Santa Monica Bay Modeling for PCB and DDT

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Overview

In order to support determination of DDT and PCB TMDLs and load allocations for Santa Monica Bay (SMB), a mass balance model was developed. The model represents key processes and contributing factors in a relatively simple manner using a box framework. It is not intended to mechanistically simulate detailed hydrodynamic or water quality processes. Indeed, a high level of model complexity is not warranted in light of current data limitations and the necessary schedule for completion. This document summarizes the conceptual model that was developed, key processes and parameters considered, and data used.

A conceptual model was developed to quantify DDT and PCB load movement into, within, and out of SMB. Although the focus of the study is on SMB proper, the analytical approach must consider contributions from the Palos Verde (PV) Shelf, interactions with the open ocean, and contributions from land-based sources. Figure 1 presents the spatial scope of the area being evaluated and shows the division of SMB and adjoining off-shore areas into analytical elements. The conceptual model includes three horizontal boxes – one representing SMB proper, one that acts as a receiver of along-shore inputs, and one that represents general ocean boundary conditions. Each of these boxes is in turn represented using multiple vertical layers and physically defined using available bathymetry data.

Conceptual Model

SMB itself is represented as a single horizontal box divided vertically into 5 water column layers and 2 sediment layers (as shown in Figure 2). Outside the SMB box, the receiver box receives along-shore flow from the PV Shelf (Q_{in}), with corresponding sediment, DDT, and PCB loads. To balance the flow, an outflow (Q_{out}) is specified at the opposite side of the receiver box. Since the box model is intended to simulate long-term average conditions in the system, a balanced flow assumption is reasonable. Outside the receiver box is an ocean boundary box which represents general ocean conditions. As with the SMB box, the receiver and boundary boxes are vertically divided into 5 water column layers and 2 bed layers.
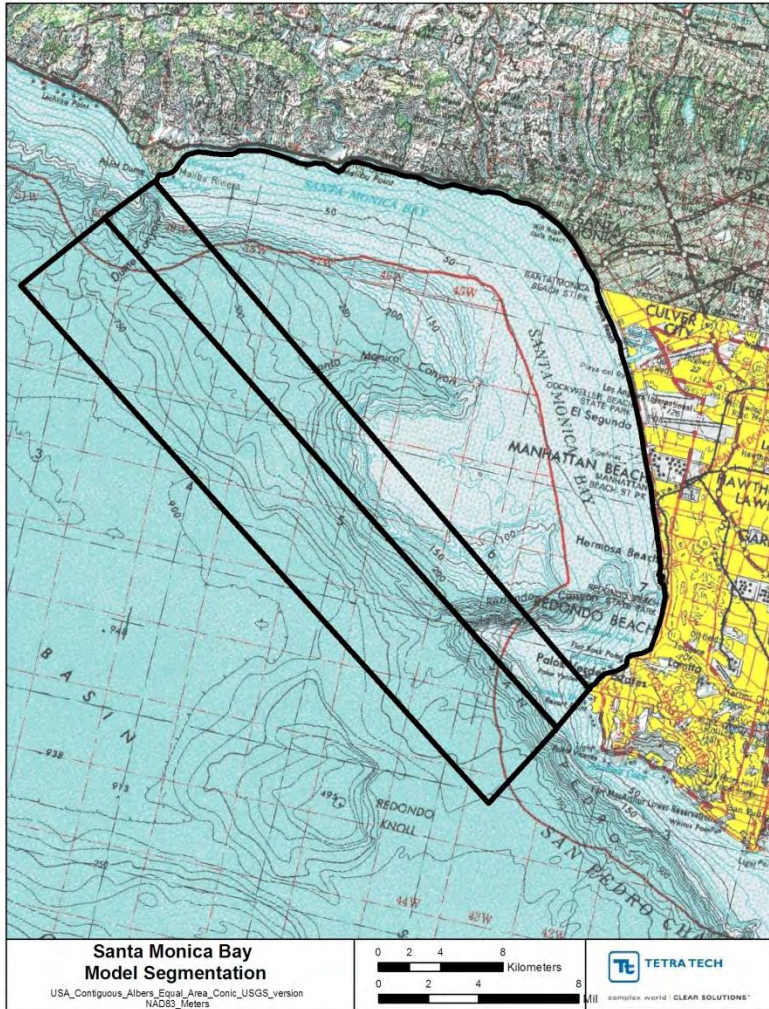
Figure 1. Santa Monica Bay Study Area and Analytical Elements

Bathymetry data downloaded from the Southern California Coastal Ocean Observing System (SCCOOS) were used to estimate average depths and volumes for the model boxes. Box volumes were calculated by multiplying the surface area (based on segmentation width and length) by the average depth. The SMB itself is represented using an overall average depth of 55 m while the receiver and boundary boxes are represented using average depths of 133 m and 286 m, respectively.
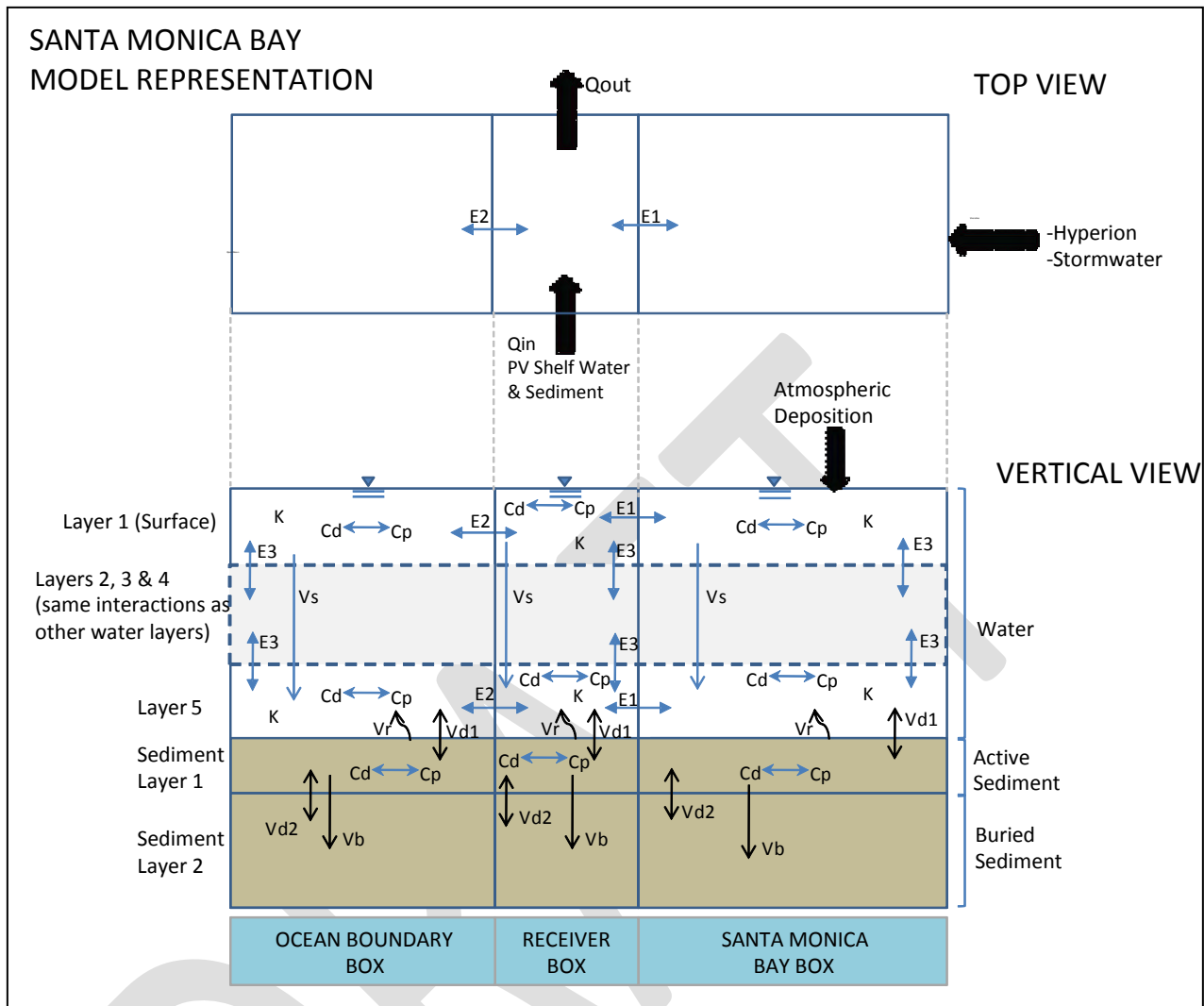
Figure 2. Schematic of the SMB model

