20 kg ($(1.2 + 0.7 + 0.7)/(3 \times 0.08) = 10.9$ kg in 7 months, ≈ 18.7 kg per year). Given the uncertainty associated with the different methods, it is difficult to determine which estimate is best (i.e., the estimate of KLI (2002, 2005) or of McKee and Leatherbarrow (2005) and McKee *et al.* (2005a)). Thus, as a first approximation, the PCB model in this study incorporates a local tributary input of **40 kg per year** as the default annual loading from local tributaries. This annual load will be adjusted during model calibration (Section III.).

Temporal Distribution Annual PCB loads from local tributaries are converted to daily PCB loads for use in the model based on the proportion of annual tributary runoff volume occurring on a given day. In other words, the model assigns a proportion of annual PCB loads occurring on a given day equal to the proportion of annual runoff occurring on that same day. Annual flow volumes are calculated for water year durations (October 1 to September 30). Daily streamflow from Guadalupe River at St. Johns Street (USGS Station 11169000) is used as input data to represent runoff patterns from local tributaries and indicate daily variability in tributary loads of PCBs. Of the 66 million cubic meters of annual flow volume discharged from Guadalupe River in WY 2000, approximately 3.1% of the annual discharge occurred on February 14th, 2000. Accordingly, the model is set up to discharge 3.1% (1.2 kg) of the WY 2000 annual PCB load (40 kg) from local tributaries on February 14th, 2000.

Guadalupe River daily flow data were selected as an indicator of tributary runoff based on an evaluation of temporal runoff patterns in several tributaries. In wet years (e.g., 1983), cumulative distributions of daily runoff in Guadalupe River are similar to those in Alameda Creek, Napa River, San Francisquito Creek, and Walnut Creek (Figure 5). However, during dry years (e.g., 1990), weaker relationships exist between tributaries. Thus, the use of Guadalupe River flow data to model runoff from other local tributaries is more appropriate during moderate to wet years than in dry years. An additional benefit of using Guadalupe River data is that the record of daily flow encompasses the entire period of the decadal hindcast (1940 to 2002).

Guadalupe River data are used as an indicator of tributary runoff and daily PCB loads in recognition of potentially significant uncertainties associated with this method. In reality, spatially heterogeneous characteristics, such as rainfall patterns and intensities, land use, geology, and PCB source distribution produce highly variable patterns of runoff and PCB transport within and between Bay Area watersheds. Furthermore, the direct correlation between runoff and PCB loads assumed in the model is not necessarily valid for many of the same reasons. As previously noted, however, this method provides a means for evaluating the long-term response of the Bay to episodic pulses (days to weeks) of runoff-driven inputs of PCBs from local tributaries. Future iterations of the model will test the sensitivity and uncertainty associated with this method.

Spatial Distribution Modeled daily PCB loads are proportionally distributed between the nine Bay Area counties according to the size of the population in each county as determined from cen-

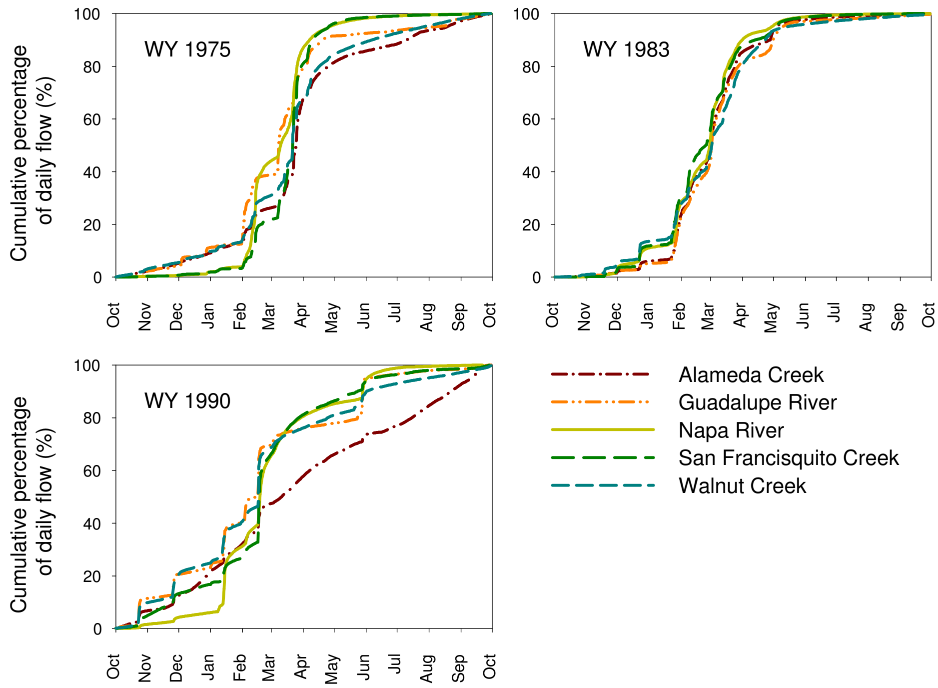

Figure 5: Cumulative daily distribution of annual runoff in local tributaries.

sus data (MTC-ABAG, 2003). Population is used as an indicator of load distribution based on findings of several studies that have found higher PCB concentrations in stream sediment collected from urban areas compared to non-urban areas (KLI, 2002). For example, Alameda County population in 2000 (1.4 million people) was approximately 21% of the entire Bay Area population (6.8 million). It follows then that the model requires that of the 1.2 kg of PCBs discharged to the Bay on February 14th, 2000, approximately 0.25 kg is discharged from Alameda County. Prior to WY 2000, the distribution of population in Bay Area counties varied significantly; therefore, PCB loads in the hindcast varied proportionally to reflect those trends.

To achieve even greater spatial resolution of PCB load distribution within counties, county-wide PCB loads are further divided into hydrologic regions used by Davis *et al.* (2000) and KLI

(2002) (Figure 6). For example, Alameda County is divided into hydrologic regions that include Berkeley, East Bay Cities, Fremont Bayside, and Alameda Creek. The PCB load discharged from Alameda County is divided into these regions based on the proportions of PCB loads for these regions determined by KLI (2002) (Table 2). In continuation of the above example for February 14th, 2000, the model requires that East Bay Cities discharge 56% (or 0.14 kg of PCBs) of the 0.25 kg of PCBs discharged by Alameda County on that day.

Figure 6: Hydrologic regions of the San Francisco Bay area from Davis *et al.* (2000).

Table 2: Local tributary loading of PCBs by county and hydrologic region.

Hydrologic Region	Assigned County[1]	% Bay Area Population per County, 2000	Current Annual PCB Load (kg)[2]	% Total Annual County PCB Load	Bay Segment	Model Boxes
Alameda Creek	Alameda	21	2.2	21	SB	7 – 8
Berkeley	Alameda		1.4	14	CB	18 – 19
East Bay Cities	Alameda		5.7	56	SB, CB	5 – 17
Fremont Bayside	Alameda		1.0	9	LSB	1 – 4
Concord	Contra Costa	14	4.3	77	CARQ, SUB	30 – 39
Pinole	Contra Costa		1.3	23	CB, SPB	20 – 29
Novato	Marin	4	1.1	30	SPB	23
San Rafael	Marin		2.7	70	CB	19 – 22, 49 – 50
Napa River	Napa	2	2.2	100	CARQ	29
San Francisco Bayside	San Francisco	11	0.4	100	CB	18 – 19, 49 – 50
San Mateo Bayside	San Mateo	10	4.5	100	SB,CB	5 – 17
Coyote Creek	Santa Clara	25	1.9	20	LSB	1
Guadalupe River	Santa Clara		2.1	23	LSB	2
Palo Alto	Santa Clara		5.3	57	LSB	2 – 4
Fairfield	Solano	6	1.8	100	CARQ, SUB	30 – 39
Petaluma Ruver	Sonoma	7	1.1	60	SPB	23 – 24
Sonoma Creek	Sonoma		0.7	40	SPB	26 – 27

[1] County designations of hydrologic regions are only approximate due to differing boundaries.

[2] Estimated PCB loads from KLI, 2002.

The model is formulated so that PCB loads from defined hydrologic regions enter the Bay into model boxes that lie directly adjacent to those regions. For large regions that are adjacent to several model boxes, the region-wide PCB load is equally distributed among each box. Thus, for example, the PCB load from East Bay Cities is equally distributed among boxes 5 through 17 (see Table 2). It is important to note that applied hydrologic regions and counties do not necessarily share common boundaries; therefore, the link between county-based population and regional distributions of PCB loads reported by KLI (2002) is only an approximation used for distributing PCB loads around the perimeter of the Bay on a daily time-step.

Wastewater Effluent

Daily inputs of PCBs from municipal wastewater effluents are incorporated into the model based on estimated PCB concentrations in effluent and annual wastewater effluent discharge estimates from Uncles and Peterson (1995, 1996). From November 1999 to February 2001, Yee *et al.* (2002) measured total PCB concentrations in effluent from nine municipal wastewater treatment plants (Table 3). For monitored treatment plants, typical PCB concentrations are multiplied by discharge volumes to obtain a daily PCB load. PCB loads enter the Bay in the upper layer of adjacent model boxes. For wastewater discharges that were not monitored in the PCB effluent studies, concentrations are estimated using data from the nearest treatment plant for which monitoring data were available.

Atmospheric Deposition

Addition of atmospherically-derived PCBs occurs through wet deposition of PCBs in rainfall in both dissolved and particulate form and through dry deposition of particles (e.g., dust). Atmospheric deposition of PCBs to the Bay is modeled on a daily time-step through wet and dry

Table 3: Wastewater effluent PCB concentrations in model boxes. 'Estimated' concentrations were based on data from the nearest monitored treatment plants.

Bay Segment	Model Boxes	Total PCB conc. (pg/L)	POTW	Source
LSB	1,2	200	SJSC, Sunnyvale	Yee et al. 2000
LSB	3	400	Palo Alto	Yee et al. 2000
SB	8,9	300	estimated	this study
CB	13	4200	EBDA	Yee et al. 2000
CB	15	2500	CCSF	Yee et al. 2000
CB	17	6800	EBMUD	Yee et al. 2000
CB	20,21,23 49,50	4000	estimated	this study
SPB	24,26,28	600	estimated	this study
CARQ	29,33	600	estimated	this study
SUB	34	1300	CCCSD	Yee et al. 2000
	37	600	Fairfield-Suisun	Yee et al. 2000
	42,45	600	estimated	this study

deposition of PCB mass to the top layer of the water column in each segment. Daily wet deposition of PCBs is modeled based on daily rainfall volumes measured in San Francisco (Null, 2004) and an estimated total PCB rainfall concentration of 1 ng/L. There are currently no published data on PCB concentrations in Bay Area rainfall; therefore, the modeled rainfall concentration is based on measured PCB concentrations of similar magnitude in studies conducted in urban areas (Zhang *et al.*, 1999; van Ry *et al.*, 2002; Park *et al.*, 2001; Hornbuckle *et al.*, 1994). Modeled rainfall is uniformly distributed across all segments of the Bay.

