REVISED CALIBRATION OF THE WATER QUALITY MODEL FOR THE DELAWARE ESTUARY FOR PENTA-PCBs AND CARBON

Staged TMDLs for Total PCBs for
Zones 2 - 6 of the Delaware River

Delaware River Basin Commission

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WEST TRENTON, NEW JERSEY

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This report is a collaborative effort of the staff of the Modeling & Monitoring Branch of the Delaware River Basin Commission staff, Dr. Victor J. Bierman, Jr. and Scott C. Hinz of Limno-Tech, Inc. (LTI), and Dr. Ferdi L. Hellweger and Dr. Dominic M. Di Toro of HydroQual, Inc.

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The approach to calibration of the PCB TMDL model for the Delaware Estuary and the mass balance components analysis were developed by Dr. Bierman and Mr. Hinz of Limno-Tech, Inc. at the request of the Delaware River Basin Commission (DRBC). The calibration approach was consistent with the recommendations of the Expert Panel convened by DRBC to provide independent scientific review of the overall modeling effort.

The decadal scale consistency check was conducted by Dr. Hellweger and Dr. Di Toro of HydroQual, Inc. in collaboration with LTI and DRBC staff. Funding for HydroQual's decadal scale consistency check was provided by the Delaware Estuary TMDL Coalition. Dr. Hellweger and Dr. DiToro wrote the Decadal Scale Consistency Check section of the Model Calibration Report.

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EXECUTIVE SUMMARY

The overall objective of the model calibration was to assess the predictive capability of the DELPCB water quality model in representing the principal environmental processes that influence the transport and fate of penta-PCBs in the Delaware River Estuary. These processes include hydrodynamics, sorbent (organic carbon) dynamics and partitioning of PCBs to organic carbon in the water column and bedded sediments. The model was calibrated to ambient data for biotic carbon (BIC) and particulate detrital carbon (PDC) in the water column, and to available data for net solids burial in the sediments. Finally, the calibrated sorbent dynamics model was used to drive a mass balance model of penta-PCBs in the water column and sediments. No adjustment of parameters for PCBs was performed following the calibration of the organic carbon model.

The model utilizes a 575 day continuous simulation period spanning September 1, 2001 through March 31, 2003. Daily loads of organic carbon and penta-PCB were estimated for each day of the period for the following source categories: contaminated sites, non-point sources, point discharges, model boundaries, tributaries, atmospheric deposition, and combined sewer overflows (CSOs). The uncertainty associated with the load estimation for each of these categories was assessed using a Monte Carlo analysis. Ambient water samples were collected from the mainstem Delaware Estuary for the analysis of particulate and dissolved PCBs, total suspended solids, and particulate and dissolved organic carbon. Twenty four main stem channel sites were sampled under a range of flows characteristic of the main tributaries of the Delaware River. The data collected allowed initial quantitation of dissolved and particulate PCB levels as well as organic carbon in the mainstem Delaware Estuary. The resultant monitoring data were used as calibration targets for the model.

The DELPCB model simulates tidal flows, and spatial and temporal distributions of organic carbon (OC) and penta-PCB. Comparisons of simulated to measured water quality concentrations indicate generally good agreement and low bias of the estimate for organic carbon and penta PCB. The correlation coefficients for particulate and dissolved penta-PCB exceed EPA's recommended correlation coefficient acceptance criteria for model calibration for water quality variables.
Short-term sensitivity analyses indicate that the impact of zeroing out the initial PCB concentrations in sediment layers has almost three times more influence on water column PCB concentrations than zeroing out the six external PCB loadings. A calibration period of 575 days is not long enough to equilibrate with other PCB sources, and thus the sediment layers remain as a source for PCBs during the calibration period. Setting the loading from the six external source categories to zero results in about a 20 percent reduction in PCB concentrations in water column in mid-Estuary. Zeroing out the 'Gaseous PCB' concentrations results in about a 10 percent reduction of PCB concentrations in Zones 3, 4 and portions of 5. Substantial influences from boundary conditions are also observed at the extreme ends of the Estuary. The sensitivity analysis results point to importance of the initial sediment conditions during the short term model calibration period.

The mass balance tracking in standard WASP5 was enhanced in order to track mass fluxes of PCBs through every model segment including water column and sediment segments, and to track model processes that would normally be aggregated (e.g., kinetic transformations, gross settling and resuspension, etc.). The approach implemented within the model code demonstrated that the model does properly track mass transport fluxes and transformations.

Historical hindcast simulations (1930-2002) were performed to check the long-term (decadal scale) behavior of the model. A review of the hindcast simulation results using the current model showed: (1) the model is in reasonable agreement with the historical water column concentrations, both observed and deduced from the dated core for the period following the 1980s; (2) the model is in reasonable agreement with the contemporary sediment data in the upper estuary (Zones 2-3); (3) the model appears to be inconsistent with the historical sediment data; (4) the model predicted time course of water column and sediment bed concentrations also appear to be inconsistent with the fish tissue concentrations. At present it is not clear what the source(s) of the two inconsistencies (sediment and fish tissue) is (are). Possible causes include error(s) in (1) forcing functions (current and/or historical), (2) the model (e.g. mixed layer depth) and/or (3) the data or how they are interpreted.

1 Introduction and Background

1.1 Introduction

As part of the development of Stage 1 TMDLs for polychlorinated biphenyls, several numerical models were developed and/or enhanced. These models included a water quality model for organic carbon and pentachlorobiphenyls (penta-PCBs) based upon the Water Quality Simulation Program (WASP) Version 5.12 (DRBC, 2003a). Following the establishment of the Stage 1 TMDLs for PCBs by the U.S. Environmental Protection Agency in December 2003, the penta-PCB model was further examined and revised as one of the first tasks conducted in developing Stage 2 TMDLs.

As a result of this effort, the following corrections, updates and enhancements to the penta-PCB model were implemented:

- Correction to parameter (VELFM) assignment for proper input of wind velocities.
- Correction to model code for volatilization.
- Corrections to loadings from selected contaminated sites.
- Updating of penta-PCB concentrations at two model boundaries: the mouth of Delaware Bay, and the Chesapeake & Delaware (C&D) Canal.
- Updating of ambient water data for several monitoring surveys in the estuary.
- Adjustment of resuspension rates for several segments to ensure net burial.
- Incorporation of source code to permit detailed mass balance calculations.
- Short-term sensitivity analyses of model parameters.

This report presents the results of the model calibration following the incorporation of these revisions. It replaces the initial model calibration report prepared by DRBC in September 2003 (DRBC, 2003b).

1.2 Model Calibration Approach

The overall objective of the model calibration was to accurately represent the principal environmental processes influencing the transport and fate of penta-PCBs in the Delaware River and Estuary. These processes include hydrodynamics, sorbent (organic carbon) dynamics and partitioning of PCBs to organic carbon in the water column and bedded sediments. The first step in the process was calibration of the hydrodynamic model to available data for tidal heights and confirmation of this calibration by using the computed hydrodynamics to drive a mass balance model for salinity (chloride). The calibrated hydrodynamic and salinity model was then used as a “hydraulic chassis” to drive a mass balance model of organic carbon sorbent dynamics. This model was calibrated to ambient data for biotic carbon (BIC) and particulate detrital carbon (PDC) in the water column, and to available data for net solids burial in the sediments. Finally, the calibrated sorbent dynamics model was used to drive a mass balance model of penta-PCBs in the water column and sediments.

The hydrodynamic, sorbent dynamics and penta-PCB models were calibrated to available data for the period from September 2001 through March 2003. This period contained the most comprehensive data for salinity, organic carbon and penta-PCBs for the Delaware River and Estuary. Continuous dynamic simulations were conducted with all three of the coupled mass balance models for this 19-month period. For a hydrophobic organic chemical (HOC) like PCBs, this approach is necessary but not sufficient to constrain all of the controlling environmental processes. In particular, water column PCB concentrations in rivers or estuaries typically respond to changes in external loadings or sorbent dynamics on time scales of days to weeks. In contrast, sediment PCB concentrations typically respond on time scales of years to decades because PCBs are much less mobile in bedded sediments. Consequently, if sediment-water interactions are important in controlling the overall response of PCBs in a system, these dynamics can only be calibrated using decadal-scale simulations and long-term historical data.

A major obstacle to conducting a rigorous decadal-scale PCB model calibration for the Delaware River and Estuary is that historical data for PCB loadings and responses are extremely limited. Nonetheless, given the importance of exercising the penta-PCB model to assess its long-term performance, a decision was made to conduct a decadal-scale consistency check on the short-term 19-month calibration. This check involved conducting a 74-year hindcast simulation for penta-PCBs from 1930 through 2003. Because reconstruction of historical penta-PCB loadings required many assumptions, emphasis was placed only on broad trends and temporal structure of the hindcast simulation results, not on absolute comparisons to historical data. Results from these simulations were used to inform decisions on sediment-water cycling rates and surface sediment layer mixed depths in the short-term 19-month calibration. These are the principal model parameters that control sediment-water PCB interactions and hence the long-term behavior of the penta-PCB model.

Figure 1.1 shows a map of the Delaware Estuary, including the Water Quality Management Zones. Figure 1.2 shows the model segmentation for the PCB TMDL water quality model.

Figure 1.1 - Map of the Delaware Estuary Including Zones

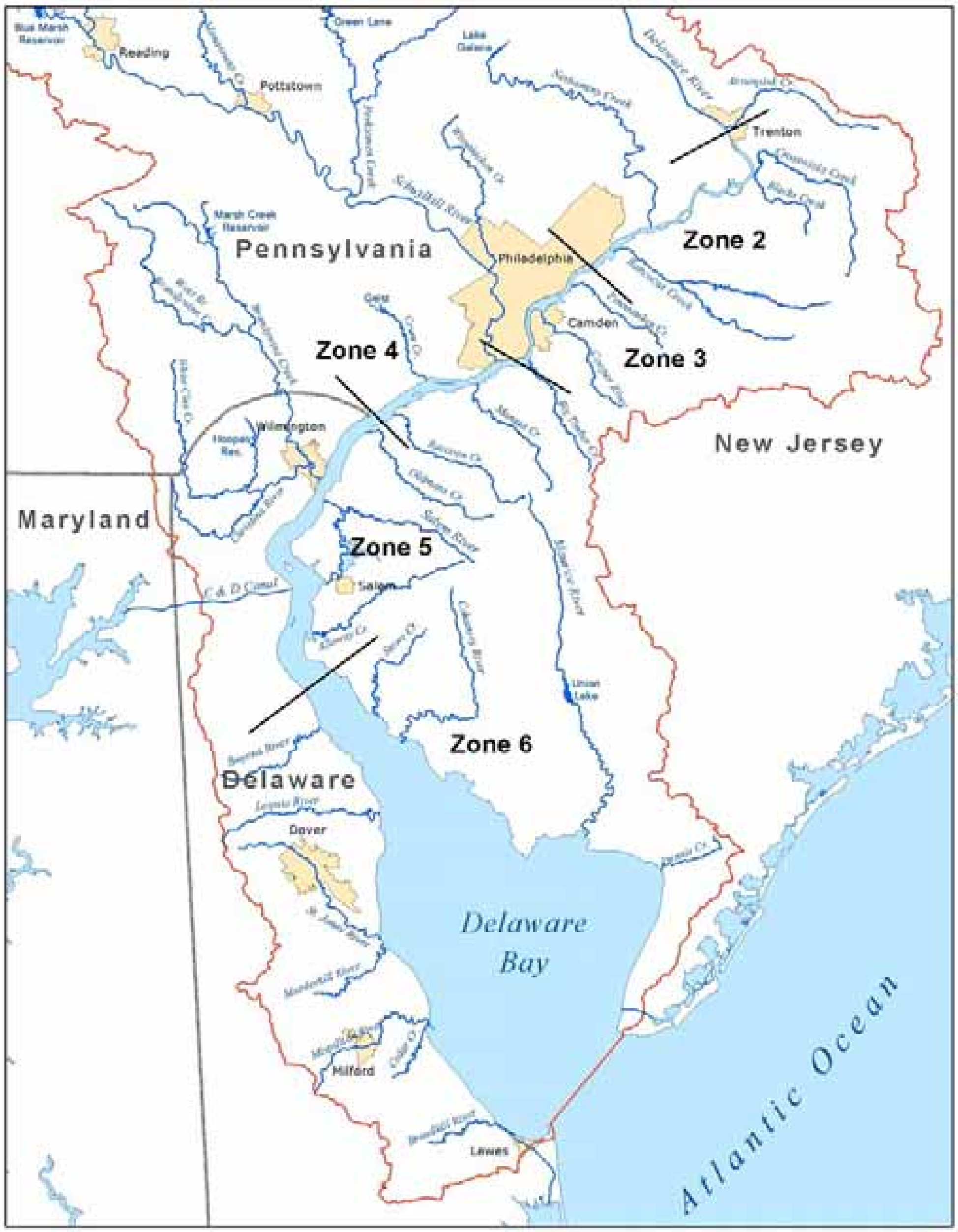
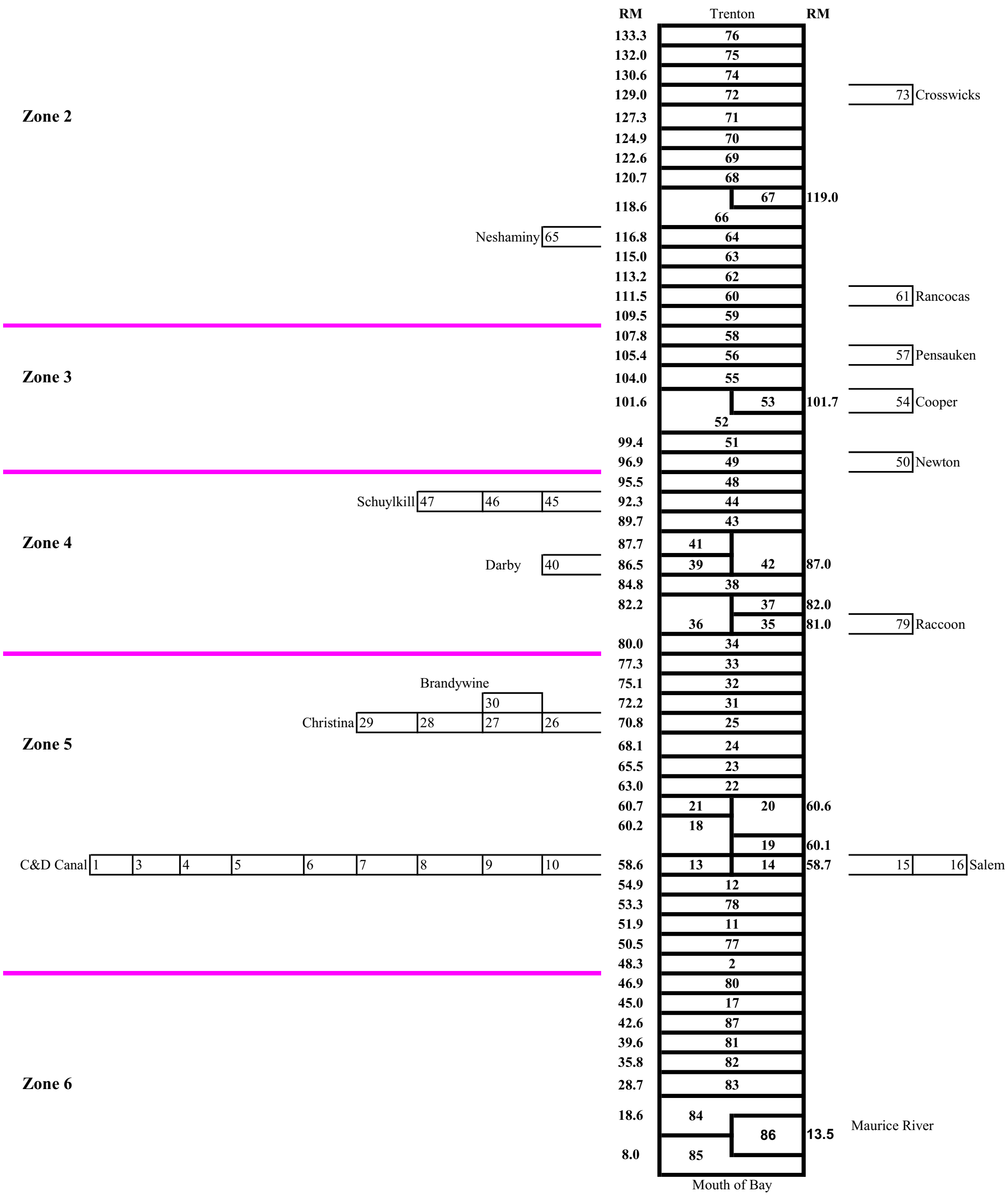


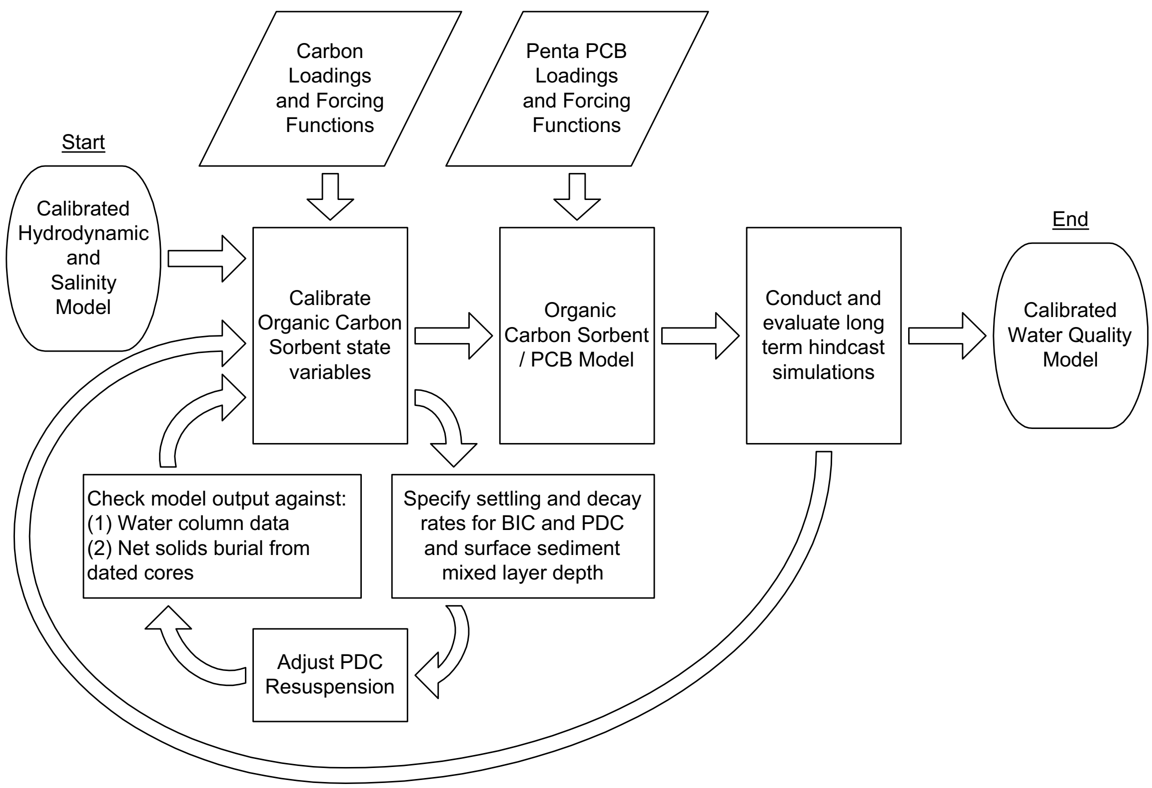
Figure 1.2 - Schematic Diagram of the PCB TMDL Water Quality Model



1.3 Model Calibration Strategy

The general calibration strategy was to specify as many external inputs and internal model parameters as possible using site-specific data or independent measurements, and only a minimal number of parameters through model calibration. Another part of the strategy was that parameters determined through model calibration were held spatially and temporally constant unless there was supporting information to the contrary. Model parameters were not permitted to assume arbitrary values in order to obtain the best "curve fits" in a strictly mathematical sense. Emphasis was placed on best professional judgment and on results from a suite of different metrics that were used collectively in a weight-of-evidence approach. Figure 1.3 shows a simplified schematic representation of the model calibration approach.

Figure 1.3 - Model Calibration Approach



1.3.2 Organic Carbon Sorbents

The calibrated hydrodynamic and salinity model was used as a "hydraulic chassis" to drive the organic carbon sorbent dynamics model. The hydrodynamic and salinity calibrations are described in a previous section of this report. The following were the principal steps in calibration of the organic carbon sorbent dynamics:

- Specify a constant net settling rate for BIC.
- Specify a constant gross settling rate for PDC.
- Specify temperature-dependent PDC and BIC decay rates in the water column.
- Specify a temperature-dependent PDC decay rate in the sediment consistent with available data for sediment oxygen demand.
- Adjust PDC resuspension rates for each spatial zone or sub-zone to achieve optimal agreement between model results and available data for water column PDC concentrations and net solids burial rates.
- Conduct sensitivity analyses on model parameters over ranges consistent with the scientific literature, other modeling studies and best professional judgment to obtain optimal agreement between computed and observed values.
- Adjust PDC gross settling and resuspension rates, and surface sediment layer mixed depths, to achieve consistency between results from the short-term 19-month calibration and the 74-year hindcast simulations.

1.3.3 penta-PCBs

The calibrated organic carbon sorbent dynamics model was used to drive the mass balance model of penta-PCBs in the water column and sediments. All external inputs and internal model parameters for penta-PCB were specified using site-specific data or independent measurements. No penta-PCB model parameters were determined through model calibration. Furthermore, there was only feed-forward from the short-term organic carbon sorbents calibration, not feed-back from the short-term penta-PCB calibration. That is, results from the short-term penta-PCB simulations were not used to retroactively adjust any of the model parameters in the short-term organic carbon sorbents calibration.

There was feed-back from the 74-year hindcast simulations to the short-term organic carbon sorbents calibration. Results from the 74-year hindcast simulations were used to inform final decisions on sediment-water cycling rates and surface sediment layer mixed depths in the short-term calibration. Sediment-water cycling rates for penta-PCBs are determined primarily by the magnitudes of PDC gross settling and resuspension velocities in the model. Surface sediment layer mixed depths are controlled by the mixing rate between the top two surficial sediment layers in the model. These model parameters can not be fully constrained during a short-term calibration period, but can only be calibrated using decadal-scale simulations and long-term historical data.

1.4 Model Calibration Metrics

To inform decisions on model parameters that were determined through calibration, a suite of different metrics was used to compare model output with available data. These metrics included both graphical and statistical methods. Results of load uncertainty analyses, discussed in Section 2.7, were also used considered. Two different sets of metrics were used, one set for the short-term calibration and another set for the decadal-scale simulations. Results from the different metrics were used collectively in a weight-of-evidence approach and all final calibration decisions were based on best professional judgment.

1.4.1 Short-Term Calibration

The following were the principal metrics used for the short-term, 19-month model calibration:

- Longitudinal plots of computed and observed annual net solids burial rates.
- Longitudinal plots of computed and observed water column concentrations for PDC, BIC and penta-PCB concentrations (total, particulate, dissolved and normalized to particulate organic carbon) at fixed points in time.
- Cumulative frequency distributions for matched pairs of computed and observed values for PDC, BIC and penta-PCB concentrations.
- Time series plots of computed and observed PDC, BIC and penta-PCB concentrations for each spatial zone.
- Bivariate plots of computed and observed values for PDC, BIC and penta-PCB concentrations.

1.4.2 Decadal-Scale Consistency Check

The following were the principal metrics used for the 74-year hindcast simulations:

- Time series plots of computed (estimated) and observed total PCB concentrations in the water column.
- Time series plots of computed (estimated) and observed total PCB concentrations in the surficial sediments.
- Time series plots of computed (estimated) total PCB concentrations in the water column and sediments, versus observed fish body burdens.
- Longitudinal plots of computed and observed penta-PCB concentrations in the surficial sediments in the final year (2002) of the 74-year hindcast simulation.
- Time series plots of computed penta and (estimated) total PCB concentrations in the water column (organic carbon normalized) and observed values from dated sediment core slices.

Because reconstruction of historical penta-PCB loadings required many assumptions, and historical data were very sparse, computed results from the 74-year hindcast simulations were expressed as estimated uncertainty ranges instead of discrete trajectories. Interpretation of these results placed emphasis on broad trends and temporal structure,

1.5 Loadings and Forcing Functions

Daily loads of organic carbon and penta-PCB were estimated for each day of the 575 day continuous simulation period spanning September 1, 2001 through March 31, 2003 for relevant source categories, including:

- contaminated sites;
- non-point sources;
- point discharges;
- model boundaries
- tributaries
- atmospheric deposition; and
- CSOs

Table 2.1 outlines the various source categories, data, and methods used for computing the loads. Each of these computations is discussed in more detail in the sections that follow.

2 Updated and Revised Model Code, Loadings, and Forcing Functions

2.1 Updates and Revisions

2.1.1 Contaminated Site Load Update

Upon review by the Loadings Subcommittee, it was determined that contaminated site loads for a subset of the sites were overestimated due to a computation error in a spreadsheet. The loads for the EPA lead sites were overestimated by a factor of 10. This error was corrected and the following revised contaminated site loads were developed. Table 2.1 shows the original and revised contaminated site loads.

Table 2.1 - Revised Contaminated Site Loads as of June 2004

Facility	Original Daily Penta PCB Load (kg/day)	Prepared by	Original 577 day load (kg)	Revised Daily Penta PCB Load (kg/day)	Revised 577 day load (kg)
Castle Ford - DE-192	1.4374E-06	EPA	8.2939E-04	1.4374E-07	8.2939E-05
Forbes Steel & Wire Corp. - DE-165	5.1989E-06	EPA	2.9998E-03	5.1989E-07	2.9998E-04
Old Airport Road Site - DE-283	0.0000E+00	EPA	0.0000E+00	0.0000E+00	0.0000E+00
Rogers Corner Dump - DE-246	1.0465E-04	EPA	6.0385E-02	1.0465E-05	6.0385E-03
Industrial Products - DE-030	5.1129E-05	EPA	2.9501E-02	5.1129E-06	2.9501E-03
Chicago Bridge and Iron - DE-038	3.2768E-03	EPA	1.8907E+00	3.2768E-04	1.8907E-01
Ludlow Industrial Park Drum Site - DE-121*	0.0000E+00	EPA	0.0000E+00	0.0000E+00	0.0000E+00
ABM-Wade, 58th Street Dump - PA-0179	1.9739E-06	EPA	1.1389E-03	1.9739E-07	1.1389E-04
O'Donnell Steel Drum - PA-0305	3.4939E-07	EPA	2.0160E-04	3.4939E-08	2.0160E-05
Conrail-Wayne Junction - PA-215	2.3043E-03	EPA	1.3296E+00	2.3043E-04	1.3296E-01
CONRAIL, Morrisville Lagoons - PA-441*	5.4056E-06	EPA	3.1190E-03	5.4056E-07	3.1190E-04
Pennwalt Corp. - Cornwells Heights - PA-0031*	3.1227E-07	EPA	1.8018E-04	3.1227E-08	1.8018E-05
Front Street Tanker - PA-2298	1.9914E-06	EPA	1.1491E-03	1.9914E-07	1.1491E-04
8th Street Drum - PA-3272	8.9655E-07	EPA	5.1731E-04	8.9655E-08	5.1731E-05
East 10th Street Site - PA-2869	1.0076E-02	EPA	5.8138E+00	1.0076E-03	5.8138E-01
Metal Bank - PA-2119	9.9092E-05	EPA	5.7176E-02	9.9092E-06	5.7176E-03
Lower Darby Creek Area Site - PA-3424	1.8481E-04	EPA	1.0664E-01	1.8481E-05	1.0664E-02
Roebling Steel Co.	4.9609E-05	EPA	2.8624E-02	4.9609E-06	2.8624E-03
Bridgeport Rental & Oil Services (BROS)	5.8140E-04	EPA	3.3547E-01	5.8140E-05	3.3547E-02
Dana Transport Inc.	3.8523E-08	EPA	2.2228E-05	3.8523E-09	2.2228E-06
Harrison Avenue Landfill	6.2542E-03	EPA	3.6087E+00	6.2542E-04	3.6087E-01
Metal Bank groundwater pathway	9.8312E-07	DRBC	5.6726E-04	9.8312E-07	5.6726E-04
AMTRAK Former Refueling Facility	1.3182E-03	DNREC	7.6059E-01	1.3182E-03	7.6059E-01
Gates Engineering	6.8226E-10	DNREC	3.9366E-07	6.8226E-10	3.9366E-07
AMTRAK Wilmington Railyard	1.6238E-03	DNREC	9.3692E-01	1.6238E-03	9.3692E-01
Diamond State Salvage	0.0000E+00	DNREC	0.0000E+00	0.0000E+00	0.0000E+00
NeCastro Auto Salvage	1.2867E-05	DNREC	7.4245E-03	1.2867E-05	7.4245E-03
Hercules Research Center	4.6121E-06	DNREC	2.6612E-03	4.6121E-06	2.6612E-03
Dravo Ship Yard	5.3216E-05	DNREC	3.0706E-02	5.3216E-05	3.0706E-02
DP&L/Congo Marsh	2.7290E-07	DNREC	1.5747E-04	2.7290E-07	1.5747E-04
American Scrap & Waste	7.4230E-04	DNREC	4.2831E-01	7.4230E-04	4.2831E-01
Pusey & Jones Shipyard	1.6033E-06	DNREC	9.2511E-04	1.6033E-06	9.2511E-04
Delaware Car Company	0.0000E+00	DNREC	0.0000E+00	0.0000E+00	0.0000E+00
Bafundo Roofing	1.5692E-04	DNREC	9.0543E-02	1.5692E-04	9.0543E-02
Kreiger Finger Property	1.5828E-04	DNREC	9.1330E-02	1.5828E-04	9.1330E-02
Clayville Dump	0.0000E+00	DNREC	0.0000E+00	0.0000E+00	0.0000E+00
Electric Hose & Rubber	8.8694E-05	DNREC	5.1176E-02	8.8694E-05	5.1176E-02
Penn Del Metal Recycling	1.1407E-04	DNREC	6.5821E-02	1.1407E-04	6.5821E-02
E. 7th Street North & South	5.7992E-05	DNREC	3.3461E-02	5.7992E-05	3.3461E-02
Delaware Compressed Steel	6.2877E-06	DNREC	3.6280E-03	6.2877E-06	3.6280E-03
Newport City Landfill	0.0000E+00	DNREC	0.0000E+00	0.0000E+00	0.0000E+00
DuPont Louviers - MBNA	9.5516E-08	DNREC	5.5113E-05	9.5516E-08	5.5113E-05
North American Smelting Co.	1.2821E-05	DNREC	7.3977E-03	1.2821E-05	7.3977E-03
RSC Realty	3.4113E-05	DNREC	1.9683E-02	3.4113E-05	1.9683E-02
AMTRAK CNOC	0.0000E+00	DNREC	0.0000E+00	0.0000E+00	0.0000E+00
Wilmington Coal Gas - N	2.2378E-06	DNREC	1.2912E-03	2.2378E-06	1.2912E-03
Del Chapel Place	2.2515E-06	DNREC	1.2991E-03	2.2515E-06	1.2991E-03
Kruse Playground	1.0643E-06	DNREC	6.1412E-04	1.0643E-06	6.1412E-04
Budd Metal	6.3450E-06	DNREC	3.6611E-03	6.3450E-06	3.6611E-03
Fox Point Park Phase II	1.1708E-04	DNREC	6.7553E-02	1.1708E-04	6.7553E-02
BENSALEM REDEV LP ELF ATOCHEM	1.7561E-05	PADEP	1.0133E-02	1.7561E-05	1.0133E-02

The original computation resulted in a 577 day site load of approximately 15.9 kg. With the computation error corrected, the revised site load is approximately 3.9 kg over 577 days. It is important to note that work of the Loadings Subcommittee is ongoing. Two changes likely to be applied to the contaminated site loads are the uniform application of the revised universal soil loss equation to all sites and the addition loads from New Jersey lead contaminated sites. In total, these changes are likely to increase the overall 577 day load for contaminated sites, such that the final estimate will be higher than 3.9 kg.

2.1.2 C&D Canal Concentration Update

After issuance of the TMDL in December 2003, analytical results from one additional sample from the C&D canal became available. The original sample collected on March 19, 2003 had a penta-PCB concentration of 901 pg/L. The new sample collected on April 1, 2003 had a penta-PCB concentration of 401 pg/L. The average of these two results suggested a concentration closer to 651 pg/L as opposed to the 901 pg/L specified prior to December 2003. This lower boundary concentration was consistent with the observations that the model was over-predicting PCB concentrations in the lower portion of the estuary. Based on the new information, a revised constant penta-PCB concentration of 651 pg/L was specified for the C&D tidal boundary segment for all simulation days.

2.1.3 Ocean Boundary Concentration Update

The penta-PCB ocean boundary concentration of 200 pg/L specified for the original Stage 1 TMDL model was derived primarily from concentrations calculated from NOAA mussel watch data for oysters in lower Delaware bay (NOAA, 1989 and 2003). This value also corresponded well to our own lower bay measurements which ranged from slightly less than 100 to slightly greater than 500 pg/L penta-PCB. After issuance of the Stage 1 PCB TMDL, additional data was released by the laboratory which consistently showed penta-PCB concentrations at the mouth of the bay at 100 pg/L. In light of the new data, the ocean boundary penta-PCB concentration was reset to 100 pg/L. This change was consistent with observations that the model was over predicting PCB concentrations in the lower portion of the estuary.

2.2 Loads

2.2.1 Carbon Load Estimates

Three forms of carbon are included in the model. They are dissolved organic carbon (DOC), particulate detrital carbon (PDC) and biotic carbon (BIC). DOC represents microparticulates (colloids) and macromolecules that cannot be separated from whole water samples by conventional filtration. PDC represents non-living particulate detrital carbon derived from varied sources including phytoplankton decomposition, zooplankton excretion, point discharge effluents, and small scale decaying vegetative matter. BIC represents particulate organic carbon contained in live phytoplankton biomass. Since DOC concentrations for the model were specified rather than computed, no DOC loading estimates were performed. In our model, Particulate Organic Carbon consists of only two sub fractions: BIC and PDC.

$$POC = BIC + PDC$$

Similarly, the sum of POC and DOC yields Total Organic Carbon (TOC).

$$TOC = POC + DOC$$

PDC and BIC loading estimates were performed for various source categories as described in the following sections. Figure 2.1 shows a comparison of the PDC load from each source category in the system. The “Boundary” category consists of PDC load from the Delaware at Trenton and the Schuylkill Rivers. It should be noted that, in the context of the model, the Delaware at Trenton and the Schuylkill are boundaries with assigned daily concentrations, as opposed to loads. The assigned daily PDC concentrations ranged from 0.22 to 3.42 mg/L, with a median value of 0.40 mg/L for Trenton. For the Schuylkill boundary, the PDC concentration ranged from 0.33 to 20.83 mg/L with a median value of 1.05 mg/L. The assigned daily concentrations are included here for purposes of comparison.

The C&D and Ocean boundaries are assigned a fixed PDC concentration of 2.62 and 0.37 mg/L respectively.

Figure 2.1 - PDC load by Source Category During the 577 Day Simulation Period

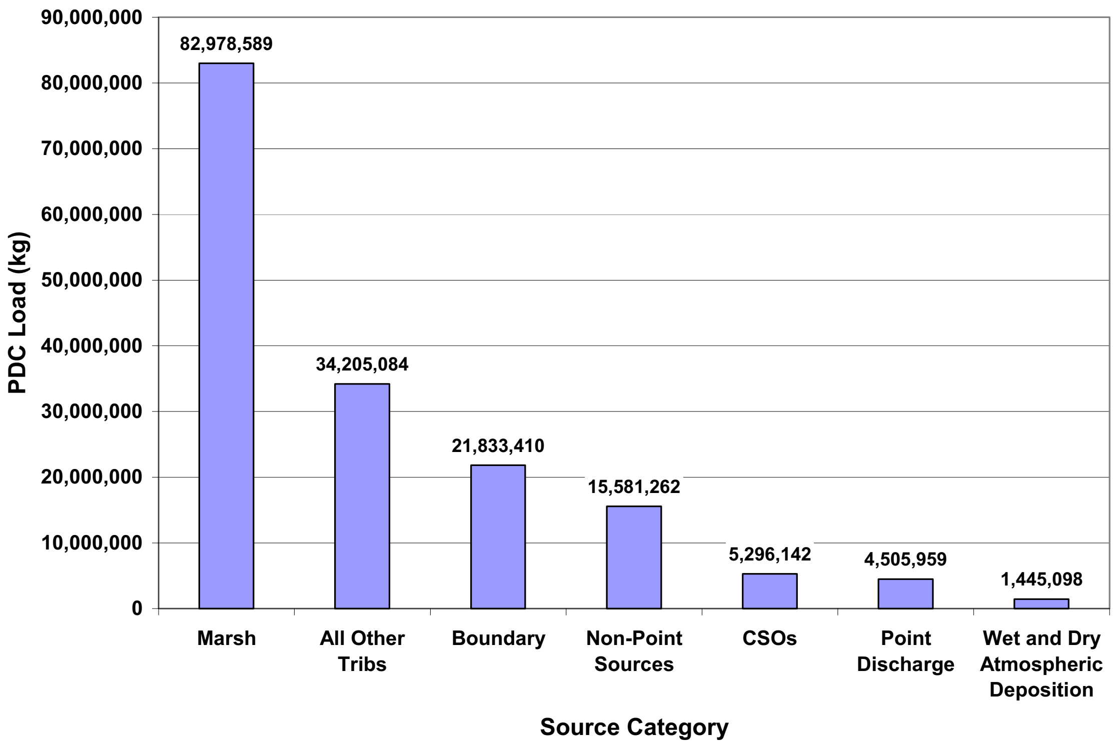
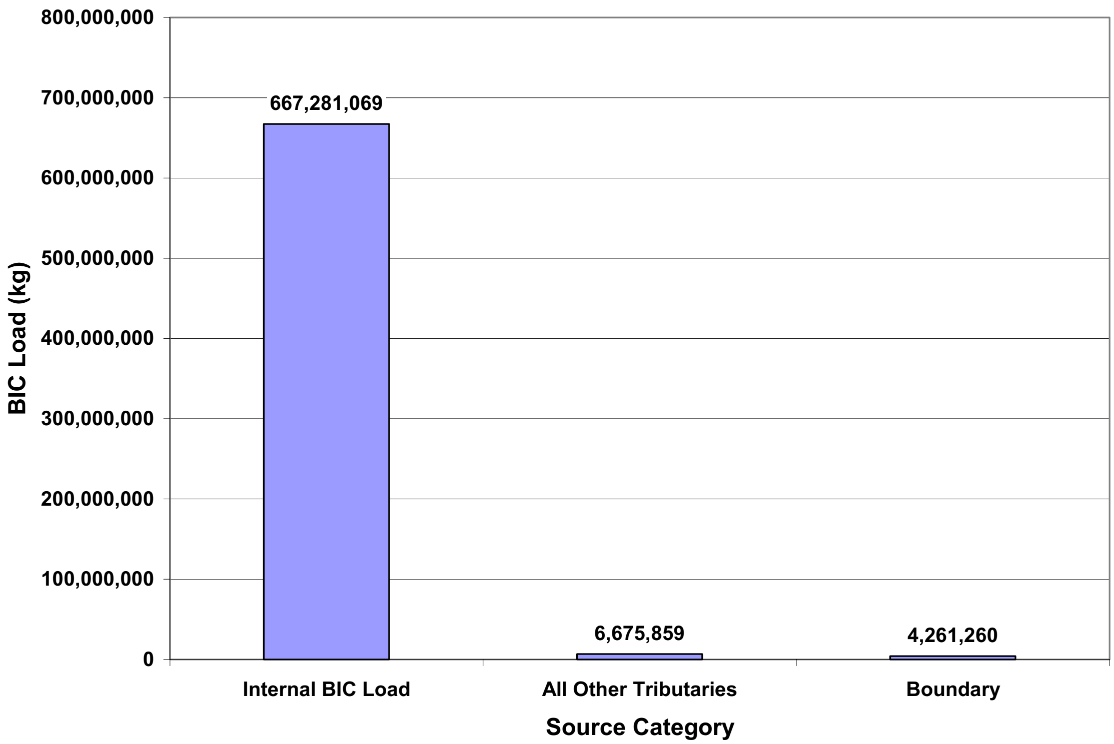


Figure 2.2 shows a comparison of the BIC load from each source category in the system. Again, the "Boundary" category refers to the Delaware at Trenton and the Schuylkill Rivers, and is not strictly a load. The term "Internal BIC Load" refers to carbon generated within the water column through primary production or the reproduction and growth of phytoplankton.