The entire model is composed of 15 water column boxes and 6 bed boxes. The SMB boxes receive sediment, DDT, and PCB loads from all direct and diffuse sources in SMB proper and from the shore (including City of LA's Hyperion Treatment Plant [Hyperion], and other NPDES discharges). Receiver boxes receive loading from the PV Shelf. Boundary boxes receive no external loading. Between the SMB and receiver boxes bi-directional exchange fluxes (E1) represent combined tidal-freshwater induced transport in the area. The load entering the SMB boxes can be transported outward to the receiver boxes, and the PV shelf load entering the receiver boxes can be transported into SMB (and deposited to the bed). Between the receiver boxes and the boundary ocean boxes, similar two-way exchange processes occur (E2) and allow sediment, DDT, and PCB to be transported to the ocean. This results in dilution of DDT and PCB levels in the receiver and SMB boxes.

Inside each box, sediment is divided into two size classes (fine sand and silt/clay), and DDT and PCB are represented in two phases (adsorbed (Cp) and freely dissolved (Cd)). The adsorption media is sediment. PCB and DDT are partitioned between the adsorbed and freely-dissolved phases based on a local equilibrium assumption. This assumes dissolved and particulate phases are in equilibrium in each time step of the model calculation. While dissolved PCB and DDT are only transported via water column transport processes, the adsorbed portion can be transported with sediment. Sediment can settle (Vs) from upper layers to lower layers and ultimately be deposited on the bed layer. Bed sediment and associated DDT and PCB can re-enter the water column via resuspension (Vr). DDT and PCB that re-enter the water via resuspension can be redistributed via desorption. In addition to resuspension, bed DDT and PCB can also enter the water column via diffusion (Vd1).

The sediment layers consist of an active sediment layer and a deeper sediment layer. The PCB and DDT are partitioned between the adsorbed and the dissolved pore water in the active layer with in-bed diffusion (Vd2) and sediment-water diffusion (Vd1) processes occurring within this layer. Loss due to burial (Vb) into deep sediment is also considered from the active layer to the deep sediment.

Various loss processes also impact DDT and PCB. In the model, these losses are not represented mechanistically. Rather, a lumped loss term is included in the mass balance equation using a first-order formulation (K).

Modeling Framework

The U.S. EPA's Water Quality Simulation Program (WASP) was selected as the basis for numerically representing the conceptual model (USEPA, 2009). WASP was selected because it is a general modeling framework that has been peer-reviewed, widely applied, and is equipped with all functionality necessary to represent the processes identified in the conceptual model discussion.

Key Toxicants Data Assumptions

The following two data assumptions were adopted for this study and were based on data from LACSD for SMB.

1) DDT is represented using DDE data. This is justified by the fact that DDE accounted for more than 96% of DDT, as shown in Figure 3.
2) For the time period when no congener data are available to quantify total PCB, the measured Aroclor data are used to approximate PCB, using the equation: $C_{PCB}=1.063C_{Aroclor}$, where C_{PCB} is the PCB concentration in ug/L; $C_{Aroclor}$ is the maximum Aroclor concentration in ug/L. This equation is derived based on data, as shown in Figure 4.
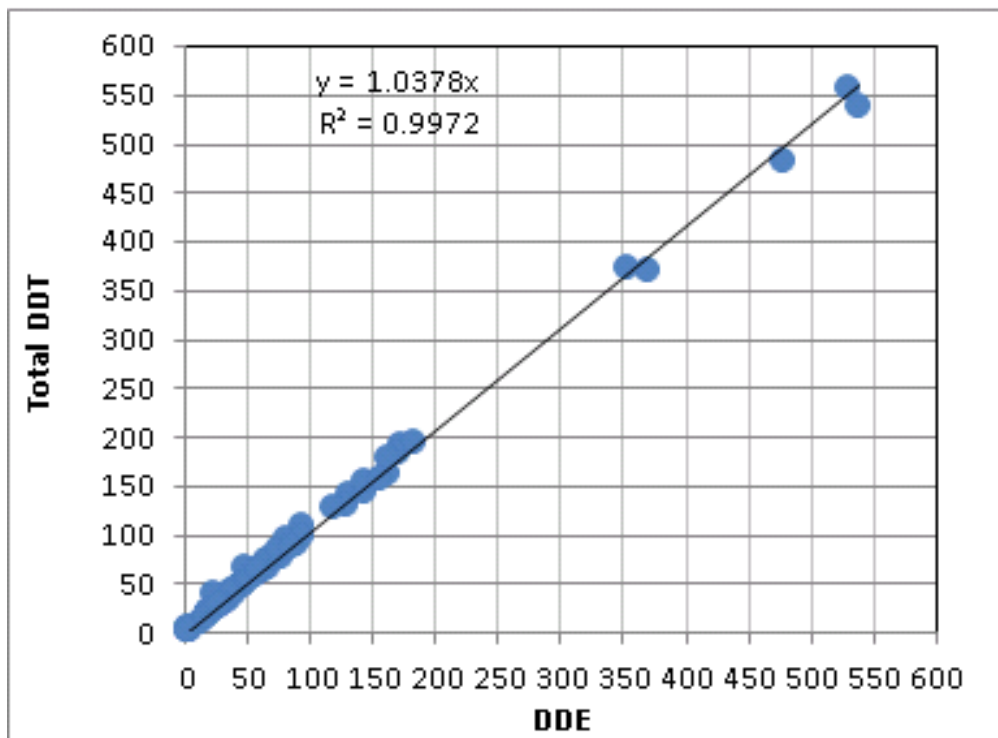
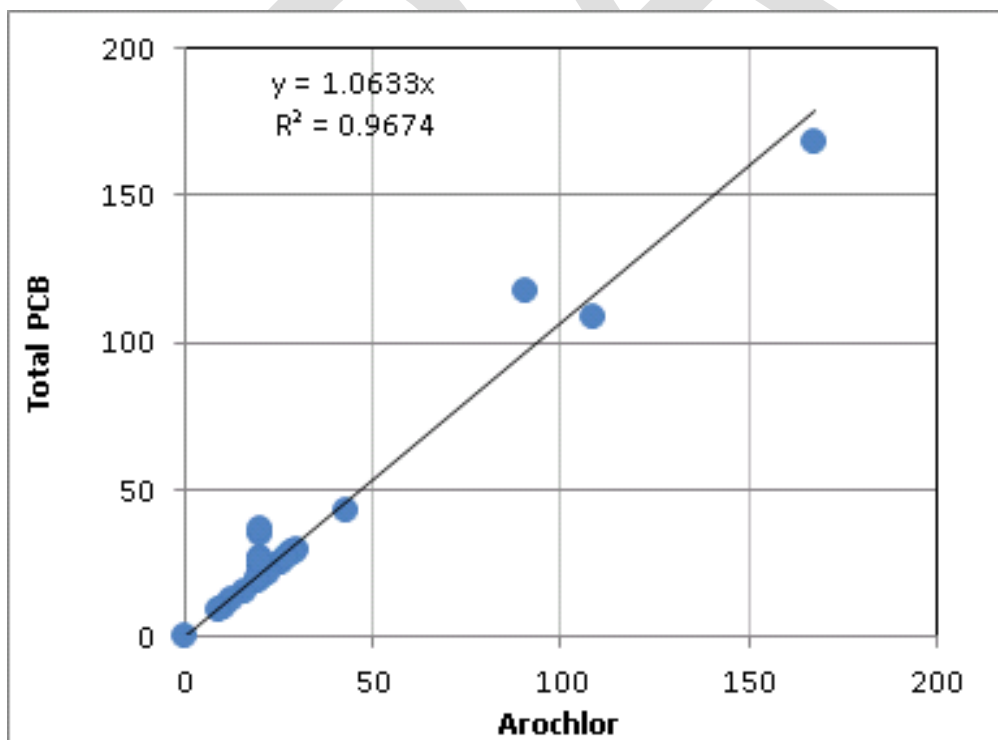**Figure 3. Relationship between DDE and total DDT**

