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TECHNICAL MEMORANDUM

To: James Vernon, Port of Long Beach
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Date: February 25, 2015

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Project: 120711-01.03

Re: Development of a Chemical Fate Conceptual Site Model for the Greater Los Angeles and Long Beach Harbor Waters

1 INTRODUCTION

This technical memorandum describes the development of a conceptual site model (CSM) for total polychlorinated biphenyl (TPCB) and total DDT (TDDT) within the Greater Los Angeles and Long Beach Harbor Waters including Consolidated Slip (Greater Harbor Waters; outlined in yellow in Figure 1) to guide future data collection and mathematical modeling efforts. This memorandum formally documents the effort presented to the Harbor Technical Work Group (HTWG) on October 22, 2013. Please refer to that presentation for additional details (Opdyke et al. 2013). Additionally, Attachment A contains a comment and response document for comments received from HTWG members.

A chemical fate CSM is a conceptual framework for understanding and quantifying chemical sources and sinks to the water column. It provides a broad, overall view of the importance of various processes or mechanisms that control the transport of chemicals into (source) and out (sink) of the water column, calculated over the long term (i.e., for steady state conditions). Chemical loading from each process is quantified using the best available site information.

The purpose for developing a chemical fate CSM for the Los Angeles/Long Beach Harbor (Harbor) is to identify the dominant sources and sinks of TPCB and TDDT to the water column and thereby guide data collection and modeling efforts. CSM development focused on the water column instead of sediments, because questions related to field programs and modeling approaches were more significant and immediate for the water column than for sediments. Modeling of the Greater Harbor Water hydrodynamics and sediment transport is currently being conducted using the WRAP Model. Based in part on this CSM, the WRAP Model will be expanded in the near future to include a chemical fate component for TPCB and TDDT.

The CSM described in this technical memorandum will continue to be updated as new information becomes available. While there are no plans to formally update this memorandum in the future, any new information and understanding related to chemical fate will be reflected in the final model calibration report associated with this project.

2 CSM COMPONENTS

Numerous processes can affect the fate of chemicals within the water column. The following processes were considered during CSM development for the Harbor (Figure 1):

- Air components (wet deposition, dry deposition, and gas exchange)
- Watershed components (gaged and nearshore contributions)
- Sediment and water column components
  - Tidal exchange
  - Net deposition
  - Sediment-water diffusion
  - Groundwater advection
  - Degradation within the water column

Other processes that would be more relevant to a surface sediment CSM, such as dredging, burial, and degradation within the sediment bed, are not included here; these processes will be addressed in the final model calibration report.

Chemical loadings for each of the processes listed above were estimated based on literature (including local studies), the WRAP Model, and professional judgment. Equations[1], data sources, and assumptions for each CSM component are described in the following sections. For each component, low, intermediate, and high values for equation variables were

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[1] For simplicity, unit conversions are omitted from all equations.

estimated to characterize uncertainty and provide a range of annual loadings; intermediate values were based on local estimates wherever possible. Most of the components were calculated on a Harbor-wide basis without calculating loadings to individual sub-waterbodies. However, information for some of the components was available on a finer scale; for these, loadings were calculated for individual total maximum daily load (TMDL) receiving waterbodies and then summed to obtain loading estimates for the entire Harbor. The estimated annual loads were compared to the equivalent load presented in the *Total Maximum Daily Load for Toxic Pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters* (Harbor Toxics TMDL; RWQCB and USEPA 2011), where possible. Loadings representing sources to the Harbor waters are positive; sinks from the Harbor waters are negative.

2.1 Air Components

2.1.1 Wet Deposition

Wet deposition is the process by which dissolved and particulate chemicals enter a waterbody via rainfall directly atop the surface of the waterbody. The annual load can be estimated using the following equation:

$$Load = Conc_{precip} \times Rate_{precip} \times SA \qquad (1)$$

where:

$Conc_{precip}$ = Chemical concentration in precipitation (ng/L)
$Rate_{precip}$ = Annual precipitation rate (in/yr)
SA = Surface area of the Greater Harbor Waters (m^2)

Chemical concentrations in precipitation were based on professional judgment and a literature review[2] of the following:

- AMEC 2013
- Glaser et al. 2006

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[2] Additional literature reviewed for air components but not directly used include McClure 1976, Rowe et al. 2007a, Sabin et al. 2003, Sobek et al. 2013, Stolzenbach et al. 2001, Tetra Tech 2011, Totten et al. 2001, and USEPA 2012.

- Hoff et al. 1996
- Leister and Baker 1994
- NJADN 2004
- Offenberg and Baker 1997
- Oram et al. 2008
- Park et al. 2001
- Poissant et al. 1997
- Sun et al. 2006
- Totten et al. 2004
- Van Ry et al. 2002

These papers included chemical concentrations in rainfall for sites across the United States as well as more locally for Long Beach Harbor (AMEC 2013). Citations describing urban locations were deemed particularly relevant to the Harbor. For TPCB, reasonable low, intermediate, and high precipitation concentrations were assumed to be 0.1, 0.5, and 2 nanograms per liter (ng/L), respectively; for TDDT, low, intermediate, and high values were 0.1, 0.4, and 1.5 ng/L, respectively.

The precipitation rate was assumed to be 13 inches per year, which is approximately the annual average for the Harbor (Current Results 2014).

Surface areas for each TMDL receiving waterbody were computed from the WRAP Model grid of the Harbor (Everest 2009). The boundary of each TMDL receiving waterbody was approximated based in Figures 5-3 and 5-8 of the Harbor Toxics TMDL (RWQCB and USEPA 2011).

Using Equation 1, loads were calculated for each TMDL receiving waterbody and then summed to obtain a total for the entire Harbor. For TPCB, low, intermediate, and high loading estimates for wet deposition were 2, 10, and 42 grams per year (g/yr), respectively; for TDDT, these estimates were 2, 8, and 31 g/yr, respectively.

2.1.2 Dry Deposition

Dry deposition is the process by which particulate-phase chemicals settle to the water surface by gravity and/or air currents. The annual load can be estimated using the following equation:

$$\text{Load} = \text{Flux} \times SA \qquad (2)$$

where:

$Flux$ = Rate of chemical mass transfer via settling of particles to water surface from air ($ng/m^2/d$)
SA = Surface area of the Greater Harbor Waters (m^2)

Flux values were based on professional judgment and a literature review of the following:

- AMEC 2013
- Hillery et al. 1998
- Holsen et al. 1991
- NJADN 2004
- Park et al. 2002
- Sabin et al. 2011
- Totten et al. 2004
- Totten et al. 2006

These papers included flux values for sites across the United States as well as more locally for Los Angeles Harbor (Sabin et al. 2011). As with wet deposition, citations describing urban locations were deemed particularly relevant to the Harbor. For TPCB, reasonable low, intermediate, and high values for flux were assumed to be 2, 8.2, and 40 nanograms per square meter per day ($ng/m^2/d$), respectively; for TDDT, low, intermediate, and high flux values were assumed to be 0.25, 10, and 20 $ng/m^2/d$, respectively. The intermediate values reflect local data (Sabin et al. 2011).

Surface areas for each TMDL receiving waterbody were computed from the WRAP Model grid of the Harbor (Everest 2009). The boundary of each TMDL receiving waterbody was approximated based in Figures 5-3 and 5-8 of the Harbor Toxics TMDL (RWQCB and USEPA 2011).

Using Equation 2, loads were calculated for each TMDL receiving waterbody and then summed to obtain a total for the entire Harbor. For TPCB, low, intermediate, and high loading estimates for dry deposition of TPCB were 46, 190, and 920 g/yr, respectively; for TDDT, these estimates were 6, 230, and 460 g/yr, respectively.

2.1.3 Air-Water Gas Exchange

Air-water gas exchange is diffusion of chemicals across the air-water interface. Because this diffusion is dependent on the concentration gradient between air and water, the transfer of chemical mass can be from air to water or *vice versa*, depending on relative concentrations. The annual load can be estimated using the following equation:

$$\text{Load} = \text{Flux} \times SA \tag{3}$$

where:

$Flux$ = Rate of chemical mass transfer between air and water ($ng/m^2/d$)
SA = Surface area of Greater Harbor Waters (m^2)

Flux values were based on professional judgment and a literature review of the following:

- Bamford et al. 2002
- Hillery et al. 1998
- Hoff et al. 1996
- Hornbuckle et al. 1994
- Hornbuckle et al. 1995
- Iwata et al. 1993
- Nelson et al. 1998
- NJADN 2004
- Park et al. 2001
- Park et al. 2002
- Rowe et al. 2007b

- Sabin et al. 2011
- Totten et al. 2003
- Totten et al. 2004
- Zhang and Lohmann 2010

These papers included flux values for sites across the United States as well as more locally for Los Angeles Harbor (Sabin et al. 2011). For TPCB, low, intermediate, and high values flux were assumed to be -10, -90, and -1,000 ng/m^2/d, respectively; for TDDT, low, intermediate, and high flux values were assumed to be -0.5, -24, and -50 ng/m^2/d. Flux values in the vast majority of the literature were consistent in direction with the latest published Southern California Coastal Water Research Project (SCCWRP) results (Sabin et al. 2011), namely that contemporary waterbodies in the United States tend, on balance, to volatilize these chemicals to the atmosphere.

Surface areas for each TMDL receiving waterbody were computed from the WRAP Model grid of the Harbor (Everest 2009). The boundary of each TMDL receiving waterbody was approximated based in Figures 5-3 and 5-8 of the Harbor Toxics TMDL (RWQCB and USEPA 2011).