Figure 2.2 - BIC load by Source Category During the 577 Day Simulation Period



BIC upstream boundary conditions were assigned with ranges from 0.04 to 0.67 mg/L for Trenton with a median value of 0.08 mg/L. The Schuylkill boundary was assigned daily BIC concentrations ranging from 0.07 to 4.07 mg/L with a median value of 0.21 mg/L. The open downstream boundaries were assigned fixed BIC concentrations of 0.07 mg/L at the ocean and 0.51 mg/L at the C&D canal.

Figure 2.3 shows a comparison of BIC and PDC load for each zone. These loads include the boundary contributions from the Delaware at Trenton, into Zone 2, and the Schuylkill, into Zone 4. It should be noted that while the BIC load is larger overall, PDC is a larger proportion of POC in Zones 2 through 5. The larger proportion of BIC in Zone 6 is due to the large surface area, and therefore high primary production, in Zone 6, as shown in Figure 2.4.

Figure 2.3 - 577 Day BIC and PDC Load for Each Zone

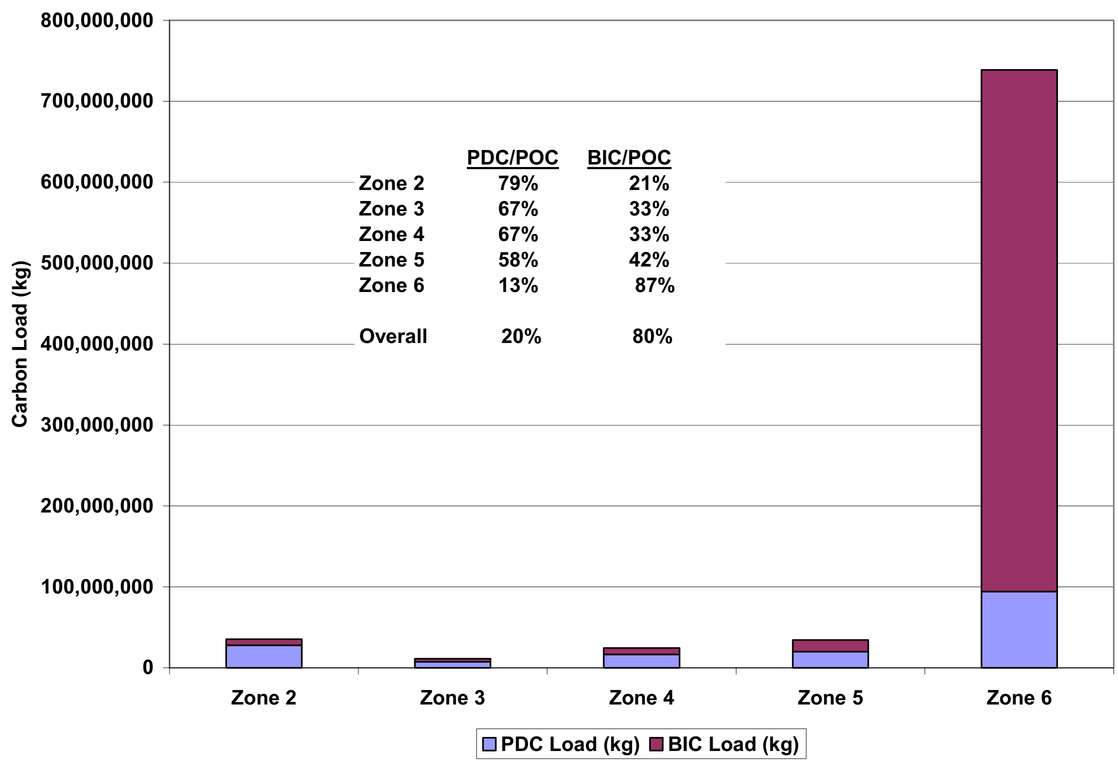
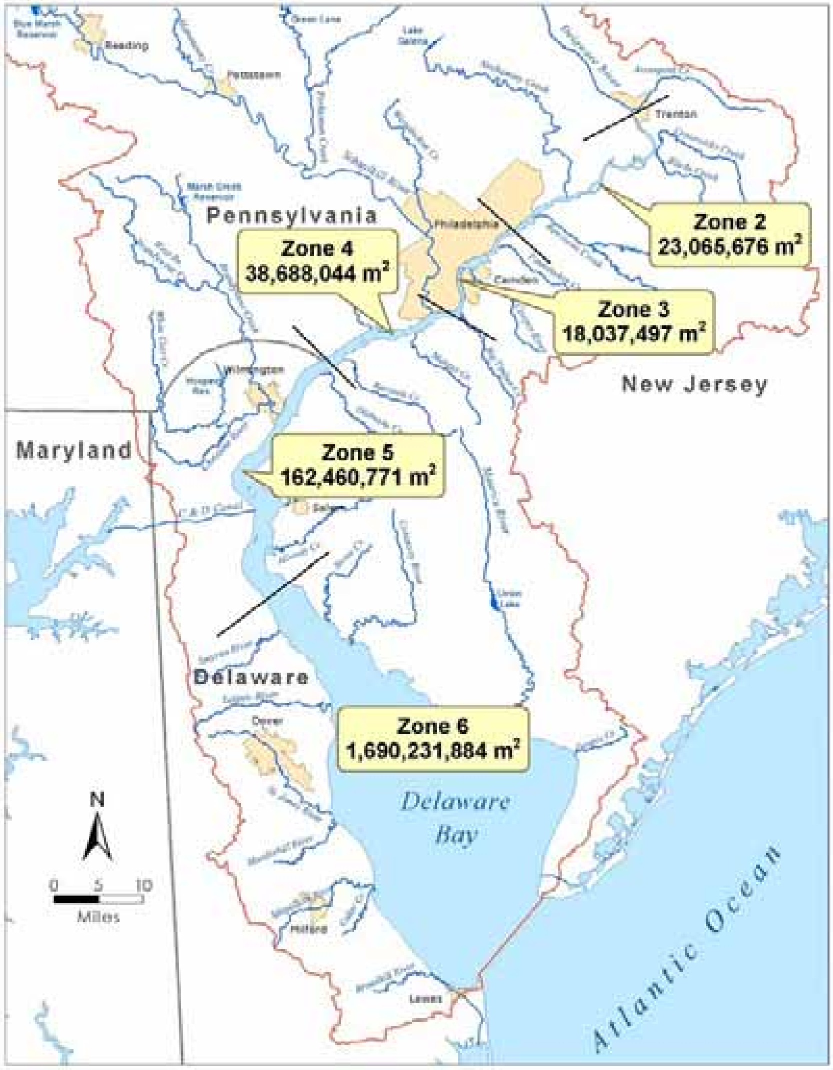


Figure 2.4 - Map of the Delaware Estuary Including Surface Area by Zone



2.2.1.2 Carbon to Chlorophyll Ratio

In order to separate measured POC into PDC and BIC fractions, we needed an estimate of the carbon to chlorophyll ratio for the Delaware estuary. The Carbon to Chlorophyll ratio provides an estimate of the portion of BIC from measured POC, as shown below:

$$Chl \times \left({}^{C}\!/_{Chl} \right) = BIC$$

and

$$POC - BIC = PDC$$

where:

Chl	=	Chlorophyll-a (mg/L)
C/Chl	=	Carbon to chlorophyll ratio
BIC	=	Biotic Carbon (mg/L)
POC	=	Particulate Organic Carbon (mg/L)
PDC	=	Particulate Detrital Carbon (mg/L)

In order to estimate an appropriate *C/Chl* for the Delaware estuary, we compiled available paired measurements of POC and chlorophyll-a, as shown in Table 2.2, and computed resultant BIC values associated with each assumed *C/Chl* and measured POC. We used two metrics to assess the appropriateness of each assumed *C/Chl*. First, the selected *C/Chl* should not result in BIC values greater than the measured POC, since BIC is a subset of POC. Second, the selected *C/Chl* should result in a BIC concentration that is roughly 15 to 25% of the POC concentration. Table 2.2 shows that *C/Chl* values between 30 and 50 generally satisfy these criteria.

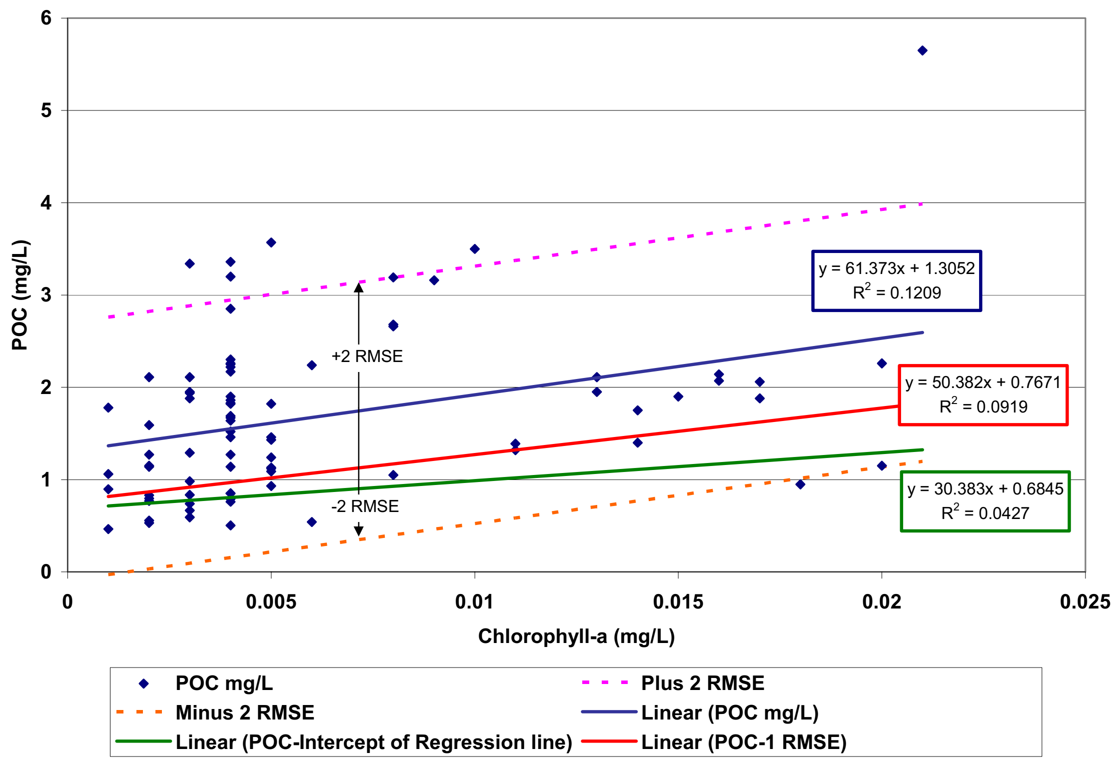
Table 2.2 - Assessment of Paired POC and Chlorophyll-a Measurements to Estimate Carbon to Chlorophyll Ratio

				C/Chl. Ratio	5	10	15	20	25	30	35	40	45	50	55	60	100	110	150
				Number of cases where BIC>POC	0	0	0	0	0	0	0	0	0	0	1	2	3	4	15
				Mean BIC/POC	2.04%	4.08%	6.13%	8.17%	10.21%	12.25%	14.29%	16.33%	18.38%	20.42%	22.46%	24.50%	40.84%	44.92%	61.25%
Date	Station	POC mg/L	Chl-A ug/L	Chl-A mg/L	Calculated BIC (mg/L)														
3/15/2002	1	3.1600	9.0	0.009	0.045	0.09	0.135	0.18	0.225	0.27	0.315	0.36	0.405	0.45	0.495	0.54	0.9	0.99	1.35
3/15/2002	2	2.2600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
3/15/2002	3	2.8500	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
3/15/2002	4	3.2000	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
3/15/2002	5	2.2400	6.0	0.006	0.03	0.06	0.09	0.12	0.15	0.18	0.21	0.24	0.27	0.3	0.33	0.36	0.6	0.66	0.9
3/15/2002	6	2.6600	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
3/15/2002	7	2.6800	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
3/15/2002	8	2.0600	17.0	0.017	0.085	0.17	0.255	0.34	0.425	0.51	0.595	0.68	0.765	0.85	0.935	1.02	1.7	1.87	2.55
3/15/2002	9	2.2600	20.0	0.02	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	2	2.2	3
3/15/2002	10	2.0700	16.0	0.016	0.08	0.16	0.24	0.32	0.4	0.48	0.56	0.64	0.72	0.8	0.88	0.96	1.6	1.76	2.4
3/15/2002	11	1.8800	17.0	0.017	0.085	0.17	0.255	0.34	0.425	0.51	0.595	0.68	0.765	0.85	0.935	1.02	1.7	1.87	2.55
3/15/2002	12	1.7500	14.0	0.014	0.07	0.14	0.21	0.28	0.35	0.42	0.49	0.56	0.63	0.7	0.77	0.84	1.4	1.54	2.1
3/15/2002	13	1.1300	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
3/15/2002	14	0.7700	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
3/15/2002	15	0.5920	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
4/11/2002	1	3.3600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/11/2002	2	2.1700	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/11/2002	3	1.4300	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/11/2002	4	1.3200	11.0	0.011	0.055	0.11	0.165	0.22	0.275	0.33	0.385	0.44	0.495	0.55	0.605	0.66	1.1	1.21	1.65
4/11/2002	5	1.4000	14.0	0.014	0.07	0.14	0.21	0.28	0.35	0.42	0.49	0.56	0.63	0.7	0.77	0.84	1.4	1.54	2.1
4/11/2002	6	2.1100	13.0	0.013	0.065	0.13	0.195	0.26	0.325	0.39	0.455	0.52	0.585	0.65	0.715	0.78	1.3	1.43	1.95
4/11/2002	7	1.9000	15.0	0.015	0.075	0.15	0.225	0.3	0.375	0.45	0.525	0.6	0.675	0.75	0.825	0.9	1.5	1.65	2.25
4/11/2002	8	2.1400	16.0	0.016	0.08	0.16	0.24	0.32	0.4	0.48	0.56	0.64	0.72	0.8	0.88	0.96	1.6	1.76	2.4
4/11/2002	9	1.9500	13.0	0.013	0.065	0.13	0.195	0.26	0.325	0.39	0.455	0.52	0.585	0.65	0.715	0.78	1.3	1.43	1.95
4/11/2002	10	1.3900	11.0	0.011	0.055	0.11	0.165	0.22	0.275	0.33	0.385	0.44	0.495	0.55	0.605	0.66	1.1	1.21	1.65
4/11/2002	11	1.0500	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
4/11/2002	12	0.8520	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/11/2002	13	0.7960	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/11/2002	14	0.5560	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/11/2002	15	0.5310	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/22/2002	1	5.6500	21.0	0.021	0.105	0.21	0.315	0.42	0.525	0.63	0.735	0.84	0.945	1.05	1.155	1.26	2.1	2.31	3.15
4/22/2002	2	3.5000	10.0	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6	1	1.1	1.5
4/22/2002	3	3.1900	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
4/22/2002	4	3.5700	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	5	1.0900	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	6	1.1200	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	7	0.9310	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	8	0.7900	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/22/2002	9	1.2400	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	10	1.4600	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	11	1.1400	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/22/2002	12	1.2700	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/22/2002	13	1.9400	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
4/22/2002	14	1.1500	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/22/2002	15	0.8340	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	1	3.3400	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	2	1.8200	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	3	1.6700	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	4	1.2700	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	5	0.7390	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	6	0.7600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	7	0.6660	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	8	0.9810	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	9	1.9500	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	10	0.8310	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
6/19/2002	11	2.1100	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
6/19/2002	12	1.5900	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
6/19/2002	13	1.7800	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
6/19/2002	14	0.8960	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
6/19/2002	15	1.0600	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
10/8/2002	1	1.8800	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
10/8/2002	2	2.1100	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
10/8/2002	3	2.2500	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	4	2.3000	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	5	1.8200	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
10/8/2002	6	1.6900	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	7	2.2200	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	8	1.5200	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	9	1.8300	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	10	1.6400	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	11	1.8600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	12	1.4600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	13	1.2900	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
10/8/2002	14	1.1400	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
10/8/2002	15	0.4650	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
9/23/2002	SBS	0.5420	6.0	0.006	0.03	0.06	0.09	0.12	0.15	0.18	0.21	0.24	0.27	0.3	0.33	0.36	0.6	0.66	0.9
9/23/2002	SJFS	1.1500	20.0	0.02	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	2	2.2	3
9/23/2002	EOC	0.9480	18.0	0.018	0.09	0.18	0.27	0.36	0.45	0.54	0.63	0.72	0.81	0.9	0.99	1.08	1.8	1.98	2.7
9/23/2002	SJL	0.5050	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
9/23/2002	LP	0.8500	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
9/23/2002	RI	1.9000	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6

To further narrow the choice for *C/Chl*, we plotted the measured POC versus measured Chlorophyll-a, along with regression line, and the regression line ± 2 root mean square error (RMSE) of the regression, as shown in Figure 2.5. In addition, we computed two new regression lines based on adjusted POC values, to assess the likely range of the slope for POC vs. chlorophyll-a. For the first adjustment, we subtracted the intercept of the regression line from the POC data and regressed those adjusted values (green line). For the second adjustment, we subtracted one RMSE from the POC data and regressed those adjusted values (red line) as well.

Adjusted data points are not shown in Figure 2.5, only the resultant regression lines. For both adjustments, negative values of POC were not included in the regressions. Although BIC is a subset of POC, the slope of BIC vs. Chlorophyll-a, which is *C/Chl*, will be equal to the slope of POC vs. chlorophyll-a since we consider BIC/POC to be constant. Therefore, Figure 2.5 further suggests a range between approximately 30 and 60 for *C/Chl.* Ultimately, we selected a value of 40 for *C/Chl* because it consistently fell centrally within the bounds of all the metrics used. Recognizing that there is some uncertainty associated with *C/Chl*, model calibration targets typically included PDC and BIC values computed from *C/Chl* values of 30, 40, and 50, to express the likely range.

Figure 2.5 - Regression of POC Vs. Chlorophyll-a Data with ± 2 RMSE and 2 Adjustments



2.2.1.3 Internal Biotic Carbon Generation

Internal generation of BIC was estimated using the long term primary production measurements made by Dr. Jonathan Sharpe in the Delaware Estuary since 1978. Dr. Sharpe provided representative long term average primary production estimates to DRBC for 5 seasons including an early spring period (Spring 1) and late spring period (Spring 2) as well as 22 spatial ranges, as shown in Tables 2.3 and 2.4, below.

Table 2.3 - Definition of Seasons for Internal Carbon Production

Dates	Season
November 17 - February 28	Winter
March 1 – April 11	Spring 1
April 12 – May 10	Spring 2
May 11 – September 12	Summer
September 13 – November 16	Fall

Table 2.4 - Internal Seasonal Carbon Production by Zone (kg C / m^2 / day)

Range (River Miles)	Spring 1	Spring 2	Summer	Fall	Winter
Below 0	4.37E-04	4.37E-04	9.60E-04	2.82E-04	2.70E-04
0 to 6.21	6.86E-04	6.86E-04	1.60E-03	9.43E-04	2.87E-04
6.21 to 12.42	6.53E-04	6.53E-04	1.51E-03	3.59E-04	2.06E-04
12.42 to 18.64	1.14E-03	1.14E-03	2.11E-03	3.26E-04	4.51E-04
18.64 to 24.85	1.37E-03	1.37E-03	1.88E-03	2.93E-04	3.89E-04
24.85 to 31.06	1.49E-03	1.49E-03	1.36E-03	3.09E-04	3.27E-04
31.06 to 37.27	1.28E-03	1.28E-03	1.12E-03	1.04E-04	1.99E-04
37.27 to 43.48	7.58E-04	7.58E-04	8.01E-04	1.16E-04	1.44E-04
43.48 to 49.7	4.40E-04	4.40E-04	5.77E-04	5.92E-05	4.09E-05
49.7 to 55.91	2.95E-04	2.95E-04	5.50E-04	7.13E-05	5.14E-05
55.91 to 62.12	2.02E-04	2.02E-04	3.31E-04	4.42E-05	2.76E-05
62.12 to 68.33	1.36E-04	1.36E-04	3.83E-04	9.04E-05	1.07E-05
68.33 to 74.55	1.27E-04	1.27E-04	4.06E-04	5.72E-05	6.48E-06
74.55 to 80.76	2.83E-04	2.83E-04	6.34E-04	9.95E-05	1.06E-05
80.76 to 86.97	3.30E-04	3.30E-04	9.70E-04	1.74E-04	1.10E-05
86.97 to 93.18	5.10E-04	5.10E-04	9.87E-04	1.02E-04	1.39E-05
93.18 to 99.39	2.56E-04	2.56E-04	1.19E-03	1.68E-04	1.08E-05
99.39 to 105.61	2.62E-04	2.62E-04	1.18E-03	2.74E-04	7.56E-06
105.61 to 111.82	2.07E-04	2.07E-04	1.38E-03	1.29E-04	1.02E-05
111.82 to 118.03	3.26E-04	3.26E-04	1.30E-03	2.46E-04	1.46E-05
118.03 to 124.24	1.90E-04	1.90E-04	1.60E-03	1.80E-04	1.23E-05
Above 124.24	1.65E-04	1.65E-04	9.57E-04	3.68E-05	8.64E-06

Each model segment was matched to the appropriate spatial range, and an internal load was specified for each simulation day by multiplying the Seasonal Carbon Production by the segment surface area, to yield an estimated daily BIC load.

2.2.1.4 Marsh Carbon Loads

In order to estimate the carbon load from marshes in the Delaware Estuary, DRBC consulted available literature for estimates of carbon production and export. The Academy of Natural Sciences (ANS) estimated a range of biomass production for emergent aquatic vegetation (EAV) in the Delaware Estuary between 241 g m^{-2} yr^{-1} for low marsh to 1305 g m^{-2} yr^{-1} for high marsh. The ANS report cites estimates of low marsh EAV production rates on the New Jersey side of the Delaware River of 863 g m^{-2} yr^{-1} by McCormick (1977) and 780 g m^{-2} yr^{-1} by Wingham and Simpson (1975). The ANS report also cites high marsh EAV production estimates ranging from 940 g m^{-2} yr^{-1} by Wingham and Simpson (1976) to 1600 g m^{-2} yr^{-1} Good and Good (1975). Combined with the ANS measured carbon proportion of approximately 40%, this results in a range of carbon production between 96.4 and 640 g C m^{-2} yr^{-1}.

Estimates of carbon export, or flux, were more limited than estimates of production. Lotrich et al., (1979) as cited in Nixon (1980) estimated the annual *flux* of organic carbon between salt marsh and coastal water at Canary Creek, Lewes, Del at 100 g TOC m^{-2} yr^{-1} with 62 g POC m^{-2} yr^{-1} and 38 g DOC m^{-2} yr^{-1}.

In other systems, Neubauer et al. (2000) measured a range of annual net macrophyte production in a tidal freshwater marsh (Pamunkey River) of 1.4 - 2 g C m^{-2} day^{-1}. This would correspond to a range of 511 – 730 g C m^{-2} yr^{-1}, which is reasonably comparable with the ranges cited for the Delaware Estuary. In order to estimate a flux from this carbon production rate, Cerco (2002 draft) assumed that carbon production represents an absolute upper bound for export, and assumed an export value of 0.3 g C m^{-2} day^{-1} for the 2nd Generation Chesapeake Bay Water Quality Model. Cerco also assumed that ⅓ of the exported carbon was in the form of DOC, ⅓ was in the form of labile particulate carbon, and ⅓ was in form of refractory particulate carbon. Since the definitions of labile and refrectory particulate carbon differ from our definition of particulate detrital carbon, we assume that Cerco's export rate should correspond to a value between 0.1 and 0.2 g PDC m^{-2} day^{-1}, which again agrees reasonably well with a flux estimate of 0.17 g POC m^{-2} day^{-1} by Lotrich et al. for marshes in Canary Creek in Lewes, Delaware.

For this iteration, we used a loading rate of 0.15 g PDC m^{-2} day^{-1} from marshes. We assumed that the marsh load consisted entirely of PDC as opposed to BIC. Marsh areas in each zone were obtained from USGS National Hydrography Dataset GIS coverages. Marsh loads were totaled for each zone and loaded into individual mainstem model segments using the relative area of the segment as a weighting factor, thus preventing inappropriately high loading rates to smaller segments. Based on observations that marsh particulate carbon is typically only available when marshes become inundated or during significant storm events, the marsh carbon load was pulsed into the system assuming 60% of the total load was released during spring tides, and 40% was released during storm events. Of the 40% released during storm events, the precipitation total for a 24 hour period divided by the total for 577 days was used as a weighting factor to distribute the storm released PDC. Thus larger storm events would release more PDC than small storm events. Similarly, on days with concurrent spring tides and storm events, both the tidal and storm portions of the PDC load were released.

2.2.1.5 Tributary Carbon Loads

Tributary carbon loads were estimated as the product of gaged or extrapolated daily flows and tributary specific mean wet and mean dry weather concentrations, toggled by precipitation data. The tributary specific mean dry weather concentration was used for any day with a 24-hour rainfall total less than 0.1-inch, and the tributary specific mean wet weather concentration was used for any day with a 24-hour rainfall total of 0.1-inch or more. Table 2.5 below shows the measured POC concentrations during the simulation period.

Table 2.5 - Summary of Tributary POC Measurements

Tributary	Date	RESULT	UNITS	BIC	PDC
Alloways Creek	7/16/2002	6.63	mg/L	1.08	5.55
Alloways Creek	12/13/2002	2.63	mg/L	0.43	2.20
Big Timber Creek	6/7/2002	0.91	mg/L	0.15	0.76
Big Timber Creek	7/18/2002	1.12	mg/L	0.18	0.94
Big Timber Creek	10/7/2002	1.35	mg/L	0.22	1.13
Big Timber Creek	12/10/2002	1.57	mg/L	0.26	1.31
Brandywine Creek	7/18/2002	0.22	mg/L	0.04	0.19
Brandywine Creek	8/29/2002	0.50	mg/L	0.08	0.41
Brandywine Creek	12/12/2002	21.20	mg/L	3.46	17.74
Brandywine Creek	12/16/2002	0.87	mg/L	0.14	0.73
Chester Creek	7/17/2002	0.37	mg/L	0.06	0.31
Chester Creek	12/10/2002	0.96	mg/L	0.16	0.80
Christina River	7/18/2002	0.62	mg/L	0.10	0.52
Christina River	8/29/2002	7.46	mg/L	1.22	6.24
Christina River	10/8/2002	0.52	mg/L	0.09	0.44
Christina River	11/12/2002	1.80	mg/L	0.29	1.51
Christina River	12/16/2002	0.92	mg/L	0.15	0.77
Christina River	12/20/2002	15.90	mg/L	2.60	13.30
Cooper River	8/1/2002	4.14	mg/L	0.68	3.46
Cooper River	10/7/2002	4.91	mg/L	0.80	4.11
Cooper River	12/10/2002	0.89	mg/L	0.15	0.75
Cooper River	2/22/2003	1.74	mg/L	0.28	1.46
Crosswicks Creek	5/13/2002	2.33	mg/L	0.38	1.95
Crosswicks Creek	7/16/2002	1.14	mg/L	0.19	0.95
Crosswicks Creek	10/7/2002	0.34	mg/L	0.06	0.29
Crosswicks Creek	10/31/2002	2.36	mg/L	0.39	1.97
Crosswicks Creek	12/10/2002	0.87	mg/L	0.14	0.73
Crosswicks Creek	3/6/2003	4.34	mg/L	0.71	3.63
Crosswicks Creek	3/27/2002	10.50	mg/L	1.71	8.79
Darby Creek	7/17/2002	1.11	mg/L	0.18	0.93
Darby Creek	10/8/2002	1.35	mg/L	0.22	1.13
Darby Creek	11/12/2002	1.33	mg/L	0.22	1.11
Darby Creek	12/10/2002	0.98	mg/L	0.16	0.82
Frankford Creek	4/25/2002	26.90	mg/L	4.39	22.51
Frankford Creek	7/17/2002	1.81	mg/L	0.30	1.51
Frankford Creek	12/10/2002	1.26	mg/L	0.21	1.05
Mantua Creek	5/18/2002	4.38	mg/L	0.72	3.66
Mantua Creek	7/16/2002	3.28	mg/L	0.54	2.74
Mantua Creek	10/7/2002	1.80	mg/L	0.29	1.51

Table 2.5 - Summary of Tributary POC Measurements (continued)

Tributary	Date	RESULT	UNITS	BIC	PDC
Mantua Creek	11/6/2002	1.11	mg/L	0.18	0.93
Mantua Creek	12/10/2002	1.82	mg/L	0.30	1.52
Neshaminy Creek	4/26/2002	0.58	mg/L	0.09	0.48
Neshaminy Creek	5/9/2002	0.64	mg/L	0.10	0.54
Neshaminy Creek	7/17/2002	0.39	mg/L	0.06	0.33
Neshaminy Creek	12/10/2002	0.43	mg/L	0.07	0.36
Pennsauken Cr.	8/1/2002	0.84	mg/L	0.14	0.70
Pennsauken Cr.	12/10/2002	1.96	mg/L	0.32	1.64
Pennypack Creek	4/25/2002	3.04	mg/L	0.50	2.54
Pennypack Creek	7/17/2002	0.22	mg/L	0.04	0.19
Pennypack Creek	12/10/2002	0.37	mg/L	0.06	0.31
Poquessing Creek	4/25/2002	4.02	mg/L	0.66	3.36
Poquessing Creek	7/17/2002	0.38	mg/L	0.06	0.31
Poquessing Creek	12/10/2002	0.34	mg/L	0.06	0.29
Raccoon Creek	5/18/2002	13.30	mg/L	2.17	11.13
Raccoon Creek	7/16/2002	3.10	mg/L	0.51	2.59
Raccoon Creek	12/10/2002	1.04	mg/L	0.17	0.87
Rancocas Creek	6/7/2002	2.56	mg/L	0.42	2.14
Rancocas Creek	7/16/2002	2.29	mg/L	0.37	1.92
Rancocas Creek	10/7/2002	2.13	mg/L	0.35	1.78
Rancocas Creek	12/13/2002	2.41	mg/L	0.39	2.02
Red Clay Creek	7/18/2002	0.63	mg/L	0.10	0.52
Red Clay Creek	8/29/2002	11.10	mg/L	1.81	9.29
Red Clay Creek	12/16/2002	0.43	mg/L	0.07	0.36
Red Clay Creek	12/20/2002	6.18	mg/L	1.01	5.17
Salem Creek	7/16/2002	1.46	mg/L	0.24	1.22
Salem Creek	12/13/2002	2.95	mg/L	0.48	2.47
White Clay Creek	7/18/2002	0.46	mg/L	0.07	0.38
White Clay Creek	8/29/2002	8.94	mg/L	1.46	7.48
White Clay Creek	12/16/2002	0.50	mg/L	0.08	0.41

POC concentrations for unsampled tributaries in Zone 6 were estimated from data reported by the University of Delaware for dry weather concentrations. The mean ratio of wet weather to dry weather POC concentration for all other tributaries was used to estimate a wet weather concentration from the dry weather concentrations reported by the University of Delaware. In addition carbon loads for Assunpink Creek and the Stowe River were estimated as the mean dry weather concentration for all other tributaries in Zones 2 through 5. Wet weather concentrations for the Stowe and Assunpink were estimated by multiplying the estimated dry weather concentration by the mean ratio of wet weather to dry weather POC concentration for all other tributaries.

Based on the analysis of paired POC and chlorophyll-a measurements in the main stem (Section 2.2.1.2), we observed that our assumed carbon to chlorophyll ratio of 40 resulted in a mean BIC/POC ratio of 0.1633. We assumed that this same relationship would hold true for the tributaries, and estimated BIC and PDC as follows:

$$BIC = 0.1633 \times POC$$

$$PDC = (1 - 0.1633) \times POC$$

2.2.1.6 Point Discharge Carbon Loads

In order to estimate the carbon load from the point dischargers, we considered two different methods for estimating POC from more routinely monitored effluent parameters (BOD_5 and TSS). For both approaches, we assumed that the point sources discharged no live carbon (i.e. BIC) and hence assigned the entire carbon load from these sources to PDC.

Method 1 is from Appendix B of the EPA report "Progress in Water Quality: An Evaluation of the National Investment in Municipal Wastewater Treatment, EPA-832-R-00-008, June 2000." This method estimates POC as a function of TSS and ratios of organic matter to total solids and carbon to dry weight of organic matter, as shown in the equation below:

$$POC \approx TSS \times \left(\frac{POM}{TSS}\right) \times \left(\frac{C}{DW}\right)$$

where

TSS	=	Total suspended solids
POM	=	Particulate organic matter
C	=	Carbon
DW	=	Dry weight

For municipal wastewater secondary treatment, EPA used values of 0.67 for POM/TSS and 0.44 for C/DW.

Method 2 is a regression developed from paired POC and BOD_5 data from 6 Water Pollution Control Plants in New York City, as part of a water quality modeling effort (Hydroqual 1999). As shown below, the equation estimates POC as a function of BOD_5.

$$POC = 4.68 + 0.31 \times BOD_5$$

To compare these two methods, we computed POC based on reported daily TSS data using Method 1 and reported daily BOD5 data using Method 2. Figures 2.6 and 2.7 show the results for two different waste water treatment facilities during December 2001.

Figure 2.6 - Comparison of 2 Methods for Estimating POC from Reported TSS and BOD_5 Data using Philadelphia SE Plant Data, December 2001

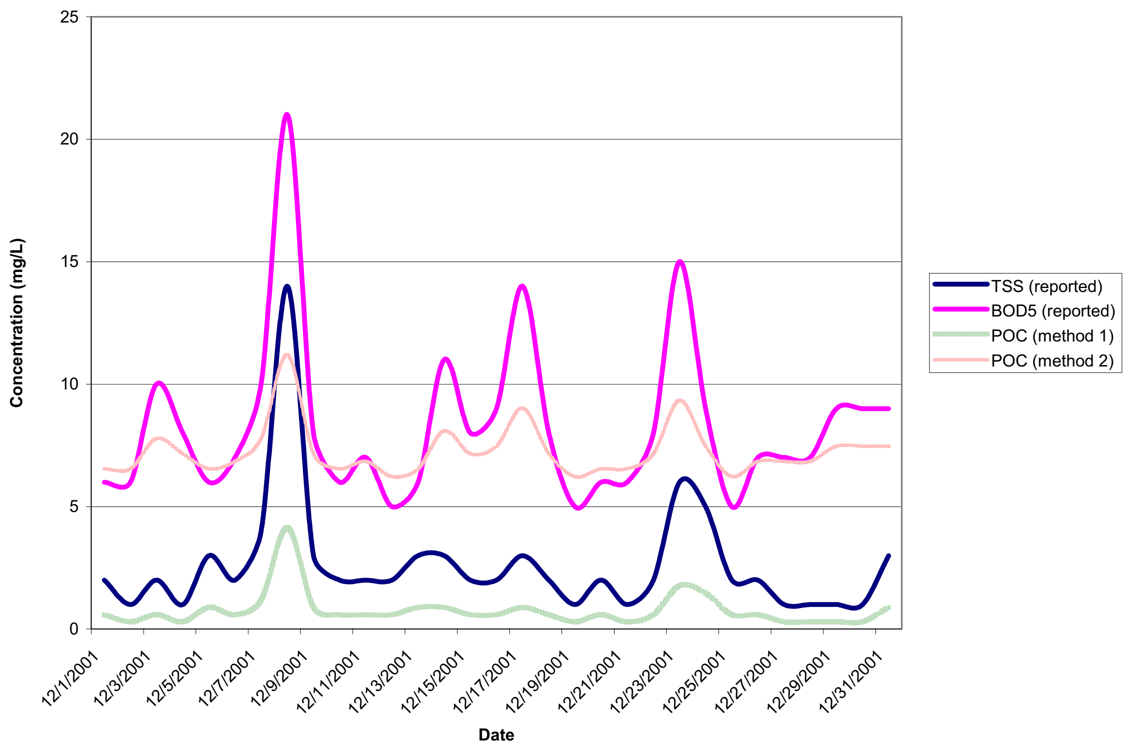
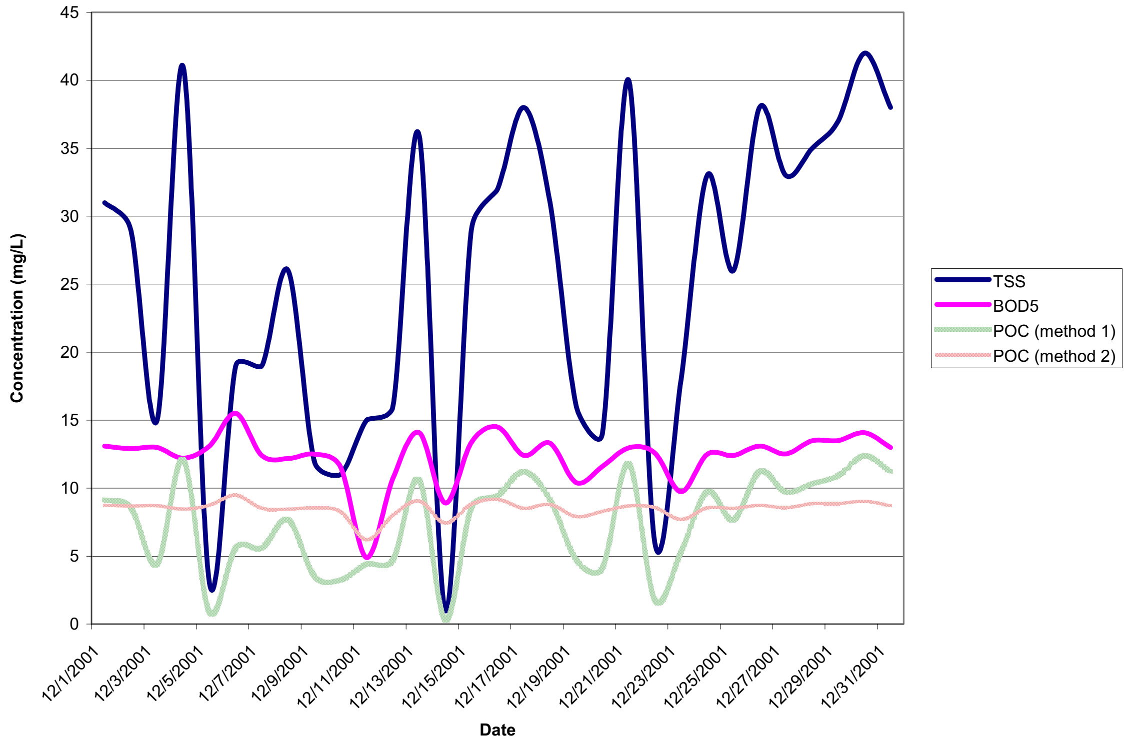


Figure 2.7 - Comparison of 2 Methods for Estimating POC from Reported TSS and BOD5 Data using Morrisville Plant Data, December 2001



Although we would expect TSS to be an upper limit for the potential value of POC, use of Method 2 frequently results in an estimated POC concentration exceeding the reported TSS concentration, as shown in Figures 2.6 and 2.7. Since Method 1 uses TSS to calculate POC, Method 1 estimated POC is always less than TSS.