Dry deposition of PCBs is modeled on every time-step and is independent of rainfall conditions. The rate of dry deposition used in the model (1 ng PCBs/m2/day) is consistent with the range reported by Tsai *et al.* (2002) at a location close to San Francisco Bay for the period June to November, 2000 (0.39 to 2.1 ng PCBs/ m2/day). Similar to rainfall, PCB inputs from dry deposition are distributed uniformly across all segments of the Bay.

2. Mixing and Advection

PCBs in the water column are physically mixed and advected according to Equation 1, with S representing daily total PCB concentration (C_t in other equations). The mixing equation is solved on a daily time-step by a matrix inversion scheme. The longitudinal and vertical current velocities used to transport PCBs are identical to those used in the salinity and sediment transport modules.

3. Partitioning

The process of PCB partitioning between dissolved and particulate fractions is modeled using the octonal-water partitioning coefficient (K_{ow}). The PCB model is developed to represent total PCBs (or the sum of congeners) and as such cannot account for differential partitioning of the various congeners. In the previous modeling study of PCBs in the Bay, Davis (2004) selected properties of PCB 118 as default values based on the rationale that PCB 118 is a good indicator of the most abundant and toxic fraction of PCBs found in San Francisco Bay. The approach in this study is consistent with that approach.

The octanol-water partitioning coefficient (K_{ow}) influences the extent to which PCBs partition between dissolved and particulate fractions in the water column. However, K_{ow} represents the partitioning of chemicals between octanol and water, while chemicals in the environment are believed to partition to organic carbon. It is therefore more appropriate to use the organic carbon-water partitioning coefficient (K_{oc}) to represent the partitioning of PCBs between water and suspended particles. The model estimates K_{oc} from K_{ow} using the following relationship (Seth *et al.*, 1999):

$$log(K_{oc}) = 1.03 \times log(K_{ow}) - 0.6 \tag{6}$$

The dissolved fraction of PCBs in the water column (ϕ_{DW}) is then calculated as a function of K_{oc} as follows:

$$\phi_{DW} = (1 + SSC \times OC \times K_{oc})^{-1} \tag{7}$$

where SSC is the modeled suspended sediment concentrations and OC is organic carbon content of the suspended particles. The default value of K_{ow} is $10^{6.7}$ (representative of PCB 118). A constant value of OC (3%) is used in the model based on a review of San Francisco Bay characteristics by Davis (2004).

Likewise, the dissolved fraction of PCBs in sediment pore water is calculated as a function of K_{oc} as follows:

$$\phi_{DS} = (1 + C_{ss} \times OC_{sed} \times K_{oc})^{-1} \tag{8}$$

where C_{ss} is the concentration of solids in sediment and OC_{sed} is the organic carbon content of sediment (range: 0.0006-0.014, (Oros and Ross, 2004)). It has been demonstrated that environmental partitioning of PCBs between water and sediment depends not only on the quantity of organic carbon present but also on the quality (or type) of organic carbon (Barring *et al.*, 2002). Given that the quantity, and likely the quality, of organic carbon content of San Francisco Bay sediments (suspended and bedded) are spatially variable (Oros and Ross, 2004), it is likely that PCB partitioning is also spatially variable. K_{oc} is, therfore, a region specific parameter. Using Equation 6, a default, spatially uniform, value of $K_{oc} = 10^{6.3}$ was used for model development. Region specific values were developed during model calibration (Section III.).

4. Volatilization

The PCB model describes the rate of volatilization of dissolved PCBs from the top layer of the water column using a series of equations presented by Davis (2004):

$$K_v = \frac{\phi_{DW} V_E}{H_u} \tag{9}$$

where K_v is the rate of PCB volatilization, ϕ_{DW} is the fraction of freely dissolved PCBs calculated in equation 7, V_E is the volatilization mass transfer coefficient, and H_u is the water depth of the upper layer. The volatilization mass-transfer coefficient (V_E) is calculated based on a two-film model commonly used to describe PCB transport across the air-water interface of surface water bodies (Hornbuckle *et al.*, 1994; Zhang *et al.*, 1999; Totten *et al.*, 2001, 2003):

$$\frac{1}{V_E} = \frac{1}{V_{EW}} + \frac{1}{K_{AW} V_{EA}} \tag{10}$$

where V_{EW} is the mass transfer rate coefficient across a stagnant water layer, V_{EA} is the mass transfer rate coefficient across a stagnant air layer, and K_{AW} is the unitless and temperature-dependent Henry's Law Constant of the PCB 118. Mass transfer rate coefficients for water and air are derived from Schmidt numbers and diffusivities based on equations in Davis (2004) and Hornbuckle *et al.* (1994):

$$V_{EW} = 0.45 W^{1.64} \left(\frac{Sc_{PCB}}{Sc_{CO_2}} \right)^{-0.5} \tag{11}$$

$$V_{EA} = (0.2W + 0.3) \left(\frac{D_{PCBA}}{D_{WA}} \right)^{0.61} \tag{12}$$

where W is wind velocity data input to the sediment transport model for calculation of erosion rates, Sc_{PCB} and Sc_{CO2} are Schmidt numbers for PCBs and carbon dioxide (CO_2), respectively.

D_{PCBA} is diffusivity of PCBs in air, and D_{WA} is diffusivity of water in air. Default values of D_{PCBA} (0.051 cm^2/s) and Sc_{PCB} (2650) are based on values reported in Hornbuckle *et al.* (1994) for pentachlorobiphenyls (e.g., PCB 118) at a temperature of 15^oC. Zhang *et al.* (1999) reported a relationship by which Sc_{CO2} changes with water temperature (T_W in units of Kelvin):

$$ln\left(Sc_{CO_2}\right) = -0.052T_W + 21.71 \tag{13}$$

The model temperature of Bay water (T_W) is held constant at 15^oC (288 K), which is the annual average water temperature from 1994 to 1996 determined by Davis (2004); therefore, Sc_{CO2} is held at a constant value of 841. At this temperature, D_{WA} is set to 0.24 cm2/s. The unitless Henry's law constant (K_{AW}) in equation 10 is also calculated as a function of T_W and Henry's law constant (H_{TW}), which itself is corrected for temperature based on equations in Hornbuckle et al. (1994):

$$K_{AW} = \frac{H_{TW}}{RT_W} \tag{14}$$

$$\log(H_{TW}) = \log(H_{298K}) + 8.76 - \frac{2611}{T_W} \tag{15}$$

where R is the universal gas constant (8.314 Pa-m3/mol-K), T_W is in units of K, H_{TW} is the temperature dependent Henry's law constant (Pa-m3/mol), and H_{298K} is the Henry's law constant at 25^oC (298 K; Pa-m3/mol).

5. Degradation

PCB degradation rates in water (K_{dw}) and sediment (K_{ds}) were selected to encompass all degradation pathways, such as hydrolysis, photolysis, and microbial degradation. Degradation rates of PCBs have not been well characterized in field studies (water or sediment); therefore a degradation rate of **3.3 x 10-5 /d** is applied to PCBs in water (dissolved and particulate) and sediment based on Davis (2004) and Gobas *et al.* (1995). Assuming first order degradation, this rate equates to an approximate half-life of 56 years.

PCB degradation in sediment is thought to decrease with increasing depth into the sediment. Compaction, limited oxygen supply, and decreased microbial activity are thought to cause the observed decrease in degradation at depth. The model accounts for this by using a depth dependent degradation rate in sediment given by:

$$K_{ds_i} = K_{ds_o} \exp\left[-\frac{z_i^2}{2\gamma^2}\right] \tag{16}$$

where K_{ds_o} is the degredation rate in sediment at the sediment surface, z_i is depth into sediment, and γ is a depth dependence parameter taken from the depth dependent vertical mixing of buried sediments (see Section 7. for more).

6. Sediment-Water Exchange

On each daily time-step, PCBs in the surface sediment layer change in response to deposition of particulate PCBs from the water column, erosion of sediment from the surface sediment layer, and diffusion of dissolved PCBs between sediment pore water and the overlying water column. Sediment erosion (R_E) and deposition (R_D) rates are calculated as part of the sediment transport module to estimate net sedimentation patterns in the Bay. Those same rates are used by the PCB module to determine the mass transfer between sediment and water due to sedimentation according to the following equations:

$$\psi_{sw} = \frac{R_E C_{s_1}}{H} - \frac{R_D A_{SW} C_t (1 - \phi_{DW})}{SSC} \tag{17}$$

$$\psi_{ws} = \frac{1}{Z_s \rho_s} \left(\frac{R_D A_{SW} C_t (1 - \phi_{DW})}{SSC} - R_E C_{s_1} \right) \tag{18}$$

where ψ_{sw} represents the net PCB mass transfer from sediment to water due to sedimentation and ψ_{ws} represents the net PCB mass transfer from water to sediment due to sedimentation.

Diffusion of dissolved PCBs between the sediment pore water and the overlying water column is modeled according to Davis (2004). The sediment-to-water diffusion rate (K_{sw}) and the water-to-sediment diffusion rate (K_{ws}) are given by:

$$K_{sw} = \frac{\phi_{DS} V_d}{(1 - \phi_{DS}) Z_s} \tag{19}$$

$$K_{ws} = \frac{\phi_{DW} V_d}{H} \tag{20}$$

where V_d is the sediment-water mass transfer coefficient.

7. Sediment Mixing

Bed sediment dynamics in San Francisco Bay greatly influence the mass of PCBs stored in sediment and time scales in which PCBs remain in circulation and affect water quality (Davis, 2004). Two distinct types of sediment processes have a significant influence on PCB fate and are incorporated into the model: 1) vertical mixing of sediment through bioturbation and physical processes, and 2) long-term net erosion and deposition of bedded sediment. Vertical mixing causes incorporation of PCBs in surface sediments into deeper sediment layers. The long-term net erosion and deposition determines the mass of PCBs transferred across the sediment-water interface (Section 6.). The combined influence of both processes ultimately determines the concentrations of PCBs in surface sediments and time scales of PCB storage in sediment.