Using Equation 3, loads were calculated for each TMDL receiving waterbody and then summed to obtain a total for the entire Harbor. For TPCB, low, intermediate, and high loading estimates for air-water gas exchange were -230, -2,100, and -23,000 g/yr, respectively; for TDDT, these estimates were -12, -550, and -1,200 g/yr, respectively.

2.1.4 Comparison to TMDL

The Harbor Toxics TMDL loading rates appear to have been based on preliminary results of a dry deposition and gas exchange flux study presented by SCCWRP in 2009 (page III-46 of RWQCB and USEPA 2011) whereas calculations presented here use the latest published SCCWRP results (Sabin et al 2011).

The Harbor Toxics TMDL estimations of air-water exchange rates accounted for dry deposition and gas exchange; Table 6-12 of RWQCB and USEPA (2011) lists “n/a” for TPCB and 680 g/yr for TDDT. The symbol “n/a” is listed because the sum of dry deposition and gas exchange was found to be negative (i.e., monitoring results show net flux from water to air). The TDDT value was based on a net flux of 29 ng/m^2/d to the water column (page III-50 of RWQCB and USEPA 2011). In comparison, the net combination of dry deposition and gas exchange in the latest published SCCWRP results (Sabin et al. 2011) used herein show an overall loss from the water column to air of -14 ng/m^2/d for TDDT (10 ng/m^2/d for dry deposition and -24 ng/m^2/d for gas exchange). For TPCB, low, intermediate, and high values for the net contribution from these two air-water exchange processes were -180, -1,900, and -22,000 g/yr, respectively; for TDDT, these estimates were -6, -320, and -740 g/yr, respectively.

In summary, from the time the TMDL was developed (using 2009 preliminary results) to the latest published SCCWRP results (Sabin et al. 2011), the magnitude of the dry deposition and gaseous TPCB flux changed (although the net direction did not) from an unspecified net flux from water to air to -1,900 g/yr, and the magnitude and net direction of TDDT flux changed from 680 to -320 g/yr.

2.2 Watershed Components

2.2.1 Gaged Inflow Load

Gaged inflow load is the chemical load from watersheds calculated using measured streamflow for tributaries combined with estimates of runoff chemical concentrations. Streamflow data are available for the San Gabriel River, Los Angeles River, Dominguez Channel, and Coyote Creek (which flows into the San Gabriel River). The annual load was estimated using the following equation:

$$Load = Conc_{runoff} \times Vol_{runoff} \tag{4}$$

where:

$Conc_{runoff}$ = Chemical concentration in runoff (ng/L)
Vol_{runoff} = Annual runoff volume (L/yr)

TPCB and TDDT concentrations in runoff were based on professional judgment and a literature review[3] of developed (e.g., urban, commercial, industrial) watersheds information that included the following:

- AMEC 2013
- ATSDR 2002
- Gilbreath et al. 2012
- Hart Crowser 2007
- Hwang and Foster 2008
- LACDPW 2012a
- Marsalek and Ng 1989
- POLA 2006
- Rossi et al. 2004
- The City of New York 2013

Most local TPCB and TDDT data were below the detection limit, with a greater than 1 ng/L detection limit; this detection limit was assumed as the intermediate value. High-resolution PCB and DDT stormwater samples are being collected this year and will be used in the chemical fate model development (AMEC 2014).

For TPCB, reasonable low, intermediate, and high TPCB concentrations in runoff were assumed to be 0.1, 1.0, and 50 ng/L, respectively; for TDDT, the values were assumed to be 0.2, 1.0, and 50 ng/L, respectively. All tributary inflows were assumed to have the same chemical concentrations.

Average annual runoff volumes for each gaged tributary were calculated from the measured tributary flows, prorated by the drainage areas between the gages and entry to the Greater Harbor Waters. The gaged drainage areas were obtained from the Los Angeles County Department of Public Works (LACDPW; 2012a, 2013); the total gaged drainage area was 1,312 square miles. The average flow for each tributary was calculated as the average of

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[3] Additional literature reviewed but not directly used include Ackerman and Schiff 2003, Davis et al. 2000, Gluchowski et al. 2012, Kinnetic 2002, Lent and McKee 2011, Parsons and Terragraphics 2007, Peng et al. 2007a, and Peng et al. 2007b.

annual average[4] flows available from 1994 through 2013 measured by the LACDPW at Dominguez Channel at S28, Los Angeles River at F319, San Gabriel River at F42B-R, and Coyote Creek at F354-R. Streamflow data for the Dominguez Channel were obtained from the LACDPW Watershed Management Division, which periodically monitors flows at Artesia Boulevard since 2003 and reports them annually (LACDPW 1999a-2012a). Streamflow data for the Los Angeles River, San Gabriel River, and Coyote Creek were obtained from the LACDPW Water Resources Division, which continuously monitors flows that are reported annually (LACDPW 1998, 1999b-2012b, 2006c, 2008c, 2013).

2.2.2 Nearshore Load

Nearshore load is the chemical load from watersheds without measured flows combined with estimated runoff chemical concentrations. The annual load can be estimated using the following equation:

$$Load = Conc_{runoff} \times DA \times Rate_{precip} \times f_{impervious} \quad (5)$$

where:

$Conc_{runoff}$ = TPCB or TDDT concentration in runoff (ng/L)
DA = Ungaged drainage area (m^2)
$Rate_{precip}$ = Annual precipitation rate (in/yr)
$f_{impervious}$ = Impervious cover fraction (−)

Runoff chemical concentrations were assumed to be the same for gaged inflows; these concentrations were based on a literature review and professional judgment. For TPCB, low, intermediate, and high concentrations in runoff were assumed to be 0.1, 1.0, and 50 ng/L, respectively; for TDDT, the values were assumed to be 0.2, 1.0, and 50 ng/L, respectively. All nearshore inflows were assumed to have the same chemical concentrations.

Drainage areas for each TMDL receiving waterbody were obtained from Table III.1-4 of the Harbor Toxics TMDL (RWQCB and USEPA 2011). The drainage area for Machado Lake was

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[4] Professional judgment was used to exclude years with an insufficient number of flow measurements to be representative of a year.

based on U.S. Environmental Protection Agency (USEPA) Nearshore Watershed model subwatersheds (Tetra Tech 2010). The total ungaged drainage area was 69 square miles. The precipitation rate was assumed to be 13 inches per year, which is approximately the annual average for the Harbor (Current Results 2014).

The impervious fraction was assumed to be 0.64, based on the industrial land use value in Table 10 in Appendix II of the Harbor Toxics TMDL (RWQCB and USEPA 2011).

2.2.2.1 Machado Lake Runoff

Machado Lake was not considered to be a gaged inflow, because flows are not routinely monitored. For the gaged watersheds, the average annual volumes were estimated based on 10 to 18 years of flow data. Flow data for Machado Lake were collected for only two wet seasons for a special study. These data were considered to be insufficient to establish the average annual volume. The flow data from Machado Lake were used to determine the percentage of runoff that discharges into the Harbor.

To account for the reduction in runoff discharges into the Harbor due to lake storage, 40 percent of the runoff from the Machado Lake drainage area was estimated to discharge into the Harbor. This percentage was based on measured average annual volume discharged into the Harbor compared to the theoretical total runoff from the watershed. The average annual volume discharged was estimated based on measured flows released from Machado Lake during the 2008/2009 and 2009/2010 wet seasons. The theoretical annual total runoff was estimated based on the volume component[5] in Equation 5 using the average rainfall wet season totals from the four closest rain gages in the drainage area of 8.39 and 17.95 inches for 2008/2009 and 2009/2010, respectively; a drainage area of approximately 64 million square meters; and an impervious fraction of 0.64. The annual load from Machado Lake was estimated using Equation 5 and then reduced by 40 percent.

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[5] $DA \times Rate_{precip} \times f_{impervious}$

2.2.3 Total Watershed Loading

Loads were calculated for each TMDL receiving waterbody based on the gaged inflow and nearshore load equations above (Equations 4 and 5, respectively) and then summed[6] to obtain the total watershed loading for the entire Harbor. For TPCB, low, intermediate, and high estimates for the total watershed loading were 61, 610, and 31,000 g/yr, respectively; for TDDT, these estimates were 120, 610, and 31,000 g/yr, respectively.

2.2.4 Comparison to TMDL

TMDL watershed loadings were estimated using Environmental Fluid Dynamics Code (EFDC) inputs provided by Tetra Tech (Tetra Tech 2010). For TPCB, the TMDL estimate was 23,000 g/yr; for TDDT, it was 10,000 g/yr. For both TPCB and TDDT, the TMDL values fall within the intermediate and high CSM estimates provided here.

2.3 Sediment and Water Column Components

2.3.1 Tidal Flushing

Tidal flushing is the process by which flood tides bring ocean water into the Harbor; the ocean waters circulate and mix with the Greater Harbor Waters and then the mixture exits during ebb tide. Thus, loading due to tidal flushing depends on hydrodynamics (inflow and outflow rates and mixing rates) as well as chemical concentrations in both the Harbor and the water outside the Harbor. This exchange was estimated using the WRAP Model and literature-based estimates (see below) of water column concentrations within the Harbor and outside the Harbor. The approach involved simulating tidal flows and mixing under a dry-weather condition to estimate the net exchange between the Harbor and ocean. The simulation included the calibrated hydrodynamic model and a conservative tracer to determine the change in contaminant concentrations for each TMDL waterbody due to tidal flushing. The simulated decrease in Harbor chemical concentrations was fitted to a first-order loss equation, from which a rate constant, k_d, was obtained.