Figure 2.8 - Comparison of 2 Methods for Estimating POC from BOD_5 and TSS

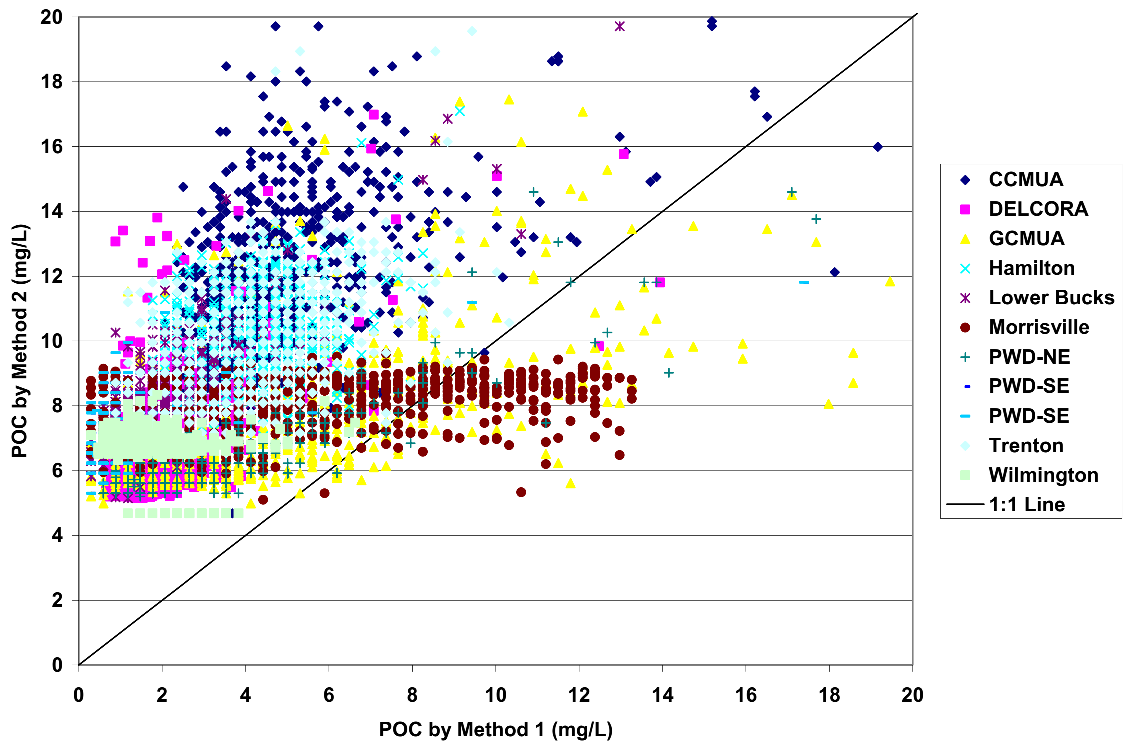


Figure 2.8, comparing POC concentration estimates using the two methods shows that Method 2 generally yields a higher POC concentration estimate than Method 1.

Given the tendency of Method 2 to result in a POC concentration higher than the measured TSS, we recommended to the Expert Panel that Method 1 be used in this iteration. The Expert Panel concurred, and Method 1 was used to estimate POC from daily TSS measurements.

For smaller municipal wastewater treatment facilities that were not required to submit daily measurements, we computed a POC concentration using Method 1 based on a typical TSS effluent concentration of 17.2 mg/L for secondary treatment as reported in *"Appendix B - Progress in Water Quality: An Evaluation of the National Investment in Municipal Wastewater Treatment, EPA-832-R-00-008, June 2000."* This results in a POC concentration of 5.07 mg/L, which is consistent with the computed POC concentrations from daily TSS measurements shown in Figure 2.8.

For facilities discharging primarily stormwater runoff, we estimated a POC concentration based on a mean general urban runoff concentration of 150 mg/L TSS, from the EPA stormwater database as reported in Horner (1994) and an assumed fraction organic carbon of 0.1. Again, we assumed that all particulate carbon from facilities discharging primarily stormwater runoff was PDC rather than BIC. This results in a PDC concentration of 15 mg/L from these facilities.

For facilities discharging primarily industrial process effluent, it is anticipated the carbon concentrations could vary widely from relatively high to undetectable concentrations. For the most part, carbon concentrations are not measured in the industrial process effluent. We presumed that, on average, industrial process effluent should have a lower carbon concentration than municipal wastewater treatment effluent. As a default, we assumed a PDC concentration of 2 mg/L for industrial process water. Since industrial process effluent flow contributes only 13% of the total point discharge flow, compared to nearly 87% contributed by municipal waste water treatment flow, errors associated with this default assumption should be minimized.

2.2.1.7 Atmospheric Deposition Carbon Loads

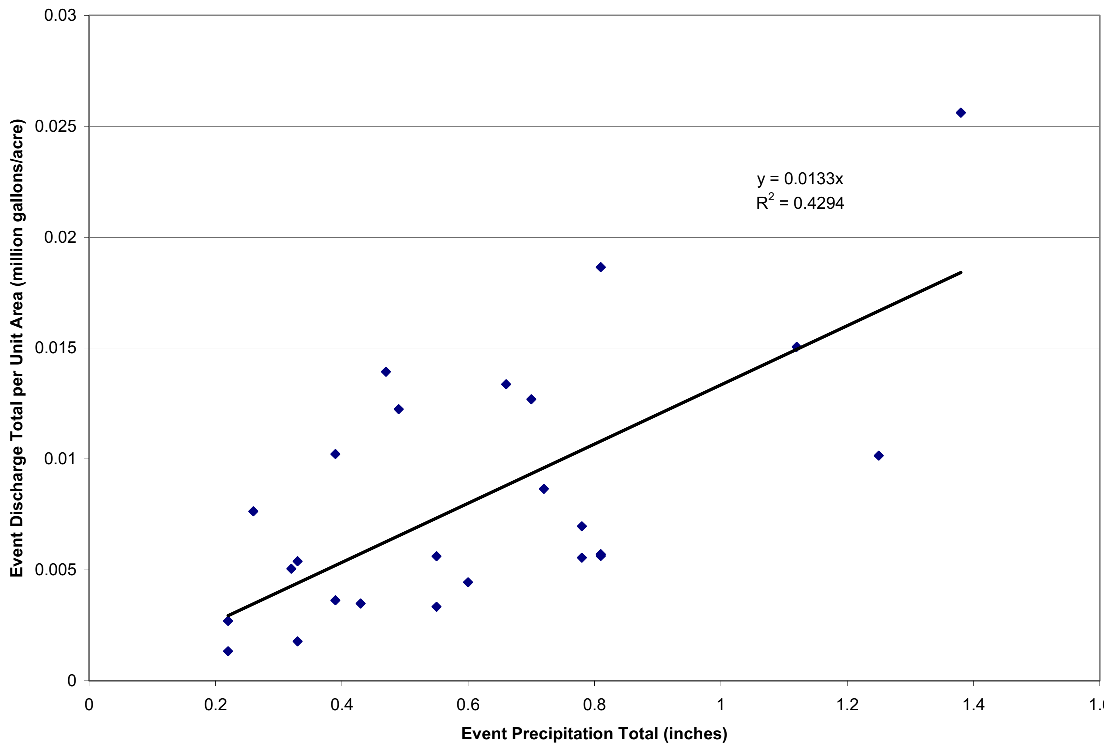
We assumed that all atmospheric particulate carbon was in the form of PDC rather than BIC. We consulted with Rutgers University to estimate the atmospheric deposition of particulate carbon. Based on Rutgers long term atmospheric particulate measurements, we assumed an atmospheric particulate solids concentration of 20 $\mu g/m^3$ with a fraction organic carbon of 0.1 and deposition velocity of 0.75 cm/s for all segments. This resulted in an atmospheric PDC deposition rate of 1.296E-6 kg PDC m^{-2} day^{-1}.

2.2.1.8 Combined Sewer Overflow Carbon Loads

To estimate PDC load from Combined Sewer Overflows, we multiplied the estimated daily flow and estimated daily PDC concentration. We assumed that all CSO particulate carbon was in the form of PDC, as opposed to BIC.

Philadelphia and DELCORA provided daily flow estimates based on their CSO discharge models. For Wilmington and Camden, we estimated CSO daily flows by regressing measured discharges with measured rainfall during those discharge events, to obtain an estimate of gallons/acre/inch. We extrapolated this estimate to the entire CSO service area and multiplied by the daily 24-hour rainfall totals for each day of the simulation period to estimate daily discharge volume. Figure 2.9 shows this analysis for two Wilmington subbasins.

Figure 2.9 - Lumped Linear Regression of Unit Area Discharge vs. Event Precipitation Totals for the Silverbrook Run and Formans Run Subbasins of the Wilmington CSO Service Area



Philadelphia and DELCORA provided daily TSS and BOD_5 measured treatment plant influent concentrations, as requested by DRBC. Plant influent concentrations are assumed to be comparable to the CSO discharge concentrations during discharge events. Wilmington and Camden declined to provide this data, so the daily values for these facilities were estimated as the mean of the Philadelphia and DELCORA TSS and BOD_5 concentrations for each day during the simulation period. We assumed that all particulate carbon associated with CSO discharges would be in the form of PDC, as opposed to BIC. We estimate the PDC concentration from the reported TSS data using the following equation from EPA (2000).

$$POC \approx TSS \times \left(\frac{POM}{TSS}\right) \times \left(\frac{C}{DW}\right)$$

where

TSS	=	Total suspended solids
POM	=	Particulate organic matter
C	=	Carbon
DW	=	Dry weight

We used the EPA recommended values for raw municipal wastewater of 0.75 for POM/TSS and 0.44 for C/DW.

2.2.1.9 Non-Point Source Carbon Loads

In order to estimate PDC loads from broad land use associated non-point sources, we modified the framework developed by Camp Dresser McKee (CDM) to estimate PCB loads (Smullen 2003). With the support of the Philadelphia Water Department, CDM developed a non-point source loading framework to estimate daily non-point source loads from the area between the tributary monitoring locations and the mainstem Delaware. CDM originally considered four (4) land use categories for non-point source loads:

- agricultural
- rural/open/ forested
- open water/wet-wetlands, and
- urban/suburban/commercial.

We estimated PDC loads from urban-suburban and rural-rural suburban land use categories. Although CDM had also included an open water category for estimating PCB non-point source loads, this category was not included for estimation of PDC, since atmospheric deposition of PDC onto the water column and marsh generated PDC were estimated explicitly in other categories.

For the urban-suburban land use category, daily PDC loads are estimated from the following:

$$L_i = A_U \times d_r \times C_i$$

where:

L_i	=	Pollutant Load Estimate from Urban-Suburban Land use areas
A_U	=	Area of urban land
d_r	=	rainfall-runoff depth as estimated by a modified rational formula approach
C_i	=	constant pollutant concentration – [Event Mean Concentration (EMC)]

For C_i, we estimated a POC concentration based on a mean general urban runoff concentration of 150 mg/L TSS, from the EPA stormwater database as reported in Horner (1994), and an assumed fraction organic carbon (f_{oc}) of 0.05. This f_{oc} is lower than the assumed f_{oc} used for industrial stormwater runoff, representing our assumption that localized higher f_{oc}'s associated with spills and accidental releases may be more concentrated at industrial sites and more diffused in the general urban landscape. We assumed that all non-point source derived particulate carbon would be in the form of PDC, rather than BIC.

For the rural/rural-suburban landuse category, we used published estimated area export rates from Horner 1992 as published in Horner 1994. We considered the land uses shown in Table 2.6

as likely components of the rural/rural-suburban category and assumed a value of 300 lbs acre^{-1} year^{-1} to represent a composite rural land use category.

Table 2.6 - Median TSS Loading Estimates for Rural subcategories.

Land Use Category	TSS Loading Median Value (lbs/ac/year)
Forest	76.5
Grass	308
Pasture	305

Again, we assumed an f_{oc} of 0.05 and treated all particulate carbon as PDC rather than BIC.

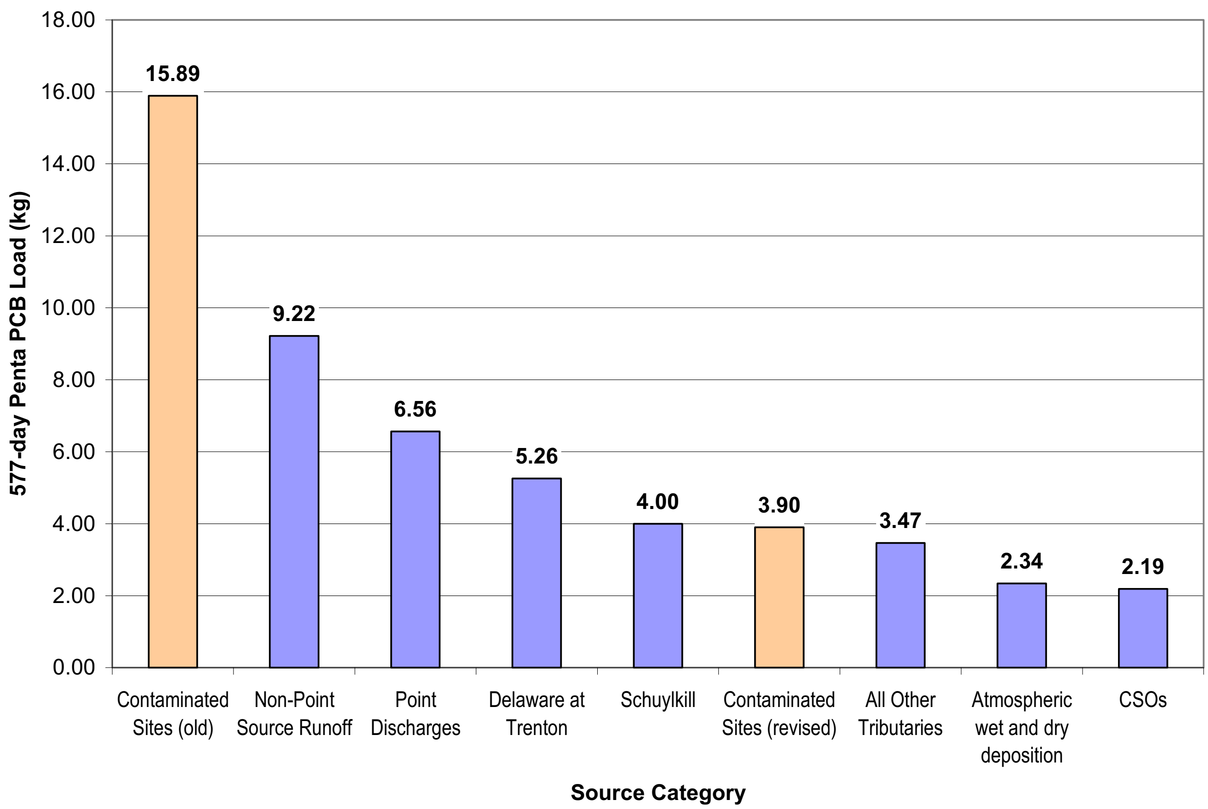
The total daily PDC load from non-point sources, therefore is the sum of the urban-suburban and rural/rural-suburban load. Since the urban-suburban load is a function of precipitation runoff, this value is equal to zero on days without precipitation, and equal to a value proportional to the rainfall total on days with precipitation. By contrast, the rural/rural-suburban load is constant on all days. Thus, the sum of these two loads yields a baseline daily load which is the same on all days without rainfall, that is proportionally increased on days with rainfall.

Finally, the original CDM load framework apportioned loads into each model segment by determining the number of subwatersheds that intersected the model segment boundaries and dividing the total load from those subwatersheds by the number of subwatersheds to approximate the discrete load to the specific segment. Since the model employs segments of varying size, we found that spatially smaller segments tended to receive higher PDC loadings than larger segments, resulting in unrealistically uneven burial rates between larger and smaller segments. To mitigate this effect, we totaled the non-point source PDC loads for each zone and then apportioned them into the specific segments using the relative surface area of each segment in the zone. Thus larger segments would receive proportionally larger loads than smaller segments. As expected, this reduced the unevenness of burial rates between larger and smaller segments.

2.2.2 Penta-PCB Load Estimates

penta-PCB loads were estimated for each day of the 575 day continuous simulation period. Figure 2.10 shows a summary of the 577 day total loads for each source category. Again, the "Boundary" category refers to the Delaware at Trenton and the Schuylkill Rivers, and is not strictly a load.

Figure 2.10 - 577 Day penta-PCB Load by Source Category



2.2.2.2 Non-Point Source penta-PCB Loads

As with PDC, in order to estimate penta-PCB loads by broad land use associated non-point sources, we used the framework developed by Camp Dresser McKee (CDM) (Smullen 2003). With the support of the Philadelphia Water Department, CDM developed a non-point source loading framework to estimate daily non-point source loads from the area between the tributary monitoring locations and the mainstem Delaware. For constant concentration model and atmospheric deposition/watershed pass-through rate model applications, four (4) land uses were developed:

- agricultural
- rural/open/ forested
- open water/wet-wetlands, and
- urban/suburban/commercial.

The framework estimates PCB loads from urban-suburban, rural-rural suburban, and open water land use categories.

For the urban-suburban land use category, daily penta-PCB loads are estimated from the following:

$$L_i = A_U \times d_r \times C_i$$

where:

L_i	=	Pollutant Load Estimate from Urban-Suburban Land use areas
A_U	=	Area of urban land
d_r	=	rainfall-runoff depth as estimated by a modified rational formula approach
C_i	=	constant pollutant concentration – [Event Mean Concentration (EMC)]

The EMC is defined as the total mass load of a chemical parameter yielded from a site during a storm divided by the total runoff water volume discharged during the event. For this project the EMC for PCBs was developed through a collaborative literature search performed by Philadelphia Water Department, CDM, and DuPont, with the EMC database being developed and maintained by DuPont.

The literature review team collected and reviewed more than 100 articles and reports dating from 1979 to the present. Articles and reports covered data from over 130 station storms from 70 sites in 20 cities in Canada, the U.S., France, Germany, and Japan. Of the 100+ articles reviewed, 12 yielded useful runoff data. Quantiles of the lognormal EMC from the literature are shown in Table 2.7.

Table 2.7 - Quantiles of the Log-Normal Event Mean Concentration

Quantile	Estimate	Units
0.01	2.20	ng/L
0.05	5.85	ng/L
0.25	23.55	ng/L
0.5	61.99	ng/L
0.75	163.20	ng/L
0.95	656.93	ng/L
0.99	1746.90	ng/L

Load estimates were based on the 50th percentile EMC value of 61.99 ng/L. In order to estimate the proportion of penta-PCB, we multiplied the total PCB EMC by the estimated proportion of penta-PCB produced as part of overall domestic PCB production. Domestic Aroclor production estimates from EPA/600/P-96/001F were combined with congener composition data for Aroclors by Frame (1996) to yield a relative penta proportion of 14.65% of domestic production.

For the agricultural, rural/open/ forested, and open water/wet-wetlands land use categories, the framework utilized atmospheric deposition data provided by Rutgers University and an assumed pass-through rate to estimate penta-PCB loads. The framework assumed pass through rates of 10% for agricultural and rural/open/ forested land use categories, and 90% for open water/wet-wetlands. The original framework utilized a single dry deposition rate for the estuary. In order to be consistent with the atmospheric deposition estimates, and to take advantage of more refined atmospheric data, we restructured the framework to use spatially varied dry deposition rates appropriate to each subwatershed.

Finally, the original CDM load framework apportioned loads into each model segment by determining the number of subwatersheds that intersected the model segment boundaries and dividing the total load from those subwatersheds by the number of subwatersheds to approximate the discrete load to the specific segment. Since the model employs segments of varying size, we found that spatially smaller segments tended to receive higher loadings than larger segments, resulting in unrealistically uneven burial rates between larger and smaller segments. To mitigate this effect, we totaled the non-point source loads for each zone and then apportioned them into the specific segments using the relative surface area of each segment in the zone. Thus larger segments would receive proportionally larger loads than smaller segments.

2.2.2.3 Point Discharge penta-PCB Loads

Daily point discharge penta-PCB loads were estimated by computing the product of daily flows and outfall specific mean or measured wet and mean or measured dry weather concentrations, as the sum of penta congeners, toggled by precipitation data. Dry concentrations were used for all days with total rainfall less than 0.1” and wet concentrations were used for all days with total rainfall equal to 0.1” or greater. For continuous discharges with minimal stormwater influence, the wet weather concentration was set equal to the dry weather concentration.

Discharger reported PCB data was used to determine the wet and dry weather concentrations. Congener concentrations were estimated for non-detect data by setting the concentration for that congener at one half of the detection limit. Data flagged with "J", indicating an estimated value, was used at the estimated value. Coeluting congener concentrations were counted one time only, to avoid artificial inflation of the penta concentration associated with assigning duplicate concentration values for two or more coeluting congeners. Data was not adjusted to account for concentrations measured in field, trip, or rinsate blanks.

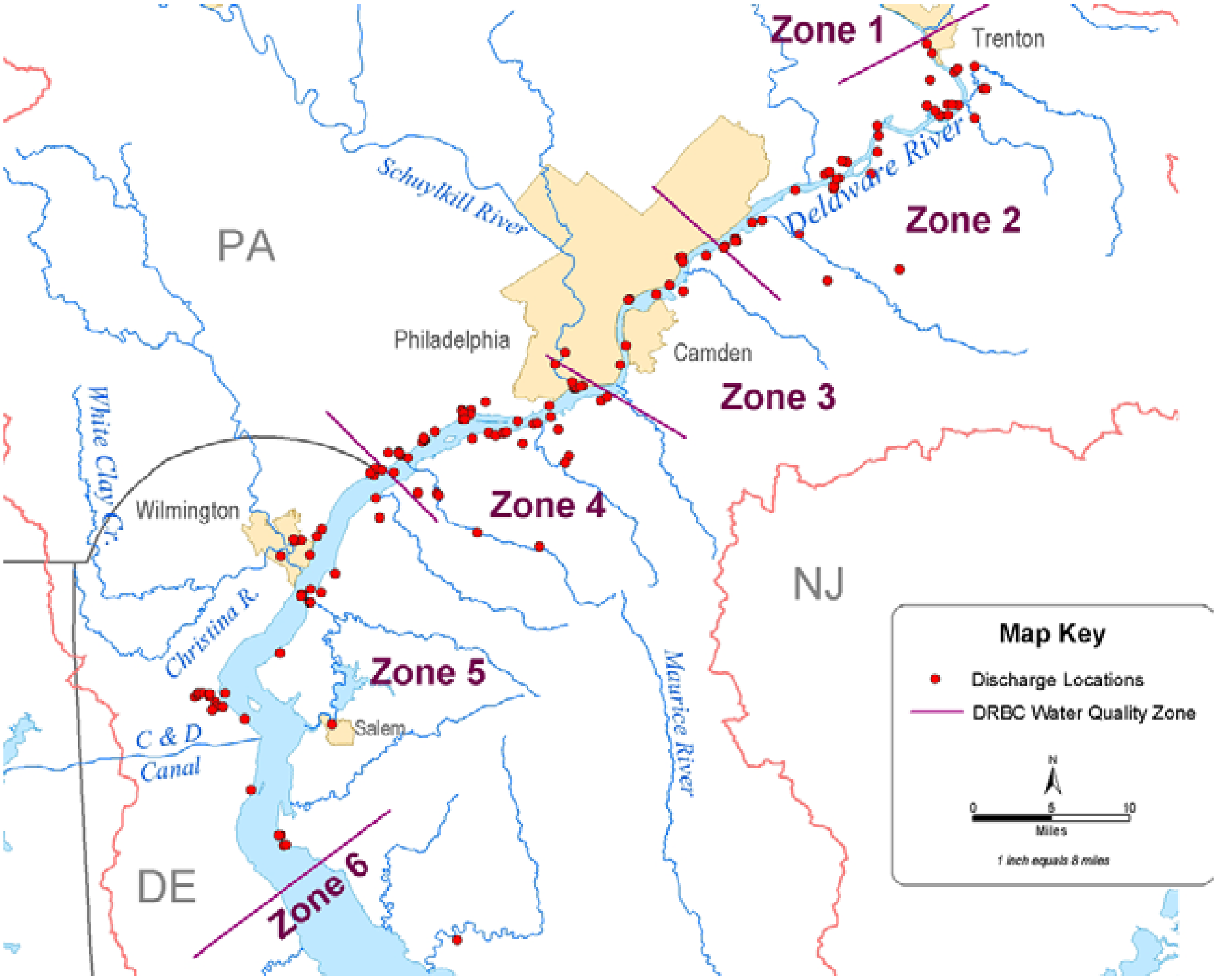
Although sampling was required for non-contact cooling water discharges, estimated loadings from these facilities were not used in this phase of modeling. A review of the influent and effluent concentration data indicated that it was not possible to determine a net load with the limited available data.

Table 2.8 shows the estimated 577 day penta-PCB load for each point discharge in the model in descending order. Discharge ID is a combination of the facility NPDES number and the outfall number or name. Figure 2.11 shows the point discharge the locations.

Table 2.8 - Estimated 577 day penta-PCB Load by Point Discharge

Discharge ID	577 Day Penta PCB Load (kg)	Discharge ID	577 Day Penta PCB Load (kg)	Discharge ID	577 Day Penta PCB Load (kg)
DE0000256-101	1.6405E+00	PA0012769-009	1.2039E-02	NJ0004391-003A	4.2689E-04
DE0020320-001	7.4880E-01	NJ0024449-001	1.1099E-02	PA0045021-001	3.7258E-04
PA0026689-001	7.1471E-01	NJ0027481-001	1.0899E-02	PA0013323-003	3.5658E-04
PA0026671-001	5.8881E-01	PA0057479-DD3	1.0296E-02	PA0013716-005	3.4763E-04
NJ0026182-001	4.7225E-01	NJ0023701-001	9.0487E-03	PA0012637-007	2.9499E-04
PA0026662-001	3.7951E-01	PA0028380-001	8.9147E-03	DE0021539-001	2.8078E-04
PA0027103-001	1.7854E-01	NJ0004286-001A	8.6842E-03	PA0013323-007	2.1883E-04
NJ0020923-001	1.4056E-01	NJ0004995-441C	7.2394E-03	NJ0005584-002A	2.0318E-04
NJ0026301-001	1.2740E-01	NJ0005045-001	7.0556E-03	NJ0004375-001A	1.9012E-04
NJ0005029-001A	9.9736E-02	NJ0027545-001	6.9896E-03	NJ0005363-017	1.6299E-04
PA0013323-002	8.8458E-02	NJ0030333-001	6.9876E-03	DE0050911-002	1.5168E-04
NJ0005100-001	7.9901E-02	NJ0021601-001	5.9230E-03	PA0013323-016	1.3569E-04
PA0026468-001	7.4536E-02	NJ0033022-001A	5.9191E-03	NJ0005185-002A	1.1314E-04
NJ0004219-001A	7.2746E-02	NJ0024856-001	5.8058E-03	DE0000051-004	9.8613E-05
NJ0022519-001	7.1610E-02	NJ0004278-001A	5.7937E-03	NJ0064696-001A	9.0635E-05
NJ0023361-001	7.1197E-02	PA0051713-001	5.2291E-03	DE0050601-016	8.5350E-05
NJ0024686-001	6.5488E-02	NJ0005240-001A	4.2929E-03	PA0013081-029	7.4575E-05
NJ0005100-662	5.9347E-02	NJ0005584-003A	4.0422E-03	PA0013716-001	7.2527E-05
PA0011533-015	5.7219E-02	NJ0020532-001	3.5158E-03	PA0012637-008	6.3916E-05
DE0020001-001	4.6842E-02	PA0012777-003	2.8323E-03	PA0057690-019	5.7861E-05
PA0013463-002	4.6443E-02	DE0000612-001	2.8184E-03	PA0057690-021	5.7861E-05
PA0012629-002	4.3794E-02	PA0013463-203	2.5395E-03	NJ0033022-002	5.2926E-05
DE0000051-001	3.9050E-02	DE0050911-001	2.4697E-03	NJ0033952-001A	5.0389E-05
NJ0025178-001A	3.8909E-02	NJ0005134-001A	2.3775E-03	NJ0004332-001B	4.0366E-05
PA0026701-001	3.7832E-02	DE0021555-001	2.3568E-03	NJ0005363-005	3.1131E-05
NJ0021598-001	3.6554E-02	NJ0021610-001	2.2231E-03	PA0011622-001	2.9746E-05
NJ0005401-001A	3.1947E-02	NJ0005240-002A	2.0267E-03	NJ0025411-462A	2.1178E-05
NJ0024015-001	3.1680E-02	NJ0022021-001	1.9017E-03	PA0013323-008	2.0217E-05
PA0057479-DD2	2.8296E-02	DE0000647-001	1.3074E-03	PA0012637-006	1.6974E-05
PA0012637-201	2.8031E-02	NJ0025411-461C	1.2856E-03	DE0050601-034	1.3333E-05
NJ0024660-002	2.6736E-02	NJ0004219-007	1.2670E-03	PA0011622-004	1.1400E-05
PA0012777-001	2.2064E-02	DE0020001-003	1.2556E-03	NJ0131342-001A	7.0549E-06
NJ0023507-001	2.1591E-02	DE0050962-003	1.1873E-03	PA0012777-007	6.7437E-06
DE0050962-004	2.0243E-02	NJ0005002-WTPA	1.1368E-03	NJ0005363-006	6.6812E-06
NJ0021709-001	2.0138E-02	NJ0005185-001A	1.0694E-03	NJ0000008-003	6.4344E-06
PA0026450-001	2.0040E-02	DE0020001-002	9.8862E-04	DE0000558-041	6.4309E-06
PA0013323-001	1.7109E-02	NJ0000008-001A	9.7524E-04	NJ0004391-002A	4.8856E-06
PA0027294-001	1.6954E-02	NJ0035394-003A	9.3212E-04	NJ0005401-003A	3.7411E-06
NJ0024007-001	1.6145E-02	NJ0005622-489	9.2285E-04	PA0057690-047	2.7909E-06
NJ0024678-001	1.5170E-02	NJ0004669-001A	8.8145E-04	DE0050601-033	2.6884E-06
NJ0024023-001	1.3390E-02	PA0011622-002	8.4941E-04	NJ0005100-011	2.1883E-06
PA0013463-103	1.3161E-02	PA0043818-001	6.8206E-04	NJ0004332-002A	9.0978E-09
PA0057690-012	1.3045E-02	NJ0005266-002A	4.6582E-04		

Figure 2.11 - Locations of Point Discharges in the Delaware Estuary



2.2.2.4 Tributary penta-PCB Loads

Tributary penta-PCB loads were estimated by computing the product of gaged or extrapolated daily flows at the monitoring location (as described in Section 2.2.2) and tributary specific mean wet and mean dry weather concentrations, toggled by precipitation data. In all, loads from 20 tributaries (not including the Delaware River at Trenton and the Schuylkill River, which are discussed in Section 2.3) were explicitly computed. The loads from tributaries in Zone 6 were estimated as part of the non-point source load category, by using the entire drainage area to the edge of the Delaware as the non-point source drainage area.

Table 2.9 - Estimated 577 Day penta-PCB Load by Tributary

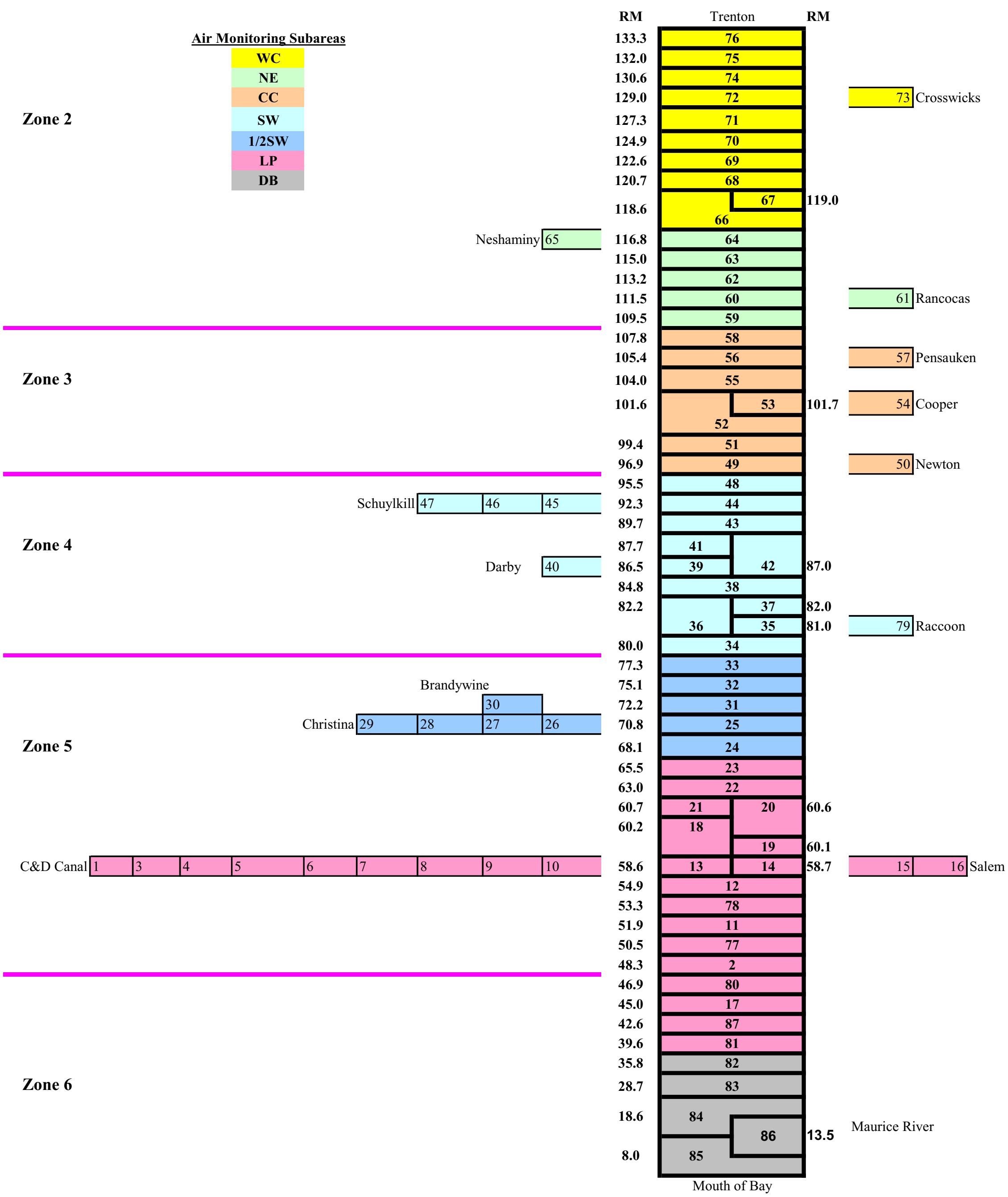
Tributary	577 Day penta-PCB Load (kg)	Tributary	577 Day penta-PCB Load (kg)
Darby	0.56	Alloways	0.12
Assunpink	0.38	Chester	0.11
Mantua	0.35	Red Clay	0.11
Cooper	0.30	Salem	0.11
Rancocas	0.23	Pennypack	0.07
Pennsauken	0.20	Christina	0.07
Frankford	0.20	Raccoon	0.06
Crosswicks	0.18	Brandywine	0.05
Big Timber	0.15	Neshaminy	0.05
White Clay	0.15	Poquessing	0.04

Although 60 tributary penta-PCB samples were collected during the calibration period, 37 results were released by the analytical laboratory in time for use in this iteration of the PCB TMDL. The remaining 23 results are still in process. As such, some tributary wet and dry weather concentrations are estimated. Specifically, the dry weather concentration for Assunpink is estimated from the mean concentration of all other tributaries, and the wet weather concentrations for Darby, Chester, Pennsauken, Cooper, Alloways, Salem, and Assunpink are estimated by multiplying their dry weather concentrations by the mean ratio of wet weather to dry weather concentration for all other tributaries. Tributary sampling is ongoing, and numerous samples have been collected after the end of the calibration period. Therefore, as more data is released by the laboratory, we anticipate refinement of the tributary loads in future phases of work.

2.2.2.5 Atmospheric Deposition penta-PCB Loads

Wet and dry atmospheric deposition was estimated using data provided by Dr. Lisa Totten of Rutgers University. Dr. Totten oversaw collection of atmospheric particulate and gas phase concentrations of PCB congeners at 6 stations over 30 sampling events between November 2001 and January 2003. Based on preliminary results, Dr. Totten estimated seasonal dry deposition rates and volume weighted rainfall concentrations for 7 subareas. The model segment assignments to specific air monitoring subareas are shown in Figure 2.12. Seasonal penta-PCB dry deposition rates and penta-PCB volume weighted mean rain concentrations are shown in Table 2.10.

Figure 2.12 - Assignment of Air Monitoring Subarea Values to Model Segments



As the remainder of the samples are analyzed, revised atmospheric deposition rates may be incorporated into future phases of work.