Figure 4. Relationship between maximum Arochlor and total PCB

Model Configuration

Model configuration involves setting the initial condition, transport coefficients, boundary conditions, external loadings, and process parameters. The information presented below summarizes the key model parameters, values used in the model, and sources of information used.

Vertical Depth Range

The average depth of the three horizontal model boxes was estimated using ArcGIS Spatial Analyst software, and the values are 97 m for the Santa Monica Bay box, 244 m for the Receiver Box, and 542 m for the Ocean Box. Each box was further divided into five layers with the depth distribution shown in Table 1.

Table 1. Vertical depth distribution of model segments (meters)

Water Layers	SMB Box (C)	Receiver Box (B)	Ocean Box (A)
Layer 5 Surface water layer	95-97	239-244	532-542
Layer 4 Intermediate shallow water layer	87-95	220-239	490-532
Layer 3 Mid depth layer	77-87	196-220	438-490
Layer 2 Intermediate deep layer	62-77	160-196	360-438
Layer 1 Bottom water layer	0-62	0-160	0-360

Initial condition

Table 2. Initial Condition-Bed

Parameter	Value	Source
Bed porosity	0.5	Blaas et al (2007)
Dry density of sand and silt/clay	2.65 kg/L	Blaas et al (2007)
Sediment distribution in bed[1]	Sand = 58%; Silt/Clay = 40%	Average from 1995 Santa Monica data provided by the City of Los Angeles Environmental Monitoring Division
Initial sediment concentration	Sand = 768.5 g/L; Silt/Clay = 530.0 g/L	Calculated based on porosity and dry density as shown above

Parameter	Value	Source
Bed layer thickness	The surface bed layer thickness is assumed to be 0.1 m; the bottom bed layer thickness is assumed to be 0.5 m.	Sherwood (2008)
Water column sediment concentration	No data have been identified; assumed value is TSS=5.0 mg/L (Sand=3.0 mg/L, Silt/Clay=2.0 mg/L) The model is not sensitive to this value because it changes very quickly once simulation begins.	Average TSS concentration in Santa Monica Bay from Bight 03 was 4 mg/l
Initial bed toxic concentrations	Surface Bed Layer: For the SMB boxes: DDT concentration = 85.7 ug/kg; No PCB congener data were available for 1995, however, arochlor data were available to derive PCB as 39.2 ug/kg. For the receiver and boundary boxes: DDT=4.0 ug/kg; PCB=1.8 ug/kg Lower Bed Layer: Set to twice as much as in surface bed.	For SMB Box: Average from 1995 Santa Monica data provided by the City of Los Angeles Environmental Monitoring Division For receiver and ocean boxes: The background value for DDT in (EPA personal communication); for PCB, use the PCB:DDT ratio in SMB to derive PCB. The receiver and ocean box bed initial concentrations do not have a significant impact on toxicant concentration in the SMB, therefore, more accurate estimates are unnecessary.
Initial water column DDT and PCB concentration	Vertical profile	LACSD, 2011.

[1] The same values are used for the SMB, receiver, and boundary boxes since data are not available for separate characterization of all boxes. This, however, is not expected to have a significant impact on model performance because the receiver and boundary boxes are both very deep.

Table 3. Initial condition-water column based on LACSD (2011) estimate (ug/L)

Area	SMB		Boundary		Receiver	
	DDE avg	PCB avg	DDE avg	PCB avg	DDE avg	PCB avg
Layer 1	7.33E-06	3.53E-06	1.00E-06	1.00E-06	1.00E-06	1.00E-06
Layer 2	5.48E-05	1.77E-05	1.00E-06	1.00E-06	3.11E-06	2.18E-06
Layer 3	1.36E-04	3.88E-05	1.21E-06	1.00E-06	3.26E-05	1.23E-05
Layer 4	2.85E-04	7.31E-05	6.68E-05	1.85E-05	2.15E-04	5.02E-05
Layer 5	4.40E-04	1.06E-04	5.70E-04	9.84E-05	6.50E-04	1.21E-04

The values in Table 3 were obtained by relating the bottom water DDT and PCB to observed bed concentration, then the values were extrapolated to the entire water column using an exponential formula. Please refer to Steele (2011) for details regarding the estimate.

Transport coefficients

Table 4. Transport Coefficients

Parameter	Value	Source
The flow from PV shelf to the receiver box	Average current velocity of 0.05 m/s. This velocity multiplied by the cross-sectional area accounts for the flow rate in cubic meter per second.	Ferre et al (2010)
Exchange (E_1)	1,000 m^2/s	Sherwood (2008)[1]
Exchange (E_2)	1,000 m^2/s	Sherwood (2008)[1]
Vertical diffusion coefficient (E_3)	1.0e-3 m2/s top and bottom layers; 2.0e-6 m^2/s for middle mixing barrier layers;	Model calibration against data in Zeng et al, 2005.
Bed diffusion coefficients	Bed-Water: 2.65e-8 m2/s Bed: 4.3E-7 m2/s	Chapra, 1997; Sherwood et al, 2002; Davis, 2003. Refined with calibration

Boundary Conditions

Two boundary conditions are specified in the model. The first represents conditions at the PV Shelf. The second represents the open ocean condition. Both of these are associated with water column transport. The sediment transport flux from the PV Shelf is addressed under External Loading.

Table 5. Boundary Conditions (ug/L)

Boundary	PV Shelf		Ocean	
	DDE avg	PCB avg	DDE avg	PCB avg
Layer 5	2.76E-03	5.93E-04	5.70E-04	9.84E-05
Layer 4	2.23E-03	5.00E-04	6.68E-05	1.85E-05
Layer 3	1.54E-03	3.76E-04	1.21E-06	1.00E-06
Layer 2	9.57E-04	2.66E-04	1.00E-06	1.00E-06
Layer 1	3.08E-04	1.18E-04	1.00E-06	1.00E-06

External Loading

These represent external sediment associated loads to the system coming from the PV Shelf, LACSD, and Hyperion.