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[6] For TPCB, low, intermediate, and high estimates for loads based on gaged inflows were 57, 570, and 29,000 g/yr, respectively; loads for ungaged flows were 4, 40, and 2,000 g/yr, respectively. For TDDT, low, intermediate, and high estimates for loads based on gaged inflows were 112, 570, and 29,000 g/yr, respectively; loads for ungaged flows were 8, 40, and 2,000 g/yr, respectively.

The annual load was estimated using the following equation:

$$Load = Conc_{wc} \times Vol \times k_d \qquad (6)$$

where:

$Conc_{wc}$ = Chemical concentration in the Harbor water column (ng/L)
Vol = Water volume (L)
k_d = First order "decay" rate constant describing loss of chemical from the Harbor (1/yr)

Initial water concentrations in the Harbor were based on water column data. Contaminant concentrations based on dry weather, mid-water column data were reviewed from multiple sources (Aderhold 2012; RWQCB 2007; Ports 2009; POLB 2009, 2010, 2011; Weston 2007a). Water column data were mostly non-detects, and the highest concentrations were observed in the Consolidated Slip. Contaminant concentrations for TPCB ranged from non-detect to 2.67 ng/L; TDDT concentrations ranged from non-detect to 1.73 ng/L. In general, the detection limits varied by study, ranging from 1 to 10 ng/L. In Greater Harbor Waters, low and high concentrations for TPCB were estimated to be 1.00 and 2.67 ng/L, respectively; the low and high values for TDDT were estimated to be 1.00 and 1.73 ng/L, respectively. The intermediate concentrations were calculated as the average of low and high values. In ocean waters, only one concentration was assumed for each chemical: 0.015 ng/L for TPCB and 0.25 ng/L for TDDT. Ocean concentrations were obtained from the Harbor Toxics TMDL EFDC modeling (RWQCB and USEPA 2011).

Water volumes by TMDL receiving waterbody were determined from the WRAP Model using the model grid of the Harbor and water surface elevation at mean sea level (MSL) (Everest 2009). The waterbody boundaries were approximated based in Figures 5-3 and 5-8 of the Harbor Toxics TMDL (RWQCB and USEPA 2011).

Loss rates (k_d) by waterbody were determined using the WRAP Model output based on tidal flushing simulations. Tidal flushing was quantified with residence time, which is the time it takes for an initial unit tracer concentration to be reduced to 1/e (RST). This RST concentration is commonly used as the criterion to determine residence time. A long residence time indicates less tidal flushing, while a short residence time indicates greater tidal flushing. Areas with less tidal flushing may have poor water quality, because pollutants remain in the water for longer periods of time. The WRAP Model simulations started with uniform chemical concentrations in the Harbor (low or high for each chemical) and ocean (one value for each chemical) and then simulated the decreasing concentrations within each waterbody over 45 days due to tidal flushing (assuming the chemicals behave as conservative tracers; Figure 2). Simulations included dry weather inflows to maintain proper hydrodynamics. As shown in Figure 2, the concentration in the Inner and Outer Harbor fluctuates, increasing and decreasing with the tides. Overall, the concentration decreases as shown by the green- and red-dashed lines. The residence time is determined when the overall concentration decreases to the RST concentration. The Outer Harbor has a residence time of about 10 days, while the residence time in the Inner Harbor is about 32 days. As expected, the residence time for the Outer Harbor indicates greater tidal flushing as compared to the Inner Harbor. This model-predicted "decay" of chemical concentrations was fitted to a first order equation to estimate the loss rate (k_d) (Table 1). The loss rate (units in per year) is the inverse of the residence time. Shorter residence times such as the Outer Harbor or San Pedro Bay correspond to a high loss rate (i.e., chemical tends to leave the Harbor). Longer residence times such as the Inner Harbor or Cabrillo Marina indicate a low loss rate (i.e., chemical tends to stay in the Harbor). High and low loss rates were determined based on the high and low TPCB and TDDT concentrations. Intermediate estimates of loss rates due to tidal flushing were calculated as the average of the low and high estimates based on the WRAP Model simulated concentrations.

Table 1
Loss Rate by Waterbody

TMDL Receiving Waterbody	TPCB Decay Rate (per year)			TDDT Decay Rate (per year)		
	Low	Intermediate	High	Low	Intermediate	High
Dominguez Channel	15.7	15.7	15.7	14.4	14.7	15.0
Consolidated Slip	12.3	12.4	12.4	8.3	9.5	10.6
Fish Harbor	23.3	23.6	23.8	12.6	15.5	18.4
Cabrillo Marina	40.9	41.3	41.7	19.0	24.4	29.8
Inner Cabrillo Beach	47.3	47.9	48.4	20.2	27.6	34.9
Inner Harbor	14.0	14.1	14.2	8.7	10.1	11.5

TMDL Receiving Waterbody	TPCB Decay Rate (per year)			TDDT Decay Rate (per year)		
	Low	Intermediate	High	Low	Intermediate	High
Outer Harbor	52.2	52.5	52.8	21.4	30.1	38.7
Los Angeles River Estuary	58.6	58.7	58.8	45.7	49.0	52.3
San Gabriel River Estuary	263.8	263.8	263.9	252.1	254.8	257.5
San Pedro Bay	53.6	53.9	54.2	29.4	36.3	43.1
Alamitos Bay	22.1	22.2	22.3	15.8	17.5	19.1

Using Equation 6, loads were calculated for each TMDL waterbody and then summed to obtain a total for the entire Harbor. For TPCB, low, intermediate, and high loading estimates for tidal flushing were -35,000, -64,000, and -94,000 g/yr, respectively; for TDDT, these estimates were -18,000, -31,000, and -47,000 g/yr, respectively.

2.3.2 Net Deposition

Deposition is the process by which particulate-bound chemicals in the water column settle and adhere to the sediment bed, resulting in a loss of chemicals from the water column; net deposition is the difference between deposition to and resuspension from the sediment bed. The annual load can be estimated using the following equation:

$$Load = Dep_{fines} \times Conc_{wc} \times \frac{1}{1+K_D \times TSS} \times K_D \quad (7)$$

where:

Dep_{fines} = Net deposition rate of fines (cohesive sediments) (kg/yr)
$Conc_{wc}$ = Chemical concentration in water column (ng/L)
K_D = Partition coefficient (L/kg)
TSS = Total suspended solids (mg/L)

The net deposition rate of fines (cohesive sediment) was based on WRAP Model simulations from 1995 to 2005. The net deposition rate based on the WRAP Model equals the difference between gross deposition and gross resuspension rates throughout the Harbor. Overall, the Harbor is a net depositional environment based on the WRAP Model results. Watershed loadings were specified based on estimates used for the Harbor Toxics TMDL (Tetra Tech 2010). A net deposition rate of 13 million kg/yr for the entire Harbor was used in the net deposition calculations. For these CSM calculations, the majority of the chemical mass was assumed to be associated (and settles) with fines. In the future, the WRAP Model will be modified to expand this assumption to include partitioning to all modeled particle size classes.

Chemical concentrations in the water column were based on mid-water column data. Dry weather chemical concentration data from the Harbor were reviewed from multiple sources (Aderhold 2012; RWQCB 2007; Ports 2009; POLB 2009, 2010, 2011; Weston 2007a). TPCB and TDDT water column data were mostly non-detects and the highest concentrations were observed in the Consolidated Slip. TPCB concentrations ranged from non-detect to 2.67 ng/L; TDDT concentrations ranged from non-detect to 1.73 ng/L. In general, detection limits varied by study, ranging from 1 to 10 ng/L. For TPCB, low and high concentrations were estimated to be 1.00 and 2.67 ng/L, respectively; for TDDT, the low and high values were estimated to be 1.00 and 1.73 ng/L, respectively. Intermediate concentrations were calculated as the average of low and high values. These concentrations were identical to those used for calculating loads from the tidal flushing component of the CSM. Because partitioning occurs between the dissolved phase and the particulate phase, the measured chemical concentration in the water (which represents the total chemical mass per water volume, not just the dissolved mass) is multiplied by a factor $[(1/(1+K_D \times TSS))]$ to determine the equivalent dissolved concentration. An average TSS value for the Harbor of 3.9 milligrams per liter (mg/L) was used, based on dry weather monthly total suspended solid (TSS) data (Everest 2007).

The partition coefficient between settling fine particulates and bottom water, K_D, was computed using sediment and porewater data collected at several Harbor locations in 2006 (Weston 2007b). Low, intermediate, and high K_D values were assigned the 20th, 50th, and 80th percentile values, respectively. For TPCB, the low, intermediate, and high K_D values were 66, 158, and 551 liters per kilogram (L/kg); for TDDT, the values were 81, 235, and 584 L/kg, respectively. The porewater data used to estimate these partition coefficients were not corrected for porewater dissolved organic carbon (DOC) concentrations; such a correction will be evaluated and potentially used in the chemical fate model development.

Low values for water column concentrations were paired with low values of K_D to produce the overall low loading estimate (and similar for the high estimate). For TPCB, low, intermediate, and high loading estimates for net deposition were -1, -4, and -19 g/yr, respectively; for TDDT, these estimates were -1, -4, and -13 g/yr, respectively.