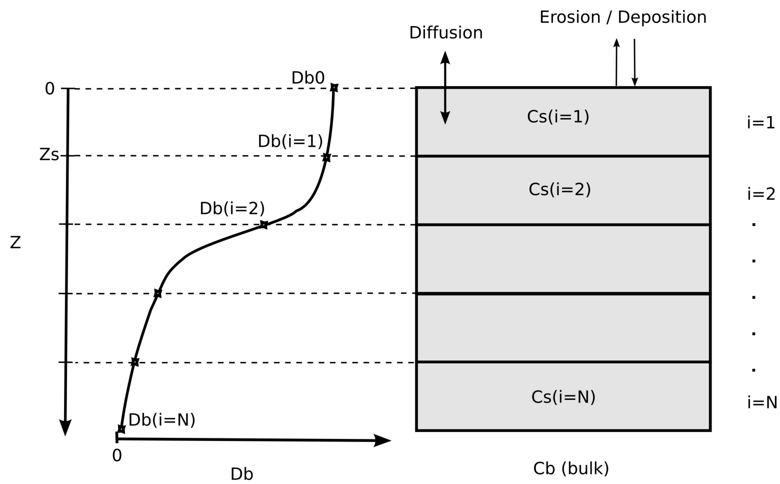

Figure 7: Schematic of the depth-dependent sediment mixing model.

The multi-box PCB model incorporates a model that describes bed sediment as N well-mixed sediment layers of thickness Z_s (Figure 7). The surface sediment layer interacts with PCBs in the water column through sedimentation (erosion and deposition) and diffusion, as described in Section 6.. The sediments are then mixed vertically, with mixing treated as a diffusive process based on relationships previously used to describe radionuclide mixing in estuarine and marine sediment cores (Fuller *et al.*, 1999; Olsen *et al.*, 1981; Peng *et al.*, 1979) (Equation 5). The vertical mixing equation also allows for the depth dependent degradation of PCBs in sediments (see Section 5.).

The depth dependent mixing rate (D_{b_i}, in Equation 5) is given by

$$D_{b_i} = D_{b_o} \exp\left[-\frac{z_i^2}{2\gamma^2}\right] \tag{21}$$

where D_{bo} is the mixing rate at the top of the sediment bed, z_i is the bottom depth of the i_{th} sediment layer, and γ is a depth dependence parameter. Selected default values are 71 cm^2/yr for D_{bo} and 9 cm for γ based on a best-fit numerical simulation of 210Pb profiles by (Fuller *et al.*,

1999) in a sediment core collected from Richardson Bay (a sub-bay of San Francisco Bay). As Fuller *et al.* (1999) noted, these best-fit values result in a reduction of D_{b_i} to approximately 0.1% of D_{b_o} at a depth of 33 cm. As a result, virtually no mixing occurs below the 33 cm depth.

8. Estimation of Historic PCB Loads

Validation of the model on a decadal time scale is necessary for constraining model parameters that influence long-term trends in PCB contamination. A hindcast was performed to ensure that model results remain within realistic bounds over long time scales. This was accomplished by back-estimating PCB loads on a daily time step to 1940, running the model from 1940 to 2002, and comparing model results to known patterns in PCB contamination of the Bay. The lack of information on historic PCB loading and concentrations (prior to 1993) precludes making extensive comparisons between model results and actual data. The PCB model can only be evaluated on on its ability to re-produce current (post 1993) patterns of PCB contamination in Bay water and sediment.

Daily PCB loads were estimated back to 1940 using methods similar to those used in the calibration of a PCB fate model for the Delaware Estuary (DRBC, 2003). Historic patterns in PCB loading were estimated based on trends in PCB emissions in the United States (Breivik *et al.*, 2002). Breivik *et al.* (2002) compiled available data on U.S. production and consumption of PCBs to estimate PCB emissions to the atmosphere for each year from 1930 to 2000 (Figure 8). Due to significant uncertainties in methods and assumptions noted by Breivik *et al.* (2002), PCB emission estimates are considered at best order-of-magnitude approximations. Despite these uncertainties, in the absence of better information these PCB emission trends were used in developing a hindcast of PCB inputs to the Bay. Following the rationale presented by DRBC (2003), the use of atmospheric emission trends as an indicator of water emission trends (e.g. runoff) is thought to be reasonable under the assumption that, during times of heavy production and use, a PCB source will have similar trends in release via different pathways.

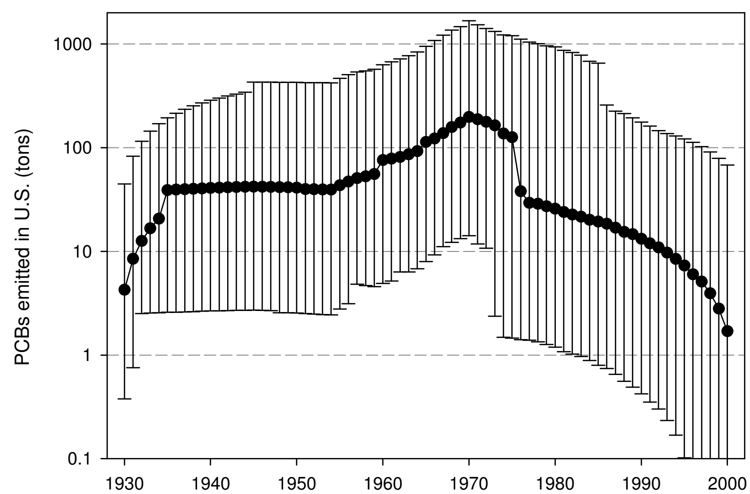

Figure 8: Estimated trends in PCB emissions to the atmosphere in the US from 1913 to 2000. Estimates compiled by Breivik *et al.* (2002).

In developing the model hindcast, PCB data used for deriving PCB loading in WY 2000 were scaled as a function of emission trends reported by Breivik *et al.* (2002). This was achieved by deriving a scaling factor based on normalization of PCB emission estimates for individual years by the PCB emission estimate for 2000. To illustrate, scaling results in a factor of one for WY 2000 and a factor of approximately 110 for 1970. As a result, a local tributary PCB load of 20 kg in WY 2000 would scale to a load of 2,200 kg in WY 1970. All of the loading pathways (local tributaries, Delta outflow, atmospheric deposition, and wastewater effluents) were adjusted using this scaling function.

Significant uncertainty is associated with these estimates of historic emissions, as noted by the large error bars in Figure 8. These estimates should therefore serve as only a generally pattern for estimating historic PCB loads to the Bay. The method of estimating historic PCB loads to the Bay was re-analyzed during model calibration. It was concluded that there is no real reason to use the exact trend observed in the estimates of Breivik *et al.* (2002), but rather to use the general trend of the estimates to develop trends in PCB loads to the Bay. With the goal of improving model results by providing a less noisy pattern of historic loads, the estimates of Breivik *et al.* (2002) were smoothed with a 10 year running filter. The resulting loading curve is seen in Figure 9. Additionally, the introduction of PCB loads to the Bay does not begin until January 1, 1950 in order to allow the sediment model to 'spin-up' for 10 years. This change was made at the recommendation of the Contaminant Fate Workgroup (CFWG), a group of experts in the field of contaminant fate modeling, and Tetra Tech, Inc. (2005) which observed an irregular 'spin-up' period in the sediment model. Any PCB mass introduced during this period could potentially be incorrectly transported. Starting PCB loading after the spin-up period avoids this potential problem.

III. PCB Model Calibration

Hindcast results of surface sediment PCBs were generally within an order of magnitude of field observations without calibration (Figure 10A). This level of agreement with field observations is reasonable, given the uncertainty surrounding model parameters and load estimates. Field observations used in this comparison were surface sediment samples taken by NOAA-EMAP in 2001 and 2002 (U.S. EPA, 2004) and results of the Regional Monitoring Program for Water Quality in San Francisco Estuary (RMP). The NOAA-EMAP field data were interpolated onto a regular 2km grid of San Francisco Bay using geospatial kriging, a method of interpolation based on the spatial correlation structure of the known data when estimating the value at unsampled locations

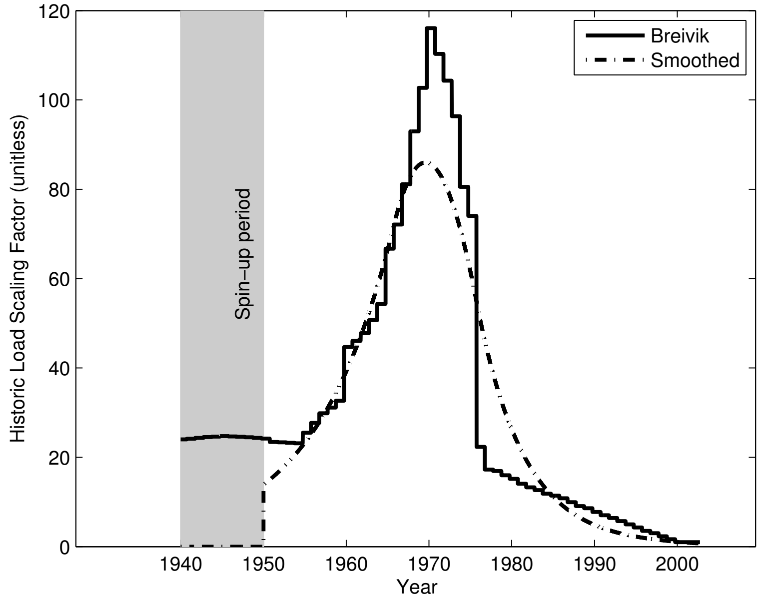

Figure 9: Smoothed historic PCB loading trend with no spin-up loading.

(Journel and Huijbregts, 1981). The interpolated data were then spatially binned to determine the mean and standard error for each Bay segment. RMP field data from 2002 to 2005 were processed using the Generalized Random Tessellation Survey (GRTS) design and analysis algorithms available for the R statistical software package (www.r-project.org). Geometric means and standard deviations were were calculated for RMP field data prior to 2002.

Figure 10B compares uncalibrated model predicted average vertical profile of PCBs in San Pablo Bay bed sediment with field observations of the PCB depth profile taken in San Pablo Bay by Venkatesan *et al.* (1999). Subsurface maxima occur at approximately the same depth in both the model output and the field observations, though the concentrations predicted by the model are significanlty higher. This level of agreement for an uncalibrated model is encouraging considering the uncertainties associated with estimating the various model input parameters.

A number of model parameters exist to calibrate model results to achieve closer agreement with field data. The most appropriate parameters to use in calibration are the magnitude and spatial distribution of external loads from local tributaries, the magnitude and temporal trends of loads from the Delta, wastewater discharge, and atmospheric depostion, and the partitioning of PCBs to suspended and bedded sediment. Changes made as a result of model calibration are outlined in the following sections. The salinity and sediment models were not altered during calibration of the PCB model, as these models were calibrated by their original developers (i.e., Uncles and Peterson (1995, 1996) and Lionberger (2003); Lionberger and Schoellhamer (2007)).