Table 2.10 - Penta-PCB Dry Deposition Rates and Rain Concentrations by Subarea

Subarea	Summer Dry deposition ($ng/m^2/d$)	Fall dry deposition ($ng/m^2/d$)	Winter dry deposition ($ng/m^2/d$)	Spring dry deposition ($ng/m^2/d$)	Volume weighted Concentration in rain (ng/L)
WC	0.26	0.79	0.74	0.63	0.11
NE	3.40	3.40	2.72	5.86	0.66
CC	10.22	6.70	16.20	7.71	0.66
SW	6.60	6.60	6.21	7.14	1.28
1/2SW	3.30	3.30	3.10	3.57	0.64
LP	1.05	1.05	1.05	1.05	0.20
DB	1.27	1.29	1.32	0.88	0.22

Dry deposition was applied on all days, regardless of rainfall. On days with rainfall, the total deposition is equal to the dry deposition applied on all days plus the wet deposition, as the product of the rainfall 24-hour total, segment area, and rain concentration.

2.2.2.6 Combined Sewer Overflow penta-PCB Loads

Combined Sewer Overflow (CSO) loads were estimated by computing the product of daily CSO flows and treatment plant specific mean wet weather influent concentrations measured in 1996 (DRBC 1998). We assumed that concentration at the plant influent would be comparable to the expected concentrations at the CSO outfalls overall, although individual outfalls may be subject to localized influences in the collection system.

During influent sampling, the Philadelphia Southeast plant was impacted by a spill event, so the concentration value for that facility was estimated using the mean penta-PCB concentration of the other five treatment plants with CSO systems (Philadelphia Northeast and Southwest, DELCOR, Wilmington, and Camden). Similarly, the Philadelphia Southwest plant received return water from sludge handling operations also impacted by the spill, in one of the two influent lines entering the plant. Only the penta-PCB concentration from the non-impacted influent line was used to estimate the Philadelphia Southwest CSO load.

2.3 Boundary Concentrations

Concentrations rather than loads are specified at model boundaries.

2.3.1 Delaware at Trenton

To estimate POC concentrations at the Delaware River at Trenton, we compared 71 paired flow and POC measurements collected by USGS between 1991 and 2001 (USGS 2003). We evaluated numerous approaches for relating POC concentration to flow, including 3 simple linear regressions (Figure 2.13), 3 stratified regressions using a median concentration for lower flows and linear regression of POC and flow for higher flows (Figure 2.14), a 2-tiered step function with a low flow median and high flow median, and the 7-regressor version of the Minimum Variance Unbiased Estimator (MVUE) (Cohn 1989, Gilroy 1990, Cohn 1992) as implemented in the software program ESTIMATOR 2000 (Cohn 2000) using both full and partial data sets. Predicted POC concentrations were plotted against observed POC, as shown in Figure 2.15, to determine which method provided the best prediction of observed POC from measured flow. In addition, we compared estuary POC measurements at the first station below the head of tide, to the concentrations predicted by selected methods. A simple linear regression, with one assumed outlier at the very high flow (~70,000 CFS) excluded, consistently yielded predictions that most closely matched both the 1991-2001 period of record, the calibration period data set at the head of tide, and the observed estuary data at the first station below the head of tide. This regression was therefore used to compute the daily POC concentration for the Delaware River at Trenton for each day of the continuous simulation period, using the measured flow for that day.

Figure 2.13 - Three Linear Regressions of POC versus Flow for the Delaware River at Trenton

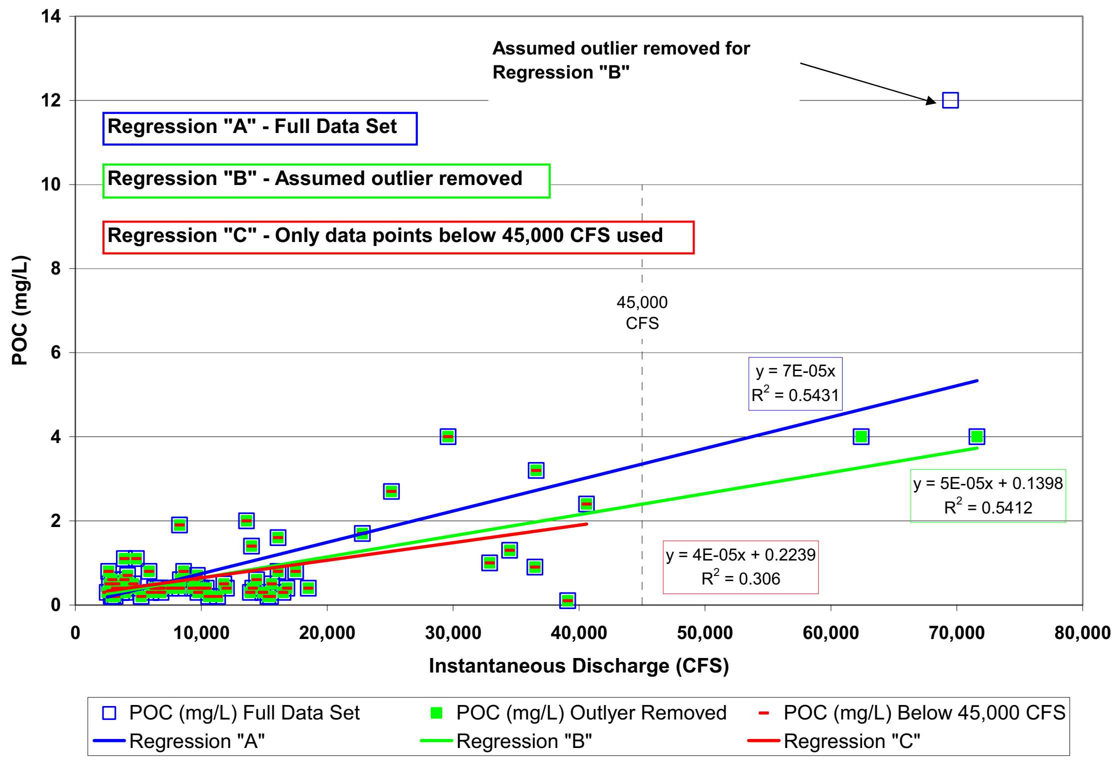


Figure 2.14 - Stratified Relationships of POC versus Flow for the Delaware River at Trenton

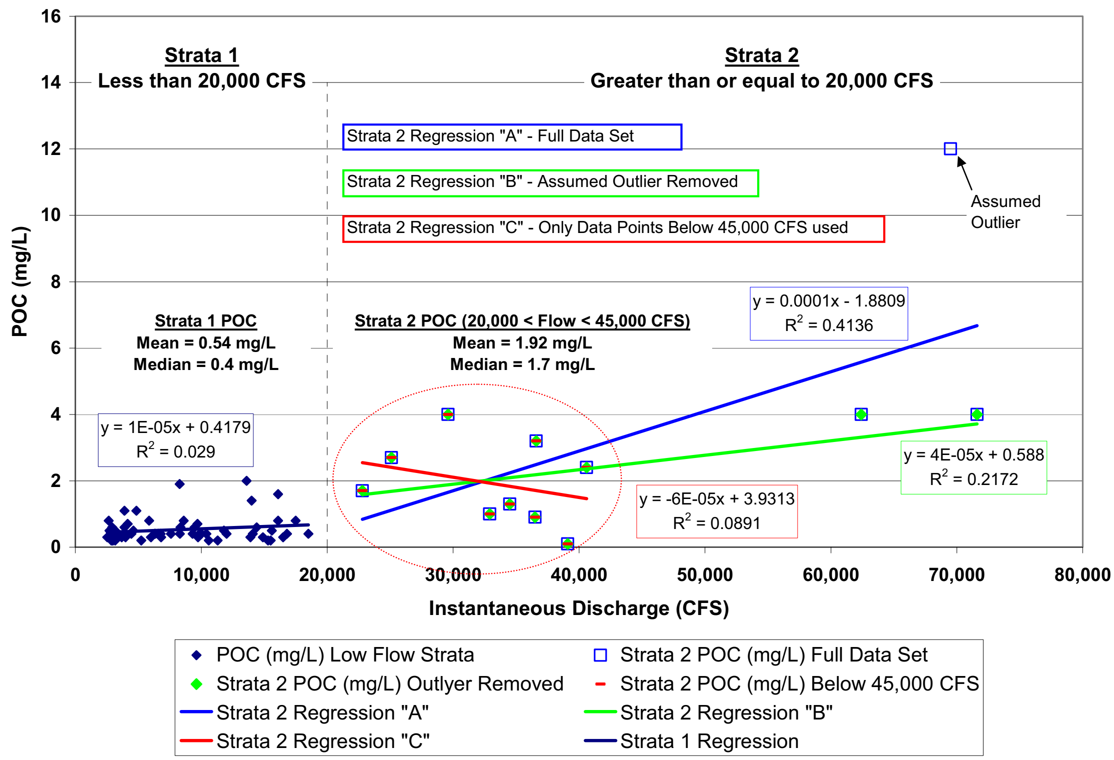
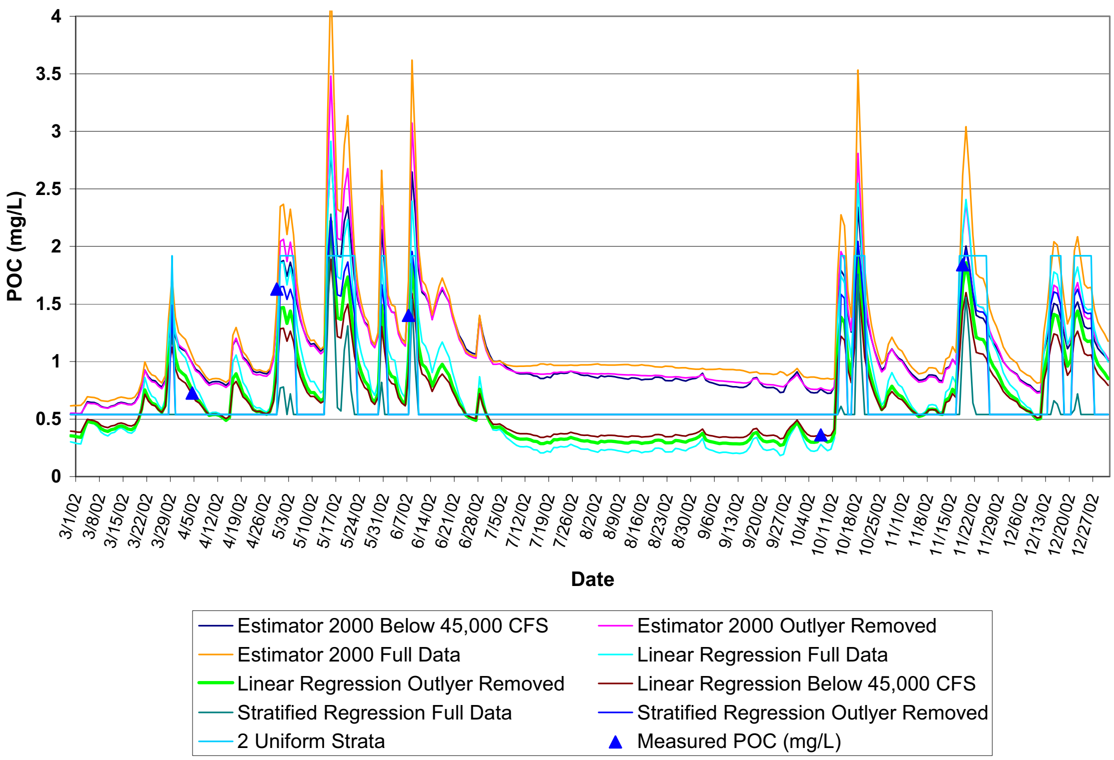


Figure 2.15 - Comparison of Predicted POC concentrations using 9 different methods to observed POC concentrations from the Delaware at Trenton



Based on the analysis of paired POC and chlorophyll-a measurements in the main stem (Section 2.2.1.2), we observed that our assumed carbon to chlorophyll ratio of 40 resulted in a mean BIC/POC ratio of 0.1633. We assumed that this same relationship would hold true for the Delaware River at Trenton, and subdivided POC into BIC and PDC as follows:

$$BIC = 0.1633 \times POC$$

$$PDC = (1 - 0.1633) \times POC$$

For penta-PCBs, dry and wet weather penta-PCB concentrations for the Delaware River at Trenton were estimated from samples collected in 2000 by USGS and in 2002 by USGS for DRBC. Results from 3 samples collected on a rising hydrograph during wet weather and 2 samples collected during dry weather were available for estimation of mean wet weather and dry weather concentrations. Dissolved and particulate PCBs were measured in the samples collected for DRBC. These fractions were summed to yield a whole matrix PCB concentration, similar to the results provided by USGS under the NAWQA program. Since the USGS data collected under the NAWQA program incorporated higher detection limits than are currently available using method 1668A, concentrations of non-detected congeners were estimated by assigning a congener concentration equal to ½ the detection limit. From these results we specified a wet weather and dry weather concentration on a daily basis for the Delaware River at Trenton. For days with a 24-hour rainfall total less than 0.1", the dry weather concentration was specified. For days with 24-hour rainfall total of 0.1" or more, the wet weather concentration was specified.

Sample collection at the Delaware River model boundary is ongoing. A larger data set will be available for specifying boundary concentrations in future phases of work.

2.3.2 Schuylkill

To estimate POC concentrations in the Schuylkill River at head of tide, we compared 28 sample records including concurrently collected flow, POC, and TSS measurements. Measurements were collected as part of several different studies by USGS, the Academy of Natural Sciences, and DRBC. Some additional data values consisting of paired flow and TSS and paired flow and POC measurements were also considered. Given the limited paired POC and flow data, and the variability of the POC measurements, we also evaluated regressions of TSS to flow, with secondary regressions of POC to TSS. Ultimately we considered numerous methods for relating POC to flow, including (**A**) linear regression of POC to TSS and linear regression of TSS to flow, (**B**) a 2-tiered step function with a POC concentration of 0.58 mg/L at flows < 10,000 CFS and 24.9 mg/L at flows ≥ 10,000 CFS, (**C**) an exponential regression of POC to flow, (**D**) POC as a function of flow from the 7-regressor version of the Minimum Variance Unbiased Estimator (MVUE) (Cohn 1989, Gilroy 1990, Cohn 1992) as implemented in ESTIMATOR 2000 (Cohn 2000), and (**E**) a linear regression of POC to flow for flows < 10,000 CFS. Other relationships including linear regression of POC from flow for the full flow regime and linear regression of POC to TSS with a 2-tiered TSS step function were considered initially, but failed to demonstrate a reasonable relationship between POC and flow. Again, predicted POC concentrations were plotted against observed POC, as shown in Figures 2.16 and 2.17, to determine which method provided the best prediction of observed POC from measured flow. Since most of the POC observations were grouped at low concentrations, with 1 observation at a high concentration, no method demonstrated an especially strong and reasonable relationship between POC and flow. Ultimately we selected a linear regression of TSS from flow for the full flow regime with a secondary regression of POC from TSS (**Line "A"**). This method tracks the observed relationships between POC and TSS and between TSS and flow, and provides some sense of increasing POC with increasing flow without the artificiality of the step functions. This relationship should be revisited as a more comprehensive database is assembled.

Figure 2.16 - Comparison of Predicted POC concentrations using 5 different methods to observed POC concentrations from the Schuylkill River

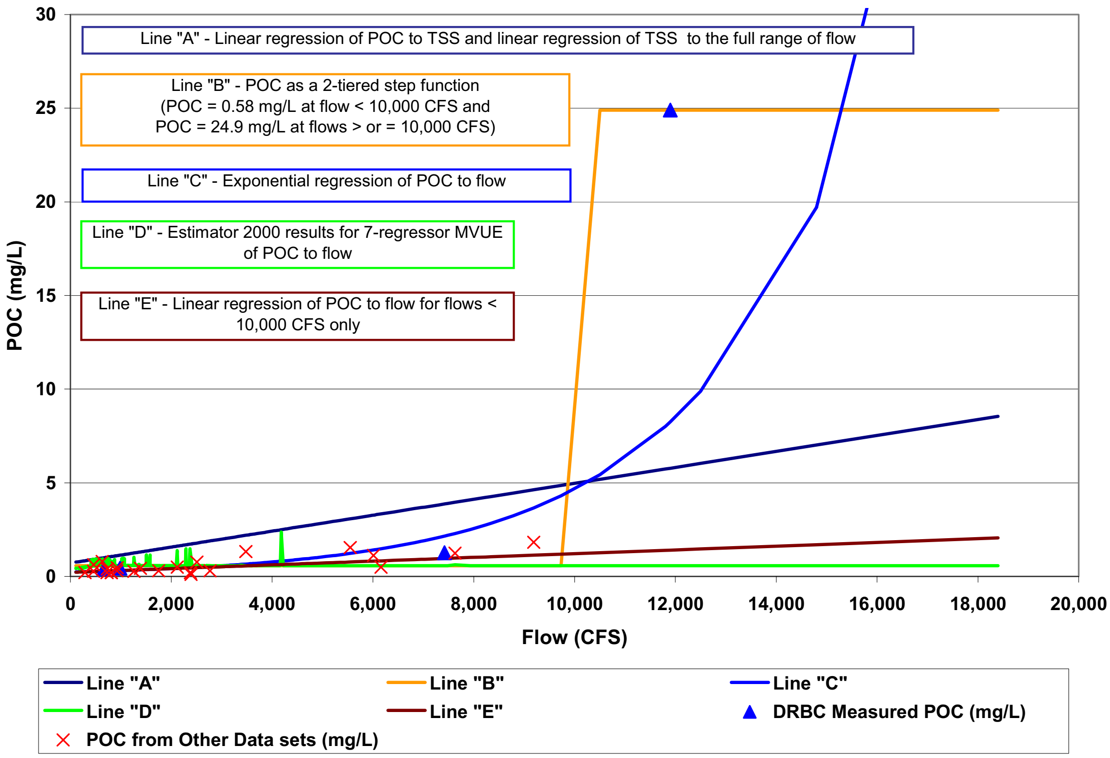
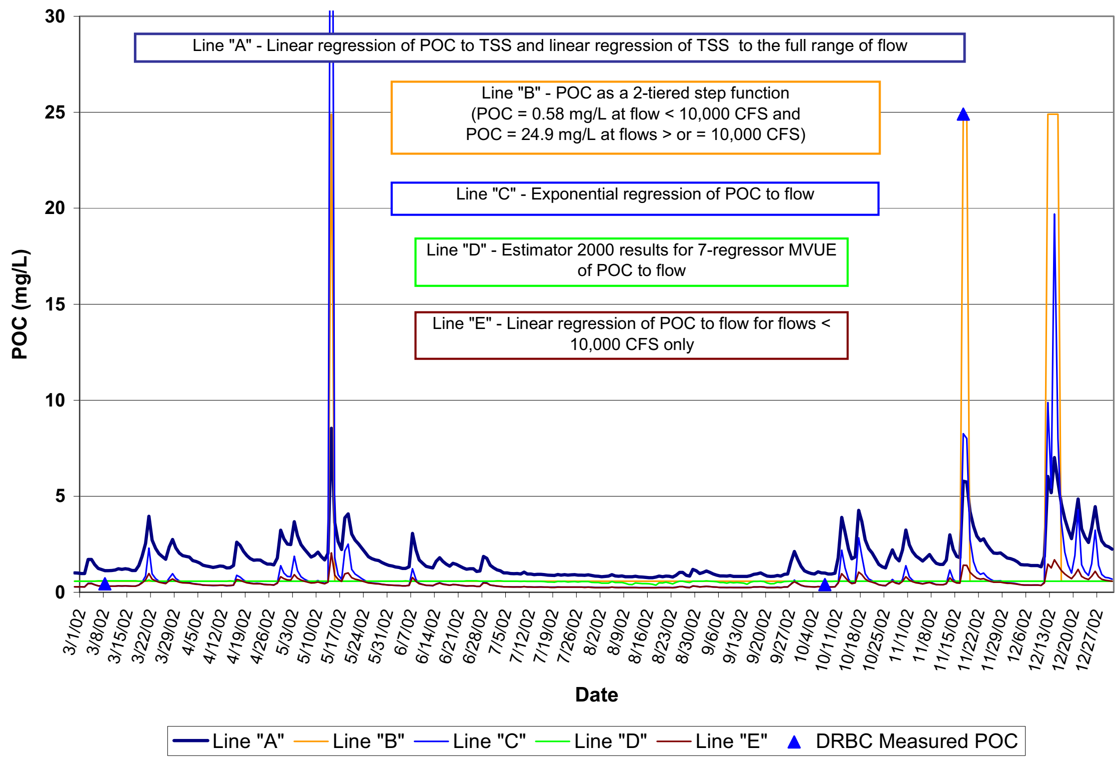


Figure 2.17 - Daily estimated POC concentrations using 5 different methods and Observed POC data from the Schuylkill River



Again, POC was subdivided into BIC and PDC fractions using the method described in the previous section.

For penta-PCBs, dry and wet weather penta-PCB concentrations for the Schuylkill River were estimated from samples collected in 2000 (by USGS) and in 2002 (by USGS for DRBC). Results from 3 samples collected on a rising hydrograph during wet weather and 3 samples collected during dry weather were available for estimation of mean wet weather and dry weather concentrations. Dissolved and particulate PCBs were measured in the samples collected for DRBC. These fractions were summed to yield a whole matrix PCB concentration, similar to the results provided by USGS under the NAWQA program. Since the USGS data collected under the NAWQA program incorporated higher detection limits than are currently available using method 1668A, concentrations of non-detected congeners were estimated by assigning a congener concentration equal to ½ the detection limit. From these results we specified a wet weather and dry weather concentration on a daily basis for the Schuylkill River. For days with a 24-hour rainfall total less than 0.1", the dry weather concentration was specified. For days with 24-hour rainfall total of 0.1" or more, the wet weather concentration was specified.

Sample collection at the Schuylkill River model boundary is ongoing. A larger data set will be available for specifying boundary concentrations in future phases of work.

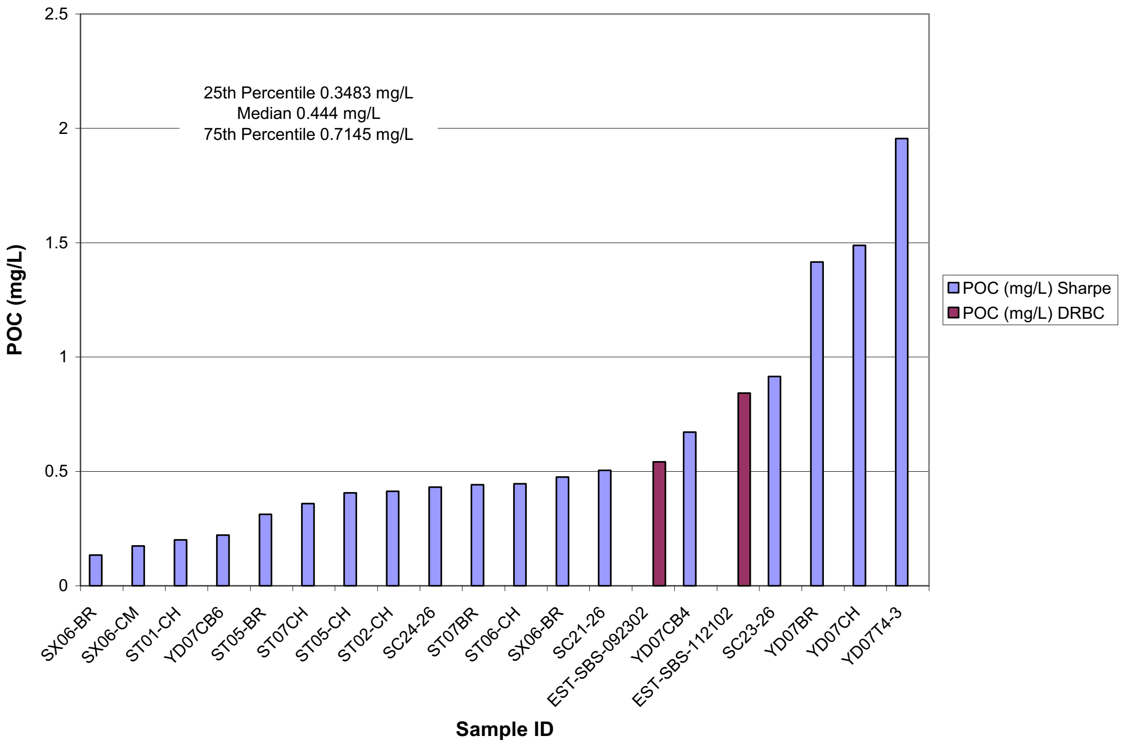
2.3.3 C&D Canal

The State of Delaware had collected TOC and DOC measurements at 3 stations within the C&D canal. Although POC can be estimated as the difference between TOC and DOC, in many cases DOC was greater than or equal to TOC in the Delaware C&D Canal data set, potentially resulting from concentrations near the lower quantitation limit for the analytical methods used. Alternatively, we specified the C&D canal concentration at 3.135 mg/L for all simulation days, which was the mean of two measurements collected by DRBC within the canal. More attention should be focused on characterizing the C&D canal concentrations in future phases of work. POC was subdivided into BIC and PDC as discussed in previous sections.

2.3.4 Ocean Boundary

To estimate the ocean boundary POC concentration, we identified 20 POC measurements from 2 different data sets collected near the mouth of Delaware Bay, as shown in Figure 2.18. The majority of the data was collected by Dr. Jonathan Sharpe of the University of Delaware, with 2 samples collected by DRBC. Results showed a median concentration of 0.44 mg/L. The boundary concentration was therefore set at 0.44 mg/L POC for all simulation days, with individual BIC and PDC fractions being estimated as discussed in the previous sections.

Figure 2.18 - POC measurements from the mouth of Delaware Bay



3 Ambient Water Quality and Sediment

3.1 Updates and Revisions

The following updates to the Calibration Report dated December 2003 have been made to this report.

In ambient water penta-PCB figures:

- Ambient water particulate, dissolved and total penta-PCB data for March 15, 2002 have been added.

- Ambient water dissolved and total penta-PCB data for April 11, 2002, April 22, 2002, and June 19, 2002 have been added .

In appendices 3A, 3B and 3C, data have been updated for April 22, 2002, June 19, 2002, and November 21, 2002.

3.2 Results

3.3 Temporal and Spatial Design of Ambient Water Column Monitoring

To support development of the Delaware Estuary Polychlorinated Biphenyl Water Quality Model (DELPCB), accurate measurements of PCB concentrations and organic carbon in the Delaware Estuary were required. Ambient water samples were collected from the mainstem Delaware Estuary for the analysis of particulate and dissolved PCBs, total suspended solids, dissolved organic carbon (DOC), chlorophyll a, and particulate organic carbon (POC). The data collected allowed initial quantitation of dissolved and particulate PCB levels as well as organic carbon in the mainstem Delaware Estuary.

The objective of the monitoring was to measure PCB concentrations at low, high and intermediate flows in the portions of the Delaware Estuary listed for TMDL development. Initially the monitoring focused on Delaware Estuary Zones 2, 3, 4 and 5 but was expanded to include Zone 6 upon the recommendations of the PCB Model Expert Panel. One data set was obtained in September 18, 2001. The data from this date was used for water column initial condition in the model. Sampling started again on March 15, 2002 and continued until March 19, 2003. The data from these monitoring dates was used as calibration targets in the model. The sampling in Zone 2, 3, 4 and 5 was conducted within the limits of available funding. Fifteen main stem channel sites were sampled under high, low, and intermediate flows for a total of eight sampling events.

The additional monitoring in Zone 6 and lower Zone 5 was conducted concurrent with previously scheduled Delaware Estuary monitoring. The nine sample sites were sampled over five additional sampling events. The overall monitoring of ambient water column consisted of twenty-four sample stations in the estuary between river miles 6.5 and 131.1 during low, high and intermediate flow conditions. The sampling stations are listed in Table 3.1 and shown in Figure 3.1.

Table 3.1 - Sampling Stations

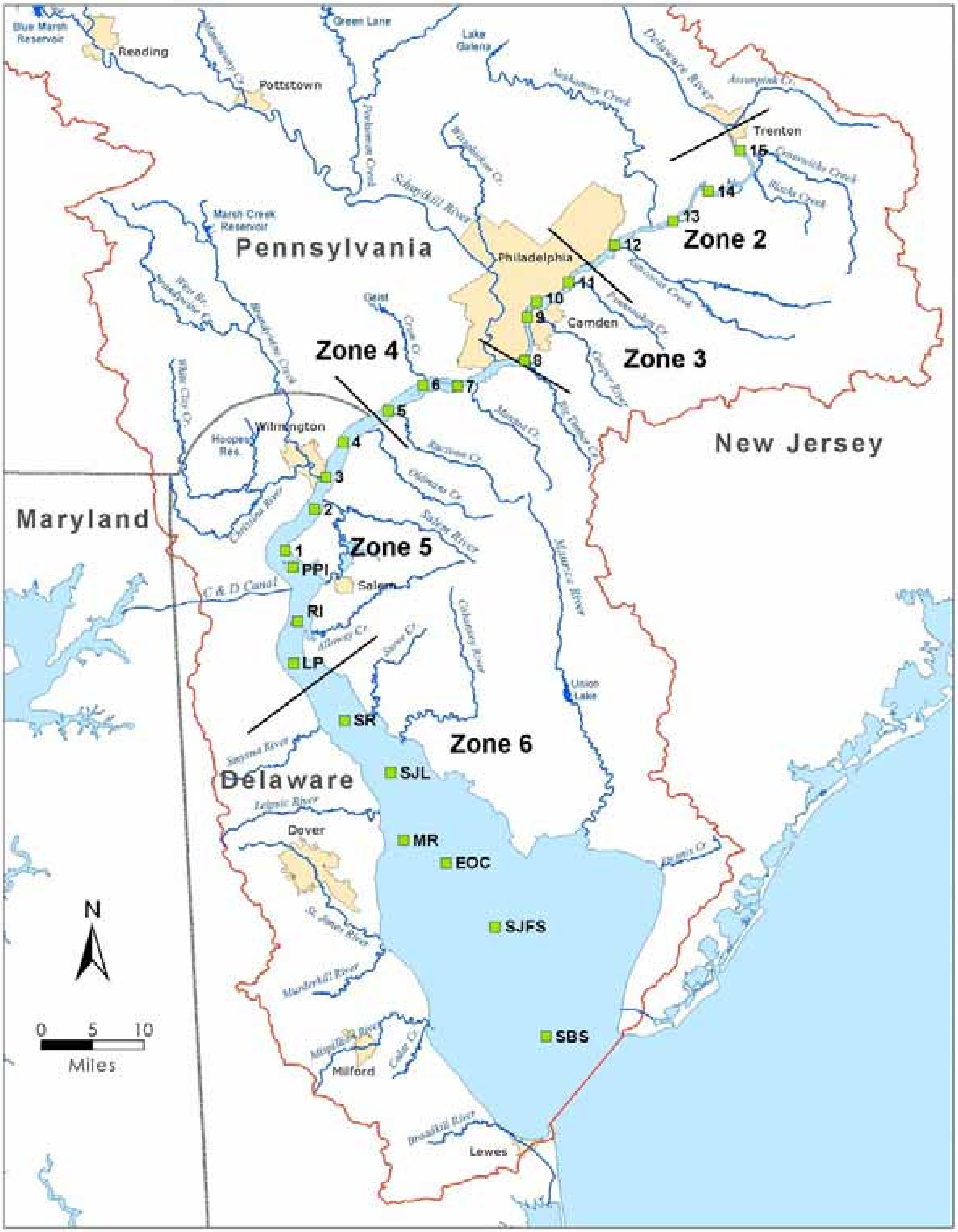
SITE	RIVER MILE	SITE DESCRIPTION	DELAWARE ESTUARY ZONE	LATITUDE AND LONGITUDE
SBS	6.5	South Brown Shoal	Zone 6	38.54000 75.06049
SJFS	16.5	South Joe Flogger	Zone 6	39.04928 75.11311
EOC	22.75	Elbow of Cross Ledge	Zone 6	39.10802 75.16460
MR	31.0	Mahon River	Zone 6	39.11030 75.22020
SJL	36.6	Ship John Light	Zone 6	39.18100 75.23050
SR	44.0	Smyrna River	Zone 6	39.22650 75.28200
LP	48.2	Liston Point	Zone 6	39.27180 75.33360
RI	54.9	Reedy Island	Zone 5	39.30770 75.33350
PPI	60.6	Pea Patch Island	Zone 5	39.35580 75.33900
1	63.0	North of Pea Patch Isl	Zone 5	39.61430 75.57706
2	68.1	South of Del. Mem. Br.	Zone 5	39.67306 75.52414
3	70.8	North of Del. Mem. Br.	Zone 5	39.71908 75.50425
4	75.1	Opposite Oldmans Pt.	Zone 5	39.76868 75.47302
5	80.0	Opposite Mouth of	Zone 4	39.81337 75.39057

		Marcus Hook Cr.		
6	**84.0**	**Eddystone**	**Zone 4**	**39.85055 75.32709**
7	**87.9**	**Paulsboro**	**Zone 4**	**39.84871 75.26406**

Table 3.1 - Sampling Stations (*continued*)

SITE	RIVER MILE	SITE DESCRIPTION	DELAWARE ESTUARY ZONE	LATITUDE AND LONGITUDE
8	95.5	Opposite Mouth of Big Timber Creek	Zone 3	39.88522 75.14074
9	99.4	Penn's Landing	Zone 3	39.94547 75.13598
10	101.6	Opposite Cooper Point	Zone 3	39.96781 75.11932
11	105.4	Mouth of Pennsauken Cr.	Zone 3	39.99477 75.05978
12	111.5	Mouth of Rancocas Cr.	Zone 2	40.04830 74.97588
13	117.8	Burlington Bristol Br.	Zone 2	40.08142 74.86790
14	122.0	Florence	Zone 2	40.12398 74.80351
15	131.1	Biles Channel	Zone 2	40.18156 74.74505

Figure 3.1 - Ambient Monitoring Locations



3.3.2 Sampling Process Design

All samples were collected at a depth of 0.6 of the depth of the water column using a 10 liter Niskin water bottle. The water samples were collected by staff from the Delaware River Basin Commission (DRBC) and the Delaware Department of Natural Resources and Environmental Control. The locations sampled are listed in Table 3.1. One field blank and one trip blank was collected on each sampling day. At each location, samples were collected at three sites on a transect across the river, and composited into one sample per location. Samples were also collected from the site composites for solids, dissolved organic carbon, particulate organic carbon, chlorophyll-a, and turbidity. Air and water temperature, pH, salinity, conductivity, dissolved oxygen, and water transparency were also measured at each site on the transects at the time of sampling. Solids and organic carbon samples were shipped to the Chesapeake Biological Laboratory of the University of Maryland for analyses, while the turbidity and chlorophyll A samples were transported by the DNREC field crew to the DNREC laboratory for analysis. The composite sample from the river locations were shipped to Axys Analytical Services, Ltd. for PCB analysis.

3.3.3 Analytical Methods

Samples were analyzed for 124 PCB congeners, solids, POC, DOC, turbidity and chlorophyll-a as shown in Tables 3.2 below. Sample filtration, for dissolved constituents, was performed by the analytical laboratory.

Table 3.2 - Summary of Analytical Parameters and Matrices

Analytical Parameter	Method	Matrix Analyzed
Particulate PCBs	Method 1668 Revision A : Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS	Solids retained on 1.0 μm nominal pore size glass fiber filter.
Dissolved PCBs	Method 1668 Revision A	Filtrate passed through 1.0 μm nominal pore size glass fiber filter.
Total Suspended Solids	Method No. 2540 D Standard Methods for the Analysis of Water and Wastewater, 19th Ed.	Solids retained on 0.7 μm glass fiber filter.
Turbidity	Method 180.1, U.S. EPA, 1983	Whole water sample
POC	Method 440.0 Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis	Solids retained on 0.7 μm glass fiber filter.
DOC	Method No. 5310 C Standard Methods for the Analysis of Water and Wastewater, 19th Ed.	Filtrate passed through 0.7 μm glass fiber filter.
Chlorophyll -a	Method 445 *In Vitro* Determination of Chlorophyll-a and pheophytin a in Marine and Freshwater Phytoplankton by Fluorescence	Solids retained on filter.

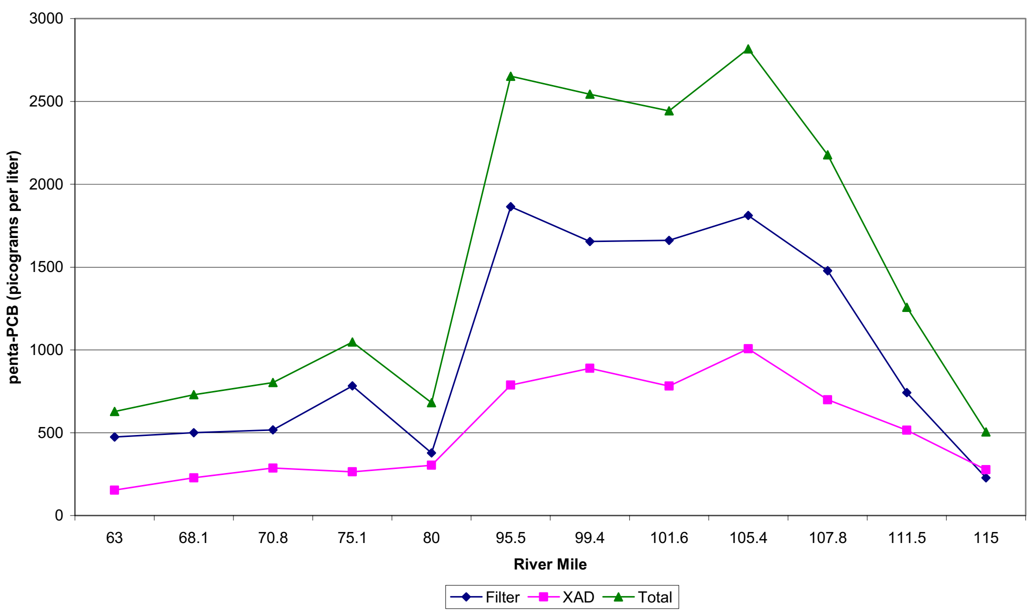
3.4 Monitoring Data

The information contained in this report is material received by the DRBC from analytical laboratories as of July 2003. Particulate organic carbon (POC) and PCB monitoring data are listed by sample date in Appendices 3A, 3B and 3C. Graphs of the particulate-PCB (filter), dissolved-PCB (XAD), and penta – PCB (total) data are also presented in Figures 3.2 through 3.8. The graphs are numbered from lowest to highest mean daily river flow at Trenton on the sampling dates. (See Section 3.3.1 for a descriptions of the penta-PCB components)

Figures 3.2 through 3.8 indicate that in general higher concentrations of penta-PCB are observed in low flow sampling dates. As the river flow increases the concentration of penta-PCB decreases. In the lower flow sampling events, the concentration of penta-PCB shows a pattern of elevated PCB between river miles 80 and 110 (Figures 3.2, 3.3, and 3.4) indicating PCB loadings in the urbanized areas of the river. A similar pattern of penta-PCB distribution is not observed in the higher flow sampling events (Figures 3.6, 3.7 and 3.8). In the higher flow sampling events, penta-PCB concentrations are lower and more evenly distributed over the sample area probably from dilution of PCB during high flow conditions.