2.3.3 Comparison to TMDL

The Harbor Toxics TMDL estimated the loss of chemicals to the sediment bed using the net deposition rate of particulates (both fines and sand) and the average existing concentration in the top 5 centimeters (cm) of the sediment bed (as a surrogate for the chemical concentration on settling particulates). Based on this approach, the TMDL estimate was -720 g/yr; for TDDT, it was -600 g/yr (Table 4-6 of the Harbor Toxics TMDL; RWQCB and USEPA 2011). The substantial differences between the values estimated in the CSM and the TMDL result because TPCB and TDDT concentrations in the surface sediments are substantially larger than concentrations calculated using partition coefficients and water column concentrations.

2.3.4 Sediment-Water Diffusion

Sediment-water diffusion is the transport of chemicals between sediment porewater and the overlying water column. The annual load to the water column due to diffusion can be estimated using the following equation:

$$Load = \left(Conc_{pw} - Conc_{wc}\right) \times K_f \times SA \tag{8}$$

where:

$Conc_{pw}$ = Chemical concentration in porewater (ng/L)
$Conc_{wc}$ = Chemical concentration at bottom of water column (ng/L)
K_f = Mass transfer coefficient (cm/d)
SA = Surface area (m^2)

Porewater concentrations were based on data collected at several Harbor locations in 2006 (Weston 2007b). The minimum, intermediate, and maximum porewater concentrations were computed for each TMDL receiving waterbody (Table 2). The minimum and maximum porewater concentrations are provided to show the range in porewater data. In some areas, porewater data have a large range due to one or two locations with high values, such as the Los Angeles Inner and Outer Harbor. The intermediate porewater concentrations were used for the sediment-water diffusion calculations and were based on the average of porewater data within for each TMDL receiving waterbody. However, no porewater data were available for several waterbodies. In general, porewater concentrations for areas without data were specified from data from a nearby area. Given that the close proximity with similar hydrodynamic and water quality conditions would provide a reasonable estimate of porewater concentrations for areas without data. For the Dominguez Channel, Consolidated Slip, and Fish Harbor, data were available from three sampling locations with detectable TPCB and TDDT porewater concentrations. F or the Dominguez Channel and Consolidated Slip, three locations were located in the Los Angeles East Basin adjacent to the Consolidated Slip. For Fish Harbor, data were from the three locations just outside of Fish Harbor. For the San Gabriel River Estuary, San Pedro Bay, and Alamitos Bay, the closest area is the Los Angeles River Estuary, where there were two locations. Because TPCB porewater concentrations for the Los Angeles River Estuary were non-detects, the average TPCB porewater concentration was specified to be the same as for the Long Beach Outer Harbor. The closest detectable TPCB porewater concentrations were located in the middle of the Long Beach Outer Harbor. These average porewater concentrations were judged to be sufficient for the CSM. Porewater concentrations will be determined by equilibrium partitioning and sediment concentrations in the chemical fate model.

Table 2
Porewater Concentrations

TMDL Receiving Waterbody	TPCB (ng/L)			TDDT (ng/L)		
	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum
Dominguez Channel[1]	46.5	97.9	149.6	68.6	75.4	82.2
Consolidated Slip[1]	46.5	97.9	149.6	68.6	75.4	82.2
Fish Harbor[1]	31.1	48.4	66.2	94.0	102.7	110.8
Cabrillo Marina	43.7	212.7	381.6	206.9	210.6	214.2
Inner Cabrillo Beach	47.0	53.2	59.4	43.9	55.5	67.0
Los Angeles Inner Harbor	25.3	182.8	757.5	38.1	154.9	454.9

TMDL Receiving Waterbody	TPCB (ng/L)			TDDT (ng/L)		
	Minimum	Intermediate	Maximum	Minimum	Intermediate	Maximum
Long Beach Inner Harbor	11.1	130.3	535.1	24.4	74.8	281.4
Los Angeles Outer Harbor	37.2	120.3	192.0	94.1	318.1	801.0
Long Beach Outer Harbor	18.0	28.5	47.4	42.1	101.5	149.3
Los Angeles River Estuary[2]	18.0	28.5	47.4	39.7	128.8	217.9
San Gabriel River Estuary[3]	18.0	28.5	47.4	39.7	128.8	217.9
San Pedro Bay[3]	18.0	28.5	47.4	39.7	128.8	217.9
Alamitos Bay[3]	18.0	28.5	47.4	39.7	128.8	217.9

Notes:
1 Based on average of three nearest detectable locations
2 PCB concentrations based on Long Beach Outer Harbor data
3 Concentrations assumed to be the same as for Los Angeles River Estuary

Ranges in contaminant concentrations of the overlying water column were determined from water column data taken within 1 foot of the sediment bed (RWQCB 2007; Weston 2007b). TPCB concentrations ranged from non-detect to 2 ng/L; TDDT concentrations ranged from non-detect to 4.3 ng/L. Detections levels varied from 0.25 to 1.25 ng/L. For TPCB, low and high values were estimated to be 0.25 and 2.0 ng/L, respectively; for TDDT, low and high values were estimated to be 0.25 and 4.3 ng/L, respectively. These values differ from those used in other CSM components, because these reflect solely the bottom waters, which participate in diffusive exchange with sediments. Intermediate concentrations used for the sediment-water diffusion calculations were computed as the average of low and high values.

Values for the mass transfer coefficient (K_f) were based on professional judgment and a literature review of Neumann 1990 and Martinez et al. 2010. Reasonable low, intermediate, and high values were assumed to be 1, 5, and 10 centimeters per day (cm/d), respectively, for both TPCB and TDDT.

Using Equation 8, loads were calculated for each waterbody and then summed to obtain a total for the entire Harbor. For TPCB, low, intermediate, and high loading estimates for sediment-water diffusion were 14,000, 71,000, and 140,000 g/yr, respectively; for TDDT, these estimates were 31,000, 160,000, and 310,000 g/yr, respectively. These estimated values are larger than the other sources and, as will be discussed below, the actual values are likely to be lower.

2.3.5 Groundwater Advection

Dissolved chemical can be transported to Greater Harbor Waters via groundwater; however, groundwater transport pathways within the Harbor are expected to be minimal. A significant groundwater source would require an extensive non-aqueous phase liquid (NAPL) plume(s) and a transport pathway. Based on available data, NAPL is largely absent in the Harbor, with aqueous TPCB concentrations at multiple stations all below the detection limit at 1 microgram per liter (µg/L) (Hovel 2013). In addition, the former Hugo Neu Proler metal recycling site, which was previously implicated as a source of PCBs to the Harbor (SCCWRP 1990), has been remediated (Yang 2012). In addition, the Harbor experiences relatively low annual precipitation and generally is characterized by high impervious cover, resulting in low infiltration. While tidal incursion into the groundwater system could provide a transport mechanism for chemicals, this incursion is not expected to be extensive. For these reasons, chemical loading from groundwater was judged to be negligible.

2.3.6 Degradation

Degradation is the process by which organic substances are broken down within the water column. This process removes chemical from the water column and is often described with a first order loss rate:

$$Load = Conc_{wc} \times Rate_{degr} \times Vol \tag{9}$$

where:

$Conc_{wc}$ = Chemical concentration in water column (ng/L)
$Rate_{degr}$ = Degradation rate constant (1/yr) (this is a negative number)
Vol = Water volume of waterbodies (L)

Chemical concentrations in the water column were based on mid-water column data. Dry weather chemical concentration data from the Harbor were reviewed from multiple sources (Aderhold 2012; RWQCB 2007; Ports 2009; POLB 2009, 2010, 2011; Weston 2007a). TPCB and TDDT water column data were mostly non-detects and the highest concentrations were observed in Consolidated Slip. TPCB concentrations ranged from non-detect to 2.67 ng/L; TDDT concentrations ranged from non-detect to 1.73 ng/L. In general, detection limits varied by study ranging from 1 to 10 ng/L. For TPCB, low and high concentrations were estimated to be 1.00 and 2.67 ng/L, respectively; for TDDT, the low and high values were estimated to be 1.00 and 1.73 ng/L, respectively. Intermediate concentrations were calculated as the average of low and high values. These Harbor concentrations were identical to those used for calculating loads from the tidal exchange and net deposition components of the CSM.

Degradation of TPCB is complicated by the fact that certain congeners may be reductively dechlorinated to other congeners, which may be described as a degradation process, but which does not reduce the mass of TPCB. Only when a congener is degraded to a non-PCB chemical can true degradation be considered to occur. Accordingly, literature values for reductive dechlorination rates are of limited use to this CSM calculation. Additionally, degradation rates of TPCB and TDDT depend on redox condition, acclimatization of organisms, and concentration (i.e., degradation is often not strictly first-order).

The rate of degradation in the water column was based on literature (Davis 2004) and professional judgment.[7] Davis 2004 presents a simple one-box mass budget model for PCBs in San Francisco Bay in which they used a half-life of 56 years. Based on this information, the degradation rate constant was assumed to be -0.01 per year for both TPCB and TDDT (-0.01 per year is approximately equal to a half-life of 56 years).

Water volumes for each TMDL receiving waterbody were based on the WRAP Model grid of the Harbor and water surface elevation at MSL (Everest 2009). See discussion in Section 2.3.1 for more details.

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[7] Other literature reviewed included Abramowicz 1993, Commandeur et al. 1996, Corona-Cruz et al. 1999, Gobas et al. 1995, Jaysankar et al. 2006, Leatherbarrow et al. 2006, Mikszewski 2004, and Nadeau et al. 1994.

Using Equation 9, loads were calculated for each waterbody and then summed to obtain a total for the entire Harbor. For TPCB, low, intermediate, and high loading estimates for degradation in the water column were -8, -14, and -21 g/yr, respectively; for TDDT, these estimates were -8, -11, and -14 g/yr, respectively. These values are small relative to other losses and indicate that while the uncertainty in degradation rates is substantial, degradation is unlikely to be an important loss mechanism from the Harbor water column.