Table 6. External Loading

Parameter	Value	Source
Load from PV Shelf[1]		
Sediment	3,600 tons/year	Ferre et al (2010)
DDT load associated with sediment	4.8 kg/yr	Based on Ferre and average sediment concentration at the PV shelf boundary using data from LACSD data (1996-2008) for Transect 1 for (excludes deep water Station 1A
PCB load associated with sediment	0.8 kg/yr	
Load from Hyperion		
Sediment	2001 –7,300 MT 2002 – 7,400 MT 2003 – 8,300 MT 2004 – 8,900 MT	Steinberger and Stein, 2004, Lyon et al 2006
DDT	8.4 kg/yr based on 2010 permit (measured loading was ND))	Hyperion Treatment Plant Permit (2010) Steinberger and Stein, 2004, Lyon et al 2006
PCB	0.9 kg/yr based on 2010 permit (measured loading was ND)	
Stormwater		
Sediment	14390 tons/yr	LA County WMMS Result (average 1996-2006)
DDT	0.46 kg/yr	Extrapolated from Curren et al 2011
PCB	1.8 kg/yr	
Atmospheric Deposition		
Sediment	0	No data to estimate. Assume negligible amount of deposition of sediment in comparison to those from other sources
DDT	1.96 kg/yr	Extrapolated from Sabin et al. 2011
PCB	1.93 kg/yr	

[1] There are two components of loading from the PV shelf. The first is associated with water column transport, and it is addressed in the boundary conditions. The second is associated with sediment transport flux from the PV Shelf in the north-west direction. In Ferre et al (2010), the sediment transport flux at site A1 (shown in Fig 12 in the journal article), which is located at the interface between the receiver box and PV Shelf, was estimated to be 0.9 ton/m/year (with an uncertainty range of 1.0). The location A1 is located at a depth of 65 m. The receiver box was extended from shoreline to a depth of 130 m, therefore 65 m is the middle of the depth range. The corresponding width of the box was estimated to be 4,000 m. Based on the width of the box, the total sediment transport flux from the PV Shelf to the receiver boxes is: 4,000 x 0.9 = 3,600 tons/year.

Process Parameters

These include the parameters related to the physical and chemical processes used to configure the model (Figure 2).

Table 7. Process Parameters

Parameter	Value	Source
Settling velocity (Vs)	Silt/Clay = 0.4 mm/s; Sand = 9.4 mm/s. A sensitivity analysis will be conducted to evaluate the uncertainty associated with these values.	Blaas et al (2007)
Resuspension[1] (Vr)	2.0e-13 m/s	Calibration
Bed-water diffusion coefficient (Vd1)	2.64e08 m^2/s	Davis (2003)
In-bed vertical diffusion coefficient (Vd2)	4.3e-7 m^2/s	Sherwood et al (2002) Calibration
DDT and PCB loss rate (K)	0.01/yr	calibration
Partitioning coefficient (Kow)	2000 L/Kg	Wilberg, P.L, and Harris, C. K. (2002) Calibration

1   Since the model is to be configured for long-term trends, event-based resuspension will not be simulated (i.e., resuspension is not dynamically simulated based on wave and current induced shear stress, which are highly variable). Resuspension will be characterized using a long term average resuspension rate. This will be estimated through the model calibration process.

Calibration Results

1) **Burial Rate**

   In Bay et al (2003), it was indicated that the annual sediment burial rate in Santa Monica Bay ranges from 0.2 cm to 2.3 cm, with an average of 1.25 cm/yr. The simulated annual burial rate is approximately 1.11 cm/yr. The minor disparity between model and data can be explained by multiple factors including that the model results and data represent different periods of time, the model is relatively coarse, and there is uncertainty in data used to define the boundary conditions and parameters.

2) **Bed DDT**

The simulated DDT concentration in the bed is plotted against the observed data in Figure 5. As shown, the predicted trend follows the observed trend. The model deviates from data for a few years, such as 1998 to 2001. This is expected, however, given the potential uncertainty in bed toxics data as well as the highly simplified nature of the model (particularly in a spatial sense).
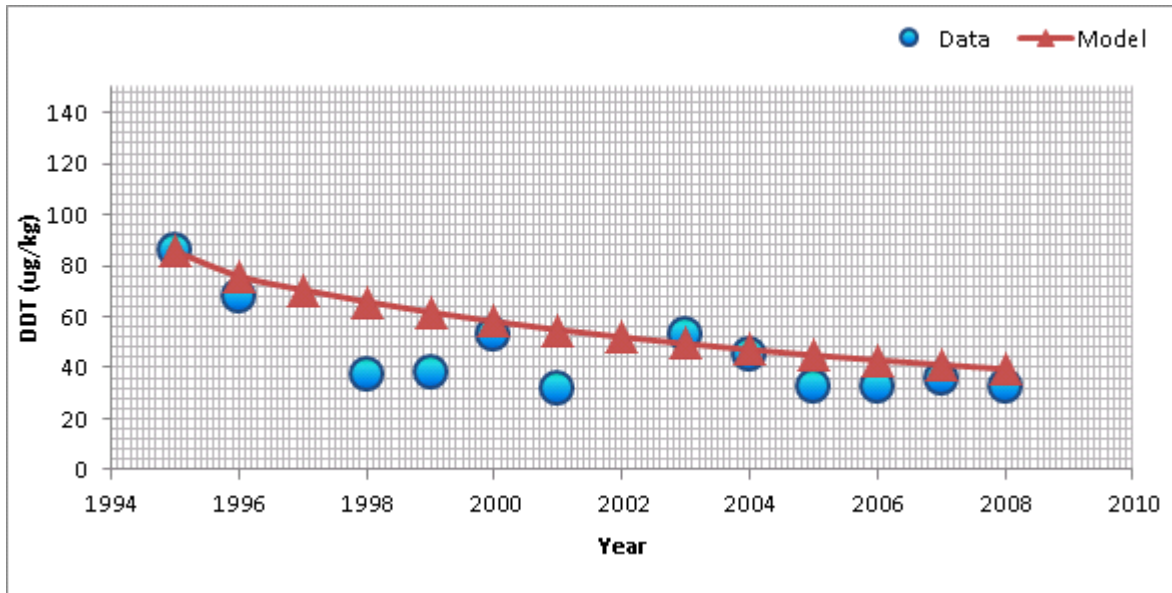