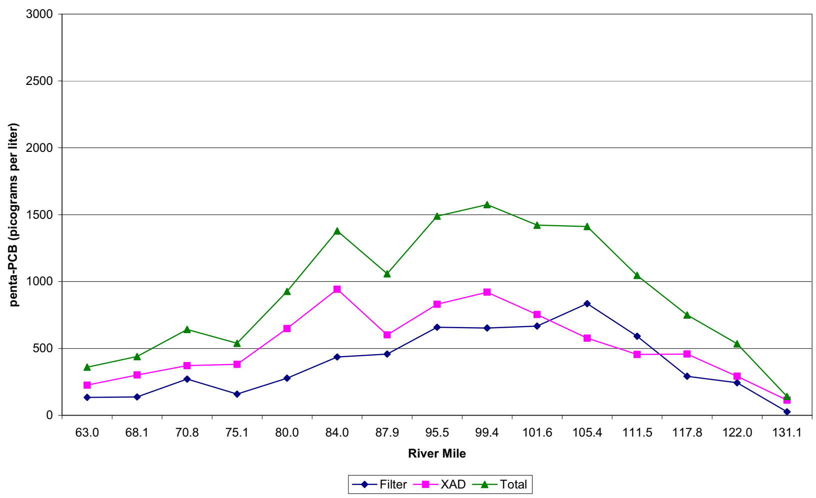
Also noteworthy is that dissolved and particulate penta-PCB are generally equivalent under intermediate flow conditions (Figure 3.7). The similar concentrations of dissolved penta-PCB (XAD) and particulate penta-PCB (filter) in the water column are not unexpected since total dissolved penta-PCB is defined as the sum of both truly dissolved and DOC bound penta-PCB. Therefore, higher concentrations in the total dissolved fraction are to be expected than would be the case in a truly dissolved fraction alone. However, dissolved and particulate PCB concentrations differ under the lowest and highest flow conditions measured. The particulate penta-PCB (filter) concentrations are higher under the lowest flow condition (Figure 3.2). The dissolved penta-PCB (XAD) concentrations are higher under the highest flow concentrations (Figure 3.8). The particulate penta-PCB (filter) fluctuate more with the river flow which is not unexpected.

Figure 3.2 - Ambient Water penta-PCBs, September 19, 2001



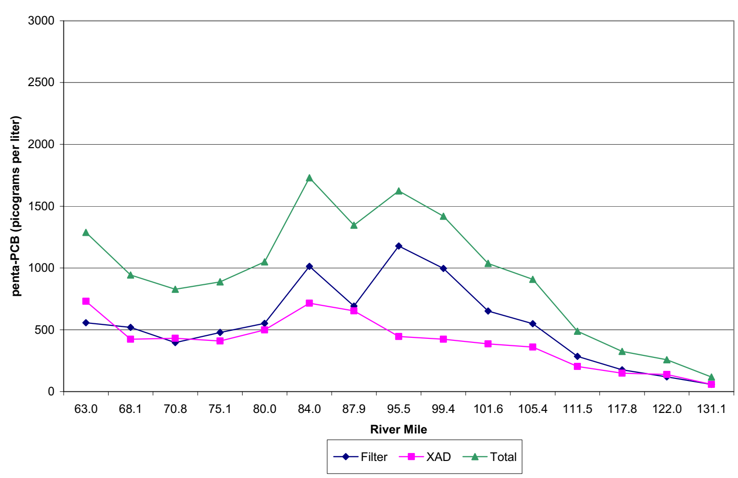
Mean Daily Flow 3,020 cfs
September 19, 2001

Figure 3.3 - Ambient Water penta-PCBs, October 8, 2002



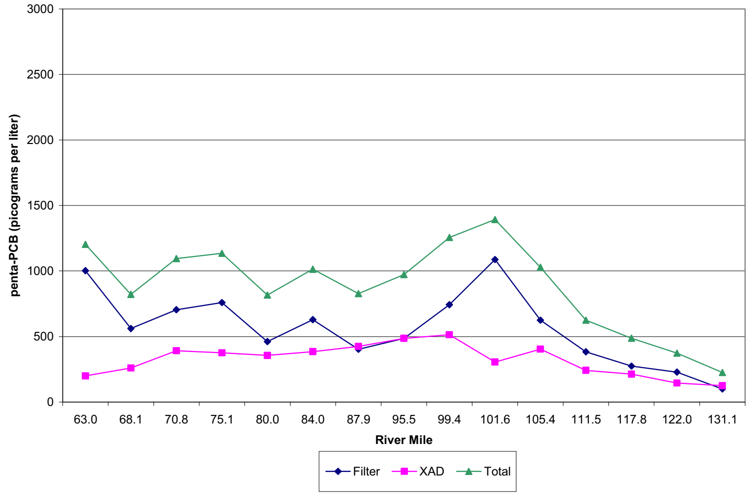
Mean Daily Flow 3,560 cfs
October 8, 2002

Figure 3.4 - Ambient Water penta-PCBs, April 11, 2002



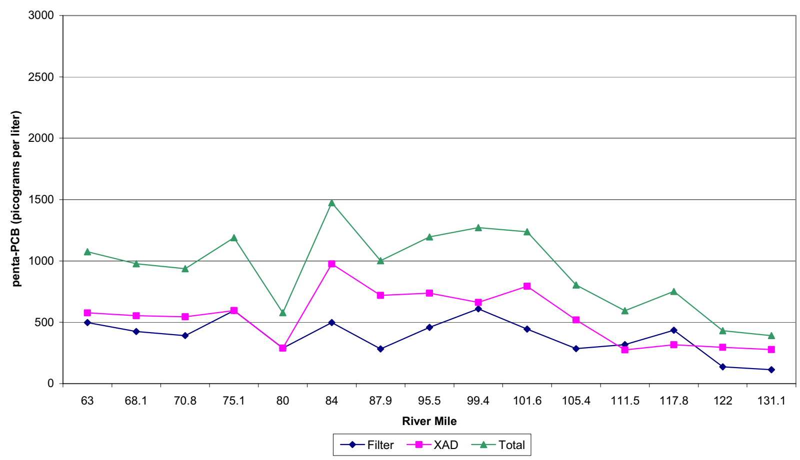
Mean Daily Flow 7,980 cfs
April 11, 2002

Figure 3.5 - Ambient Water penta-PCBs, April 22, 2002



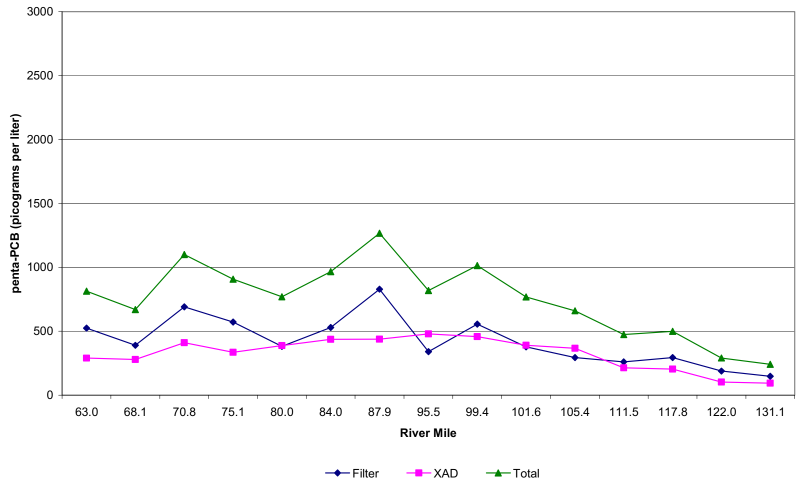
Daily Mean Flow 8,860 cfs
April 22, 2002

Figure 3.6 - Ambient Water penta-PCBs, June 19, 2002



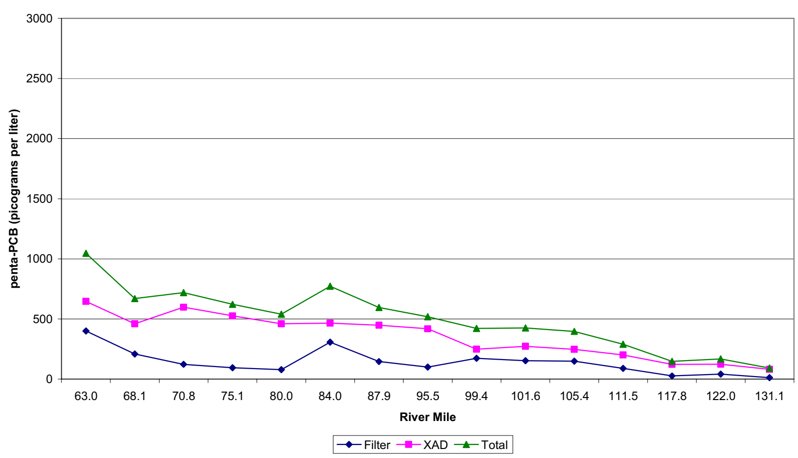
Daily Mean Flow 14,800 cfs
June 19, 2002

Figure 3.7 - Ambient Water penta-PCBs, May 6, 2002



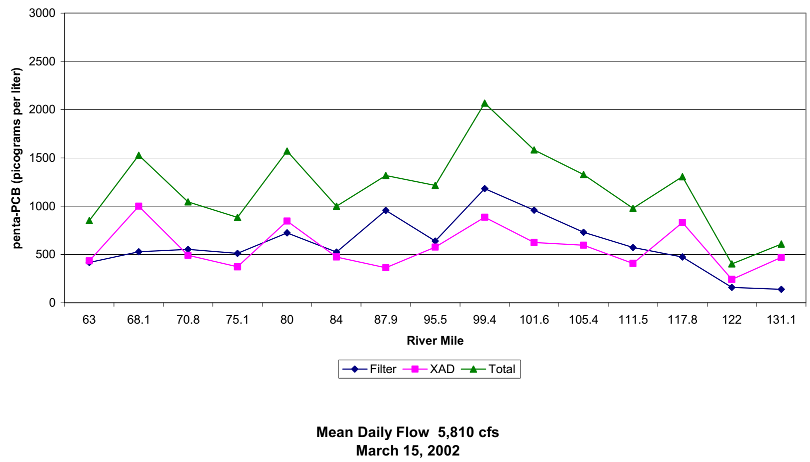
Mean Daily Flow 16,100 cfs
May 6, 2002

Figure 3.8 - Ambient Water penta-PCBs, March 19, 2003



Mean Daily Flow 36,100 cfs
March 19, 2003

Figure 3.9 - Ambient Water penta-PCBs, March 15, 2002



3.5 Calibration Targets

The PCB model calibration targets for water column (WC) and surficial sediment segment are a compilation of observed and derived data. The calibration targets used in the model are listed in three tables in Appendices A, B and C.

3.5.1 Water Column Calibration Targets

The water column data consists of total dissolved penta-PCB, particulate penta-PCB, the sum of all penta-PCB (total), and particulate organic carbon (POC) measured in ambient waters of the Delaware Estuary during the DRBC sampling period. All results for penta-PCB include the same 33 penta-congeners. A description of each component of PCBs in the water column data is as follows:

- The penta-PCB (total) in the water column is the sum of truly dissolved penta-PCB and DOC bound penta-PCB as well as particulate penta-PCB in the water column.

- The total dissolved penta-PCB is the sum of truly dissolved and DOC bound penta-PCB in the water column which is measured in the XAD fraction of Method 1668a.

- The WC-particulate penta-PCB is particulate bound penta-PCB in the water column which is measured in the > 1.0 µm filter fraction of Method 1668a.

Biotic carbon (BIC) in the calibration targets is derived from observed POC data based on a calculated estimate of the percent of POC that is BIC in the estuary. POC was measured concurrently with the PCB measurements. The estimate of the percent of POC that is BIC in the estuary was calculated at 12.25, 16.33, and 20.42% for carbon to chlorophyll-a ratios of 30, 40 and 50, respectively. These percentages were calculated based on the mean BIC/POC ratio for each carbon to chlorophyll-a ratio using observed chlorophyll-a data and observed POC data. Particulate Detrital Carbon (PDC) in the calibration targets is POC minus BIC. (See Section on Carbon to Chlorophyll Ratio)

3.5.2 Sediment Calibration Targets

The sediment data consists of penta-PCB, total organic carbon (TOC) and inorganic suspended solids (ISS) derived from several studies of sediment in the Delaware Estuary by the DRBC, NOAA, A.D. Little Inc. and Corp of U.S. Army Engineers. (See Section on Short Term Calibration Results) The sediment penta-PCB values are Zone medians of penta-PCB concentrations by dry weight sediment for each Zone converted to bulk volume (pg/L) to obtain the units used in the model. The TOC and ISS values are 13 bin rolling weighted averages of observed data.

For the 575 day short-term water quality model calibration, the sediment calibration "targets" are more accurately defined as sediment initial conditions. The details of the data averaging methods selected to define both the sediment penta-PCB and POC (essentially equivalent to TOC for the sediment bed) are presented in Section 3.4.2.

In order to normalize PCB for organic carbon in both the water column and sediment, R_1 and R_2 values were calculated for each segment of the model. R_1 is water column particulate-penta-PCB divided by the water column POC. R_2 is the sediment penta-PCB divided by sediment-TOC. These values are listed in Appendices A, B and C.

3.6 Initial Conditions

The WASP model framework requires that the user specify the starting concentration for each water column and sediment segment.

3.6.1 Water Column

Water column segments were set to the concentrations measured on 9/18/01 where the sample station was within the segment limits. We assumed a BIC/POC ratio of 16.33%, which corresponds to a *C/Chl* ratio of 40. The boundary segments for the Delaware at Trenton, Schuylkill, C&D Canal, and Ocean Boundary were set equal to the boundary concentrations on the first day of simulation (9/1/2001). Values for all other segments were linearly interpolated between the nearest upstream and downstream segments. Lateral segments other than the C&D canal and Schuylkill were set equal to the mainstem segment into which they discharge.

3.6.2 Sediment

Sediment initial concentrations for the penta-PCBs, PDC, and inorganic solids (ISS) were estimated using existing surficial sediment data collected by DRBC, NOAA, the U.S. Army

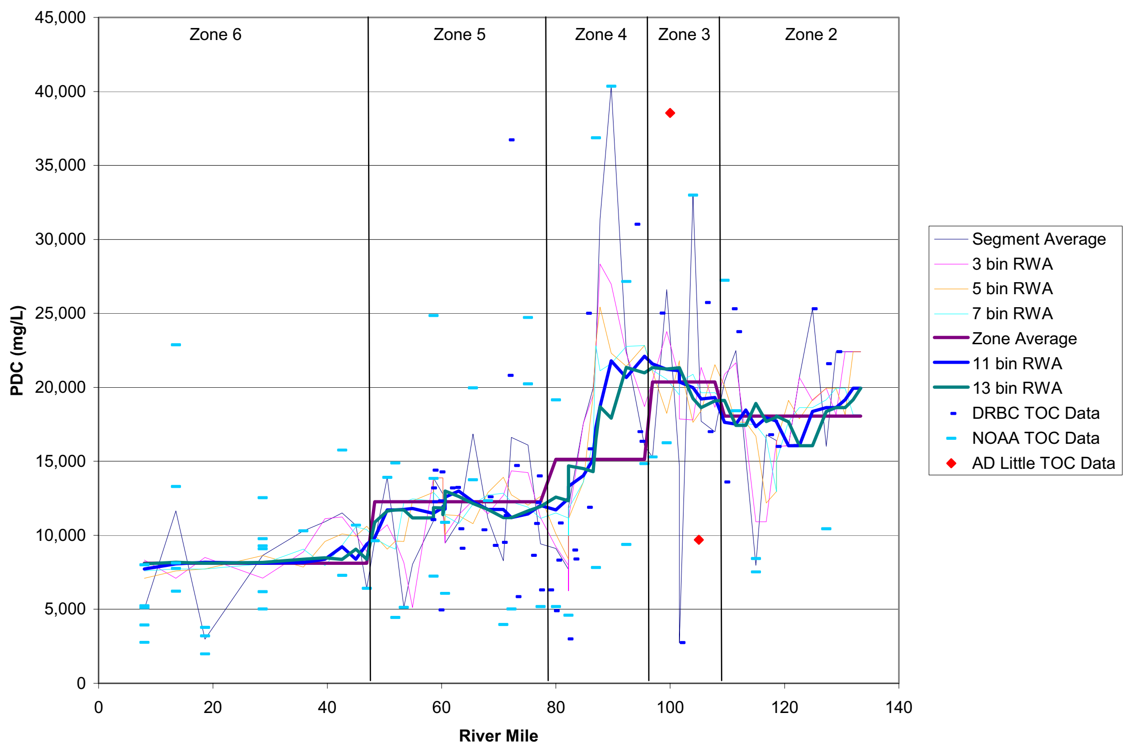
Corps of Engineers, and A.D. Little associates. Table 3.3 shows the available data for each model segment and zone.

Table 3.3 - Inventory of Sediment Sample Results for Specifying Sediment Initial Conditions

Sediment Segment	Corresponding WC Segment	River Mile	Zone	No. of Sediment Samples				
				DRBC	NOAA	COE	AD Little	Total
163	76	133.3	2					
162	75	132	2					
161	74	130.6	2					
159	72	129	2	1				**1**
158	71	127.3	2	1	1			**2**
157	70	124.9	2	1				**1**
156	69	122.6	2					
155	68	120.7	2	1				**1**
153	66	118.6	2	1				**1**
154	67	118.6	2					
151	64	116.8	2	1				**1**
150	63	115	2		2			**2**
149	62	113.2	2					
147	60	111.5	2	2	1			**3**
146	59	109.5	2	1	1			**2**
145	58	107.8	3	1				**1**
143	56	105.4	3	1			1	**2**
142	55	104	3		1			**1**
139	52	101.6	3	1				**1**
140	53	101.6	3					
138	51	99.4	3	1	1		1	**3**
136	49	96.9	3		1			**1**
135	48	95.5	4	2	1			**3**
131	44	92.3	4	1	2			**3**
130	43	89.7	4		1			**1**
128	41	87.7	4					
129	42	87	4		2	1		**3**
126	39	86.5	4					
125	38	84.8	4	3				**3**
122	35	82.2	4					
123	36	82.2	4	3	1			**4**
124	37	82.2	4					
121	34	80	4	4	2	1		**7**
120	33	77.3	5	3	1			**4**
119	32	75.1	5	2	2			**4**
118	31	72.2	5	4	1			**5**
112	25	70.8	5	2	1			**3**
111	24	68.1	5	3	1			**4**
110	23	65.5	5		2			**2**
109	22	63	5	3				**3**
107	20	60.6	5	3	2			**5**
108	21	60.6	5					
105	18	60.2	5					
106	19	60.2	5					
100	13	58.6	5	5	3			**8**
101	14	58.6	5					
99	12	54.9	5					
165	78	53.4	5		1			**1**
98	11	51.9	5		2			**2**
164	77	50.5	5		1			**1**
89	2	48.3	5		1	1		**2**
167	80	46.9	6		1			**1**
104	17	45	6		1			**1**
174	87	42.6	6		2			**2**
168	81	39.6	6					
169	82	35.8	6		1			**1**
170	83	28.7	6		6			**6**
171	84	18.6	6		3			**3**
173	86	13.5	6		5			**5**
172	85	8	6		5			**5**

In order to estimate sediment values in segments without sample results, and to address sediment heterogeneity, several approaches for interpolating and grouping sediment data were tested. These approaches included zone median values, zone mean values, and rolling weighted means using several different bin sizes. Ultimately, we determined that a 13 bin rolling weighted mean for PDC and ISS yielded the most reasonable sediment results for these values, and a zone median yielded the most reasonable results for penta-PCB. Furthermore, zone median penta-PCB specification is consistent with establishment of a zone by zone TMDL anticipated for this project. A 13 bin rolling weighted average PDC concentration allows for specification of each segment while maintaining and more accurately portraying the gradual shift in sediment composition from the head of tide to the mouth of the bay evidenced by the data. Figure 3.9 shows a comparison of several different methods for specifying sediment PDC concentrations.

Figure 3.9 - Comparison of Methods for Specifying Sediment Initial PDC Values



Since different data sets were analyzed for different numbers of penta-PCB congeners, it was necessary to identify an appropriate scaling factor to adjust all the data sets to the same basis. For example, the NOAA data set included analysis of 4 penta-PCB congeners, while the DRBC data set included analysis of 33 penta-PCB congeners. To estimate this scaling factor, we sub-sampled the DRBC results using only the congeners analyzed in the other data sets, and compared these results to the results using the sum of the DRBC congeners. A strong linear relationship suggests that the other data sets could be scaled up by multiplying the penta-PCB results by the slope of a line fit through those data points. Figure 3.10 shows this analysis conducted for the NOAA data set. Thus by multiplying the NOAA penta-PCB results by a factor of 2.8376, we can approximate what those results would have been if 20 congeners had been analyzed. Similar comparisons were conducted for both the Corps of Engineers and A.D. Little data sets as well.

Figure 3.10 - Comparison of the penta-PCB as the sum of DRBC congeners and the Sum of NOAA Congeners using the DRBC data Set

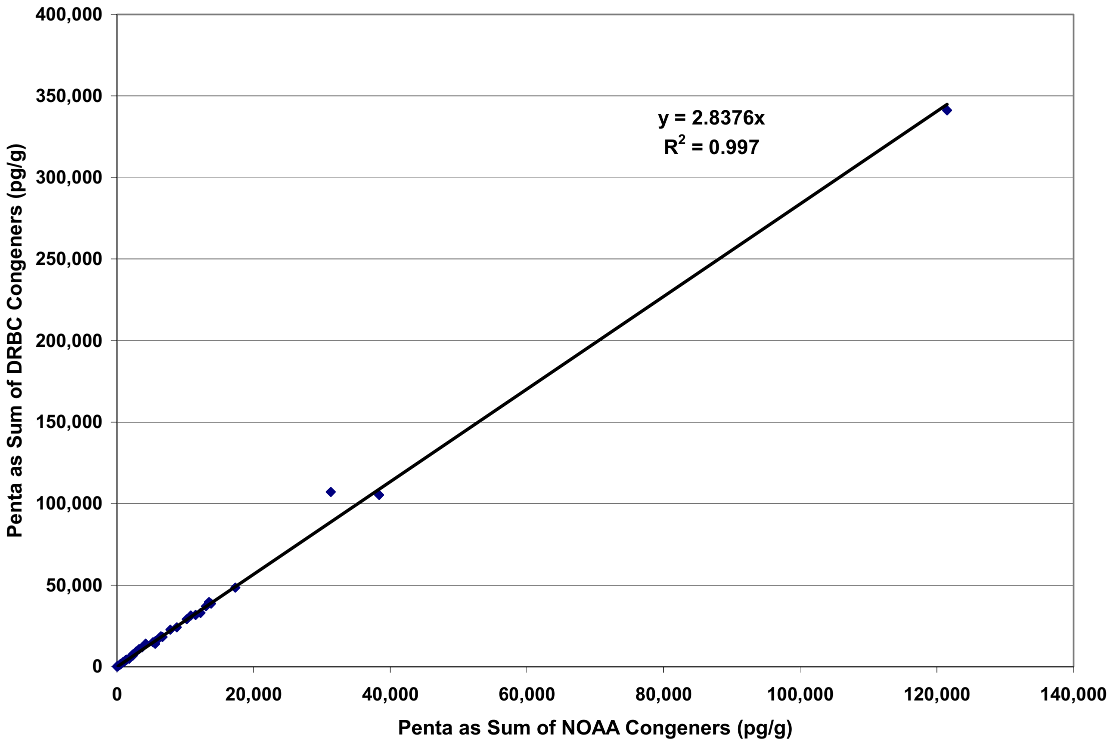
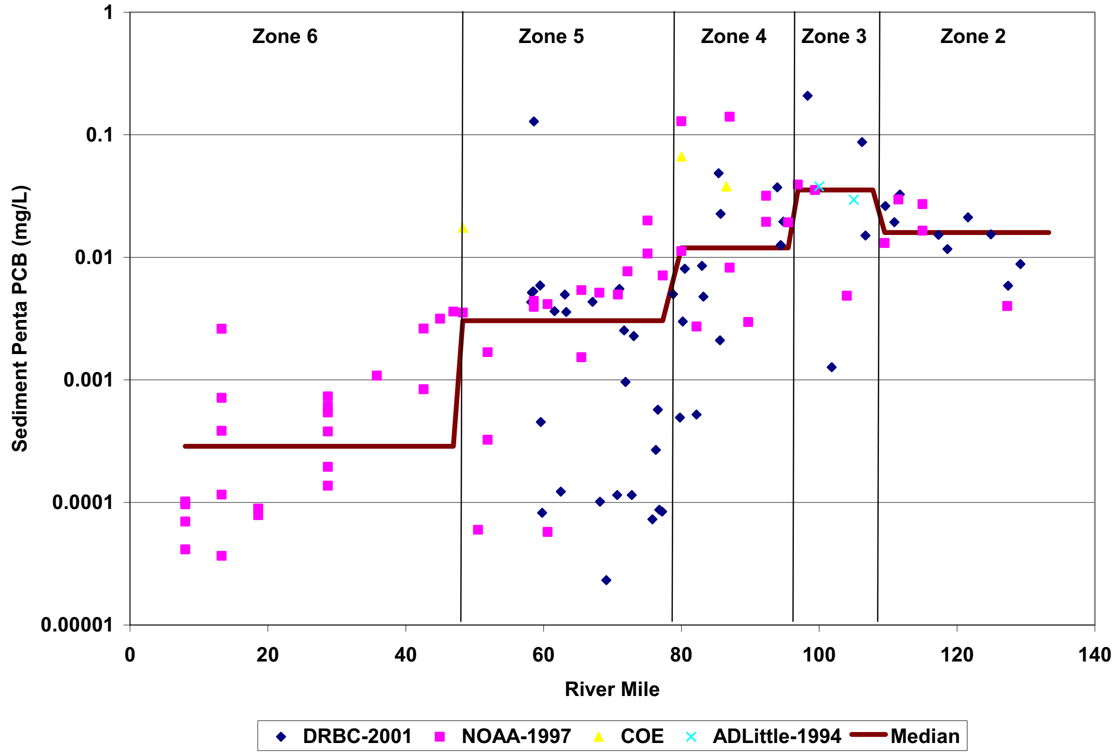


Figure 3.11 shows the sediment penta-PCB concentrations from the 4 data sets used and computed zone median penta-PCB values. Note that the general agreement between the DRBC data set and NOAA data set in range and distribution tends to support the scaling method described above.

Figure 3.11 - Sediment penta-PCB Data and Computed Zone Median Values



4 Short-Term Model Calibration

4.1 Calibration Approach and Strategy

As discussed in Section 1, the Delaware River Basin Commission and Limno-Tech, Inc. enhanced EPA's Water Quality Simulation Program (WASP) Version 5.12 in 2003 to develop a general purpose sorbent dynamic penta-PCB model for the Delaware River Estuary (DELPCB). The model simulates spatial and temporal distributions of organic carbon (OC) and penta-PCB utilizing biotic carbon (BIC) and particulate detrital carbon (PDC) state variables as well as one inorganic solid as a pseudo-state variable. The inorganic solid pseudo-state variable is not a sorbent; it serves only to ensure that sediment bulk density, porosity, and burial rate are accurately calculated at each time step.

The model treats the two OC sorbents as non-conservative state variables that are advected and dispersed among water segments, settle to and erode from benthic segments, move between benthic segments through net sedimentation or erosion, and decay at user specified rates. In this model, penta-PCBs partition to particulate- PCB (by sorbing to BIC and PDC), truly dissolved-PCB, and dissolved organic carbon (DOC) bound-PCB phases.

The general calibration strategy was to specify as many external inputs and internal model parameters as possible using site-specific data or independent measurements, and adjust only a minimal number of parameters through model calibration. Another part of the strategy was that parameters determined through model calibration were held spatially and temporally constant unless there was supporting information to the contrary. Model parameters were not assigned arbitrary values in order to obtain the best "curve fits" in a strictly mathematical sense. Emphasis was placed on best professional judgment and on results from a suite of different metrics that were used collectively in a weight-of-evidence approach.

4.1.1 A Brief Overview of the Definition for Model Calibration and Validation

Calibration and validation have been defined by Thomann and Mueller (1987), as follows:

- Calibration — The first stage testing or tuning of a model to a set of field data, preferably a set of data not used in the original model construction; such tuning to include a consistent and rational set of theoretically defensible parameters and inputs.
- Validation — Subsequent testing of a calibrated model to additional field data preferably under different external conditions to further examine model validity.

Model validation is an extension of the calibration process. Its purpose is to ensure that the calibrated model properly addresses all the variables and conditions that may affect model results. The most effective procedures for model validation are to use a portion of the observed data for calibration and apply the remaining period of observed data for validation. In view of the dynamic nature of the model development and the continuing collection of field data for use in the model calibration, a running calibration approach was used rather than setting aside a portion of a limited data set. This approach proved to be especially useful since the 575 day model calibration period ultimately included a range of flows that approximated the flow duration curve for both the Delaware River at Trenton and the Schuylkill River at Philadelphia.

Model performance assessments and calibration/validation usually include both graphical comparisons and statistical tests. Comparisons of simulated and observed state variables were be performed for different flow regimes, e.g., high- flow events from March through April, low-flow events from May to November, and intermediate-flow events between November and March. Statistical tests were performed (see section? for details).

4.1.2 Summary of Calibration and Validation Procedures

As discussed in the report entitled "PCB Water Quality Model for the Delaware Estuary," DELPCB includes three mass balances calculations: flow, organic carbons (BIC and PDC), and PCB mass balance. These three mass balance components are the focus of the model calibration and are in the terms of hydrodynamic, sorbent dynamic, and PCB mass transport. In general, we calibrate hydrodynamic model first by comparing chloride concentrations between predicted values and ambient data. Second, with an assigned PDC gross settling velocity and given decay rate of BIC for water column and PDC decay rates for both water column and sediment, we then adjust the resuspension rates, which may vary within the same zone, to compare the predicted values with BIC and PDC in the water column for sorbent dynamic model calibration. Thirdly, for the PCB calibration, we specify partition coefficients of PCB to the organic carbons, Henry's Law constant for air water exchange, and assume no PCB decay.

In this report, we used the calibrated DYNHYD5 model that was used in December 2003 TMDL development. Only minor changes of PDC resuspension rates are made to maintain a net deposition rate of 1 cm/year for each surface segment.

4.2 Updates and Revisions

The following updates to the Calibration Report dated December 2003 have been made to this report.

4.2.1 Source codes of DELPCB Model

- In air-water exchange subroutine VOLAT.FOR, on line 122 under "Implementation Of Thomann and Fitzpatrick's Algorithm and Mills et al., for liguid and gas film tansport formula has been modified from 0.0372***(SWIND**2.)/SDEPTH))** to 0.0372***(SWIND**2.))/SDEPTH)** which makes XKL's unit become meter/day.

4.2.2 Input File of TOXI5/WASP5

- In Parameter Card G, VELFM has been set to zero
- Based on the available data, Ocean boundary and C&D canal have been updated. PCB input value of 9.02E-7 mg/L has been changed to 6.51E-7 mg/L for C&D Canal and value of 2.00E-7 mg/L has been changed to 1.00E-7 mg/L for Ocean.
- As indicated in section 3, revised estimates of PCB loadings from contaminated site will be included to replace the old estimate.
- Minor modifications have been made to PDC resuspension rates to ensure a net solids deposition rate of 1 cm/year or less while its gross settling remain the same (1 m/day).

4.3 Calibration Targets

Section 3.5 describes the water column and sediment calibration targets used in the short-term calibration. The specific water column parameters used as targets were biotic carbon (BIC), particulate detrital carbon (PDC), total penta-PCB, particulate penta-PCB and total dissolved penta-PCB (the sum of truly dissolved and dissolved organic carbon-bound penta-PCB.

The sediment calibration targets are more accurately defined as initial sediment conditions (see Section 3.5.2). Initial sediment conditions for each of the model sediment layer segments were established for penta-PCB, total organic carbon (TOC) and inorganic suspended solids (ISS) (see Section 3.4.2).

4.4 Model Calibration Results

4.4.1 Graphical Presentation of Results

The results for both the initial and revised short-term, 19-month model calibrations (TMDL 2003 - green line in plots) and (IAC JUNE2004 - red line in plots) are illustrated in three types of plots:

- **Spatial Plots** - Spatial (longitudinal) plots of computed and observed water column concentrations for PDC, BIC and penta-PCB concentrations (total, particulate, total dissolved and normalized to particulate organic carbon or R1) at fixed points in time. These plots (Figures 4.1 to 4.13) are presented for each of the thirteen (13) ambient surveys that were conducted between March 15, 2002 and March 19, 2003. Note that 7 of these surveys encompassed Zones 2 – 5 of the Delaware River between the C&D Canal and Trenton, NJ. Six (6) of the surveys occurred in Zone 6 (Delaware Bay) and lower Zone 5.

- **CFD Plots** - Figures 4.14 through 4.19 present cumulative frequency distribution plots (CFD) of computed and observed water column concentrations of BIC, PDC, dissolved penta-PCB (DDPCB), particulate penta-PCB (PPCB) and total PCB (TPCB). In these plots, the cumulative percentile is plotted on the X axis while the observed and simulated water column concentrations are plotted on the Y axis.

- **Bivariate Plots** - Figures 4.20 through 4.24 present plots of observed water column concentration data on the X axis and model simulation results on the Y axis along with the regression equations between the two variables. If all model simulation results match ed the observed water column concentrations then all points should lie on the line bisecting the graph (i.e., the slope of the line would equal 1.0, and the intercept of the line would pass through 0.0). The graph also contains the square of the correlation coefficient or r^2 value. This value represents the amount of the total variation in the data explained by the regression equation (i.e., the degree to which the model predictions explain the observed water column concentrations).

4.4.2 Summary of Model Results

Modeling results are summarized as follows:

- Upon implementing the changes discussed in Section 4.1, the difference between the two model simulation results is negligible.
- **No** adjustment of parameters for PCBs was performed following the assignment and adjustment of settling velocities, resuspension rates and decay rates during the calibration of the organic carbon model.
- The model reasonably simulates spatial and temporal distributions of organic carbon (OC) and penta-PCB with the exception of BIC and PDC in lower Zone 5.
- Around RM 63 in Zone 5, model consistently under-predicted organic carbon concentrations, which indicates the possible influence of processes related to the

estuarine turbidity maximum (ETM). Such evidence suggests that additional physical, chemical, and hydrodynamic functions are not included in the current model. To better describe the ETM, additional modeling and field investigations are needed.

- There are no obvious differences between the old and the new runs which means that the minor adjustments of resuspension rates for sediment burial does not impact the model results.
- Corrected contaminated site loads and volatilization fluxes have been implemented with minor impacts on simulated results.
- From the CFD plots in Figure 4.14, the BIC data appears in good agreement with predicted values except for Zone5. For Zones 2-5 and all Zones, the plots show that predicted values generally overlay observed values.
- From the CFD plots in Figure 4.15, PDC has a flat slope compared with data. The differences are likely due to the influence of the ETM (see the first figure for Zone5 in the right column.).
- Comparisons of simulated to measured water quality concentrations generally indicate good agreement, low bias of the estimate for DDPCB, but a slight overprediction of the particulate PCB and total PCB. Such behavior suggests that a closer examination of the PCB loads, physical and chemical functions is needed.
- Bivariate plots for BIC and PDC (Figures 4.20 and 4.21) also indicate the underprediction of these two parameters in Zone 5.
- Bivariate plots for dissolved PCBs (DDPCB), particulate PCB (PPCB) and total PCB (TPCB) indicate reasonable correlations between observed and predicted water column concentrations in Zones 2 – 6 of 0.63, 0.72 and 0.74, respectively. These values exceed EPA's recommended correlation coefficient acceptance criteria for model calibration for water quality variables.

4.4.3 Discussion and Conclusions

At the conclusion of this stage of model calibration, the following issues, problems, study questions, and information needs were identified to be addressed and resolved as DELPCB is expanded to other PCB homologs in Stage 2 of the model development:

- Around RM 63 in Zone 5, the model consistently under-predicts organic carbon concentrations, which indicates the influence of Estuary Turbidity Maximum (ETM). Such evidence suggests that additional physical, chemical, and hydrodynamic functions are not included in the current model. To better describe ETM, additional modeling and field investigations are samplings are needed.
- BIC data appears in a good agreement with predicted values except for Zone5. For Zones 2-5 and all Zones BIC plots, the predicted values overlay observed values. However, PDC has a flat slope compared with data. Such differences appear to be due to the influence of ETM on observed concentrations.
- Comparisons of simulated to measured water quality concentrations indicate generally good agreement, low bias of the estimate for DDPCB, but somewhat over-predicted the PPCB and total TPCB. Refined estimates of PCB loads including tributaries, boundaries (especially the Delaware and Schuylkill Rivers, and the C&D Canal), and the ocean based upon additional field surveys are needed.

- Additional ambient surveys in Zone 6 are needed to examine the spatial variability of carbon and PCB in Delaware Bay.
- From sensitivity analysis results, the initial surface sediment PCB concentrations accounted for ~50% of the water column PCB concentrations. Such behavior suggests that a re-analysis of the sediment data used for establishing model initial conditions (f_{oc}, density, inorganic solids, TOC, PCBs) is required. Inclusion of additional sediment data in conjunction with a more detailed sediment analysis, and related sediment measurements such as particle size classes in a geostatistical analysis are recommended.
- It is essential to continue the efforts to reduce uncertainties in external loading source categories. Specific attentions should be put on contaminated sites, non-point sources, as well as the aforementioned tributaries and the external boundaries.

4.5 Future Refinements of DELPCB Model

1. Revise the existing spatial representation of the estuary in terms of Zones 2-6. Develop new spatial zones based on an assessment of a suite of data-based metrics. For example, use geostatistical results for sediment f_{oc}, density, inorganic solids, percent fine/coarse grain size, TOC, PCBs and R2. If time and funding permit, include relevant historical data (e.g, additional sediment cores), where appropriate, especially data that could be used to better define lateral variability. Develop GIS coverages for each parameter and use overlays to inform judgments on revised spatial representations. Also use bathymetry and locations of significant tributaries, inflows and loading sources.

2. Continue efforts to reduce uncertainties in external loading source categories. Place emphasis on contaminated sites, non-point sources, tributaries (including the Delaware and Schuylkill) and the external boundaries.

3. Depending on results of the geostatistical analysis of percent fine/coarse grain sediment data, scale the gross PDC resuspension rates on a segment-specific basis.