3 LOADING SUMMARY

3.1 Preliminary Loading Estimates

Table 3 and Figure 3 summarize the preliminary low, intermediate, and high loading approximations for each CSM component. Values are deemed preliminary, because estimates will be refined using data collected during upcoming field programs. The dominant process currently contributing chemical to the water column appears to be sediment-water diffusion; for loss of chemical from the water column, tidal exchange appears to be the most important. Gas exchange is a moderate sink, whereas contribution from the watershed provides a moderate source of chemical. The least important sources of chemical to the water column are wet and dry deposition as well as groundwater advection. The least important sinks are net deposition and degradation in the water column.

Table 3
Preliminary Loading Summary

CSM Component	TPCB Load (g/yr)			TDDT Load (g/yr)		
	Low	Intermediate	High	Low	Intermediate	High
Air Components						
Wet Deposition	2	10	42	2	8	31
Dry Deposition	46	190	920	6	230	460
Gas Exchange	-230	-2,100	-23,000	-12	-550	-1,200
Watershed Components						
Watershed	61	610	31,000	120	610	31,000

CSM Component	TPCB Load (g/yr)			TDDT Load (g/yr)		
	Low	Intermediate	High	Low	Intermediate	High
Sediment and Water Column Components						
Tidal Exchange	-35,000	-64,000	-94,000	-18,000	-31,000	-47,000
Net Deposition	-1	-4	-19	-1	-4	-13
Sediment-Water Diffusion	14,000	71,000	140,000	31,000	160,000	310,000
Degradation	-8	-14	-21	-8	-11	-14
Total[1]	**-21,000**	**5,900**	**57,000**	**14,000**	**130,000**	**300,000**

Notes:

1 Total is the sum of values for individual components before rounding; rounding was performed on values for individual components after summation.

Positive and negative values indicate sources to and sinks from the water column, respectively.

3.2 Loading Imbalance

Table 3 indicates that estimated sources and sinks are out of balance, especially for TDDT. These results are not unexpected, because the estimates of the mass balance components are based on limited data. These estimates will be refined using the upcoming field programs planned by the Ports. In addition, one key benefit of the fate and transport model is that it balances mass; thus, the results of the field studies will be incorporated into the model, resulting in a refined mass balance. For the purposes of this document, a sensitivity analysis was performed by varying key components to achieve balance. The purpose of this sensitivity analysis is to determine what insights this analysis may provide regarding the major loads of contaminants to the waters of the Harbor.

3.3 Sensitivity Analysis

One key question for decision making that can be addressed by this mass balance and by the fate and transport model is the relative importance of ongoing watershed loads and loads from sediments. In the preliminary loading estimate, loads from sediments dominate (Table 3). Therefore, to address the imbalance, a sensitivity analysis was performed by balancing mass by reducing sediment-water diffusive exchange to address positive total loads (TPCB load intermediate and high cases and TDDT load low, intermediate, and high cases) and increasing watershed loads to address negative total loads (TPCB load low case).

For the cases using the intermediate loads and for the TDDT load low case, sediment-water diffusion is still the dominant source to the water column (Table 4). However, for the TPCB load low and high cases and the TDDT load high case, source loads from the watershed and sediment-water diffusion are of similar order of magnitude. These two key loads will be addressed directly by the Ports. A field study is underway to measure DDT and PCB concentrations in the primary watershed sources. In addition, the diffusive exchange loads will be refined in the model by the use of the extensive sediment data and partitioning calculations. Figure 4 shows the middle value for each component, with error bars indicating range.

Table 4

Loading Sensitivity Analysis

CSM Component	**TPCB Load (g/yr)**			**TDDT Load (g/yr)**		
	Low	**Intermediate**	**High**	**Low**	**Intermediate**	**High**
Air Components						
Wet Deposition	2	10	42	2	8	31
Dry Deposition	46	190	920	6	230	460
Gas Exchange	-230	-2,100	-23,000	-12	-550	-1,200
Watershed Components						
Watershed	*21,000*	610	31,000	120	610	31,000
Sediment and Water Column Components						
Tidal Exchange	-35,000	-64,000	-94,000	-18,000	-31,000	-47,000
Net Deposition	-1	-4	-19	-1	-4	-13
Sediment-Water Diffusion	14,000	*66,000*	*86,000*	*18,000*	*30,000*	*17,000*
Degradation	-8	-14	-21	-8	-11	-14
Total[1]	**0**	**0**	**0**	**0**	**0**	**0**

Notes:

[1] Total is the sum of values for individual components prior to rounding; rounding was performed on values for individual components after the summation.

Positive and negative values indicate sources to and sinks from the water column, respectively.

Italicized values = updated values, as compared to Table 3

4 CONCLUSIONS

Through the development of the chemical fate CSM, the following conclusions can be made regarding the importance of processes contributing to the gain or loss of TPCB and TDDT to the Greater Harbor Waters as a whole:

- Wet and dry deposition, groundwater, and degradation in the water column are probably not important processes. Consequently, further field efforts focused on estimating these processes are not likely to be as useful as efforts to estimate more important processes. It is possible that degradation of TPCB and/or TDDT in the sediment bed itself is a meaningful loss process from sediments; degradation will be investigated during the construction of the WRAP Model.
- Losses due to gas exchange may be important. Estimates of these losses for the Los Angeles Harbor were recently presented by Sabin et al. (2011). Accordingly, no new field work has been proposed and the information in Sabin et al. (2011) will form the basis for quantifying this mechanism in the chemical fate model.
- Watershed loadings may be important. Of the processes evaluated, chemical loading from the watershed ranked in the middle. Its potential importance provides motivation for a stormwater study to better quantify loadings during high flow events, when the majority of watershed loadings to a waterbody typically occur. On a smaller spatial scale (e.g., within specific Greater Harbor Waters), the watershed load is likely to be important for those waterbodies with tributary inputs. Finally, watershed loadings are important not just as direct sources of chemical to the water column of the Harbor but also as sources of contaminated particles settling on the Harbor sediment bed.
- Water column concentrations are important in the calculation of several CSM components, one of which was found to be an influential component evaluated for the CSM (i.e., tidal exchange). Water column concentrations used in calculating net deposition, tidal exchange, and degradation were based on studies between 2003 and 2012; the high percentage of non-detect data results in high uncertainty in these CSM calculations. This uncertainty is particularly influential in the calculation of tidal exchange, because tidal exchange was found to be a significant sink for chemicals in the Harbor. The importance of tidal exchange provides incentive for a water column

study to better measure chemical concentrations in water both inside and outside the Harbor.

- Tidal exchange is important. The importance of tidal exchange also provides impetus for expanding the WRAP Model to include a chemical fate component in the near future to allow effects of tidal exchange on chemical load to be better quantified.
- Sediments appear to be an important source of TPCB and TDDT to the water column. The WRAP fate and transport Model will permit refinement of the estimate of the strength of this source as well as estimates of anticipated future trends in sediment chemical concentrations.

The CSM provides a broad, overall view of the current sources and sinks of chemical to the Greater Harbor Waters. Caveats for the usage of the CSM include:

- Smaller, more enclosed waterbodies may be controlled to some degree by transient sources and sinks (e.g., inputs and outputs during discrete storm events). Accordingly, mass balances on smaller waterbodies are not the focus of this CSM discussion but will be estimated with the fate and transport model.
- Dominant sources and sinks for specific waterbodies within the Harbor (e.g., Consolidated Slip and Fish Harbor) may be different.
- The CSM cannot be used to predict future conditions.

The CSM is a living framework. Future data collection and hydrodynamic, sediment transport, and chemical fate and transport modeling will refine our understanding of the site.