Figure 5. Comparison of simulated bed DDT and data

3) **Bed PCB**

The simulated PCB concentration in the bed is plotted against the observed data in Figure 6. The model represents a decreasing trend in PCB concentration, similar to that for DDT. Data for 2005 through 2007, however, don't necessarily match this trend. Based on the model predictions and PCB loads from all known sources, the high 2005 through 2007 are unrealistic throughout the entire SMB modeling domain. That is, only if there is a tremendous amount of PCB loading (on the order of several hundred kilograms per year) entering SMB directly would it be possible to produce the 2005-2007 levels system-wide. Given that the data represent limited locations and time periods, it is reasonable to assume that they do not accurately represent conditions throughout SMB.
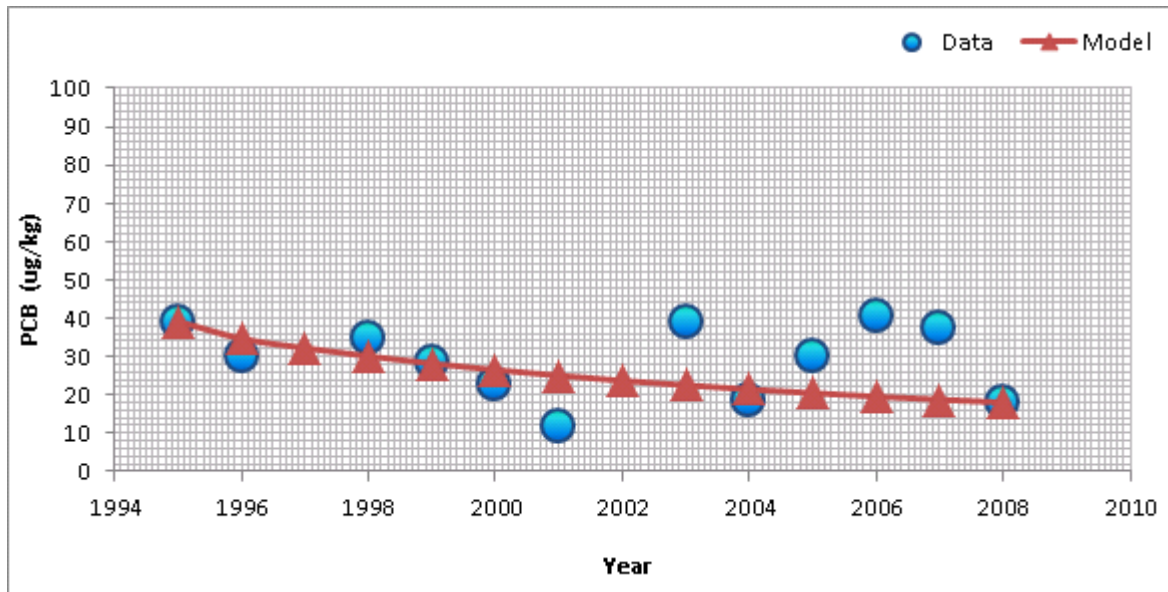
Figure 6. Comparison of simulated bed PCB and data

4) **Water Column DDT**

No long-term water column data for DDT are available. Thus it is not possible to directly compare long-term average conditions predicted by the model to data. Long-term model predictions were, however, compared to available short term data to evaluate the model's ability to simulate general trends. Figure 7 plots the long-term average model results against the short term data in Zeng et al (2005). The data were collected in 2003 and 2004 at different depths: 2 m (21 samples), 10 m (20 samples), 20 m (4 samples), 35 m (13 samples) above bed, and 2 m (16 samples) below air-water interface.   The model reproduces the general characteristics of the observed vertical profile, particularly when considering the wide variability in the observed values.

As an additional check, the model simulated vertical profile was also compared to that derived using bed concentration and a vertical exponential formula by LACSD (2011). As shown in Figure 7, the model results match the data based estimate well too, suggesting a reasonable representation of conditions in Santa Monica Bay.
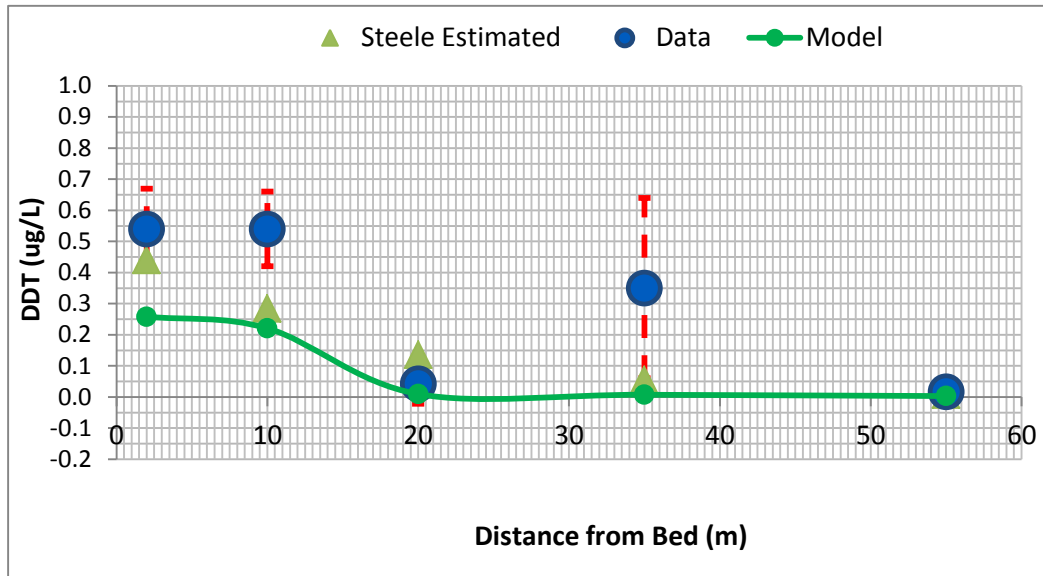
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Figure 7. Simulated water column DDT profile versus data

Primary Flux Calculation

Based on the calibrated dynamic model, the flux of DDT and PCB was calculated and is shown in Figures 8 and 9. Although a significant amount of DDT and PCB loads originate from the PV Shelf, only a very small amount actually ends up inSMB. This is because the predominant flow direction outside the mouth of SMB is parallel to the Bay. The toxics load entering the receiver box is subjected to three major transport processes: net advective flux in the north-west direction, tidal exchange with the ocean, and tidal exchange with the bay. Since the water column toxics concentration in SMB is generally higher than that in the receiver box, the net toxics flow between these two areas is towards the receiver box. And since the ocean toxics concentration is lower than that in the receiver box, a positive gradient of DDT and PCB concentration remains between the receiver box and the open ocean. This causes a large amount of DDT and PCB to be lost to the ocean across the gradient.