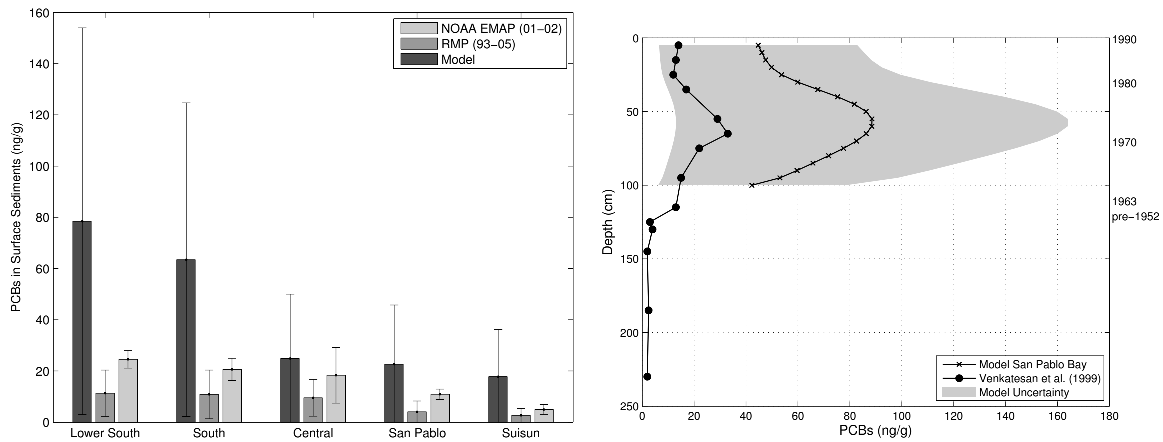

Figure 10: Uncalibrated hindcast model results: (A) Surface sediment PCB concentrations compared with NOAA-EMAP and RMP field observations, (B) Vertical profiles of modeled PCBs in bed sediments compared to observations from Venkatesan *et al.* (1999). Error bars on NOAA-EMAP and RMP data represent the segment variability of observations. Error bars and shading on model results represent aggregate model uncertainty at the 95% confidence level.

A. TRIBUTARY LOADS

A default estimate of 40 kg of PCBs per year loaded from local tributaries was used during model development. Uncalibrated model results at the end of the hindcast, while reasonable for a first guess, significantly exceeded field observations (Figure 10). Improved recent information on loading estimates from local tributaries (KLI, 2002, 2005; McKee and Leatherbarrow, 2005; McKee *et al.*, 2005a, e.g.) suggested that an annual PCB load of 40 kg was too high. A careful review of existing loading studies conducted by the Sources, Pathways, and Loadings Workgroup of the RMP resulted in a new estimate of **20 kg per year** for the annual PCB load for WY 2000 (Lester McKee, San Francisco Estuary Institute, personal communication).

B. DELTA LOAD

The comparison of observed to model-predicted surface sediment PCB concentrations in the northern Estuary (i.e., Suisun and San Pablo Bays, abbreviated SPB and SuB respectively in Figure 10) indicated that estimated PCB loads from the Delta should be scaled down. Thus, a scaling factor, Υ_{Delta}, was applied to the Mallard Island regression equation as follows:

$$L_{Delta} = (89.72 \times \log(SSC) + 106.77) \times Q_{Delta} \times \Upsilon_{Delta} \tag{22}$$

where Q_{Delta} is the daily Delta outflow. The model was run iteratively until a reasonable fit was observed in Suisun Bay surface sediment PCB concentrations. The final value of the scaling factor was $\Upsilon_{Delta} = 0.5$, indicating either that the regression equation relating PCBs to SSC (Figure 4) overpredicts PCB loads from the Delta or that the model unrealistically retains PCB mass in the northern Estuary. An RMP pilot study is currently being conducted to investigate the latter. This pilot study hypothesizes that a considerable portion of the loads of water, sediment, and associated contaminants delivered during episodic high-flow events via the Delta actually exit the Bay through the Golden Gate within a few tidal cycles. Measurements of material fluxes at Mallard Island therefore may be an overestimate of the mass passing through the Delta that is actually retained within the Bay.

C. PCB PARTITIONING

Preliminary testing of model version 1.0 indicated that results were highly sensitive to changes in PCB partitioning between water and sediment (Leatherbarrow *et al.*, 2005). Moreover, environmental partitioning is a highly variable processes that is difficult to characterize. Partitioning coefficients were therefore an obvious candidate for model calibration.

An estimator of model bias (MB^*) was developed to provide an objective means of finding best values for region-specific PCB partitioning coefficients (K_{oc}). The model bias estimator incorporates the regional-scale deviation of model-estimated PCB concentrations in water and sediment from field observations (RMP data used for particulate and dissolved concentrations; NOAA-EMAP data used for surface sediment concentrations). The determination of MB^* requires that the model bias (MB) of particulate, dissolved, and sediment PCBs on a regional basis be calculated first:

$$MB_{ij} = \frac{Model\ PCB\ Concentration\ in\ Matrix\ i\ and\ Region\ j}{Observed\ PCB\ Concentration\ in\ Matrix\ i\ and\ Region\ j} \tag{23}$$

where i represents either particulate, dissolved, or surface sediment and j represents the Bay segment (i.e., Suisun, San Pablo, Central, South, or Lower South Bay). Next, the mass-weighted model bias for all matrices (MB_j^*) is calculated for each segment:

$$MB_j^* = \frac{\sum_i M_{ij} MB_{ij}}{\sum_i M_{ij}} \tag{24}$$

where M_{ij} is the PCB mass in matrix i and segment j. Finally, MB^* is the mean of the individual segment model biases:

$$MB^* = \frac{1}{N}\sum_{j=1}^{N} MB_j^* \tag{25}$$

where N is the number of Bay segments ($N = 5$). The model was run iteratively using different values for each regional partitioning coefficient, with care taken to ensure that coefficients did not change outside the realm of what is conceptually acceptable. The overall model bias (MB^*) was determined for each iteration until an optimum value (value closest to one) was obtained.

After many iterations, the following calibrated region specific partitioning coefficients were obtained: Lower South Bay = $8.0e5$, South Bay = $8.0e5$, Central Bay = $7.5e6$, San Pablo Bay = $4.0e6$, Suisun Bay = $8.0e5$, Delta = $8.0e5$.

D. Summary of Calibration Efforts

During initial model development it was obvious that uncertainties associated with estimating magnitudes and spatial patterns of historic loads and PCB partitioning coefficients would translate into significant uncertainties in model results. Therefore, calibration efforts focused on refining historic loads and partitioning. Other PCB-related model parameters, such as volatilization or degradation rates, could have been changed through trial-and-error calibration procedures. However, these parameters are based on previous studies and their relative uncertainty is often unknown. Further, the uncertainty in model results that can be attributed to these parameters was not so obvious. Future uncertainty analysis will help determine which model parameters are most influential and may be appropriate to use in further calibration efforts.

IV. Uncertainty Analysis

A. INDEPENDENT PERFORMANCE EVALUATION

An independent analysis of the multibox PCB model was performed by Tetra Tech, Inc. to assess the uncertainty of model predictions and identify ways to improve model performance (Tetra Tech, Inc., 2006). Multiple input parameters (Table 5) were varied simultaneously using random sampling techniques. 10,000 model runs were executed and model performance was evaluated by prescribed performance standards that measured how well model predictions compared to observed data in different Bay segments. Of the 10,000 model runs, only 389 were found to surpass calibrated model results. Analysis of these 389 model runs suggested partitioning coefficients, tribuatry loads, and particle settling velocities as the key model input parameters responsible for the improved performance. Coincidently, two of these three parameters were used during model calibration (e.g., partitioning and tributary loads).

B. ASSESSMENT OF AGGREGATE UNCERTAINTY

Extensive analyses were performed to assess the aggregate of uncertainty of model estimates resulting from uncertainties in model input parameters. For the analyses, the uncertainty and/or variability of each sediment- and PCB- related model input parameter was represented by statistical distributions (Table 4). These distributions express how the input parameters 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. A total of 10,000 model runs were generated for this analysis. The same set of 10,000 runs were originally used by Tetra Tech, Inc. (2006) in their independent testing of the multibox model.

Analyses were performed on a Bay segment basis. Figure 11a illustrates how the distribution of the 10,000 model runs was used to determine the uncertainty of modeled PCB concentrations in surface sediments in South Bay. In analyzing the results for other model outcomes and Bay segments it became evident that a relationship between model uncertainty (expressed by twice the standard deviation of the 10,000 runs, an approximation of the 95% confidence interval) and average model estimates existed. Figure 11b shows this relationship for PCBs in South Bay surface sediments. In this example the uncertainty of model results was estimated to be approximately equal to mean of all runs. In other words, the uncertainty of modeled PCB concentrations in South Bay surface sediments is $\pm 100\%$. Results for other Bay segments and model outcomes are summarized in Table 5.

Strong correlations between the mean and uncertainty of model runs were observed for the majority of the model outcomes and Bay segments (Table 5). These relationships were used to extrapolate model uncertainty to all other model runs (i.e., those not used in uncertainty analysis).

A relatively low degree of uncertainty in model predicted PCB concentrations in water and sediment was observed in the northern reach of the Bay (Table 5). This trend is an artifact of the spatial distribution of PCB loads from local watersheds and the range over which PCB loads from the Delta were tested during uncertainty analysis.

The northen reach of the Bay receives less PCBs from local watersheds than do the central and southern reaches (Figure 12). PCB loads from local watersheds are known to be key drivers of model-predicted PCB concentrations in water and sediment (Leatherbarrow *et al.*, 2005; Tetra Tech, Inc., 2006). However, it reasonable to expect a relatively localized effect of varied PCB loads from local watersheds. Hence, the variability in model-predicted PCB concentrations due to varied PCB loads from local watersheds was restricted to the Bay segments that recieve the highest proportion of those loads.

Additionally, the northern reach of the Bay is known to be controlled by freshwater flows from the Delta (Conomos, 1979). Delta outflow and associated loads of sediment and PCBs were varied over a relatively small range during uncertainty testing (seddeltafac in Table 4), thereby limiting the associated variability in model predictions in the northern reach.