4. Consider spatially variable PDC gross settling velocity and/or BIC net settling velocity to more accurately describe erosional and depositional areas in the estuary, and the estuarine turbidity maximum or ETM. If necessary, modify the existing model segmentation in these areas and consider lateral segmentation if necessary.

5. Explicitly incorporate the impacts of dredging on the PCB budget. Investigate impacts of dredging scenarios on: (1) long-term hindcast simulations; (2) short-term calibration; and (3) decadal-scale forecasts.

6. Conduct additional long-term hindcast simulations as part of the overall model calibration process. These should be conducted with zone- or region-specific loadings as information becomes available from dated cores in different portions of the estuary.

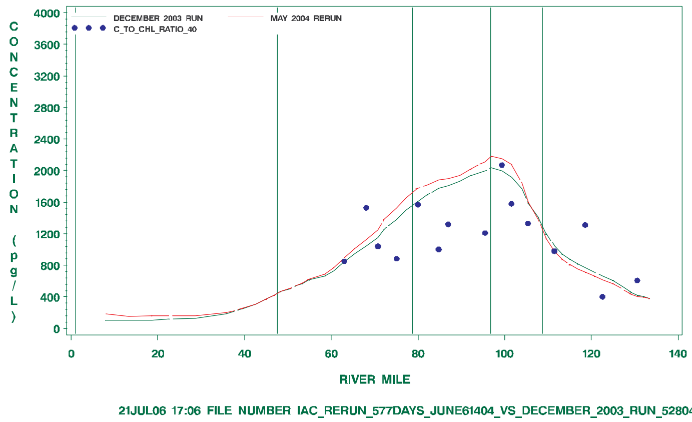
FIGURE 4. 1

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

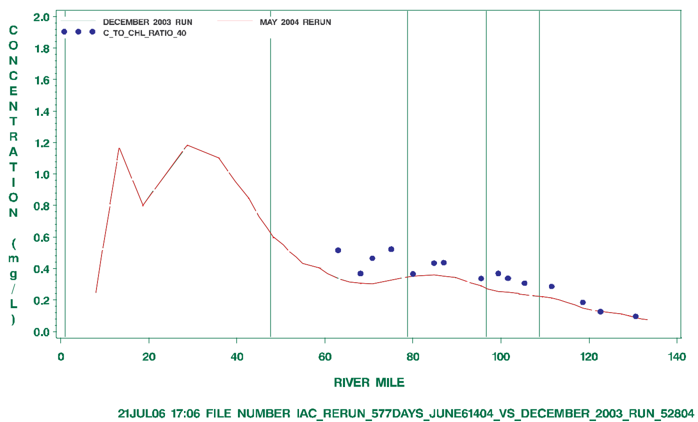
SHORT TERM CALIBRATION RESULTS

3 – 15 – 2002

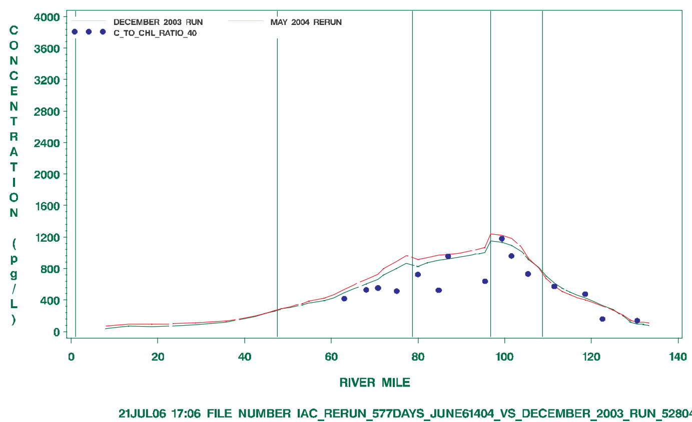
SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 195



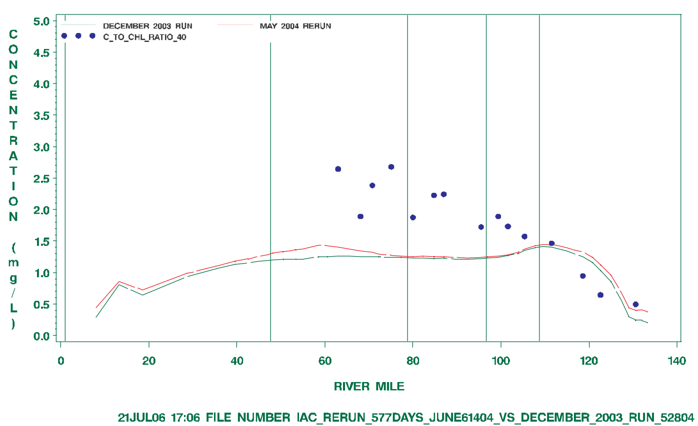
SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 195



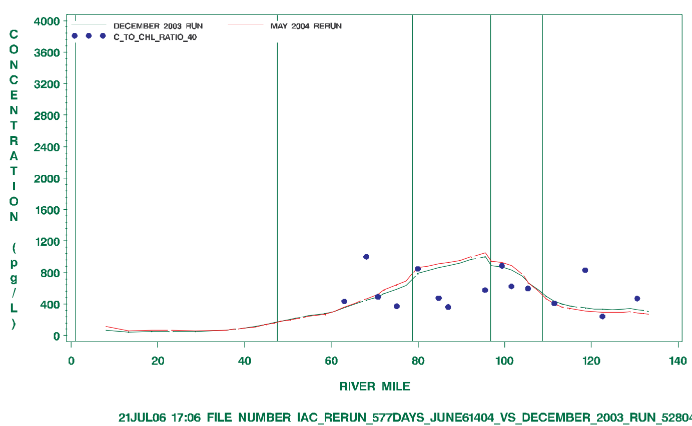
SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 195



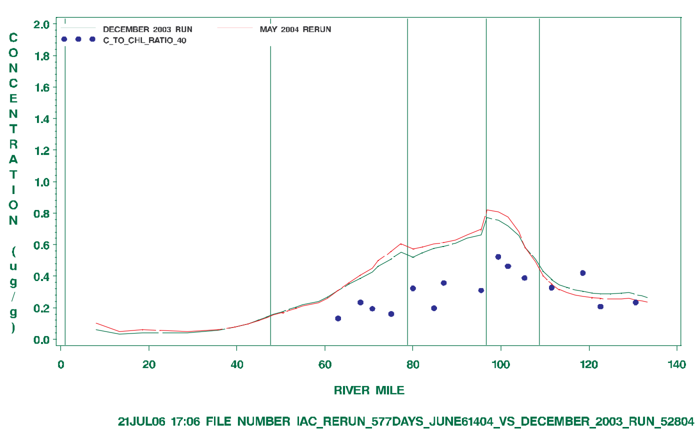
SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 195



SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 195



SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 195



SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 195

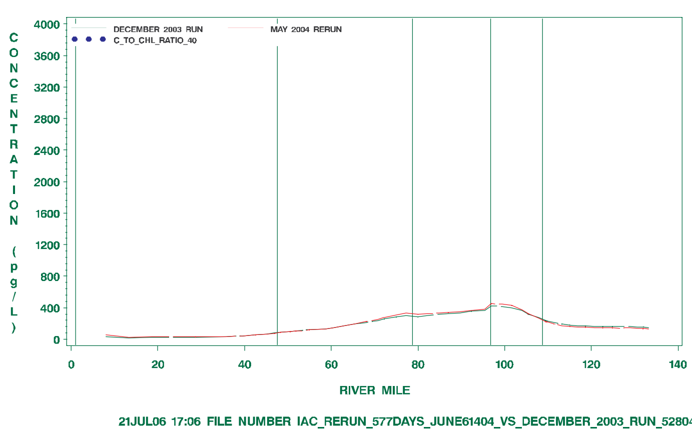


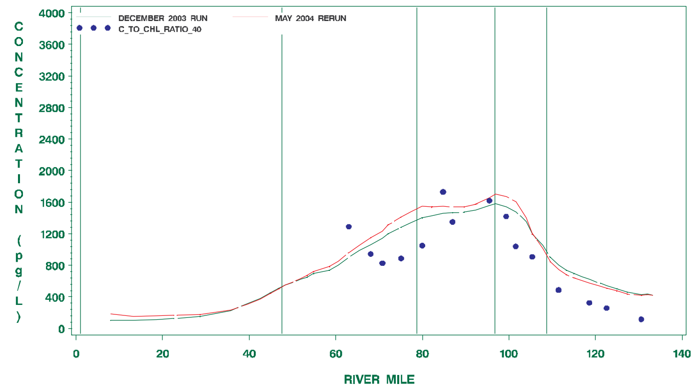
FIGURE 4. 2

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

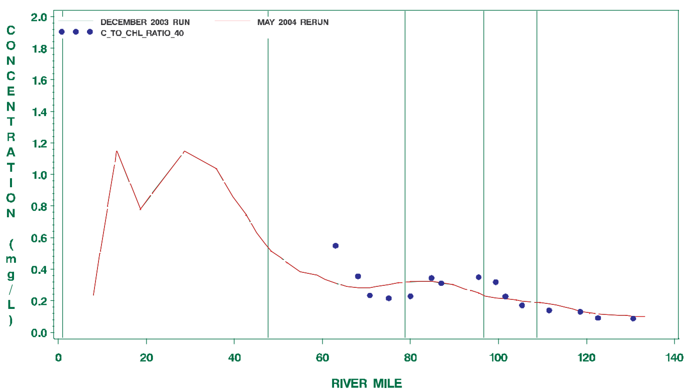
4 – 11 – 2002

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 222



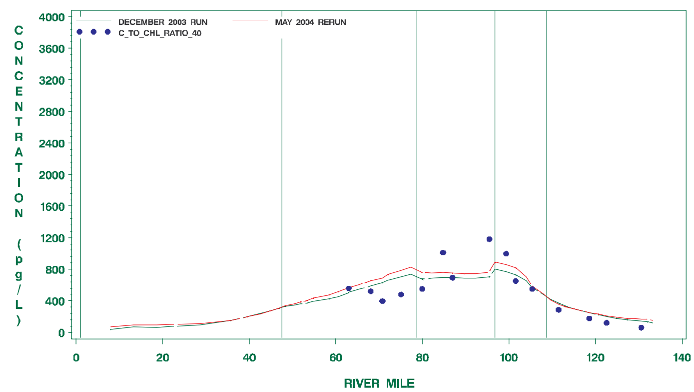
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 222



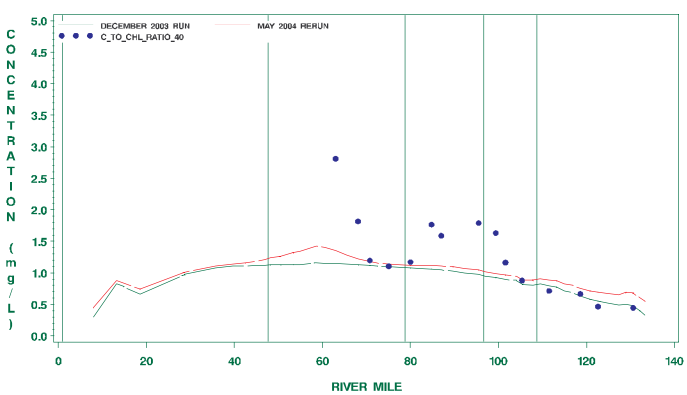
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 222



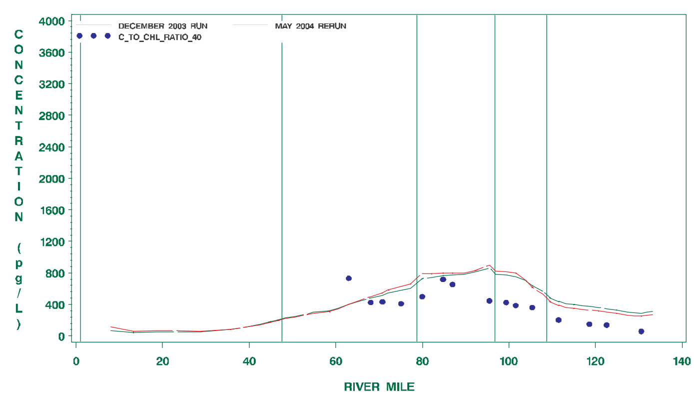
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 222



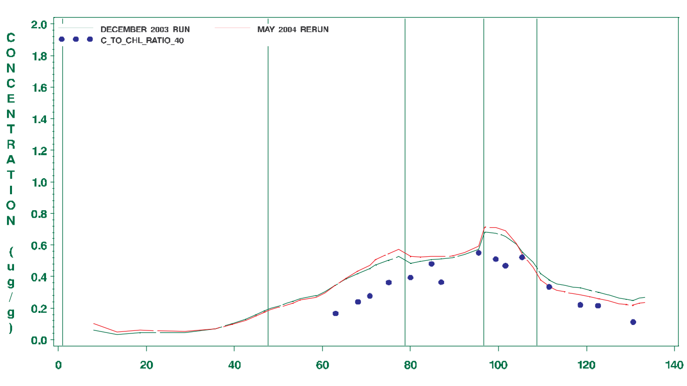
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 222



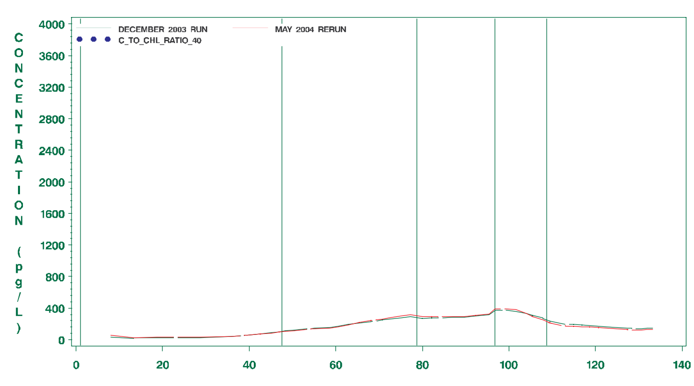
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 222



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 222



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

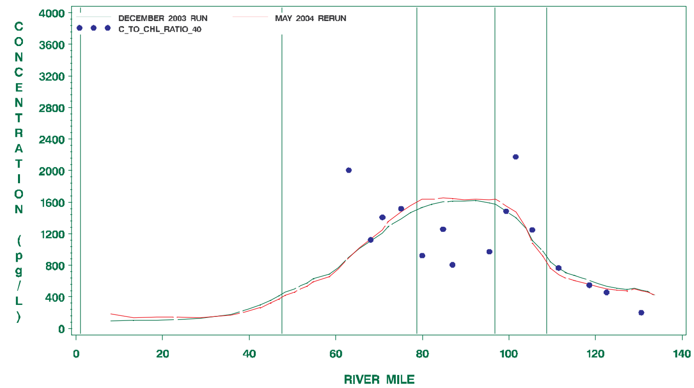
FIGURE 4. 3

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

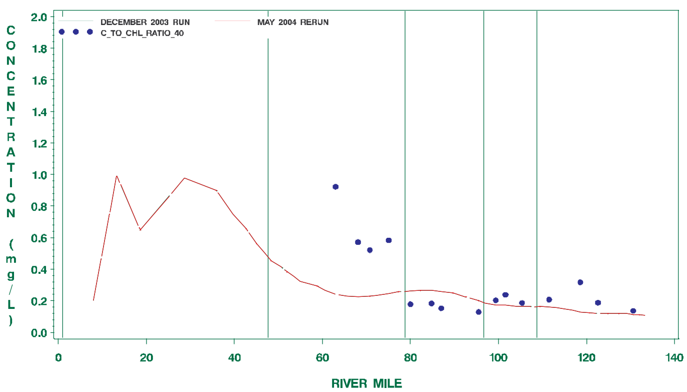
4 – 22 – 2002

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 233



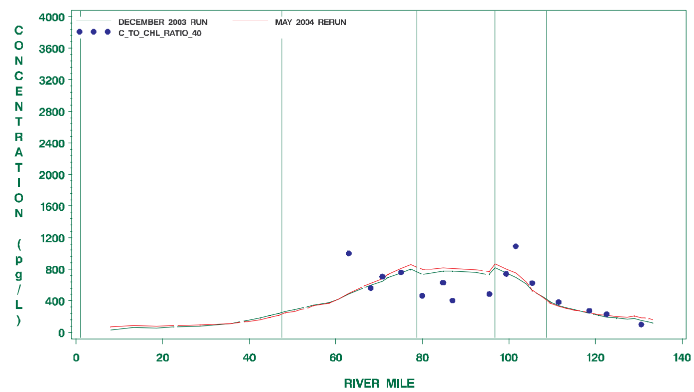
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 233



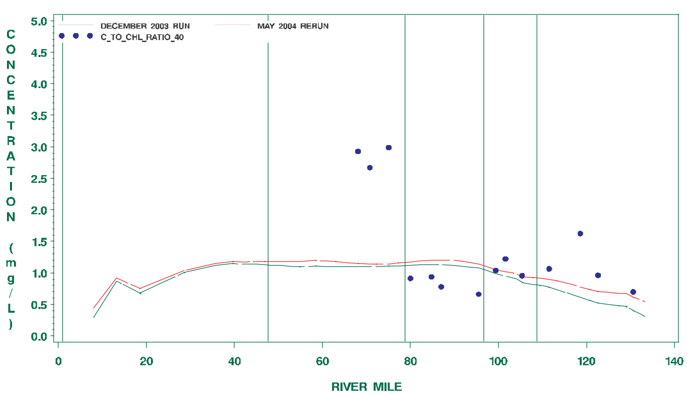
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 233



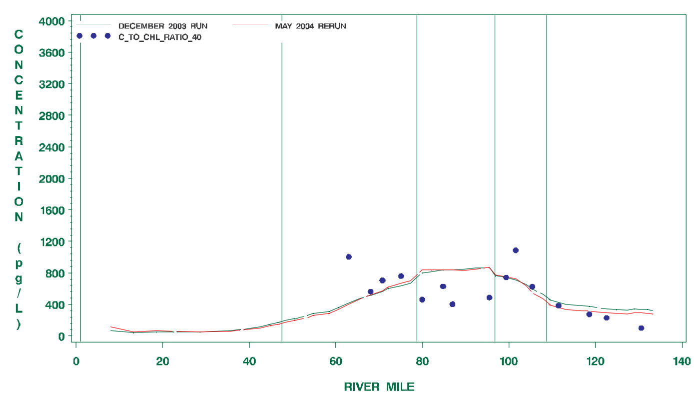
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 233



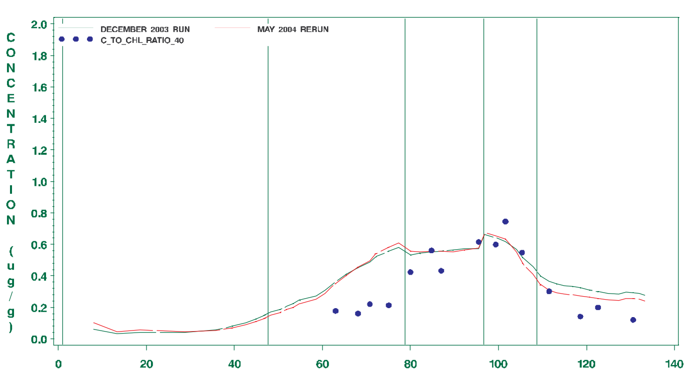
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 233



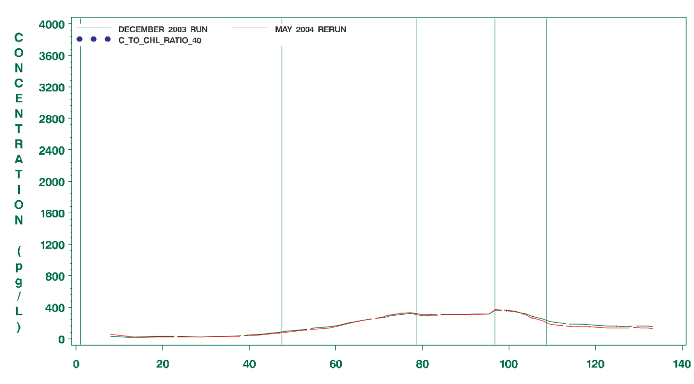
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 233



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 233



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

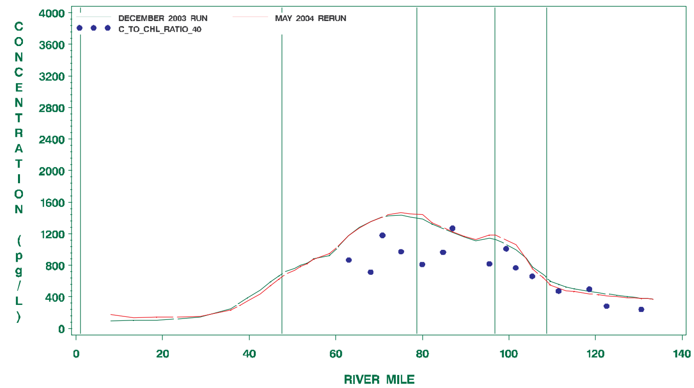
FIGURE 4. 4

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

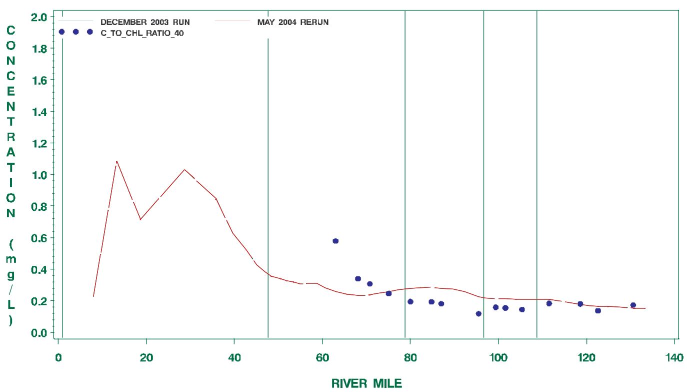
5 – 06 – 2002

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 247



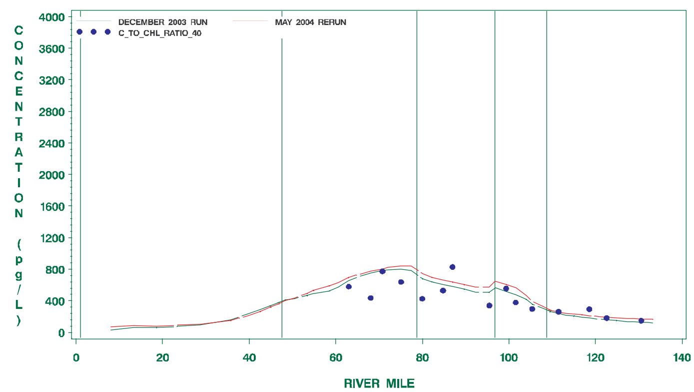
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 247



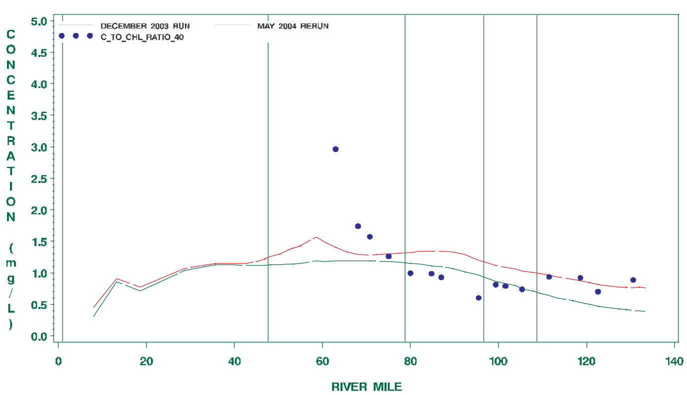
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 247



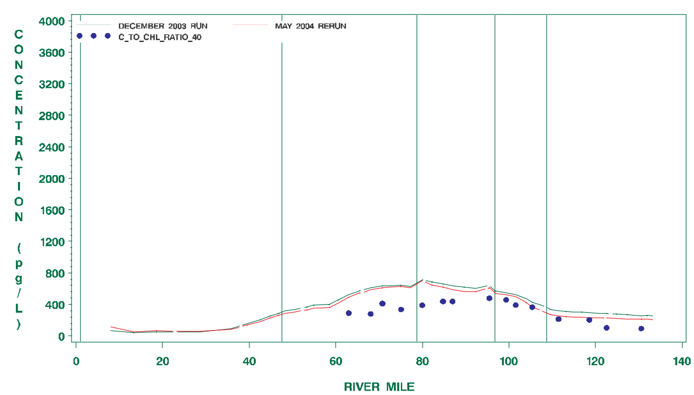
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 247



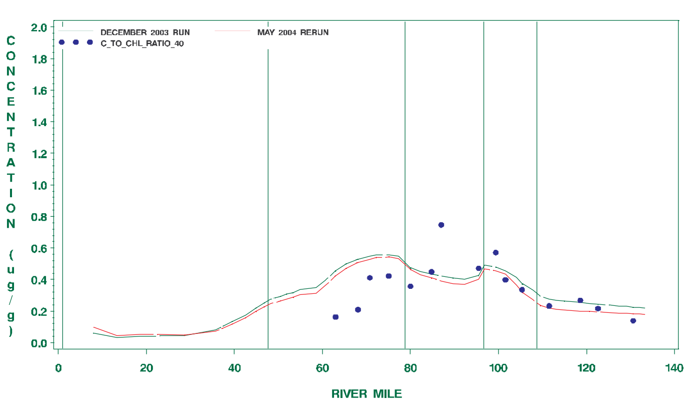
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 247



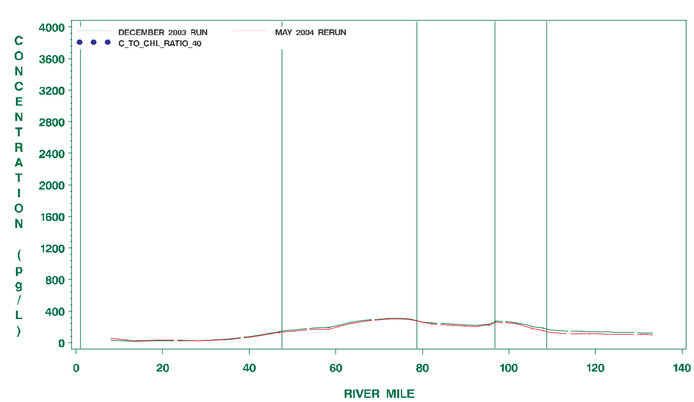
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 247



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 247



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

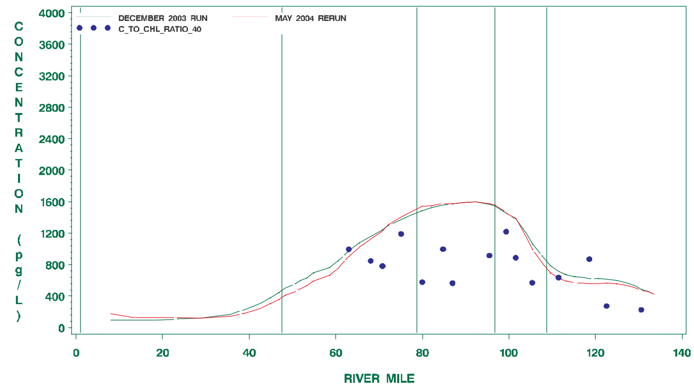
FIGURE 4. 5

SPATIAL PLOTS OF WATER COLUMN
BIC, PDC, TPCB, R1
PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

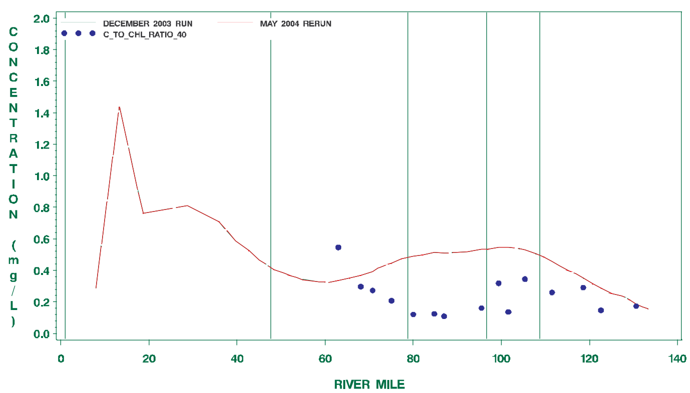
6 – 19 – 2002

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 291



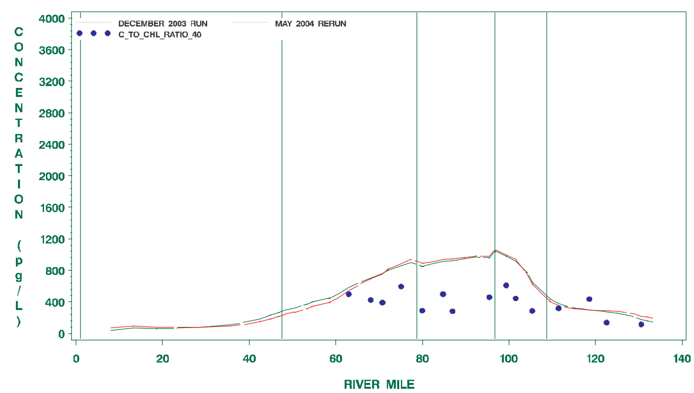
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 291



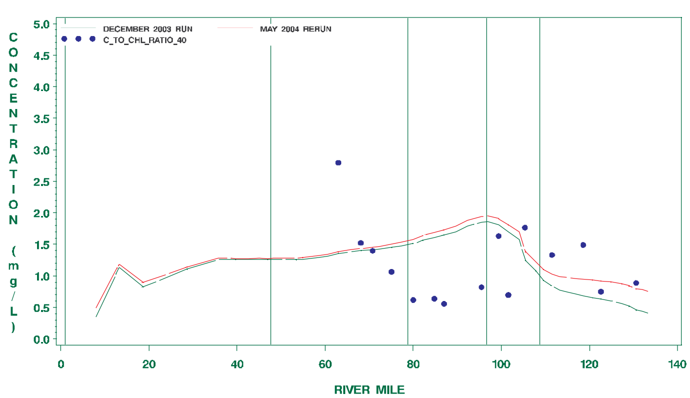
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 291



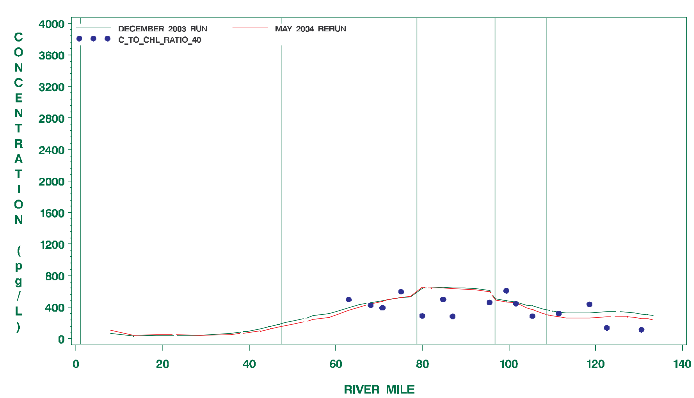
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 291



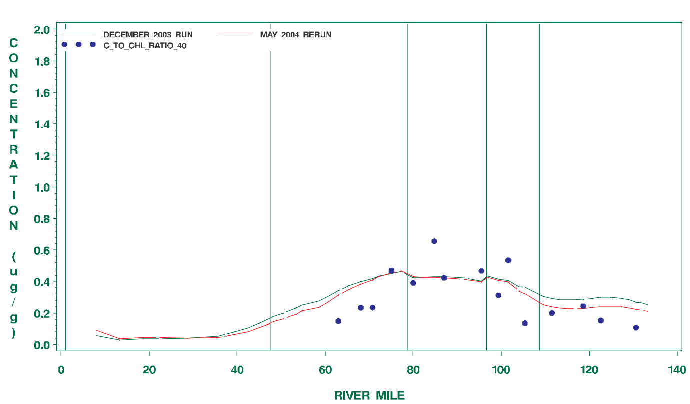
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 291



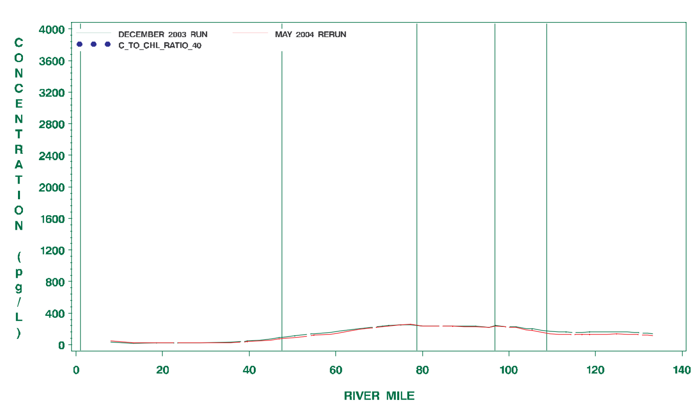
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 291



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 291



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

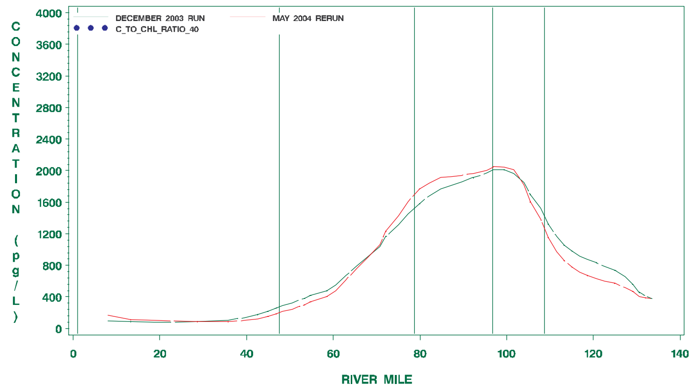
FIGURE 4. 6

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

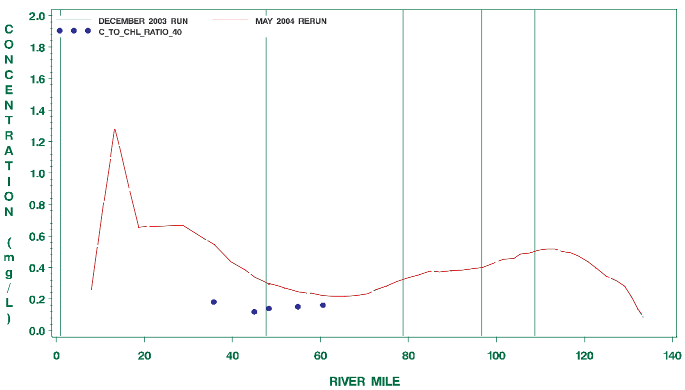
8 – 05 – 2002

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 338



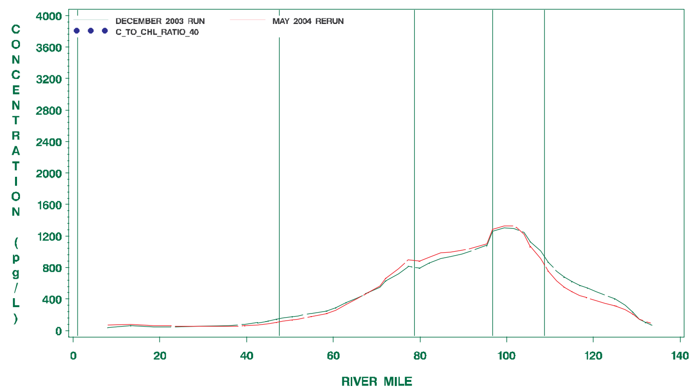
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 338



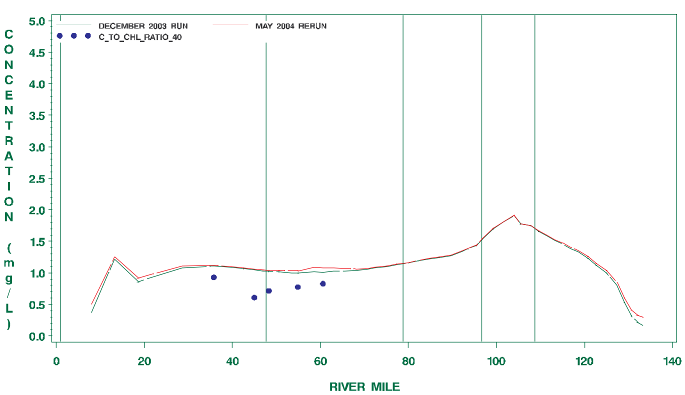
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 338



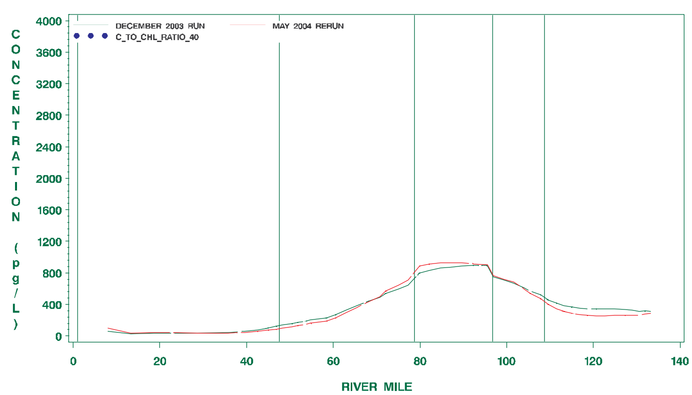
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 338



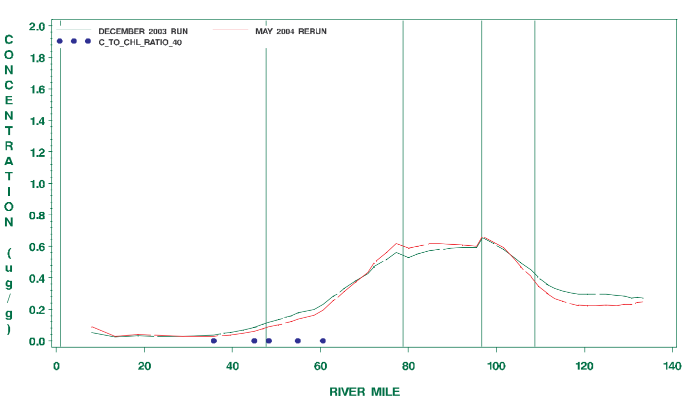
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 338



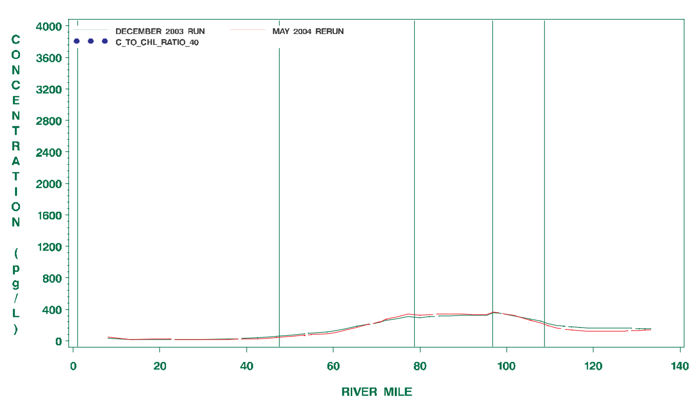
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 338