It is possible that more DDT and PCB enter Redondo Canyon due to local effects, however these effects are not represented within the current simplified box model. Obtaining a more accurate estimate of the local fate and transport of toxics in this area would require a high resolution, coupled hydrodynamic, sediment transport, and toxic s model. Even with the uncertainty in modeling due to simplification in the spatial resolution, it is not expected that much higher toxics contributions to the Bay from the PV Shelf would occur.
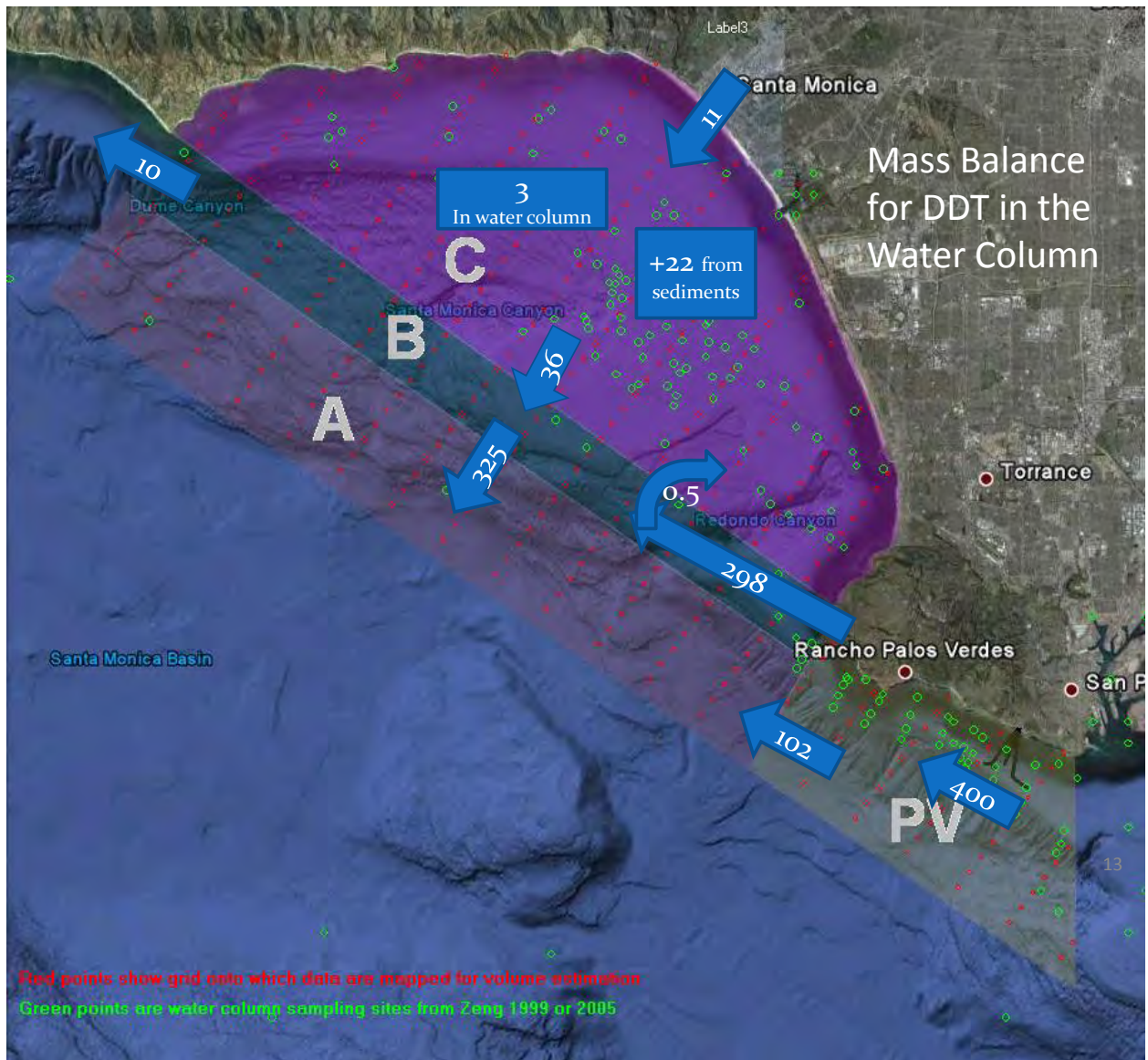
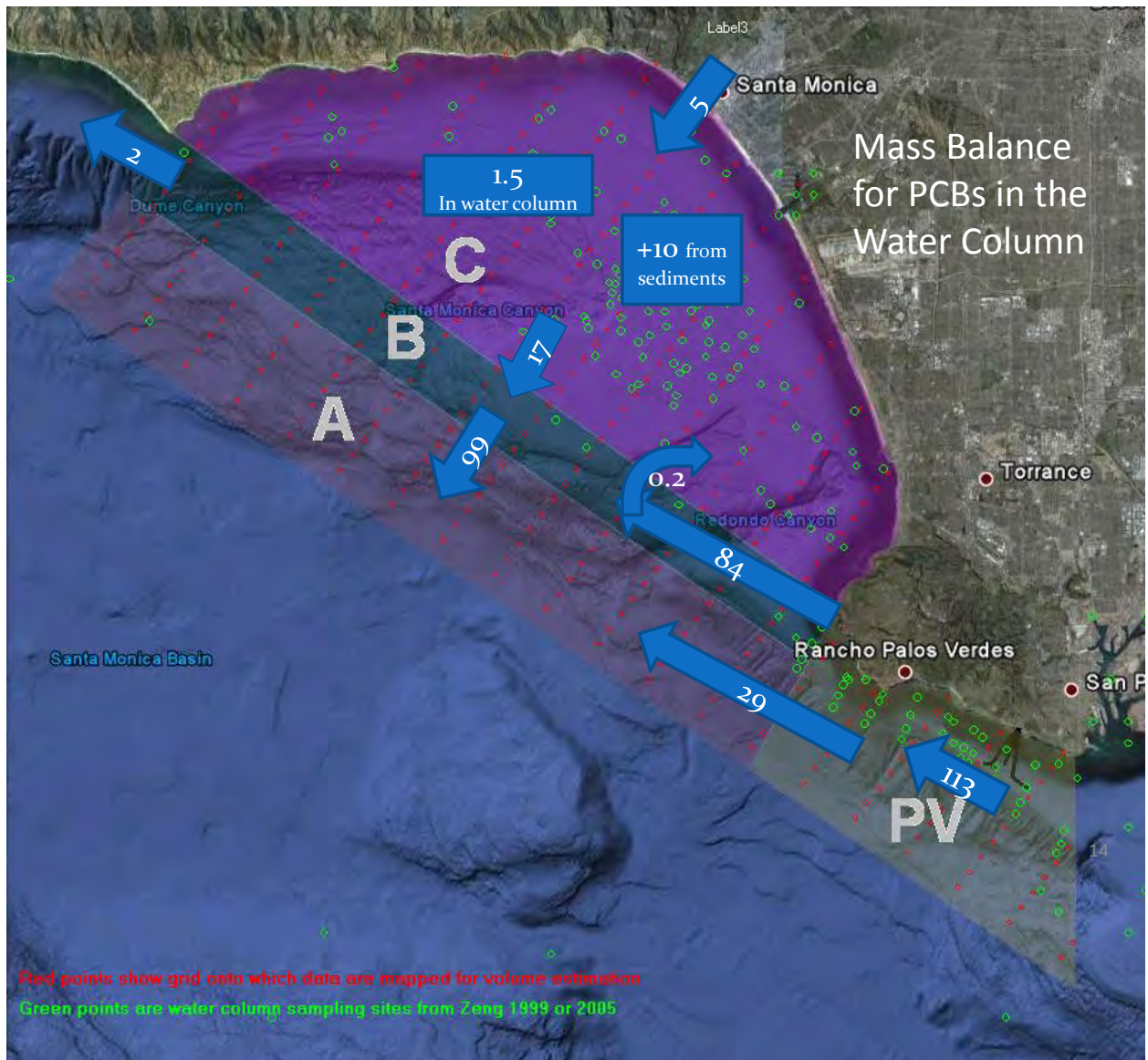**Figure 8. Simulated annual DDT flux (kg/yr)**

Figure 9. Simulated annual PCB flux (kg/yr)

Sensitivity Analysis

The SMB model was configured in a highly simplified manner. Therefore it inherently includes some level of uncertainty. To quantify the potential impact of model parameterization on results, a sensitivity analysis was conducted. The analysis involved perturbing key parameters one-by-one and evaluating the response of bed DDT and PCB concentrations. Figures 10 and 11 present the results. Table 8 below provides a key to the different sensitivity analysis and their description. The results indicate that although the simulated average DDT and PCB concentrations respond to changes in parameter values, the predicted values appear to be relatively stable – particularly with regard to a 50% change.