Table 4: Model input parameters and distributions used for uncertainty analysis. Table originally presented in Tetra Tech, Inc. (2006)

Parameter	FORTRAN variable name	Distribution	Units	Best Estimate	Lower Limit	Upper Limit
Surface sediment mixing coefficient	**Dbo**	**Uniform**	cm^2/yr	71	12	130
Half Gaussian depth dependence	**gam**	**Uniform**	cm	9	5	13
PCB Degradation rate	**deg**	**Lognormal**	1/yr	0.012	0.0012	0.12
PCB Degradation in sediment			same as above			
Erosivity scaling factor	**constefac**	**Uniform**	unitless	1	0.95	1.05
Scale factor for wind shear and current shear	**constwfac**	**Uniform**	unitless	1	0.95	1.05
Settling velocity scale factor	**constdfac**	**Uniform**	unitless	1	0.95	1.05
Water sediment mass transfer coefficient	**Vd**	**Lognormal**	m/d	0.0024	0.00024	0.024
Tributary SSC loading scaling factor	**sedtribfac**	**Uniform**	unitless	1	0.95	1.05
Tributary PCB load	**pcbtload**	**Uniform**	kg/yr	20	5	35
Delta SSC scaling	**seddeltafac**	**Uniform**	unitless	1	0.95	1.05
PCB concentration in rain	**pcbrain**	**Uniform**	pg/l	1000	50	1950
Atmospheric PCB dry deposition rate	**pcbdry**	**Uniform**	pg/m^2/d	1000	390	1610
Wastewater PCB scaling	**pcbwwfac**	**Uniform**	unitless	1	0.9	1.1
Organic carbon content of suspended sediment	**ocss**	**Uniform**	unitless	0.03	0.01	0.05
Organic carbon content of sediment-LSB	**ocsed**	**Uniform**	unitless	0.014	0.004	0.024
Organic carbon content of sediment-SB	**ocsed**	**Uniform**	unitless	0.012	0.002	0.022
Organic carbon content of sediment-CB	**ocsed**	**Uniform**	unitless	0.009	0.005	0.013
Organic carbon content of sediment-SPB-SUI	**ocsed**	**Uniform**	unitless	0.012	0.006	0.018
Organic carbon content of sediment-Delta	**ocsed**	**Uniform**	unitless	0.006	0.003	0.009
Water Temperature	**tw**	**Uniform**	K	288	285	291
Suspended sediment density	**rhoss**	**Uniform**	kg/L	1.1	0.7	1.5
Concentration of solids in sediment	**css**	**Uniform**	kg/l	0.5	0.4	0.6
Octanol-water partition coefficient for PCB-118	**kow**	**Lognormal**	unitless	5.50E+06	4.0+05	7.6E+07
Kh constant for PCB-118	**Kh**	**Uniform**	Pa-m3/mol	3.94	1.01	6.87

Best estimate = Median value of truncated lognormal distributions
1/2 (lower limit plus upper limit), uniform distributions
Lower limit = minimum value of truncated lognormal distributions
Smallest value, uniform distribution
Upper limit = Maximum value of truncated lognormal distributions
Largest value, uniform distributions

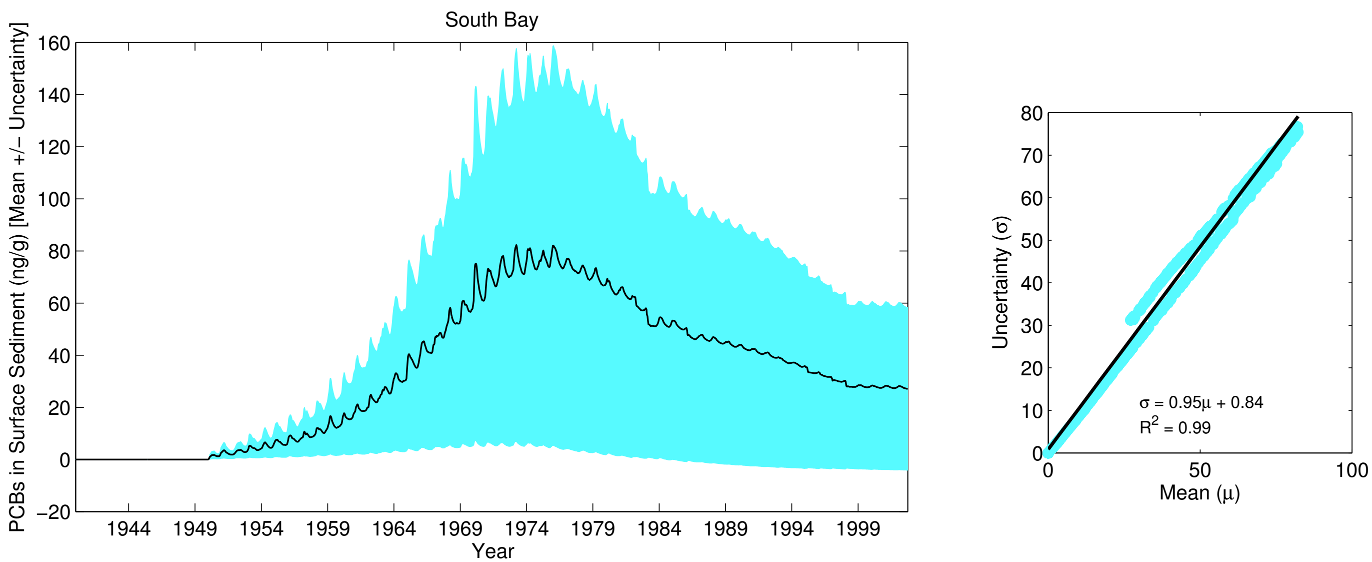

Figure 11: Uncertainty of modeled PCB concentrations in surface sediments (top 5 cm) in South Bay. The black line indicates the average of all 10,000 model runs. The shaded region indicates the uncertainty of model results.

Table 5: Summary of linear regressions of average model outcome versus the uncertainty (twice the standard deviation) of all uncertainty analysis model runs.

Model Outcome	Subregion	Slope	Intercept	R^2
Total PCBs in water	Suisun Bay	0.34	179.39	0.72
	San Pablo Bay	0.68	41.77	0.97
	Central Bay	0.72	19.25	0.99
	South Bay	0.84	264.50	1.00
	Lower South Bay	0.86	353.87	1.00
PCBs in surface sediments	Suisun Bay	0.69	0.31	0.98
	San Pablo Bay	0.82	0.48	0.99
	Central Bay	0.99	0.61	0.99
	South Bay	0.95	0.84	0.99
	Lower South Bay	0.94	1.83	1.00
SSC	Suisun Bay	0.11	-2.76	0.73
	San Pablo Bay	0.08	0.13	0.95
	Central Bay	0.08	0.08	0.89
	South Bay	0.08	-0.08	0.66
	Lower South Bay	0.06	3.88	0.67
Sediment deposited	Suisun Bay	-0.07	6.70E+08	0.98
	San Pablo Bay	-0.13	-3.84E+07	0.99
	Central Bay	-0.24	-6.08E+08	0.95
	South Bay	-0.09	2.18E+08	0.99
	Lower South Bay*	0.00	3.76E+08	0.02

* Uncertainty is difficult to estimate in Lower South Bay as the sediment model is specifically calibrated to net sedimentation in this segment.

V. Results and Discussion

A. Validation: Salinity and SSC

The underlying hydrodynamic and sediment transport models were calibrated and validated for daily salinity by Uncles and Peterson (1995, 1996) and for long-term sedimentation by Lionberger (2003); Lionberger and Schoellhamer (2007). This study provides an added validation of hindcast salinity and SSC to ensure consistency in model behavior among studies and to bolster confidence

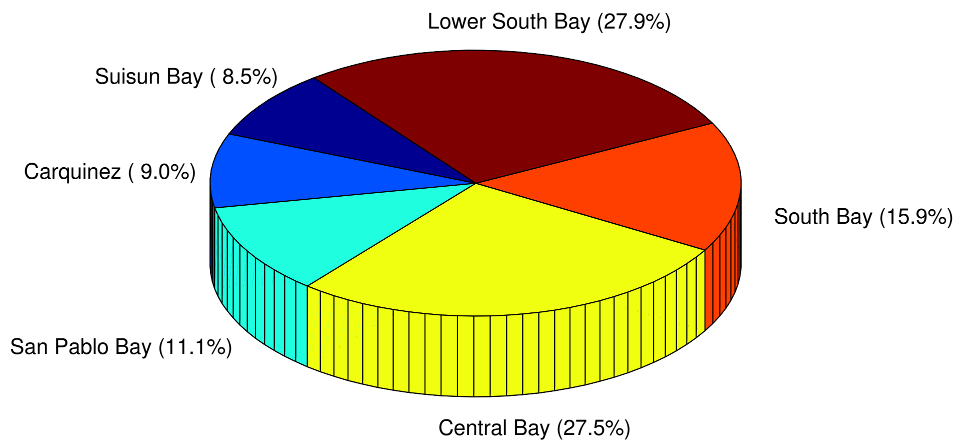

Figure 12: Percent of WY 2000 PCB loads from local watersheds loaded into each Bay segment.

in model results.

Modeled salinity and SSC for WY 1999 were compared to observations at Pier 24 (Central Bay; Figure 13). Modeled upper and lower layer salinity and depth averaged SSC trended with observations and captured observed variability on a seasonal to sub-seasonal (i.e., spring-neap cycle) basis but underestimated daily variability. A similar comparison of modeled SSC to observed SSC at Channel Marker 17 (Lower South Bay) again illustrated the models ability to reproduce the seasonal to sub-seasonal variability (Figure 14). The fact that the model was able to reproduce WY 1999 observations of both salinity and SSC after approximately sixty years of simulation indicates that the model captures the key physical processes governing water and sediment transport in the Bay. The agreement of modeled and observed daily SSC is particularly encouraging given that the sediment model was calibrated to long-term net sedimentation, leaving SSC as a free parameter. The SSC comparison is thus a true validation of model performance.