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 338



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

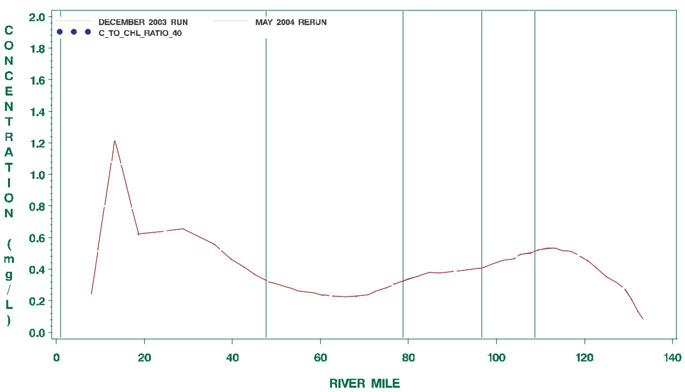
FIGURE 4. 7

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

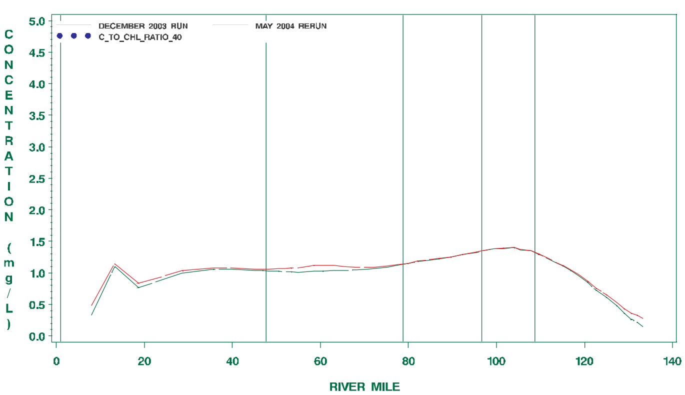
8 – 19 – 2002

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 352



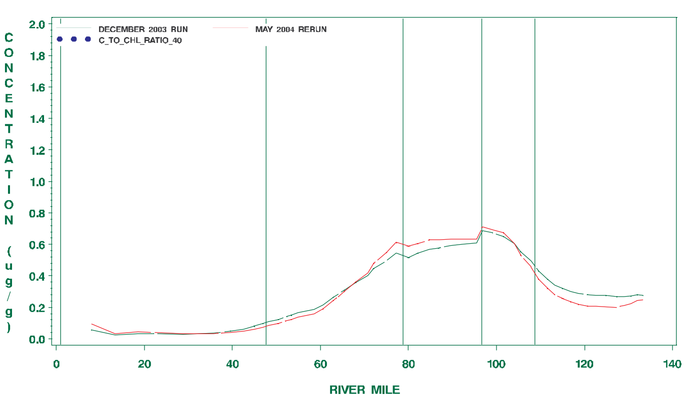
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 352



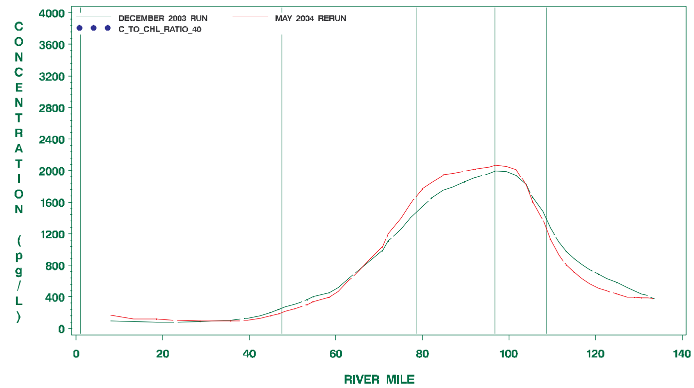
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 352



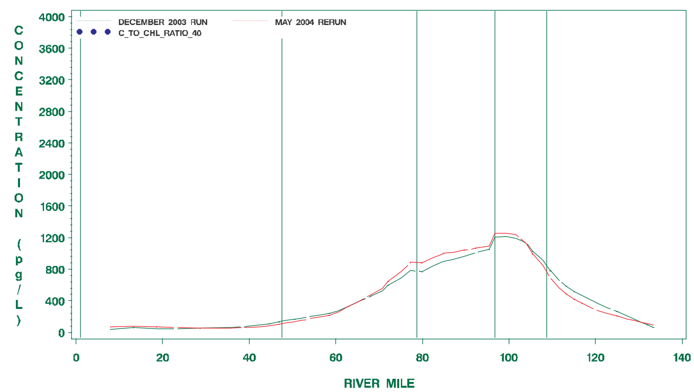
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 352



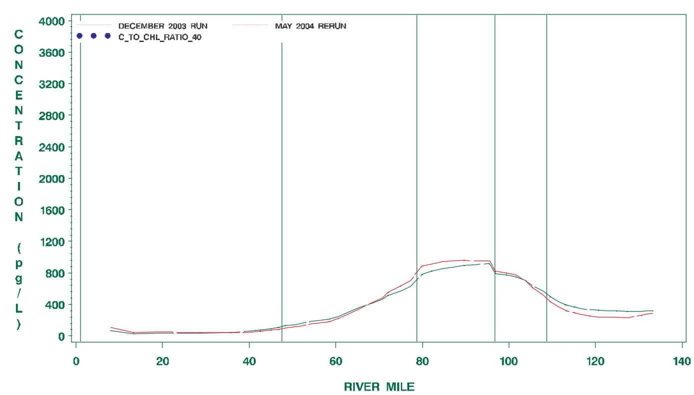
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 352



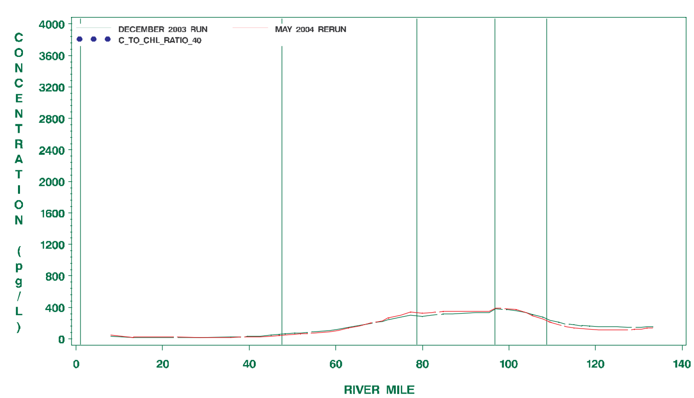
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 352



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 352



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

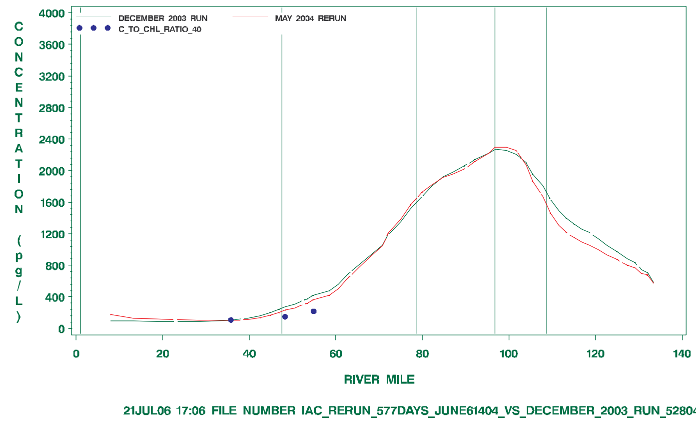
FIGURE 4. 8

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

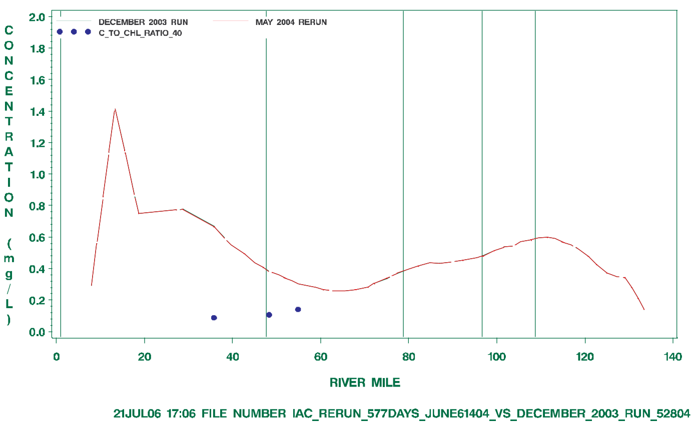
SHORT TERM CALIBRATION RESULTS

9 – 03 – 2002

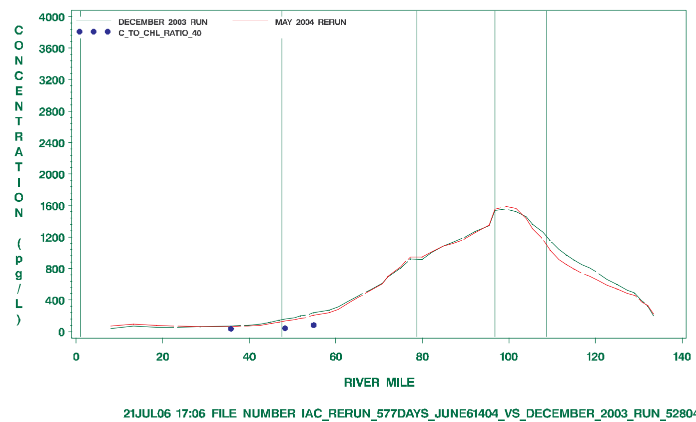
SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 367



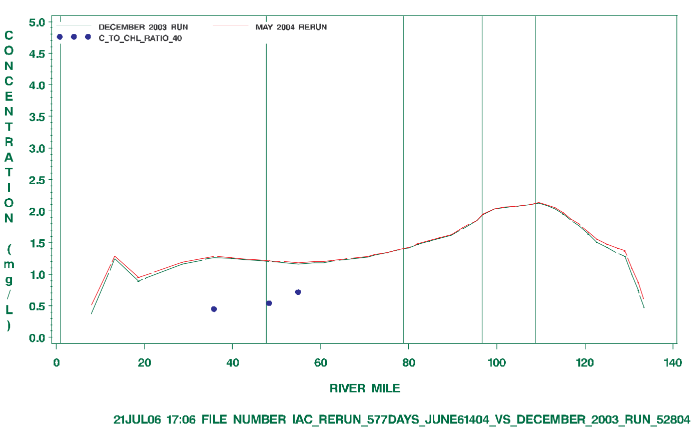
SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 367



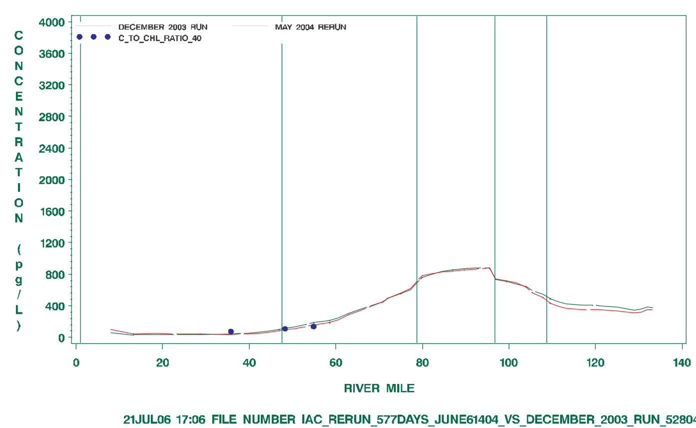
SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 367



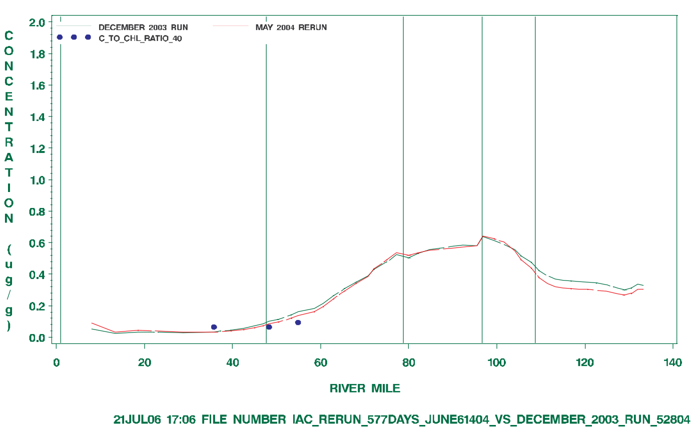
SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 367



SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 367



SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 367



SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 367

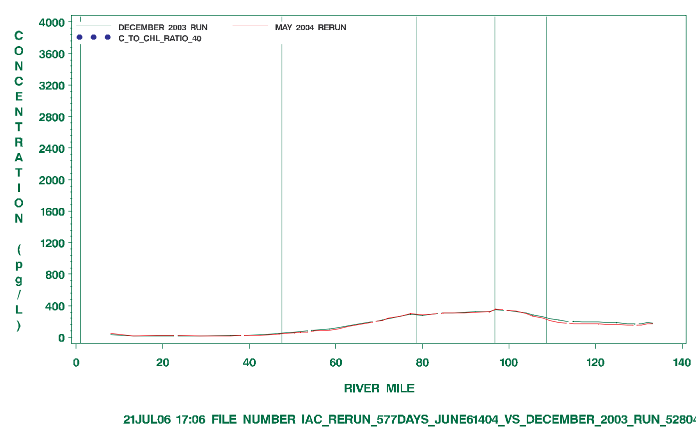


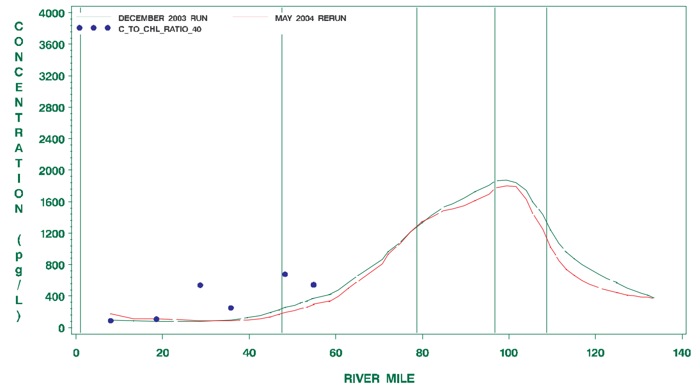
FIGURE 4. 9

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

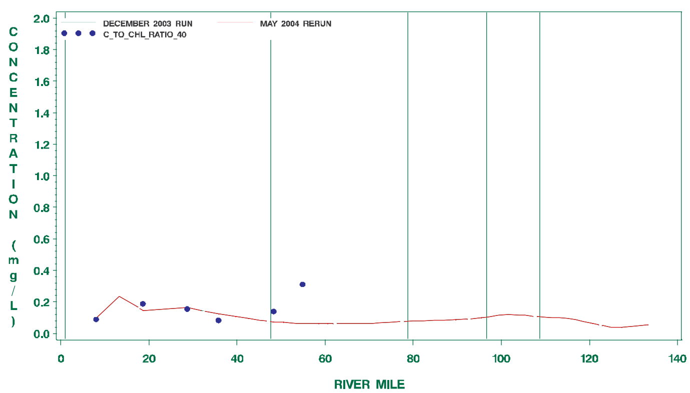
9 – 23 – 2002

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 387



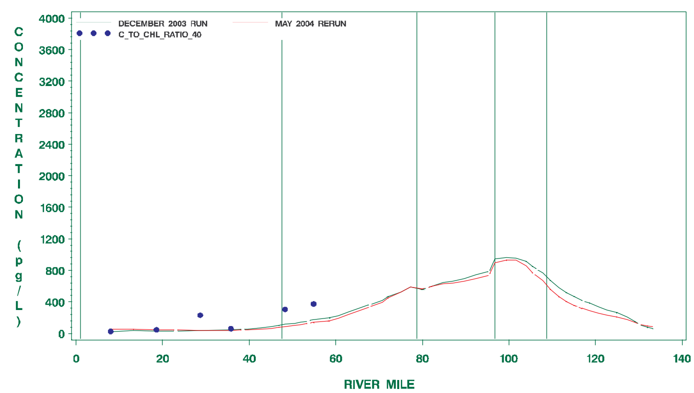
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 387



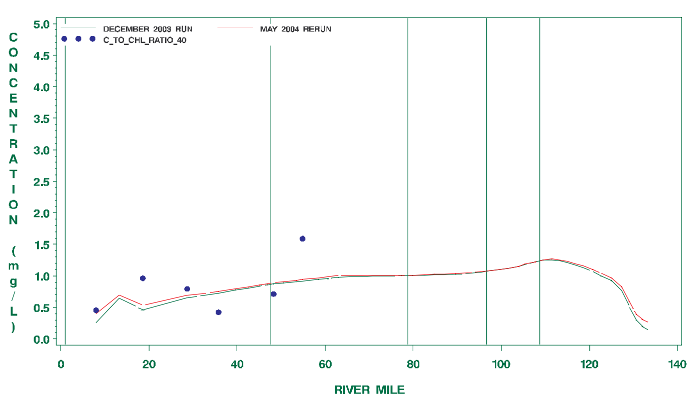
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 387



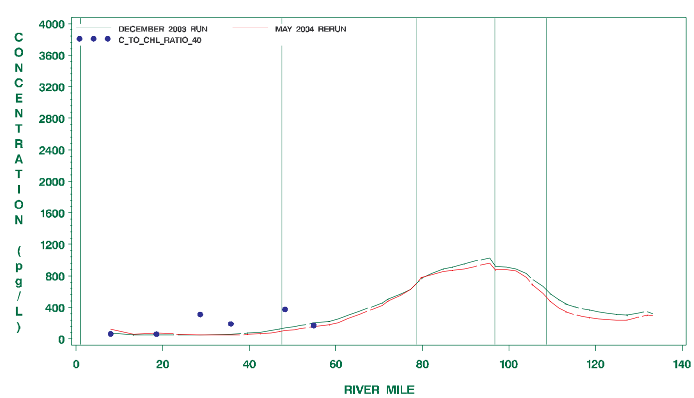
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 387



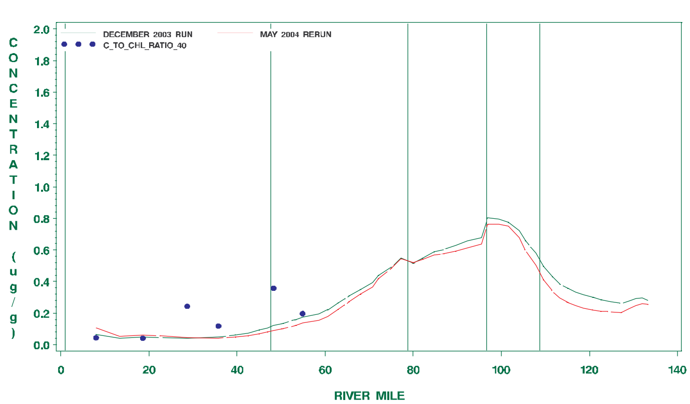
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 387



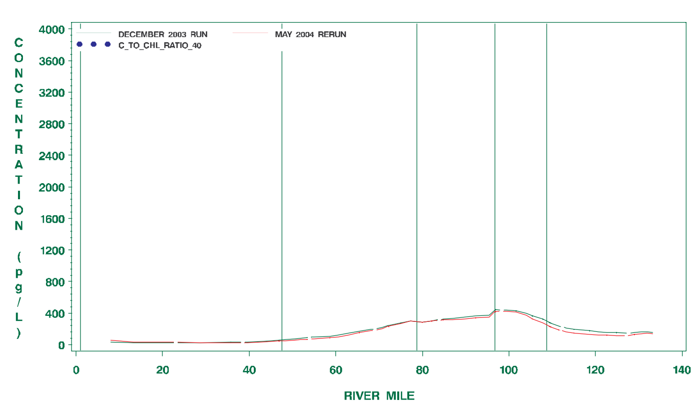
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 387



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 387



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

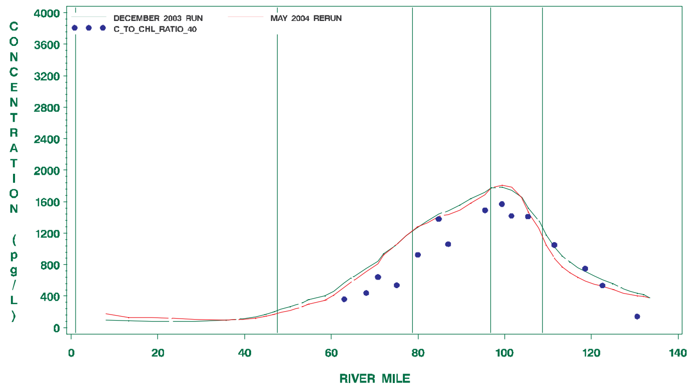
FIGURE 4. 10

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

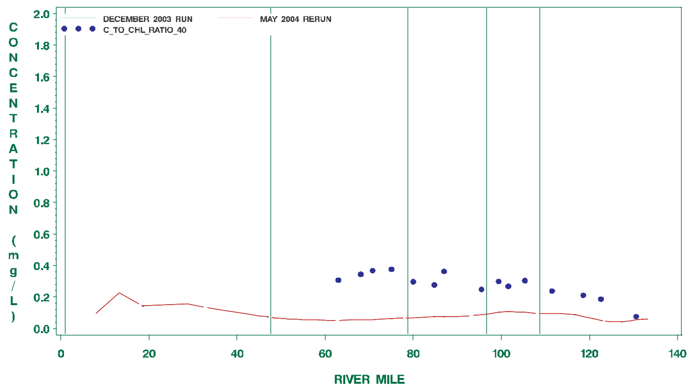
10 – 08 – 2002

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 402



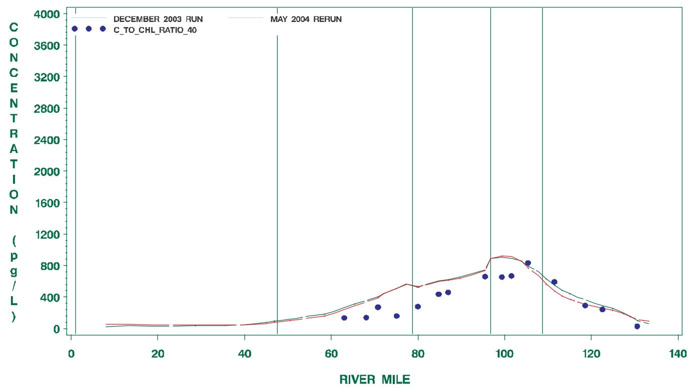
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 402



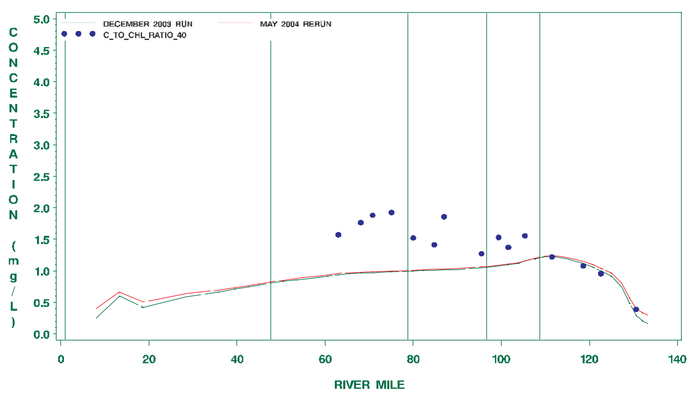
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 402



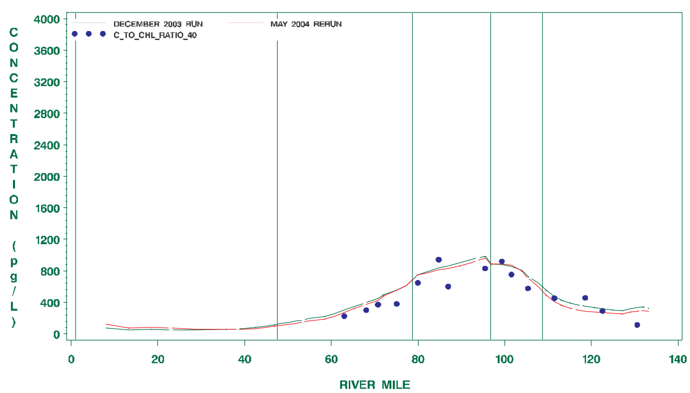
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 402



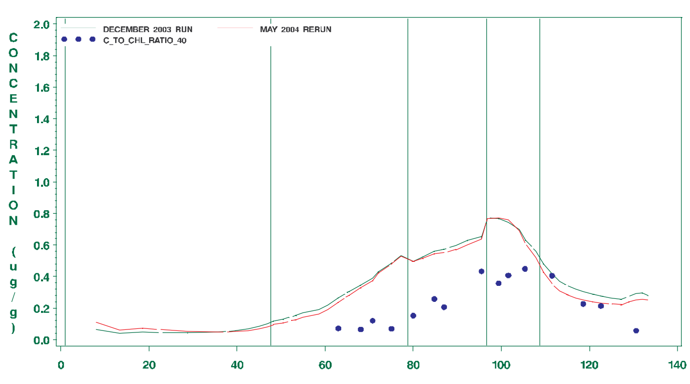
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 402



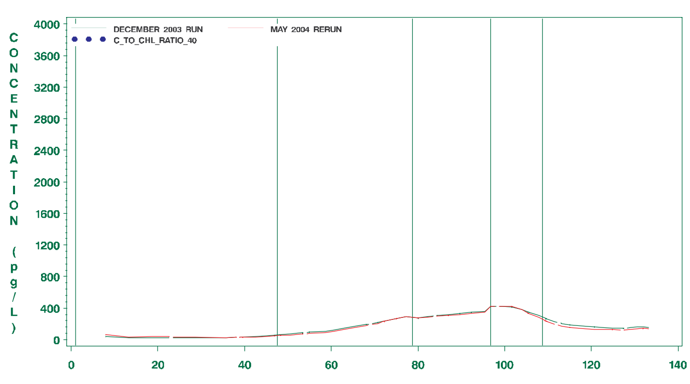
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 402



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 402



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

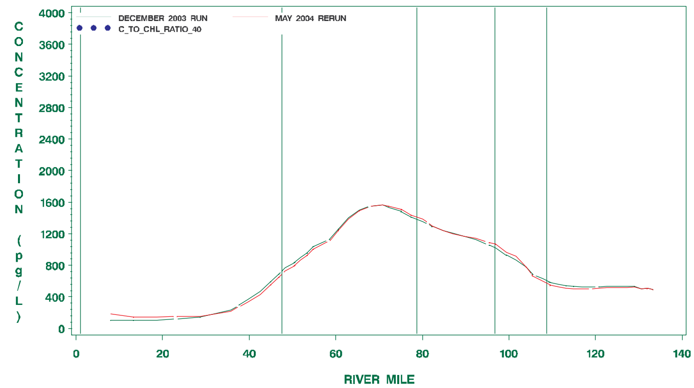
FIGURE 4. 11

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

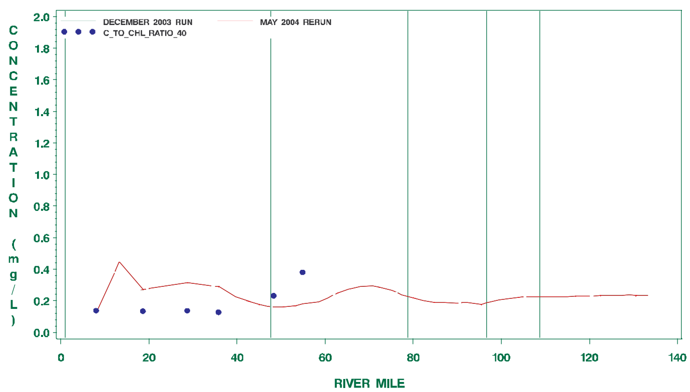
11–21–2002

SPATIAL PLOT FOR TPCB –OBSERVED VS SIMULATED FOR DAY 446



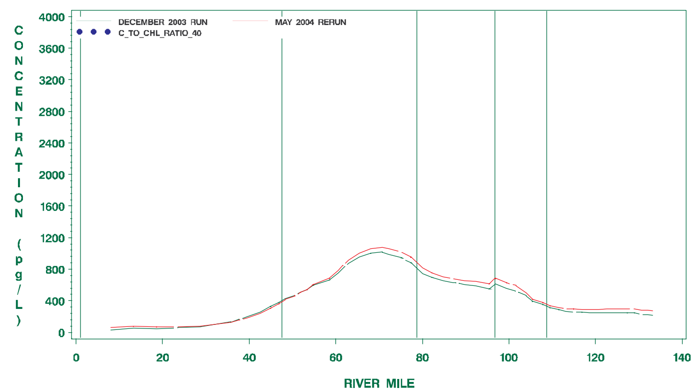
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC –OBSERVED VS SIMULATED FOR DAY 446



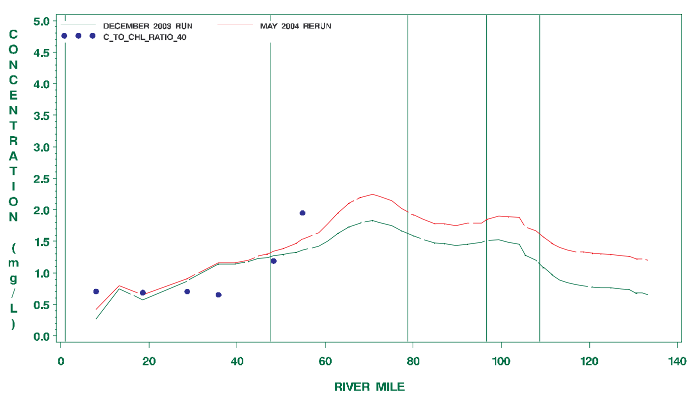
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB –OBSERVED VS SIMULATED FOR DAY 446



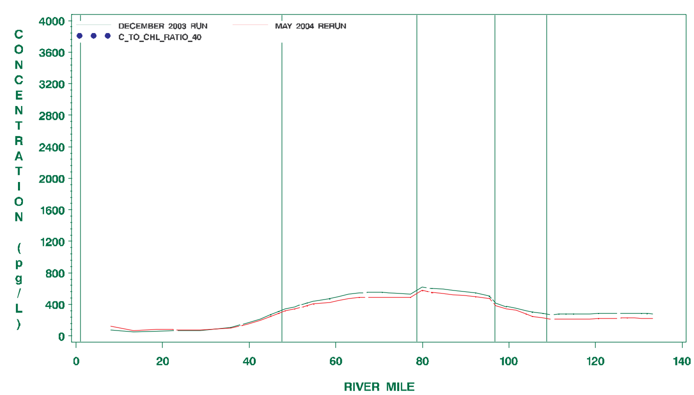
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC –OBSERVED VS SIMULATED FOR DAY 446



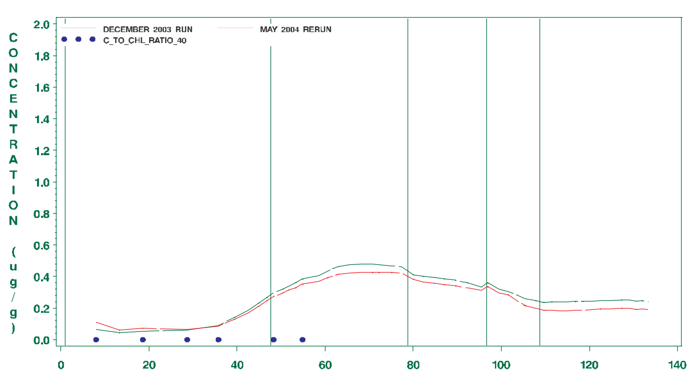
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB –OBSERVED VS SIMULATED FOR DAY 446



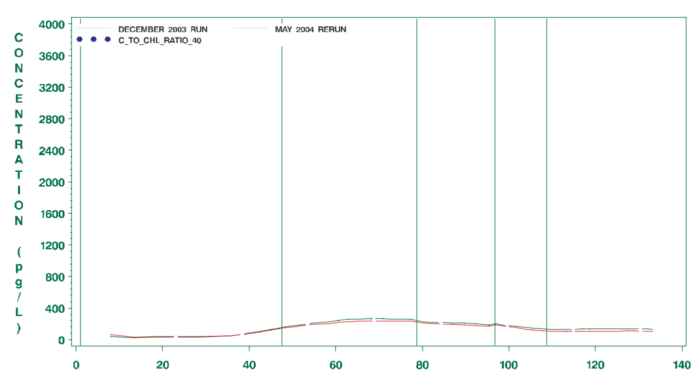
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 –OBSERVED VS SIMULATED FOR DAY 446



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB –OBSERVED VS SIMULATED FOR DAY 446



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

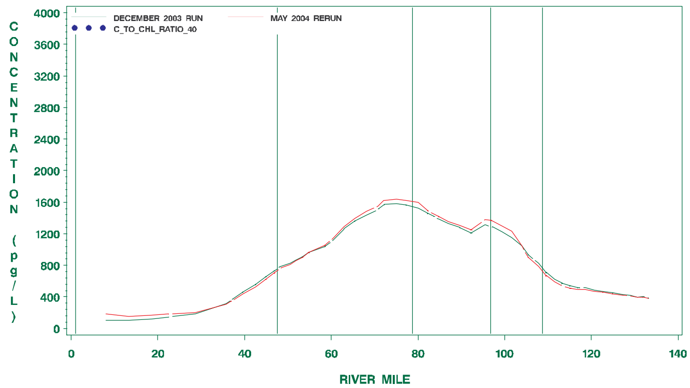
FIGURE 4. 12

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

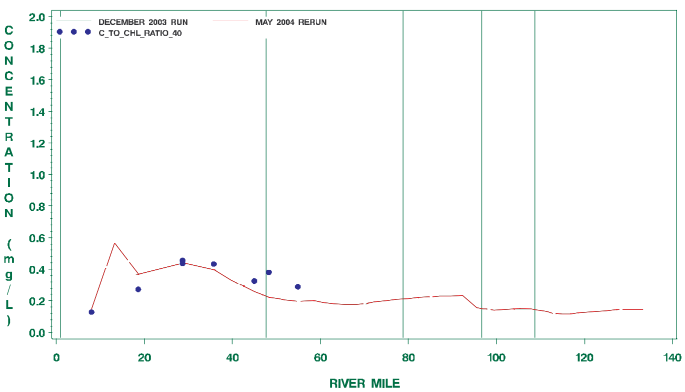
3–10–2003

SPATIAL PLOT FOR TPCB –OBSERVED VS SIMULATED FOR DAY 555



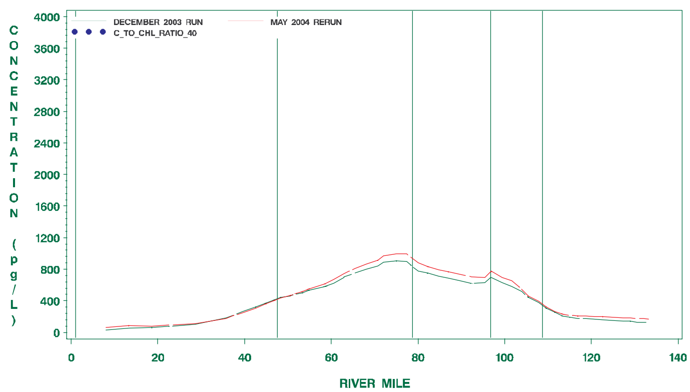
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC –OBSERVED VS SIMULATED FOR DAY 555



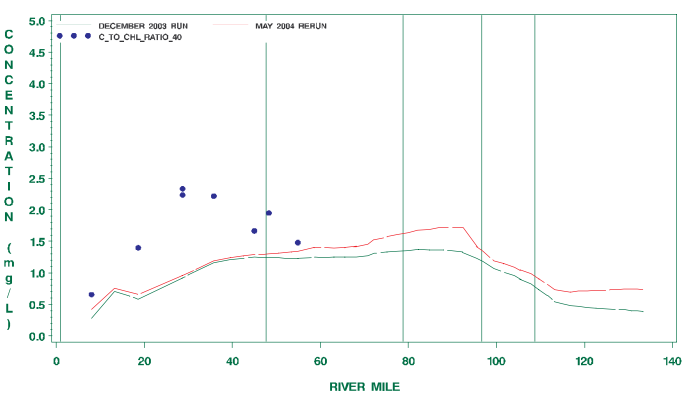
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB –OBSERVED VS SIMULATED FOR DAY 555



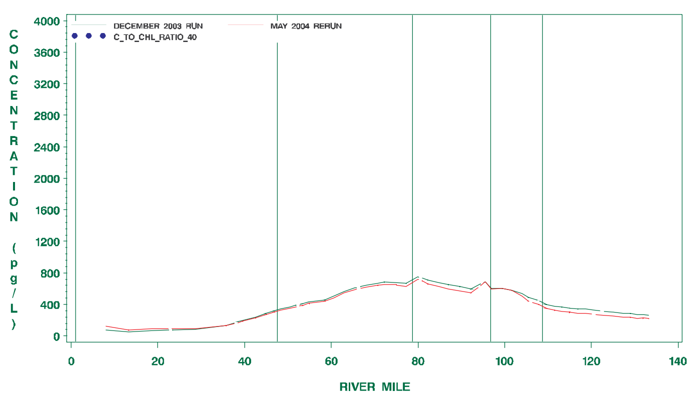
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC –OBSERVED VS SIMULATED FOR DAY 555



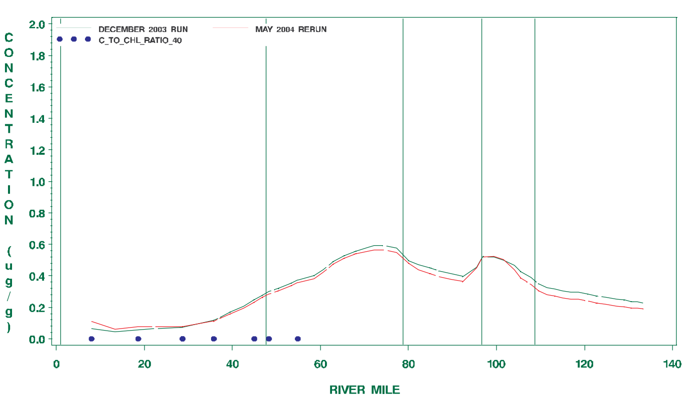
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB –OBSERVED VS SIMULATED FOR DAY 555