Table 8. Description of Sensitivity Analysis Matrix

| Sensitivity Analysis	Descriptions
Cali	Calibration
S1	50% lower decay rate in both water and bed
S2	50% higher decay rate in both water and bed
S3	50% higher horizontal exchange coefficient
S4	50% lower horizontal exchange coefficient
S5	50% lower partitioning coefficients in both water and bed
S6	50% higher partitioning coefficients in both water and bed
S7	No resuspension
S8	No bed-water diffusion
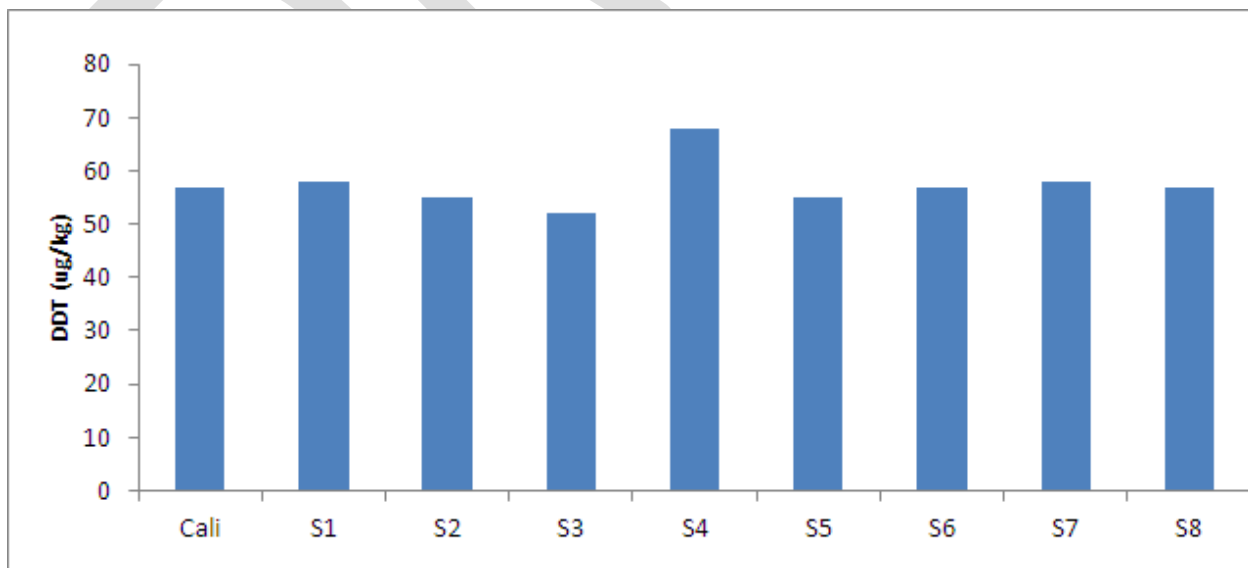
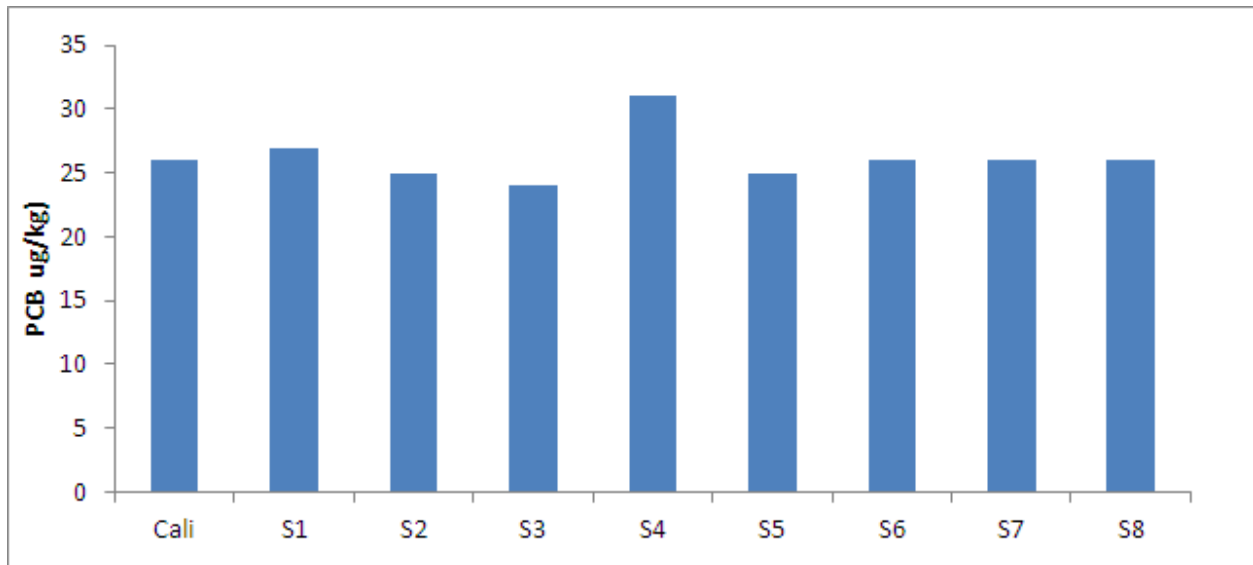**Figure 10. Sensitivity of average modeled DDT concentration to parameters**

Figure 11. Sensitivity of average modeled PCB concentration to parameters

Scenario analysis

The calibrated model was reconfigured to run for a longer time period. The goal was to evaluate the time of recovery until compliance is met in both the water column and the active bed. The simulation period was extended to cover the years from 1995 to 2094. All current loadings were assumed to last for the entire period. Figures 12 through 15 show the simulated time series for DDT and PCB in both the water column and active bed of SMB. Note that the water column concentrations were calculated as volume weighted average concentrations for the five layers. Also note that the targets in the water column are:

- DDT= 0.17 ng/L
- PCB=0.019 ng/L

Targets in the active bed are:

- DDT= 23 ng/g
- PCB=7 ng/g

The water column targets are met under the current condition based on vertical average concentration. It is noted that the concentrations in the bottom waters would still violate the targets in the scenario analysis, due to the static nature of the boundary condition. That is, the concentrations of DDT and PCB remained unchanged in the boundary conditions. This doesn't reflect the change in ocean water and PV shelf water due to natural recovery and management actions.   Bed DDT and PCB concentrations,

however, violate targets. Model results indicate that the bed toxic concentrations decrease with time, and compliance is predicted to be reached in approximately 2024 for DDT and 2036 for PCB.

As indicated in Figures 8 and 9, only a small amount of DDT and PCB that originates in the PV Shelf ultimately ends up in Santa Monica Bay. Additionally, loss of DDT and PCB in the bed layer due to burial is significant and estimated to be an order of magnitude higher than the external loadings.
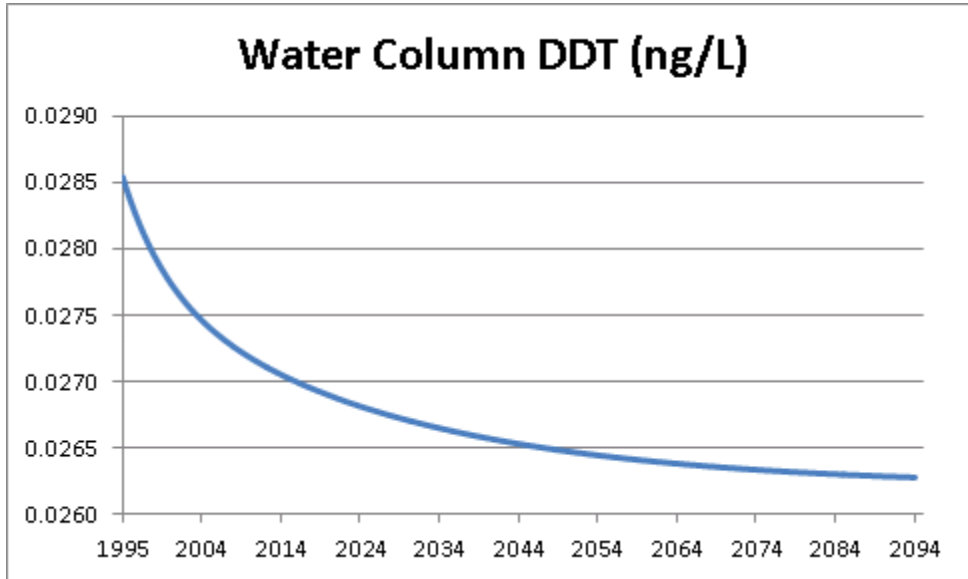