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FIGURES

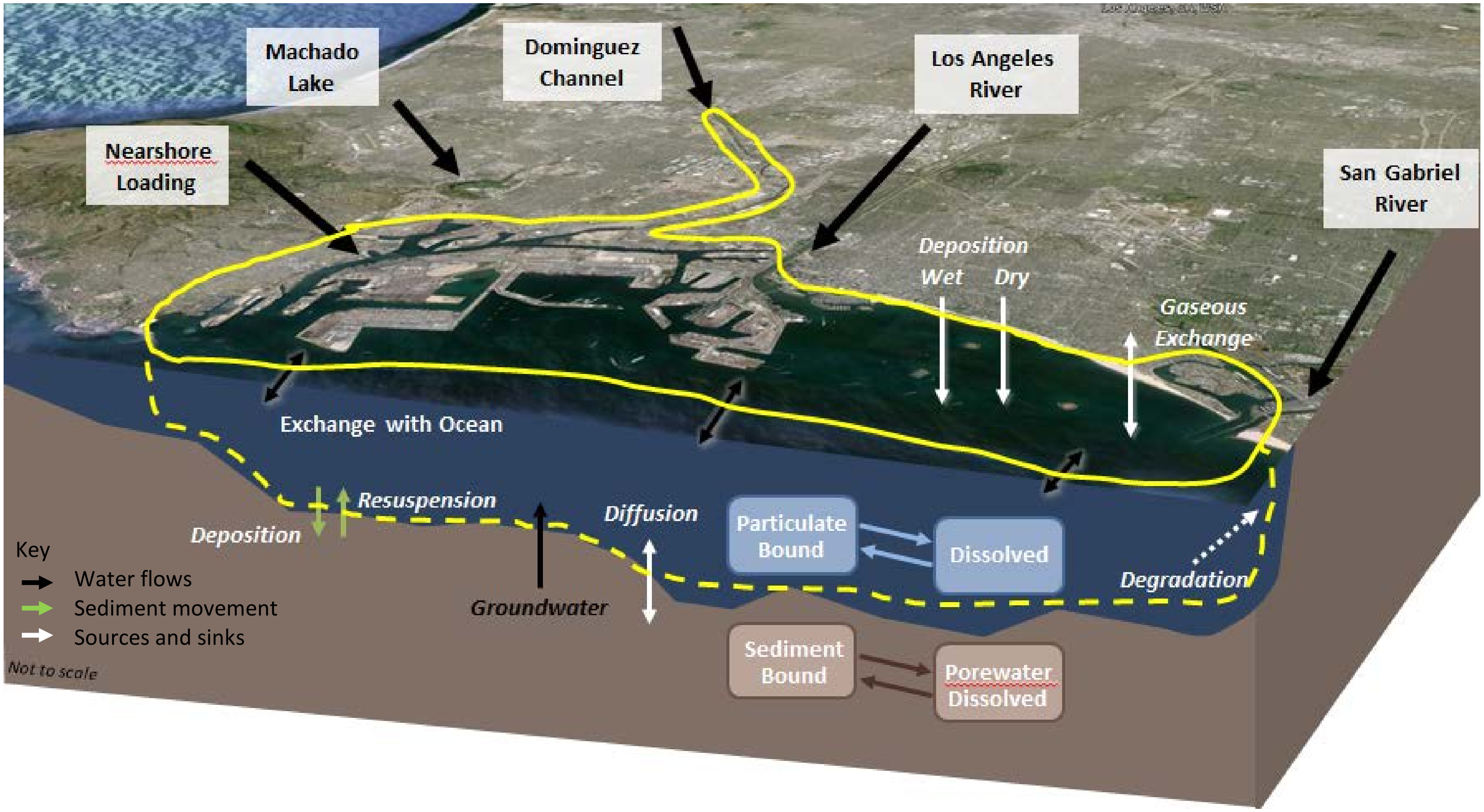


Figure 1
Processes Affecting Chemicals in the Water Column
Greater Los Angeles and Long Beach Harbor Waters

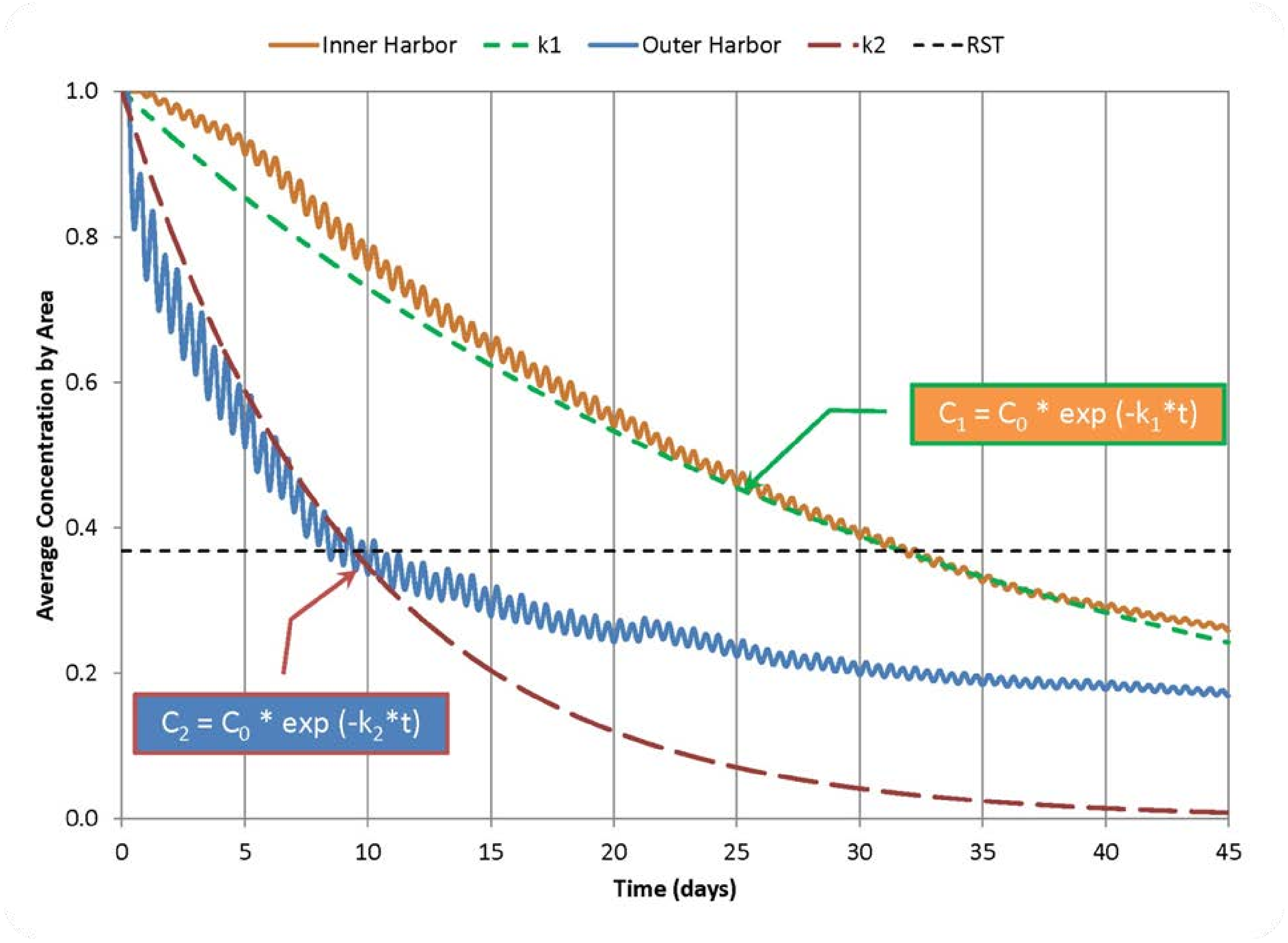
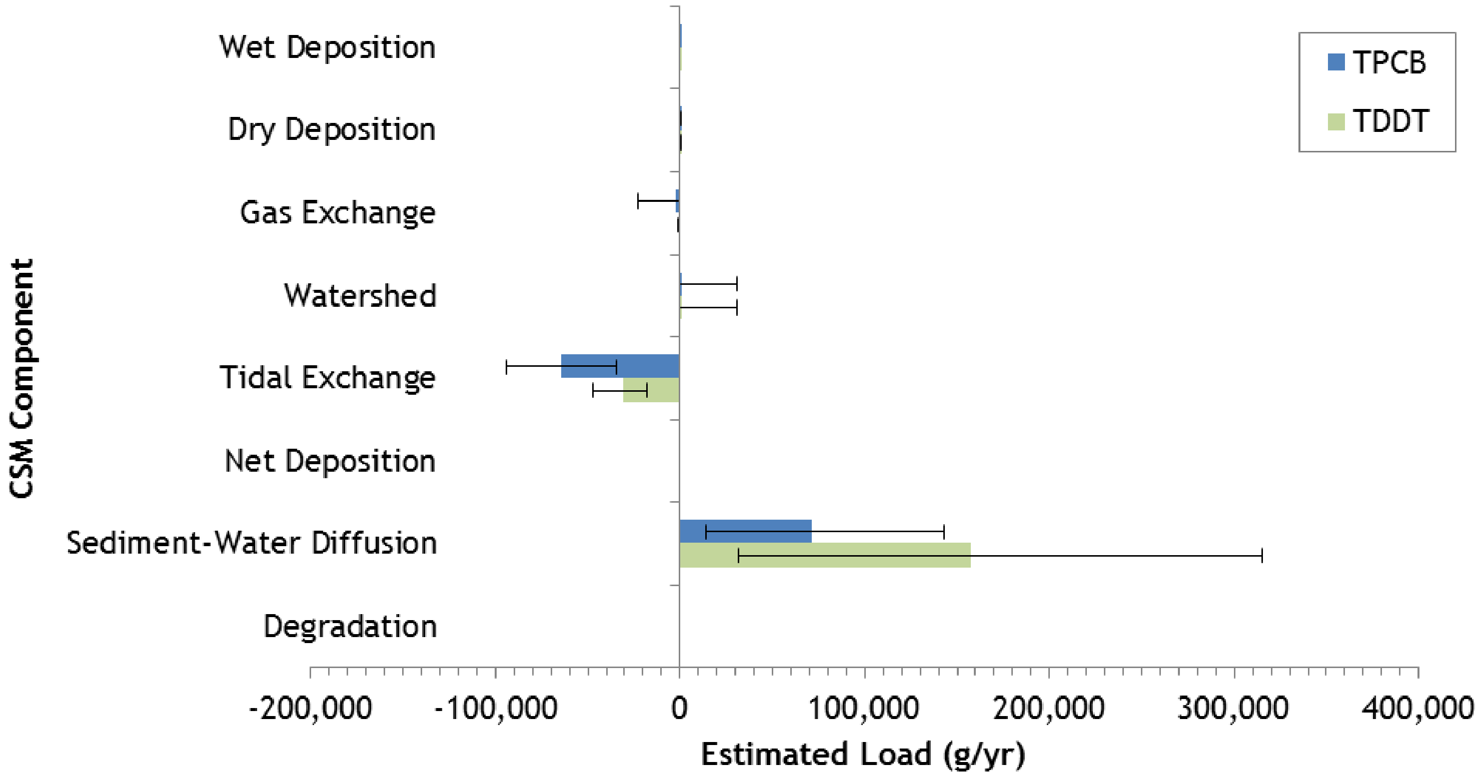
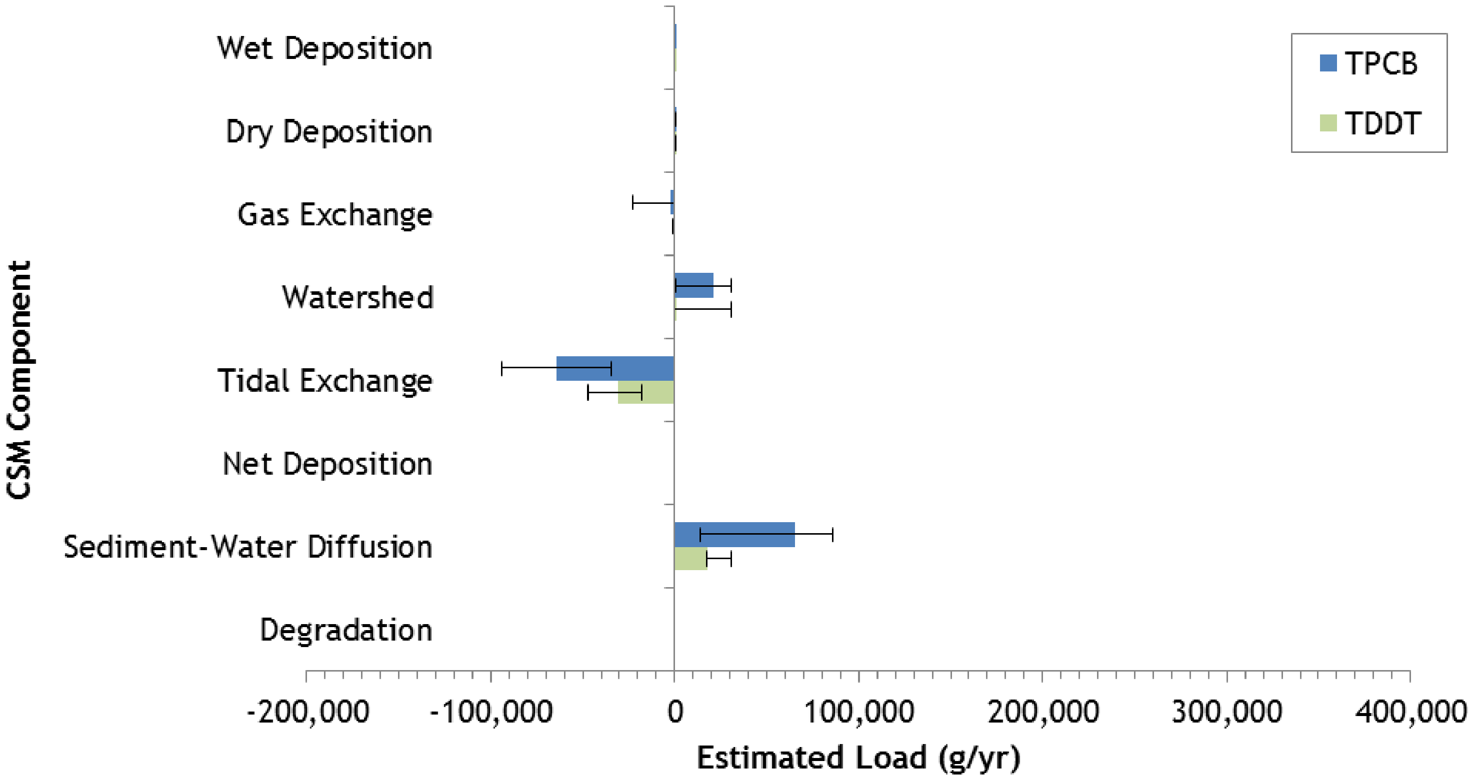