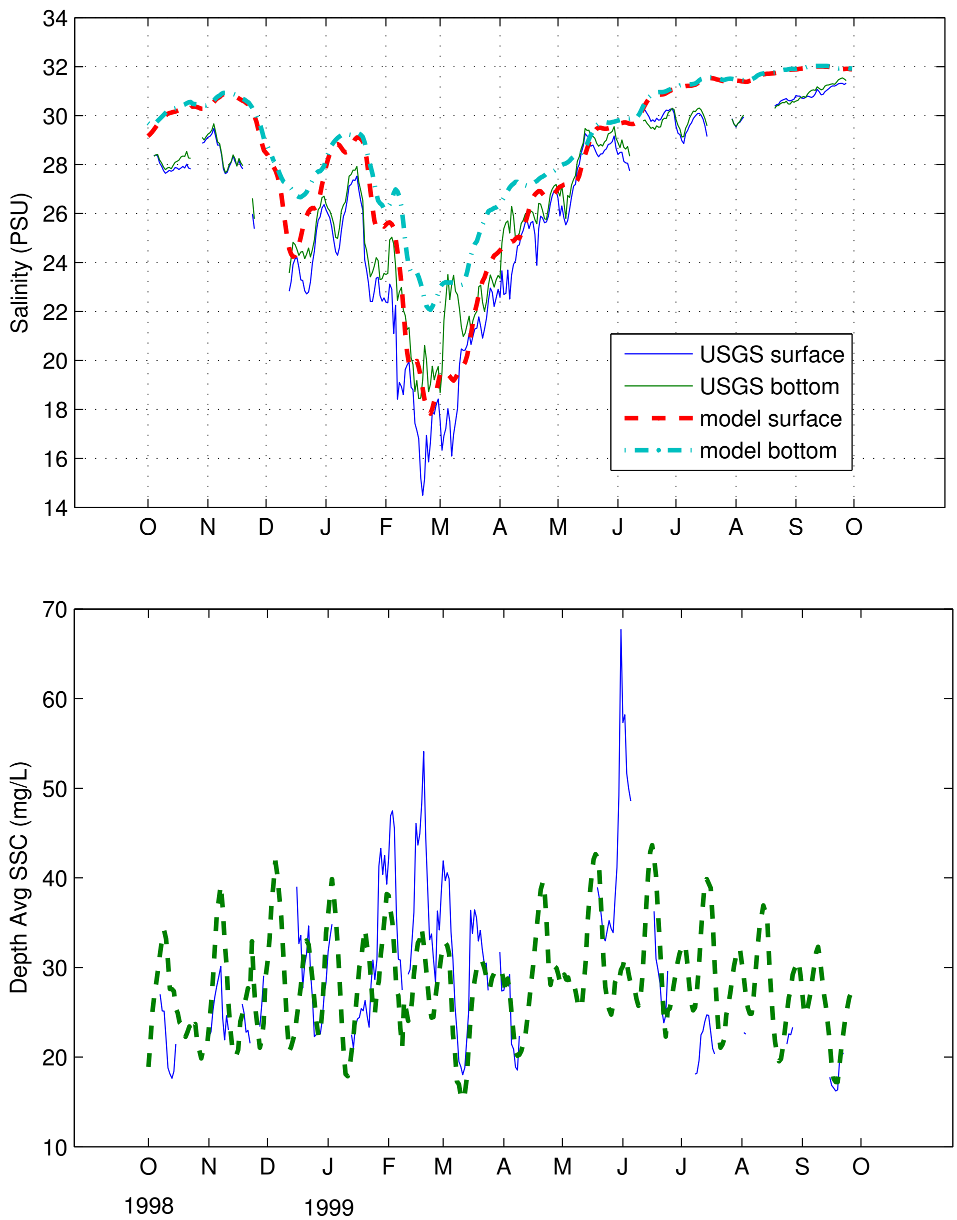

Figure 13: Validation of modeled daily salinity (top) and SSC (bottom) at Pier 24 (Central Bay) for WY 1999.

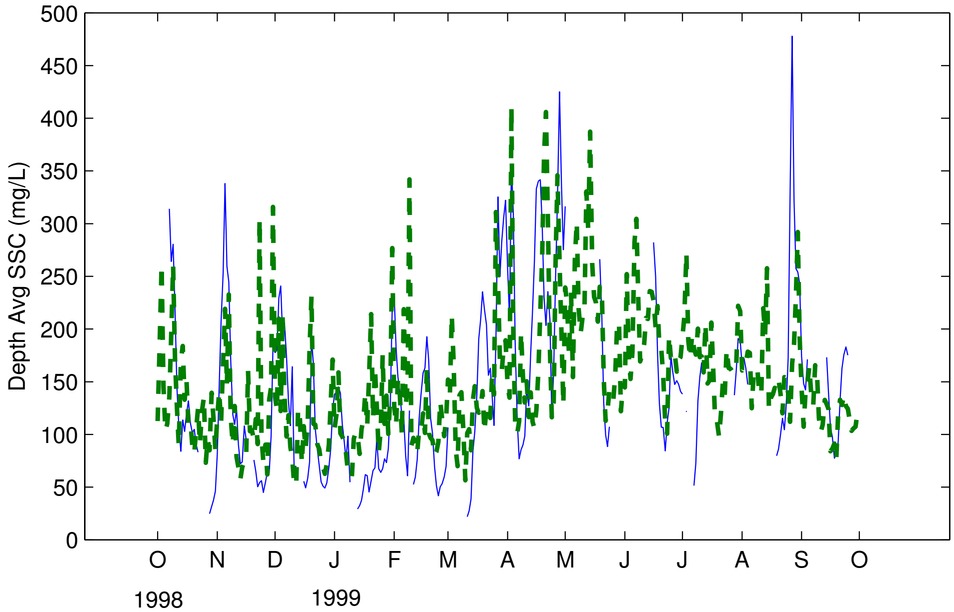

Figure 14: Validation of modeled SSC at Channel Marker 17 (Lower South Bay) for WY 1999.

B. REPRODUCING CURRENT PCB PATTERNS

Surface Sediments

Hindcast PCB concentrations in sediment were compared to patterns and trends observed in sediment cores and surface sediments to validate the PCB model. The lack of historic PCB observation in the Bay limits our ability to evaluate the performance of the model in describing long-term historic trends in surface sediment PCBs. Instead, PCB data collected by the RMP since 1993 and NOAA-EMAP sediment monitoring in 2001 and 2002 were used to evaluate whether the model could reproduce the current spatial distribution of PCBs in surface sediments.

Figure 15 shows modeled PCB concentrations in surface sediments at the end of the hindcast compared to RMP and NOAA-EMAP field observations. Overall, the model reproduced the between-segment variability observed in both sets of field observation, with the same general trend of decreasing concentrations from south to north observed in both modeled and measured results. The magnitudes of model results were generally within the variability of the field observations. Furthermore, when considering the uncertainty of model estimates, results are statistically similar to observations (i.e., no statistical difference at the 95% confidence interval).

Notable differences are observed beween NOAA-EMAP and RMP field data (Figure 15), which could potentially be explained by the different site locations of each study. The NOAA-EMAP data were collected in 2001 and 2002 and sampled mostly the shallow margins of the Bay. Some sites even targeted potential hot-spots (e.g., Hunter's Point, Richmond Harbor). In contrast, RMP data used for the comparison include samples collected from 1993 to 2005. Data prior to 2002 were collected at fixed locations along the central axis of the Bay, mostly in deep channels. In 2002 the RMP implemented a probabilistic study design which located sites in both shallow and deep locations. It is believed that the shallow margins of the Bay should exhibit higher concentrations of PCBs as these regions are closer to diffuse sources in the urbanized watersheds. That concept will be tested as RMP monitoring efforts continue.

Sediment Depth Profiles

The mass of PCBs stored in sediment is highly dependent on the relative amounts of erosion and deposition occurring over time. In a strictly erosional regime, mass is transferred into sediments by diffusion and bioturbation. Sediment cores in such regions provide very limited information on historic trends. In a depositional regime, large amounts of PCB mass can move into the sediments both by advective (e.g., deposition) and diffusive processes. Sediment cores in these regions will display layers of varying PCB concentrations giving a detailed profile of historic trends. A very limited number (two) of sediment cores with detailed chronolgy have been collected in San Francisco Bay and analyzed for PCBs. Venkatesan *et al.* (1999) measured PCB concentrations in sediment cores collected from San Pablo Bay in 1990 and from Richardson Bay in 1992. The multibox model does not have the spatial resolution necessary to make a meaningful comparison with the Richardson Bay core; Richardson Bay is modeled as part of one homogenously mixed box in Central Bay. Hindcast model results were compared to the San Pablo Bay core to validate model performance. This type of temporal comparison is the only real means presently available for validating the PCB models ability to reproduce historic patterns of PCB concentrations in Bay sediments.

Figure 16 shows the hindcast model core in San Pablo Bay compared to the observations of Venkatesan *et al.* (1999). Model results represent an average of seven lower-layer model boxes in San Pablo Bay, which collectively represent the channel sediments for the San Pablo Bay segment. Three key features of the modeled sediment core agree well with the observed core: 1) the surface concentrations are comparable (observed concentrations are within the 95% confidence interval of the model), 2) the shapes of the profiles are comparable, with the PCB concentrations increasing in the upper 50-70 cm and then decreasing again, and 3) the depths and magnitudes of the maximum PCB concentration are similar (not statistically different at the 95% confidence interval). Most striking is the similarity in the date of the maximum PCB concentration. According to the core by Venkatesan *et al.* (1999), the maximum deposition of PCBs in San Pablo Bay occurred in the early- to mid-1970s. From Figures 17 and 18, it is evident that the maximum PCB concentration in the modeled profile (≈ 50 ng/g at ≈ 50 cm) was also estimated to occur in the early-1970s.

The agreement between modeled and observed depth profiles lends credibility to model results and bolsters confidence in its internal mechanics. Modeled PCB concentrations in surface sediments are further validated by the agreement of subsurface PCBs, which indicates that the parameterizations of historic loads and internal processes are reasonable. The subsurface agreement suggests that the reasonably accurate prediction of PCB concentrations in surface sediments was not due to chance but rather to accurate and detailed accounting of historic patterns in PCB use, loading, and in-Bay transport.

VI. Conclusions

A multibox mass budget model was developed to improve understanding of the long-term fate of PCBs in San Francisco Bay. The model was built upon two existing models; a tidally-averaged hydrodynamic model previously used to interpret daily to decadal variability in salinity concentrations and a sediment transport model used to estimate long-term bathymetric change. 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 observed patterns of PCB impairment. Extensive

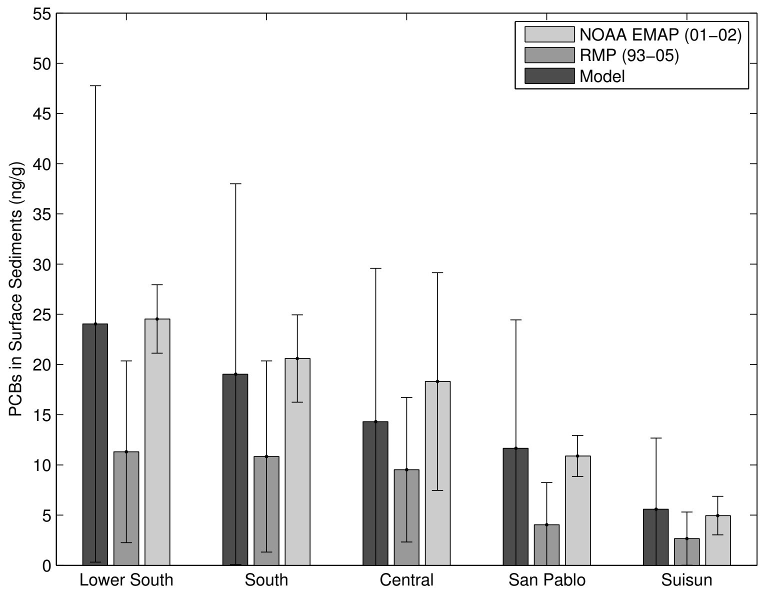

Figure 15: Calibrated hindcast model results for surface sediment PCB concentrations compared with NOAA-EMAP and RMP field observations. Error bars on NOAA-EMAP and RMP data represent the segment variability of observations. Error bars on model results represent aggregate model uncertainty at the 95% confidence level.

uncertainty analyses were conducted to establish a quantifiable degree of confidence in model predictions.