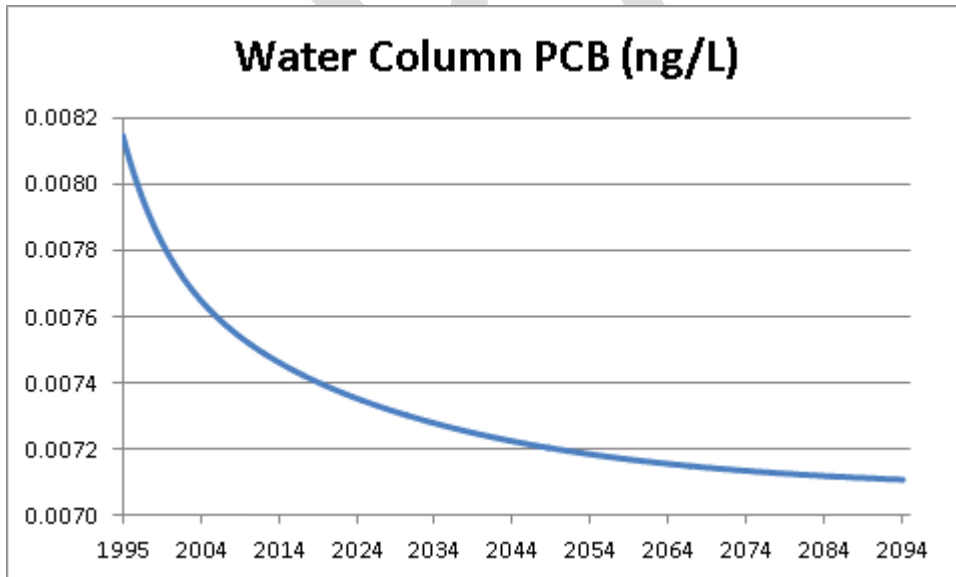**Figure 12. Simulated water column DDT concentrations in Santa Monica Bay**

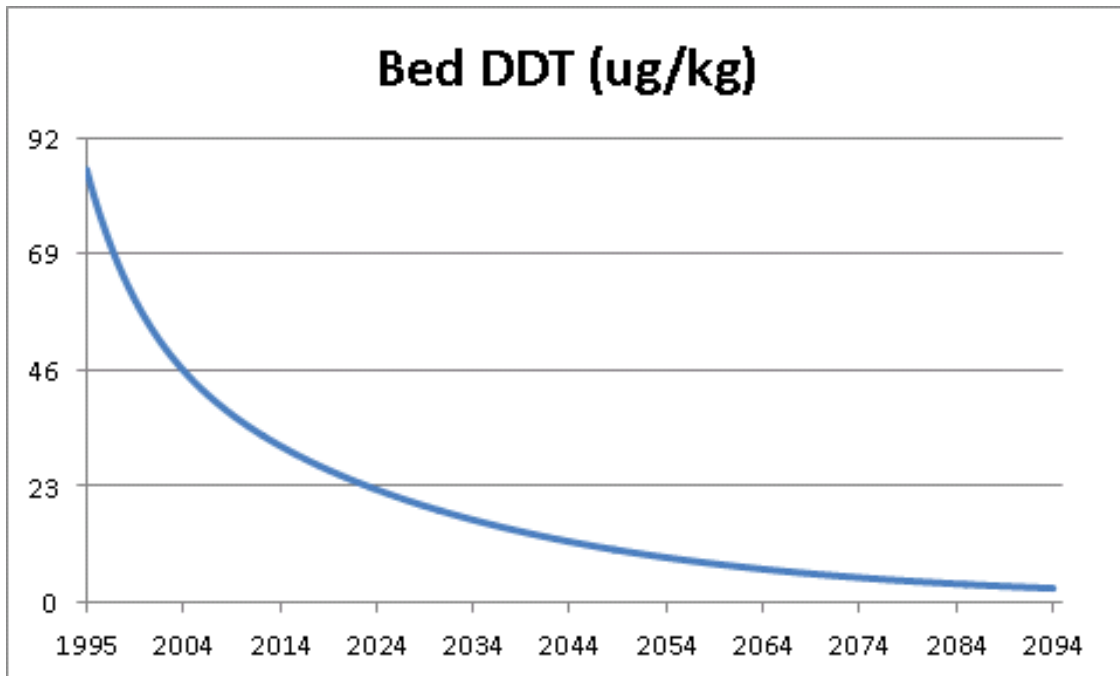**Figure 13. Simulated water column PCB concentrations in Santa Monica Bay**

Figure 14. Simulated active bed DDT concentrations in Santa Monica Bay
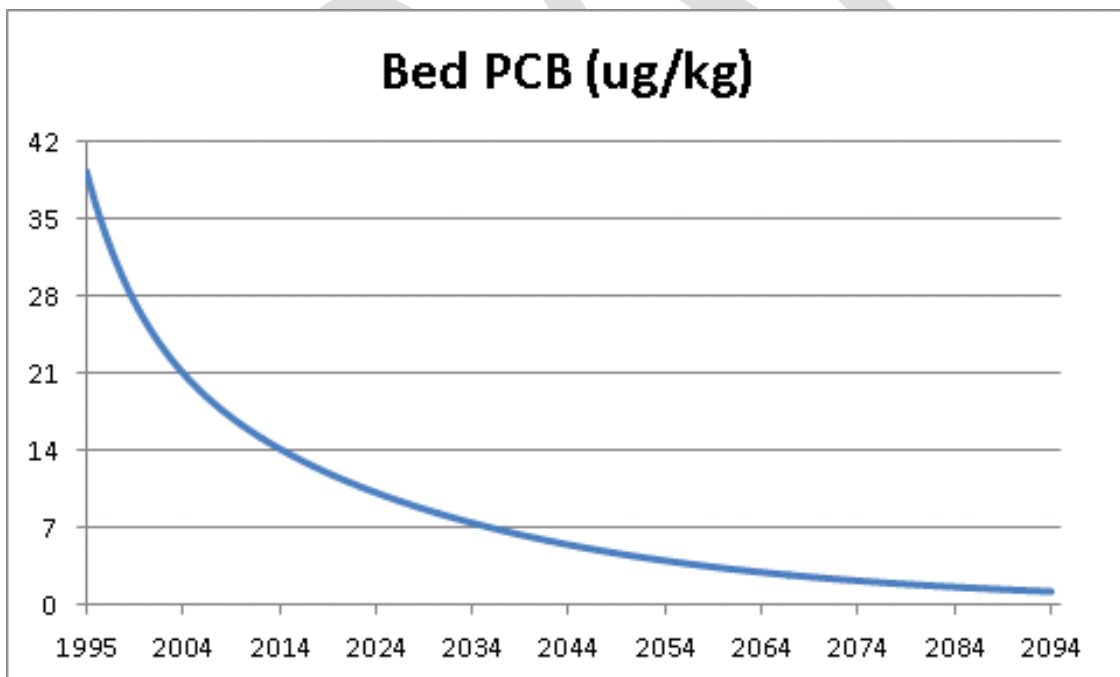

Figure 15. Simulated active bed PCB concentrations in Santa Monica Bay

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