Figure 2
Tidal Flushing – Determination of Loss Rate
Greater Los Angeles and Long Beach Harbor Waters



Note: Bars represent intermediate estimates; error bars indicate low and high estimates.

Figure 3
Preliminary Loading Summary
Greater Los Angeles and Long Beach Harbor Waters



Note: Bars represent middle values for each component; error bars indicate ranges.

Figure 4
Loading Sensitivity Analysis
Greater Los Angeles and Long Beach Harbor Waters

ATTACHMENT A
RESPONSE TO COMMENTS

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RESPONSE TO COMMENTS

TECHNICAL MEMORANDUM: DEVELOPMENT OF A CHEMICAL FATE CONCEPTUAL SITE MODEL FOR THE GREATER LOS ANGELES AND LONG BEACH HARBOR WATERS

Comment Number	Page Number	Commenter	Comment	Response
1	1	Steve Bay	Why is the CSM focus on the water column when the TMDL focus is on sediment contaminants. A better description of why this CSM is needed for developing a sediment management plan.	As stated, the goal of the CSM is to "guide future data collection and mathematical modeling efforts." It was decided during the initial scoping of the CSM effort that while contaminated sediments are the focus of the TMDL, questions related to field programs and modeling approaches were more significant and immediate for the water column than for the sediments. Development of a CSM for sediments would not have importantly informed proposed sediment field studies (e.g., geochronology cores and sedflume study) or modeling approaches. This clarification has been added to Section 1.
2	2	Steve Bay	Implies a separate sediment CSM is in development. Will that be presented to the HTWG in the near future?	A separate CSM for sediments is not in development; Section 2 has been revised for clarity. Sediments will be included in the chemical fate model.
3	2	Steve Bay	Some of the estimates appear to make extensive use of data from other regions, which could be a large source of error considering regional loads, especially for DDTs. For each section, a description of how the various estimates relate to local vs. literature values. I suggest that the intermediate values should be based on local estimates wherever possible.	We agree. The intermediate values are based on local estimates, wherever possible. High and low estimates are included to provide an understanding of likely variability and uncertainty. Text has been added in Section 2 to clarify that intermediate values were based on local estimates, wherever possible.
4	5	Steve Bay	It is surprising that DDT deposition estimates are similar/lower than PCBs, considering local DDT contamination patterns. Do these fluxes reflect patterns seen in local data?	Intermediate values (for which DDT deposition is slightly higher than PCB deposition) reflect local data (Sabin et al. 2011). High and low estimates are drawn from literature and generally reflect other urban locations. A sentence has been added in Section 2.1.2 to state specifically that intermediate values reflect local data.
5	9	Steve Bay	Similarity of DDT and PCB concentrations doesn't match expectations based on local sources of DDTs. There needs to be a better description of how these assumed concentrations relate to local conditions in So. Calif.	Existing stormwater data are generally non-detect for PCBs and DDTs, with a detection limit of 1 ng/L or greater. The intermediate value of 1 ng/L used for both PCBs and DDTs is consistent with this detection limit. However, existing data are sparse and accordingly provide an uncertain understanding of local runoff concentrations. Data from other urban areas were used to define appropriate high and low estimates. Section 2.2.1 has been edited to clarify the source of intermediate values. In addition, text has been added to note that additional stormwater data are being collected in 2014.
6	10	Steve Bay	The total areas used for gauged vs. nearshore load estimates should be stated for clarity.	Total areas used for gaged and nearshore load estimates have been added to Sections 2.2.1 and 2.2.2.
7	10	Steve Bay	Seems like nearshore concentrations should be higher due to local sources of PCBs and DDTs from industrial activities.	Nearshore data do not exist to quantify these differences.
8	11	Steve Bay	Why isn't Machado lake included in gauged load estimate if flow data are available?	Machado Lake is not considered to be a gaged inflow, because flows are not routinely monitored. Flow data for Machado Lake were collected for only two wet seasons during a special study. These data were considered to be insufficient to establish the average annual volume. For the gaged watersheds, the average annual volumes were estimated based on 10 to 18 years of flow data. A clarification has been added to Section 2.2.2.1.
9	11	Steve Bay	Separate estimates should also be provided for gauged and nearshore loads.	Gaged and nearshore load estimates have been added to Section 2.2.3.