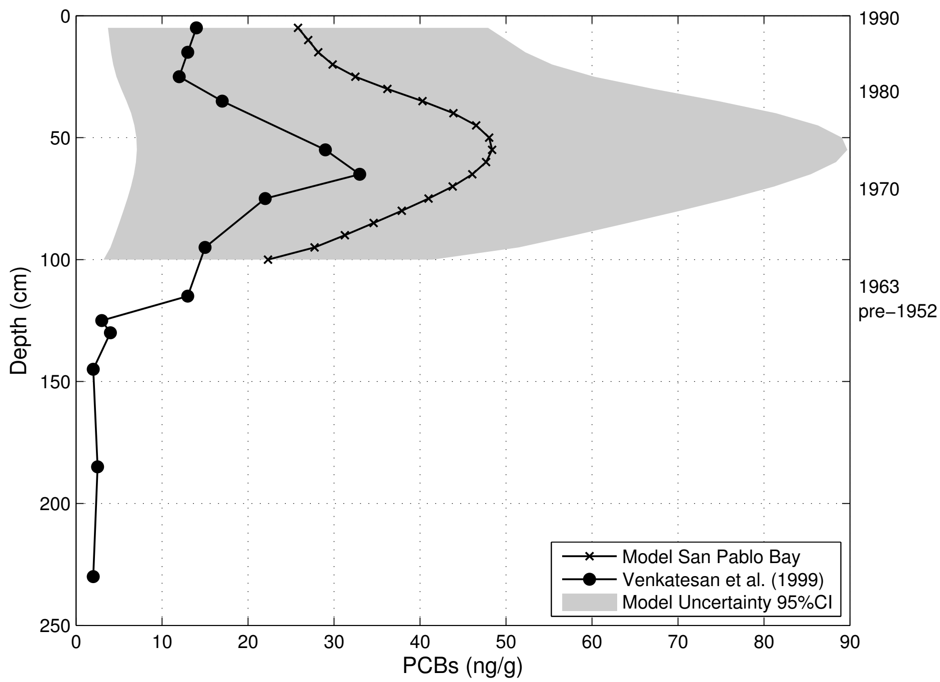

Figure 16: Calibrated hindcast model results of the vertical profile of in bed sediments compared to observations from Venkatesan *et al.* (1999). Shading on model results represents aggregate model uncertainty at the 95% confidence level. Numbers at the right indicate the chronology of the Venkatesan *et al.* (1999) sediment core in San Pablo Bay, not the model core.

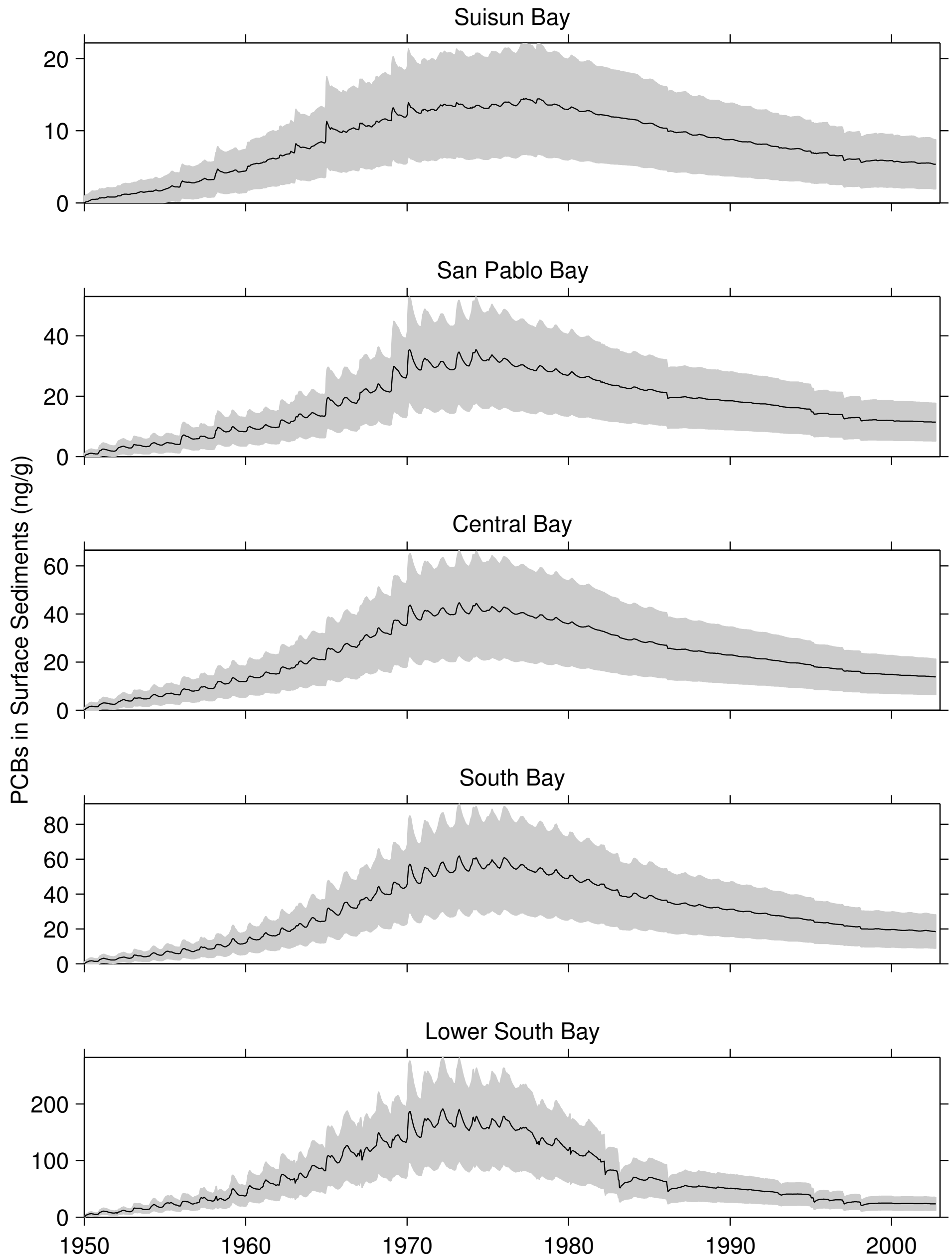

Figure 17: Hindcast PCB concentrations in surface sediment (top 5 cm) from 1940 to 2002. Shading indicates model uncertainty at 95% confidence level.

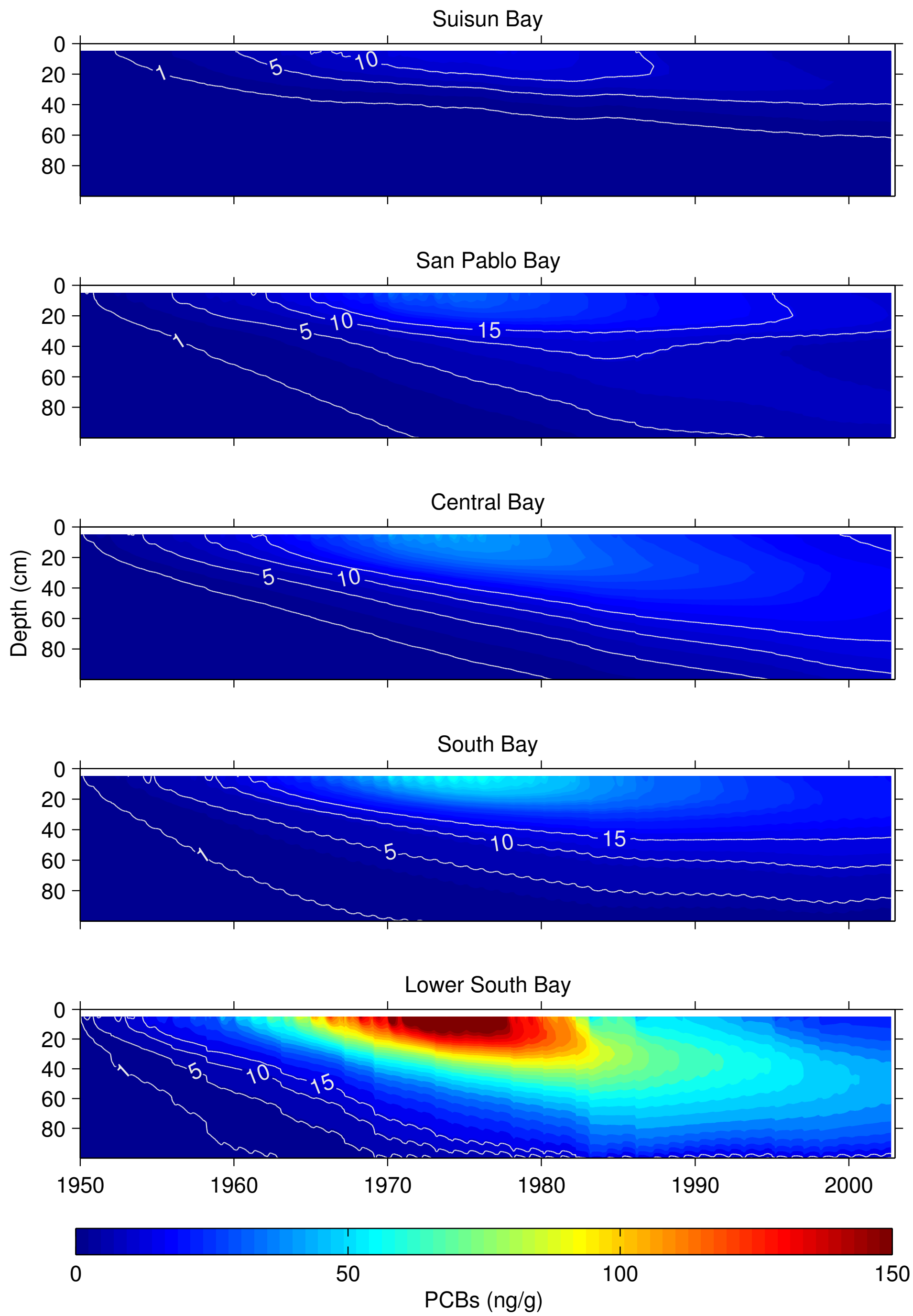

Figure 18: Hindcast PCB concentrations in 100 cm of sediment from 1940 to 2002.

VII. LITERATURE CITED

Barring, H., Bucheli, T. D., Broman, D., and Gustafsson, O. (2002). Soot-water distribution coefficients for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polybrominated diphenylethers determined with the soot cosolvency-column method. *Chemosphere*, **49**, 515–523.

Breivik, K., Sweetman, A., Pacyna, J. M., and Jones, K. C. (2002). Towards a global historical emission inventory for selected 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. In T. J. Conomos, editor, *San Francisco Bay: The Urbanized Estuary*, pages 47–84. Pacific Division of the American Association for the Advancement of Science, San Francisco, California.

Davis, J. A. (2004). Long-term fate of polychlorinated biphenyls in San Francisco Bay (USA). *Environmental Toxicology and Chemistry*, **23**(10).

Davis, J. A., McKee, L. J., Leatherbarrow, J. E., and Daum, T. H. (2000). Contaminant loads from stormwater to coastal waters in the San Francisco Bay region. A Presentation to the Bay Area Stormwater Management Agencies Association. San Francisco Estuary Institute, Oakland, CA. www.sfei.org/sfeireports.htm.

DRBC (2003). Calibration of the PCB water quality model for the Delaware Estuary for penta-PCBs and carbon. Technical report, Delaware River Basin Commission, West Trenton, NJ. http://www.epa.gov.reg3wapd/tmdl/pdf/delaware_tmdl/ModelCalibrationReport.pdf.

Foxgrover, A. C., Higgins, S. A., Ingraca, M. K., Jaffe, B. E., and Smith, R. E. (2004). Deposition, erosion, and bathymetric change in South San Francisco Bay: 1858-1983. Open file report 2004-1192, U.S. Geological Survey.

Fuller, C. C., van Green, A., Baskaran, M., and Anima, R. (1999). Sediment chronology in San Francisco Bay, California, defined by ^{210}Pb, ^{234}Th, ^{137}Cs, and $^{239,240}Pu$. *Marine Chemistry*, **64**, 7–27.

Gobas, F., Z'Graggen, M., and Zhang, X. (1995). Time response of the Lake Ontario ecosystem to virtual elimination of PCBs. *Environmental Science and Technology*, **29**, 2038–2046.

Hornbuckle, K. C., ands C W Sweet, J. D. J., and Eisenreich, S. J. (1994). Seasonal variations in air-water exchange of polychlorinated biphenyls in Lake Superior. *Environmental Science and Technology*, **28**, 1491–1501.

Jaffe, B. E., Smith, R. E., and Zink Torresan, L. (1998). Sedimentation and bathymetric change in San Pablo Bay 1856-1983. Open file report 98-0759, U.S. Geological Survey.

Journel, A. G. and Huijbregts, C. J. (1981). *Mining Geostatistics*. Academic Press, New York, NY.

KLI (2002). Final Report, Joint Stormwater Agency Project to Study Urban Sources of Mercury, PCBs, and Organochlorine Pesticides. Technical report, Kinnetic Laboratories, Inc. / EOA, Inc., Santa Cruz, CA.

KLI (2005). Errata to the Final Report, Joint Stormwater Agency Project to Study Urban Sources of Mercury, PCBs, and Organochlorine Pesticides. Technical report, Kinnetic Laboratories, Inc. / EOA, Inc., Santa Cruz, CA.

Knowles, N. (1996). *Simulation and prediction of salinity variability in San Francisco Bay*. Masters thesis, Scripps Institution of Oceanography, University of California, San Diego.

Knowles, N. and Cayan, D. R. (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., McKee, L. J., Schoellhamer, D. H., Ganju, N. K., and Flegal, A. R. (2004). Concentrations and loads of organic contaminants and mercury associated with suspended sediment discharge to San Francisco Bay from the Sacramento-San Joaquin River Delta, California. Rmp technical report: Sfei contribution 405, San Francisco Estuary Institute, Oakland, CA.

Leatherbarrow, J. E., Oram, J. J., and Davis, J. A. (2005). A model of long-term PCB fate and transport in San Francisco Bay, CA. Draft Technical Report: SFEI Contribution 388, San Francisco Estuary Institute, Oakland, CA.

Lionberger, M. A. (2003). *A tidally-averaged sediment transport model of San Francisco Bay, California*. Masters thesis, University of California, Davis.

Lionberger, M. A. and Schoellhamer, D. (2007). A tidally-averaged sediment transport model of San Francisco Bay, California. Technical report, USGS. In preparation.

McKee, L. J. and Leatherbarrow, J. E. (2005). Concentrations and loads of mercury, PCBs, and OC pesticides in the lower Guadalupe River, San Jose, CA: Water Years 2003 and 2004. A Technical Report of the Regional Watershed Program: SFEI Contribution XX, San Francisco Estuary Institute, Oakland, CA.

McKee, L. J., Oram, J. J., Leatherbarrow, J. E., Bonnema, A., Hein, W., and Stephenson, M. (2005a). Concentrations and loads of mercury and PCBs, and PBDEs in the lower Guadalupe River, San Jose, CA: Water Years 2003, 2004 and 2005. A Technical Report of the Regional Watershed Program: SFEI Contribution 424, San Francisco Estuary Institute, Oakland, CA.

McKee, L., Ganju, N., and Schoellhamer, D. (2005b). Estimates of suspended sediment entering San Francisco Bay from the Sacramento and San Joaquin Delta, San Francisco Bay, California. *Journal of Hydrology*. submitted.

MTC-ABAG (2003). Bay Area Census Report. Metropolitan Transportation Commission - Association of Bay Area Governments, Oakland, CA. http://www.bayareacensus.ca.gov/historical/copop18602000.htm.

Null, J. (2004). Golden Gate Weather Services, Personal Communication.

Olsen, C. R., Simpson, H. J., Peng, T. H., Bopp, R. F., and Trier, R. M. (1981). Sediment mixing and accumulation rate effects on radionuclide depth profiles in Hudson Estuary sediments. *Journal of Geophysical Research*, **86**(C11), 11020–11028.

Oros, D. R. and Ross, J. R. M. (2004). Polycyclic aromatic hydrocarbons in San Francisco Estuary sediments. *Marine Chemistry*, **86**, 169–184.

Park, J. S., Wade, T. L., and Sweet, S. (2001). Atmospheric deposition of organochlorine contaminants to Galveston Bay, Texas. *Atmospheric Environment*, **35**, 3315–3324.

Peng, T. H., Broecker, W. S., and Berger, W. H. (1979). Rates of benthic mixing in deep-sea sediment as determined by radioactive tracers. *Quaternary Research*, **11**, 147–149.

Schoellhamer, D. and Lionberger, M. (2004). USGS, Personal Communication.

Seth, R., Mackay, D., and Muncke, J. (1999). Esitmating the Organic Carbon Partition Coefficient and its Variability for Hydrophobic Chemicals. *Environ. Sci. Technol.*, **33**, 2390–2394.

Tetra Tech, Inc. (2005). Results of independent testing of SFEI's multibox model for PCB fate and transport. Prepared for the Clean Estuary Partnership, Tetra Tech, Inc., Lafayette, CA.

Tetra Tech, Inc. (2006). Uncertainty analysis of SFEI's multibox model for PCB fate and transport in San Francisco Bay. Prepared for the Clean Estuary Partnership, Tetra Tech, Inc., Lafayette, CA.

Totten, L. A., Brunciak, P. A., Gigliotti, C. L., Dachs, J., Glenn, T. R., Nelson, E. D., and Eisenrich, S. J. (2001). Dynamic air-water exchange of polychlorinated biphenyls in the New York-New Jersey Harbor Estuary. *Environmental Science and Technology*, **35**(19), 3834–3840.

Totten, L. A., Gigliotti, C. L., Offenberg, J. H., Baker, J. E., and Eisenreich, S. J. (2003). Re-evaluation of air-water exchange fluxes of PCBs in Green Bay and Southern Lake Michigan. *Environmental Science and Technology*, **37**, 1739–1743.

Tsai, P., Hoenicke, R., and Yee, D. (2002). Atmospheric concentrations and fluxes of organic compounds in the Northern San Francisco Estuary. *Environmental Science and Technology*, **36**(22), 4741–4747.

Uncles, R. J. and Peterson, D. H. (1995). A computer model of long-term salinity in San Francisco Bay: sensitivity to mixing and inflows. *Environmental International*, **21**(5), 647–656.

Uncles, R. J. and Peterson, D. H. (1996). The long-term salinity field in San Francisco Bay. *Continental Shelf Research*, **16**(15), 2005–2039.

United States Geological Survey (2004). San Francisco Bay Bathymetry Web Site. [URL: http://sfbay.wr.usgs.gov/access/Bathy/].

U.S. EPA (2004). Environmental Monitoring and Assessment Program (EMAP). http://www.epa.gov/emap.

van Ry, D. A., Gigliotti, C. L., Glenn, T. R., Nelson, E. D., Totten, L. A., and Eisenreich, S. J. (2002). Wet depostion of polychlorinated biphenyls in urban and background areas of the mid-Atlantic states. *Environmental Science and Technology*, **36**(15), 3201–3209.

Venkatesan, M. I., de Leon, R. P., van Green, A., and Luoma, S. N. (1999). Chlorinated hydrocarbon pesticides and polychlorinated biphenyls in sediment cores from San Francisco Bay. *Marine Chemistry*, **64**, 85–97.

Yee, D., Leatherbarrow, J. E., and Davis, J. A. (2002). Organic contaminants concentrations in Bay Area effluents. Presentation to Regional Monitoring Program Technical Review Committee, San Francisco Estuary Institute, Oakland, CA.

Zhang, H., Eisenrich, S. J., Franz, T. R., Baker, J. E., and Offenberg, J. H. (1999). Evidence for increased gaseous PCB fluxes to Lake Michigan from Chicago. *Environmental Science and Technology*, **33**(13), 2129–2137.

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