Comment Number	Page Number	Commenter	Comment	Response
10	11	Steve Bay	Why did loads need to be calculated from inputs, rather than use values from TMDL? Please clarify	The TPCB and TDDT annual loads of the four major watersheds were not provided in the TMDL. In the TMDL, watershed loadings were provided as daily loadings rates (e.g., kg/day) for wet and dry conditions and no information was provided on the definition of wet and dry conditions. Conversion of reported daily loading rates to the annual loadings would require assumption of the number of wet and dry days per year. For the CSM analysis, TMDL watershed loadings were directly computed from the EFDC inputs rather than assuming a conversion from the reported daily loadings to an annual loading.
11	13	Steve Bay	Please define rst parameter in Figure 2. Why is it important?	RST is the concentration 1/e (0.368), which is commonly used as the criterion to determine residence time, which is used to compute the loss rate. The residence time corresponds to tidal flushing (i.e., movement out of the harbor). The residence time is determined as the time it takes for an initial unit tracer concentration to be reduced to 1/e (RST). The loss rate is then calculated as the inverse of the residence time. A long residence time indicates less tidal flushing and a low loss rate (i.e., chemical tends to stay in the harbor), while short residence times indicate greater tidal flushing and a high loss rate (i.e., chemical tends to leave the harbor). A clarification has been added to Section 2.3.1.
12	13	Steve Bay	Include units for decay rate. Please provide some basic explanation as to why decay rate varies so much between waterbodies. Is it related to volume of waterbody?	Each day tidal currents move harbor water along with contaminants out of the harbor replacing it with "clean" ocean water; this process is commonly referred to tidal exchange. The loss rate represents how fast a contaminant will leave the harbor due to tidal exchange. A low loss rate indicates it takes longer for a contaminant to leave the harbor. A high loss rate indicates a contaminant quickly leaves the harbor. The loss rate in the different waterbodies is expected to be different depending on how close it is to the ocean. Areas farthest from the ocean have less tidal exchange with the ocean, such as the Dominguez Channel or Consolidated Slip. Areas closest to the ocean like the Outer Harbor or San Pedro Bay have high loss rates due to the proximity to and the greater mixing with the ocean. Units for decay rate are included in the heading for the table, which is 1 per year. A clarification has been added to Section 2.3.1.
13	14	Steve Bay	Tidal flushing losses are 100x greater than watershed inputs, which seems greatly out of balance. Confidence in these numbers should be discussed in report.	Reasonable values for low, intermediate, and high for each component are included in the memorandum to provide consideration of confidence (uncertainty). Tidal losses are expected to exceed watershed inputs, because flux from sediments to the water column is substantial. We agree that 100 times may be out of balance. The stormwater and low detection limit water column programs will better define both watershed inputs and tidal exchange.
14	14	Steve Bay	Why is resuspension not discussed/estimated? This process was identified as important in CSM description.	The net deposition rate based on the WRAP Model accounts for the transport, deposition, and resuspension of sediment throughout the harbor due to tidal and fluvial actions; hence net deposition has included the net effect of sediment deposition and resuspension. Overall, the harbor is a net depositional environment based on WRAP Model results. A clarification has been added to Section 2.3.2.
15	16	Steve Bay	Provide particulate concentration values used in TMDL and those estimated for CSM calculations for comparison. My simple estimate of particulate concentration based on 1 ng/l and 4mg/L TSS suggests about 250 ng/g PCB, which is probably similar to or higher than surface sediments.	The TMDL (Appendix III, Part 1, Table III.1-2) uses TPCB concentrations in the surface sediments from 2 to 236 µg/kg. The median sediment TPCB concentration in all 11 waterbodies is 15 µg/kg. The calculation you present assumes that 100 percent of TPCBs are sorbed to particles. While the partition coefficient of TPCB is high, the concentration of suspended sediments is low. The equation to determine the fraction dissolved is as follows: $F_d = \frac{1}{(1 + K_{oc} f_{oc} TSS)}$ Based on literature and Weston (2007) data, estimates of K_{oc} and f_{oc} are $1e^{6}$ L/kg and 0.02. Using a TSS value of 4 mg/L, the fraction dissolved is 93 percent, leaving the particulate (sorbed) fraction (F_p) as 7 percent. The TPCB concentration in the particulates is then given by $r = \frac{CF_p}{TSS}$ Using a water concentration (C) of 1 ng/L, the particulate TPCB concentration is 18 µg/kg, which is similar to the median sediment concentration reported in the TMDL.

Comment Number	Page Number	Commenter	Comment	Response
16	17	Steve Bay	This section needs to be clarified. A consistent approach should be used to estimate porewater concentrations for areas without data. Seems like different approach used for DC, CS, and FH than used for other areas. Clarify source of estimates for SGRE, SPB, and AB, since LARE data were nondetect. No mention is made of DDT concentration assumptions.	The general approach to estimate TPCB and TDDT porewater concentrations for areas without data was to use data from a nearby area, given that the proximity with similar hydrodynamic and water quality conditions would provide a reasonable estimate of the porewater concentrations for areas without data. For Dominguez Channel, Consolidated Slip, and Fish Harbor, data were available from three sampling locations with detectable TPCB and TDDT porewater concentrations. For the Dominguez Channel and Contaminated Slip, three locations were positioned in the Los Angeles East Basin adjacent to the Consolidated Slip. For Fish Harbor, data were from the three locations just outside of Fish Harbor. For the San Gabriel River Estuary, San Pedro Bay, and Alamitos Bay, the closest area is the Los Angeles River Estuary, where two locations are positioned. However, the Los Angeles River Estuary had only detectable porewater concentrations for TDDT. Thus, the Los Angeles River Estuary TDDT data were used for the San Gabriel River Estuary, San Pedro Bay, and Alamitos Bay. Note that the Pier J location is also close, but this location was not used because it was judged to be not representative of the San Gabriel River Estuary, San Pedro Bay, or Alamitos Bay due to the enclosed area. For the TPCB porewater estimates of the Los Angeles River Estuary, San Gabriel River Estuary, San Pedro Bay, and Alamitos Bay, the nearest detectable concentrations were located further away within the Long Beach Outer Harbor. However, the closest locations to San Pedro Bay within the Outer Harbor were also non-detect for TPCB. Because the nearest detectable TPCB porewater concentrations were geographically further away, it was determined that the overall average from the entire Long Beach Outer Harbor would be more appropriate to represent the Los Angeles River Estuary, San Gabriel River Estuary, San Pedro Bay, and Alamitos Bay. In addition, determination of the "nearby area" would be more difficult, because data are geographically closer in the Long Beach Inner Harbor, but the hydrodynamic and water quality conditions in the Inner Harbor may vary compared to the Los Angeles River Estuary, San Gabriel River Estuary, San Pedro Bay, and Alamitos Bay.
17	17	Steve Bay	High values seem counterintuitive, relative to known sources and nearby values. Do they correspond to surface sediment concentration patterns? If not, might be better to estimate porewater conc. with equilibrium partitioning models.	In general, high values are from only one or two locations in the receiving waterbody, particularly for the Los Angeles Inner and Outer Harbor, indicating a large range in porewater concentrations in the harbor. For the CSM, average porewater concentrations were used as an estimate for each receiving waterbody area, which was judged to be sufficient for this preliminary estimate. Porewater concentrations will be determined by equilibrium partitioning and sediment concentrations in the chemical fate model. A clarification has been added to Section 2.3.4.
18	22	Steve Bay	This is confusing, please give example to illustrate method.	The sensitivity analysis has been simplified by balancing mass by reducing sediment-water diffusive exchange to address positive total loads and increasing watershed loads to address negative total loads. Text in Sections 3.2 and 3.3 has been revised and values shown in Table 4 and in Figure 4 have been adjusted to reflect results from the new sensitivity methodology.
19	24	Steve Bay	Dry deposition is of same order of magnitude as watershed loadings, don't agree with conclusion it is not important. Please clarify.	The intermediate value for dry deposition is approximately one-fifth that for watershed loadings. More importantly, watershed loadings are currently highly uncertain, as exemplified by high values that are 50 times the intermediate values (and 30 times the high value for dry deposition). All estimated levels (low, intermediate, and high) of dry deposition are small, compared to other sources and sinks; accordingly, we concluded that it is "probably not important" and have not proposed field investigations. High estimates for watershed loadings are large enough to warrant the conclusion of "may be important" and watershed loadings are being measured in the field.
20	24	Steve Bay	Gas exchange appears to be relatively important. This process, and the confidence in the estimates, should be discussed.	We agree. Gas exchange appears to be relatively important and may be included in the chemical fate model. The following paragraph has been added to Section 4: Losses due to gas exchange appear to be relatively important. Such losses are extraordinarily difficult to measure directly. Estimates of these losses for the Los Angeles Harbor were recently presented by Sabin et al. (2011). Accordingly, no new field work has been proposed and the information in Sabin et al. (2011) will form the basis for quantifying this mechanism in the chemical fate model.
21	3-8	Thanhloan Nguyen and C.P. Lai	Air components section only take into account the wet and dry direct air deposition. Indirect air deposition should be included	Indirect air deposition is implicitly included in the estimates of watershed loading. Direct deposition occurs in the harbor waters (i.e., the "control volume" for which sources and sinks are quantified). Indirect deposition occurs in the watershed and estimates of chemical concentration in runoff include all sources of chemicals, including this deposition.

Comment Number	Page Number	Commenter	Comment	Response
22	3-8	Thanhloan Nguyen and C.P. Lai	In order to compare the results to the TMDL loading rate, detail spreadsheet calculating load for each receiving water body should be provided, not just the TPCB or TDDT. Providing only estimated range of TPCB and TDDT to compare air deposition loadings are not sufficient	The implicit assumptions in CSM calculations become less appropriate as smaller and smaller waterbodies are considered. More accurate loads will be computed and presented on a waterbody basis following calibration of the chemical fate model.
23	8-11	Thanhloan Nguyen and C.P. Lai	Again, detail spreadsheet calculating loading for each receiving water body should be provided	Please see response to Comment 22.
24	--	Thanhloan Nguyen and C.P. Lai	Due to serious loading imbalance of the estimated sources and sinks of contaminants to the harbor, refinement of CSM TPCBs and TDDT should be done with appropriate assumptions of pollutants loading from different sources, updated data, and better results/understanding of hydrodynamic, sediment transport modeling.	We agree that the loading imbalance indicates that additional work is necessary. Several field programs are currently underway to better define the most important CSM components. Study results will be included into the calibration of the chemical fate model and refinements to the loading estimates will be available at that time.

Notes:
µg/kg = micrograms per kilogram
DDT = dichlorodiphenyltrichloroethane
CSM = Conceptual Site Model
EFDC = Environmental Fluid Dynamics Code
kg/day = kilograms per day
mg/L = milligrams per liter
ng/L = nanograms per liter
PCBs = polychlorinated biphenyls
TDDTs = total DDTs
TMDL = total maximum daily load
TPCBs = total PCBs
TSS = total suspended solids
WRAP = Water Resources Action Plan