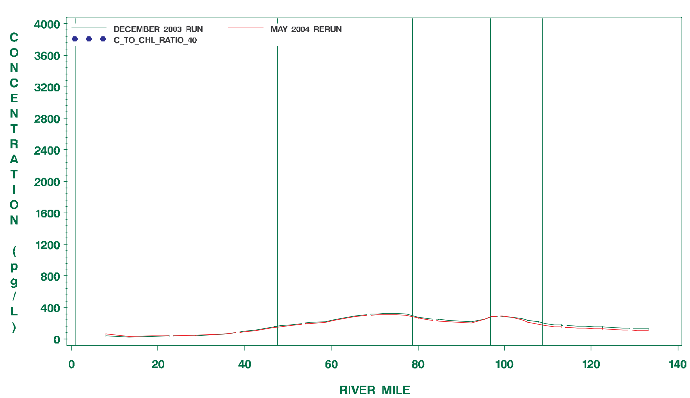
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 –OBSERVED VS SIMULATED FOR DAY 555



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB –OBSERVED VS SIMULATED FOR DAY 555



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

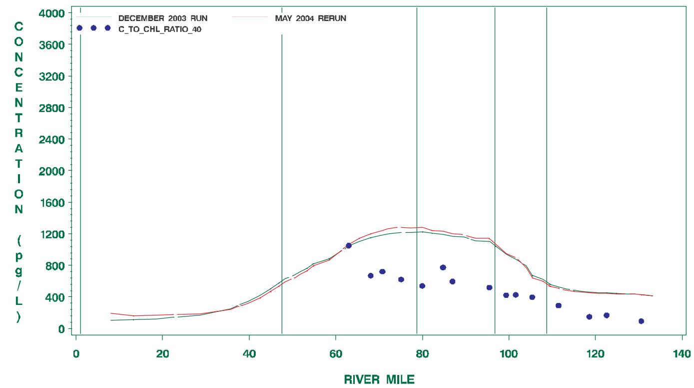
FIGURE 4. 13

SPATIAL PLOTS OF WATER COLUMN BIC, PDC, TPCB, R1 PPCB, DDPCB, AND DPCB

SHORT TERM CALIBRATION RESULTS

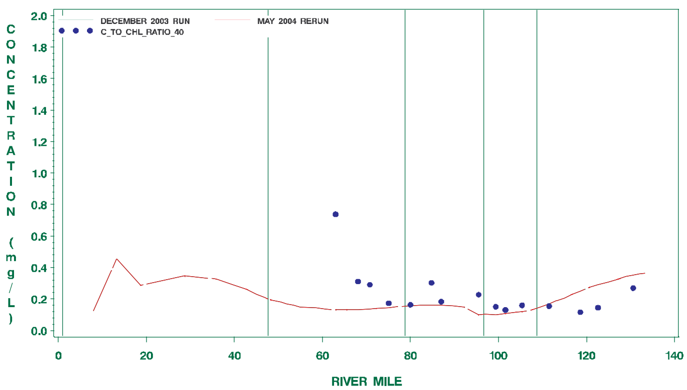
3 – 19 – 2003

SPATIAL PLOT FOR TPCB – OBSERVED VS SIMULATED FOR DAY 564



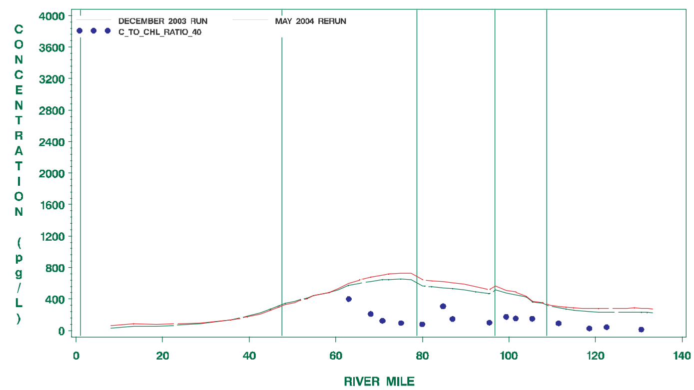
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR BIC – OBSERVED VS SIMULATED FOR DAY 564



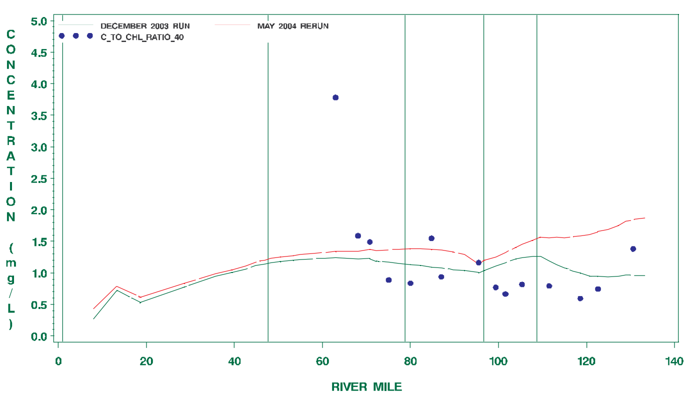
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PPCB – OBSERVED VS SIMULATED FOR DAY 564



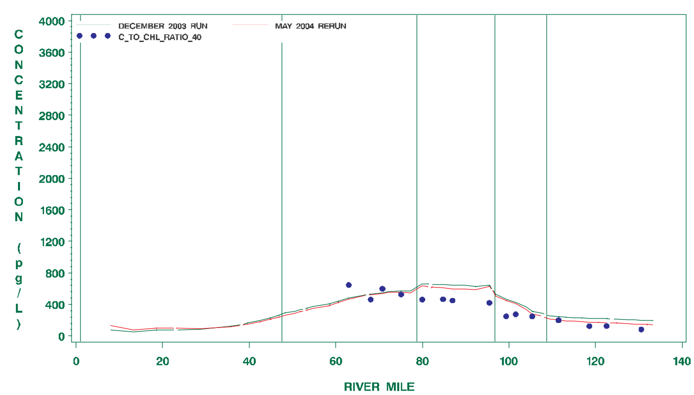
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR PDC – OBSERVED VS SIMULATED FOR DAY 564



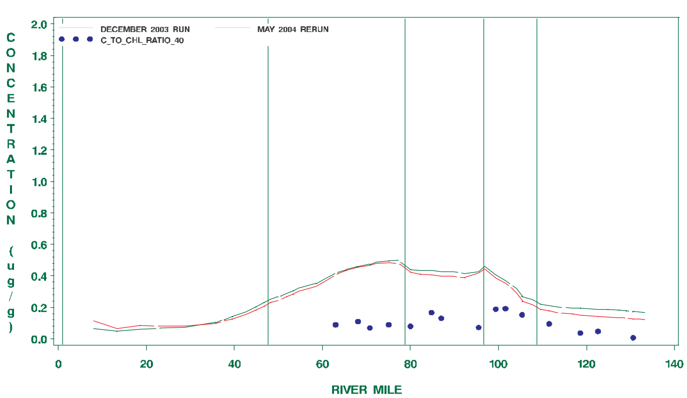
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DDPCB – OBSERVED VS SIMULATED FOR DAY 564



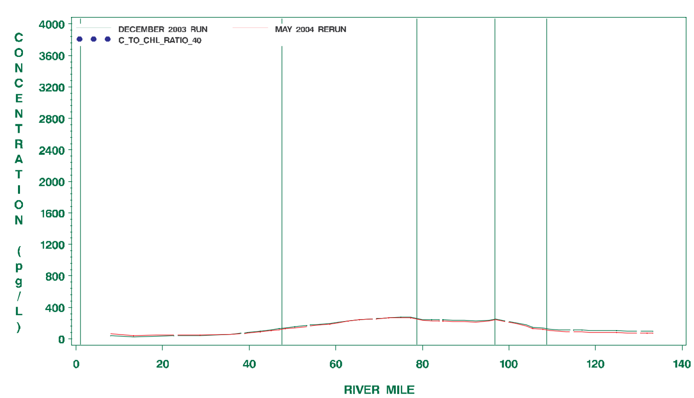
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR R1 – OBSERVED VS SIMULATED FOR DAY 564



21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

SPATIAL PLOT FOR DPCB – OBSERVED VS SIMULATED FOR DAY 564



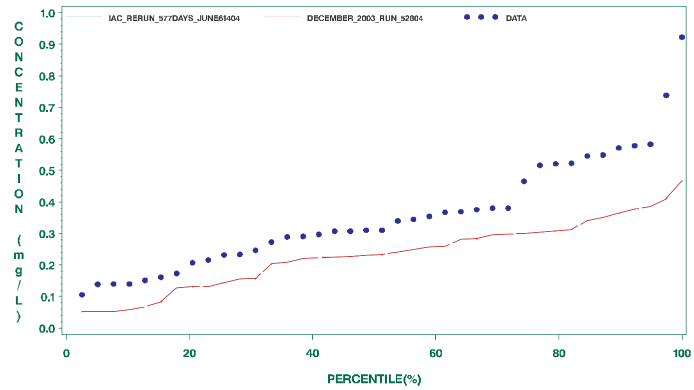
21JUL06 17:06 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

FIGURE 4. 14

CFD PLOTS OF WATER COLUMN ZONE COMPARISONS FOR BIC

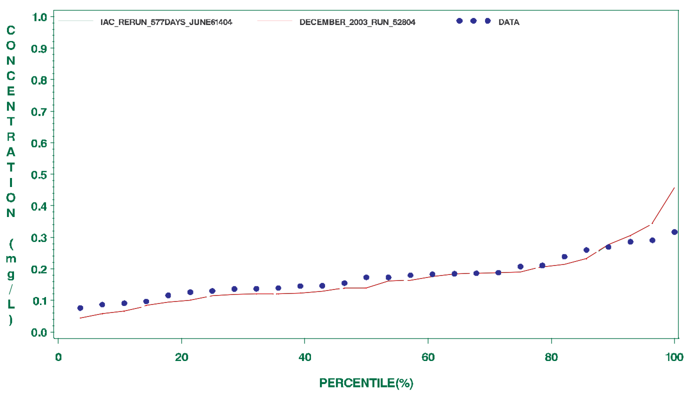
SHORT TERM CALIBRATION RESULTS

CFD PLOTS OF BIC – OBSERVED VS SIMULATED FOR ZONE 5



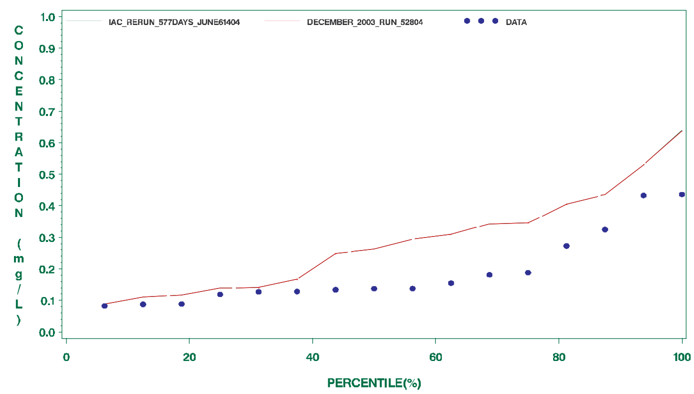
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF BIC – OBSERVED VS SIMULATED FOR ZONE 2



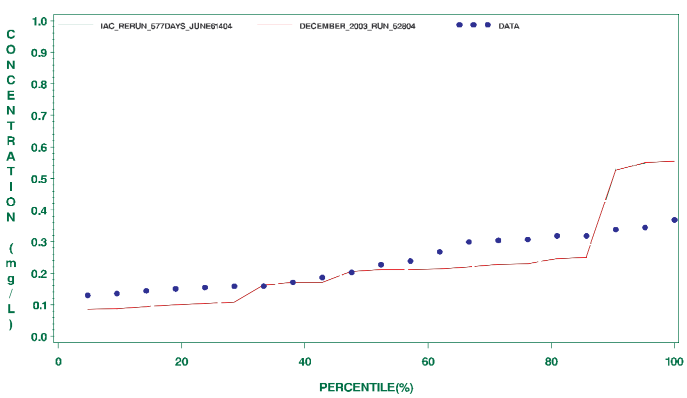
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF BIC – OBSERVED VS SIMULATED FOR ZONE 6



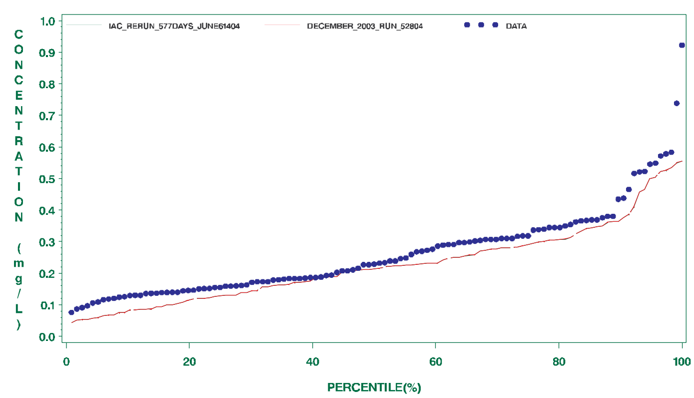
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF BIC – OBSERVED VS SIMULATED FOR ZONE 3



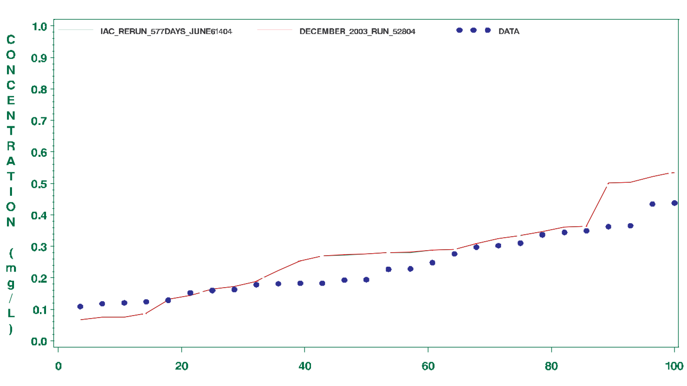
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF BIC – OBSERVED VS SIMULATED FOR ZONE 2–5



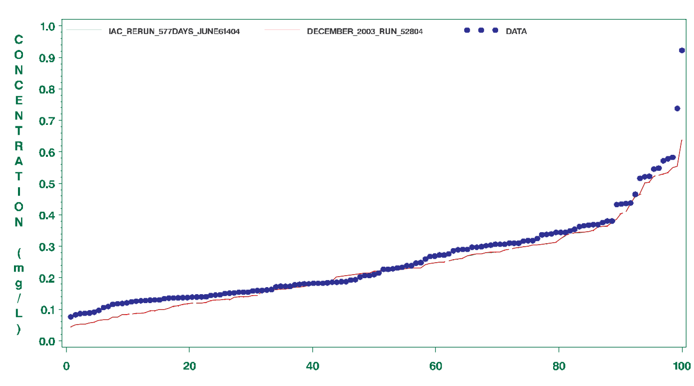
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF BIC – OBSERVED VS SIMULATED FOR ZONE 4



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF BIC – OBSERVED VS SIMULATED FOR ALL ZONES



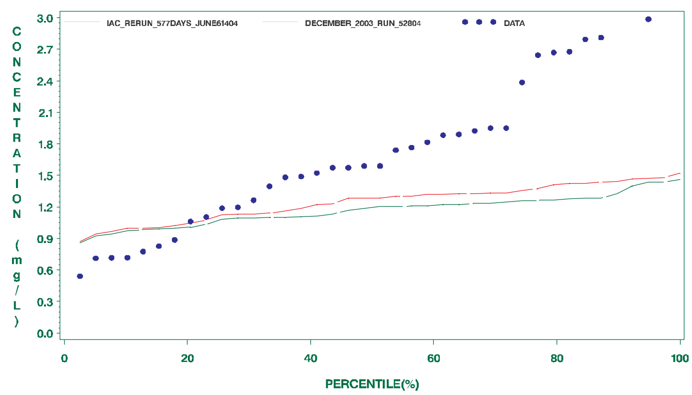
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

FIGURE 4. 15

CFD PLOTS OF WATER COLUMN ZONE COMPARISONS FOR PDC

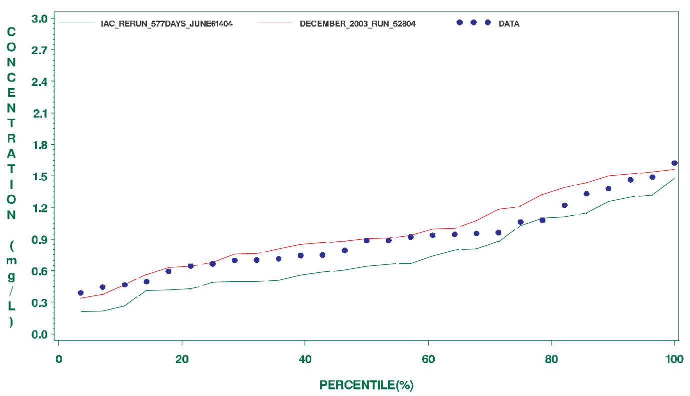
SHORT TERM CALIBRATION RESULTS

CFD PLOTS OF PDC –OBSERVED VS SIMULATED FOR ZONE 5



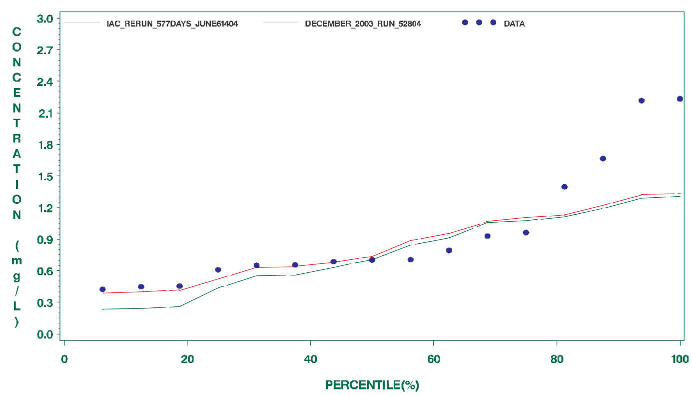
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PDC –OBSERVED VS SIMULATED FOR ZONE 2



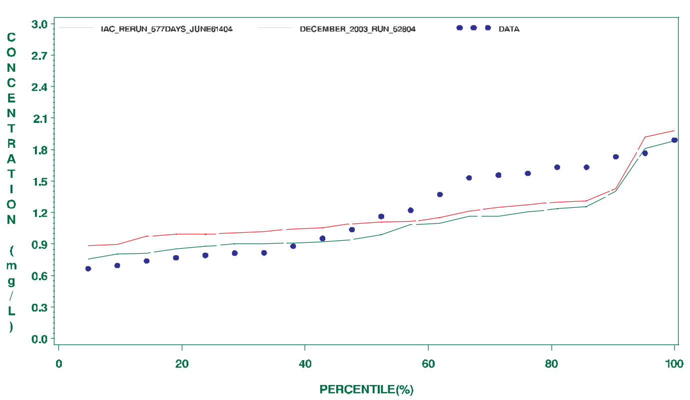
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PDC –OBSERVED VS SIMULATED FOR ZONE 6



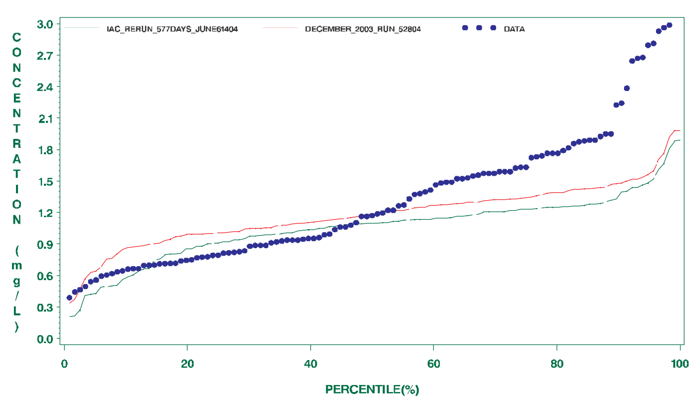
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PDC –OBSERVED VS SIMULATED FOR ZONE 3



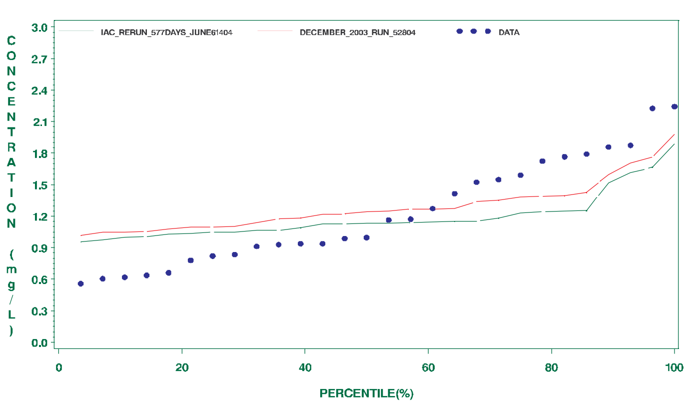
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PDC –OBSERVED VS SIMULATED FOR ZONE 2–5



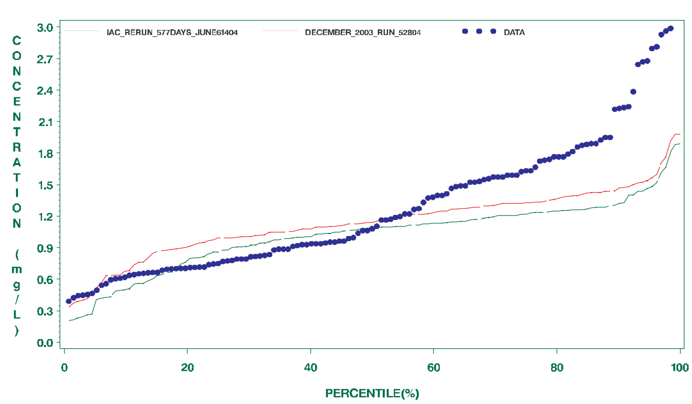
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PDC –OBSERVED VS SIMULATED FOR ZONE 4



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PDC –OBSERVED VS SIMULATED FOR ALL ZONES



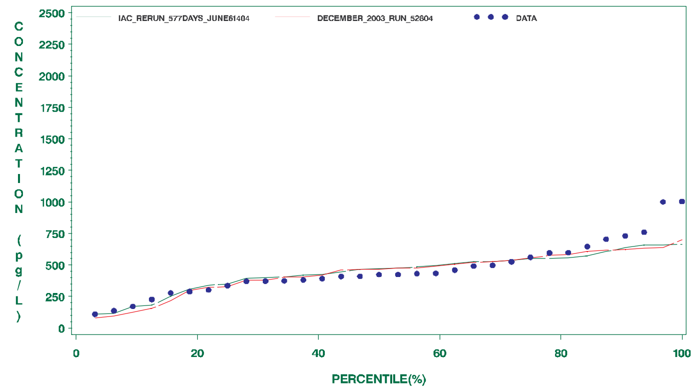
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

FIGURE 4. 16

CFD PLOTS OF WATER COLUMN ZONE COMPARISONS FOR DDPCB

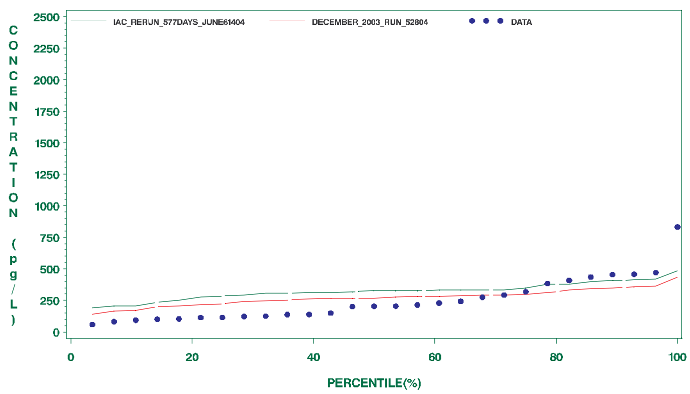
SHORT TERM CALIBRATION RESULTS

CFD PLOTS OF DDPCB —OBSERVED VS SIMULATED FOR ZONE 5



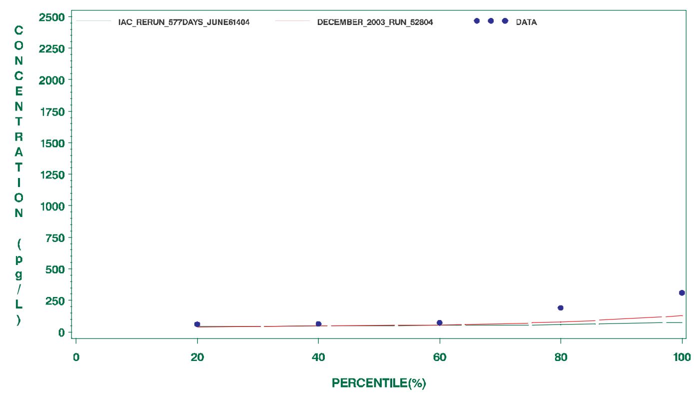
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF DDPCB —OBSERVED VS SIMULATED FOR ZONE 2



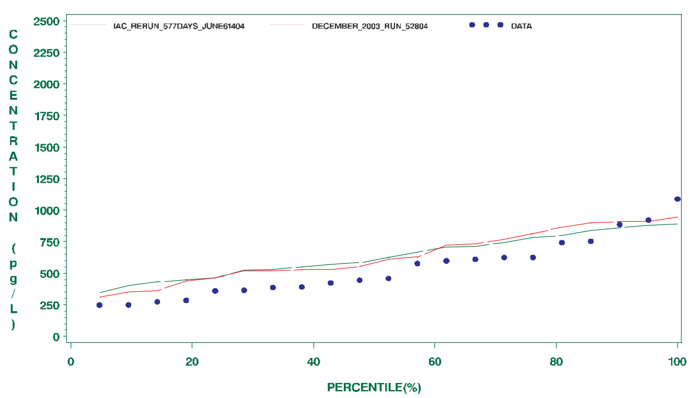
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF DDPCB —OBSERVED VS SIMULATED FOR ZONE 6



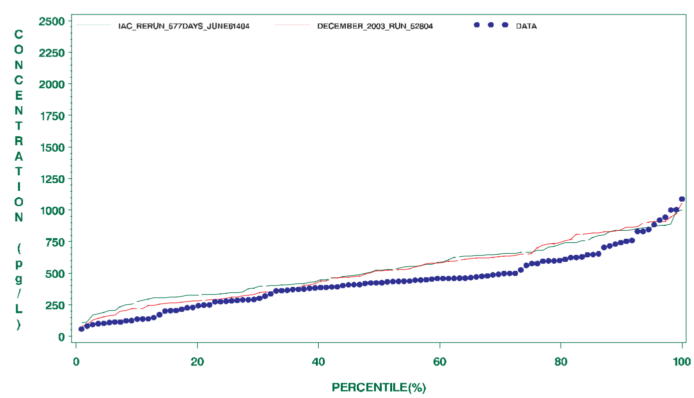
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF DDPCB —OBSERVED VS SIMULATED FOR ZONE 3



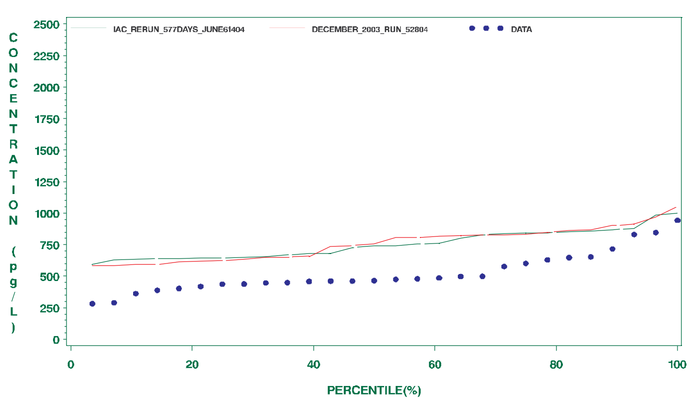
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF DDPCB —OBSERVED VS SIMULATED FOR ZONE 2—5



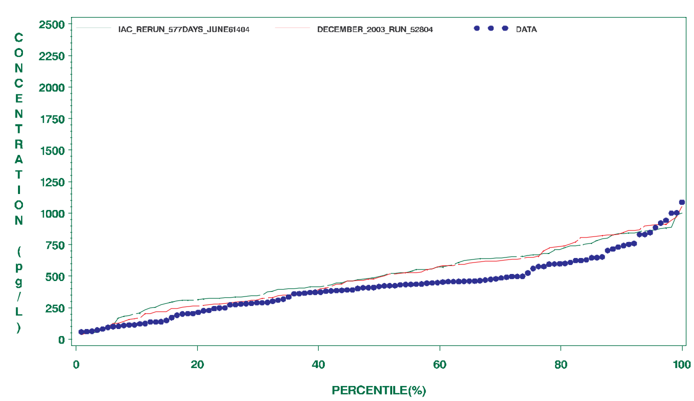
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF DDPCB —OBSERVED VS SIMULATED FOR ZONE 4



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF DDPCB —OBSERVED VS SIMULATED FOR ALL ZONES



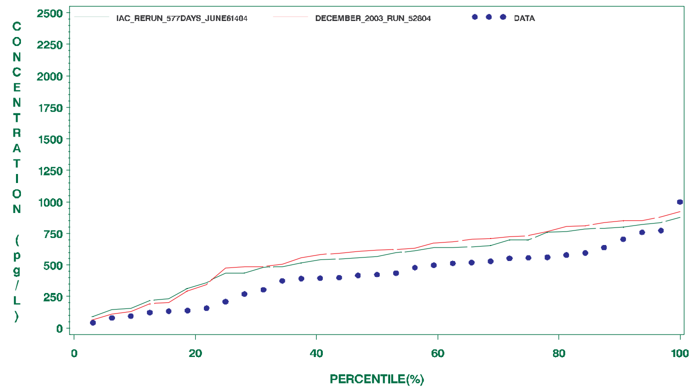
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

FIGURE 4. 17

CFD PLOTS OF WATER COLUMN ZONE COMPARISONS FOR PPCB

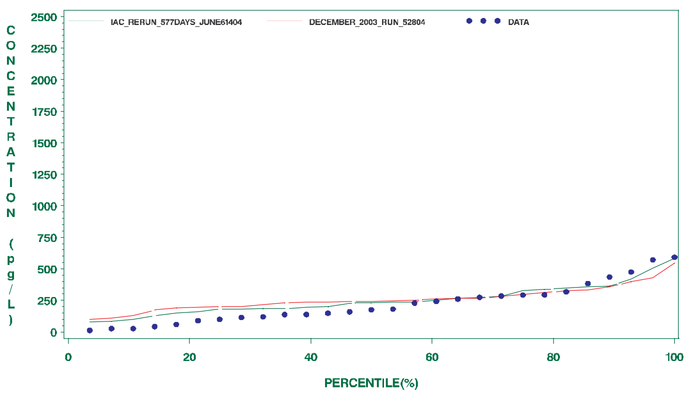
SHORT TERM CALIBRATION RESULTS

CFD PLOTS OF PPCB – OBSERVED VS SIMULATED FOR ZONE 5



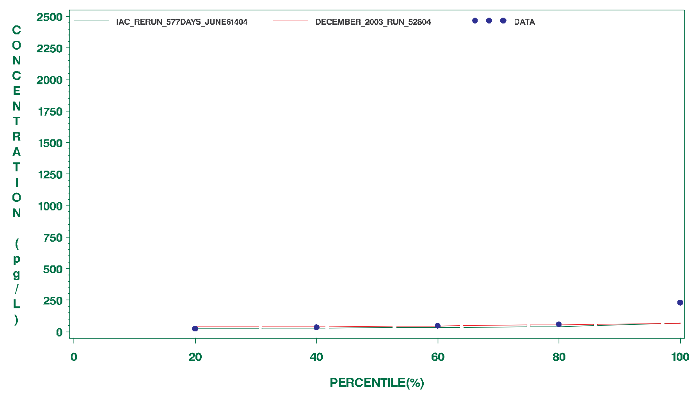
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PPCB – OBSERVED VS SIMULATED FOR ZONE 2



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PPCB – OBSERVED VS SIMULATED FOR ZONE 6



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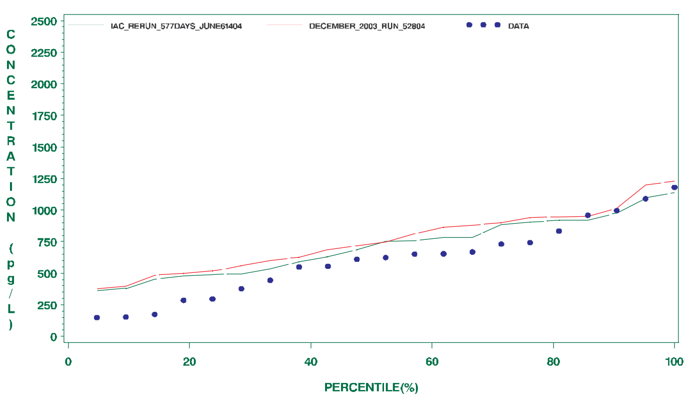
CFD PLOTS OF PPCB – OBSERVED VS SIMULATED FOR ZONE 3



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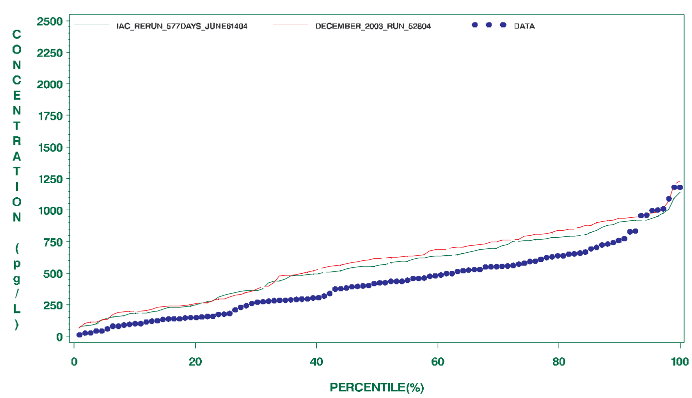
CFD PLOTS OF PPCB – OBSERVED VS SIMULATED FOR ZONE 2 – 5



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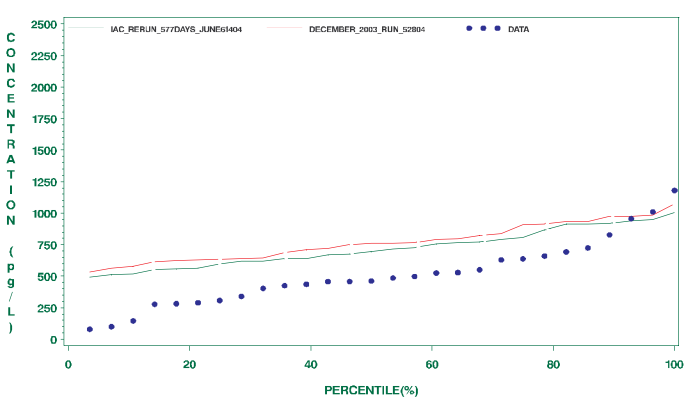
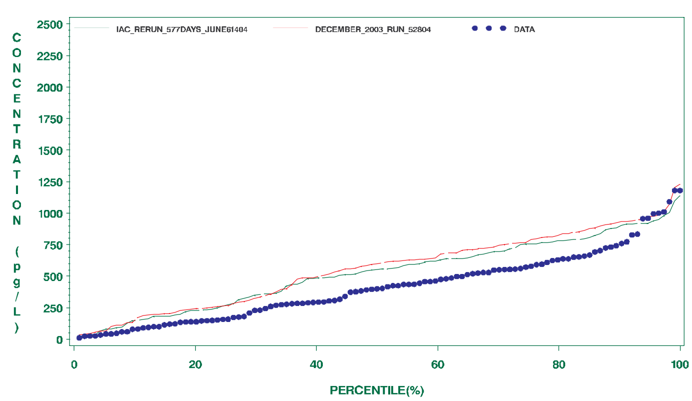
CFD PLOTS OF PPCB – OBSERVED VS SIMULATED FOR ZONE 4



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF PPCB – OBSERVED VS SIMULATED FOR ALL ZONES



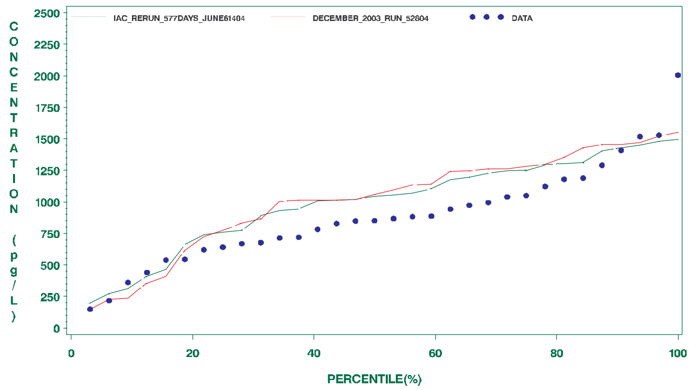
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

FIGURE 4. 18

CFD PLOTS OF WATER COLUMN ZONE COMPARISONS FOR TPCB

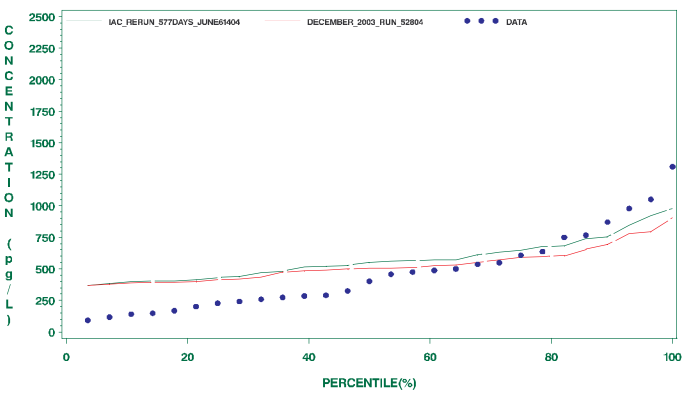
SHORT TERM CALIBRATION RESULTS

CFD PLOTS OF TPCB – OBSERVED VS SIMULATED FOR ZONE 5



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF TPCB – OBSERVED VS SIMULATED FOR ZONE 2



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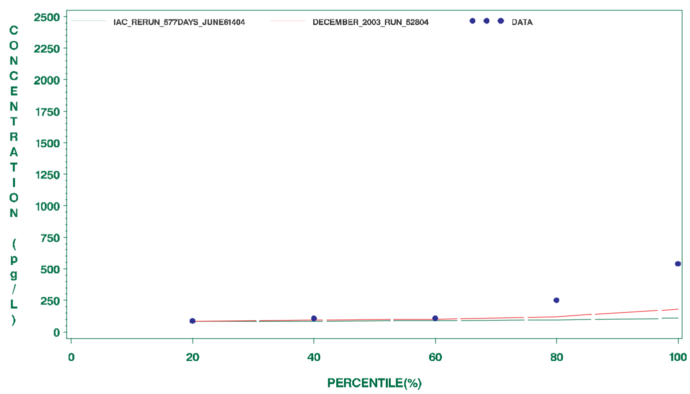
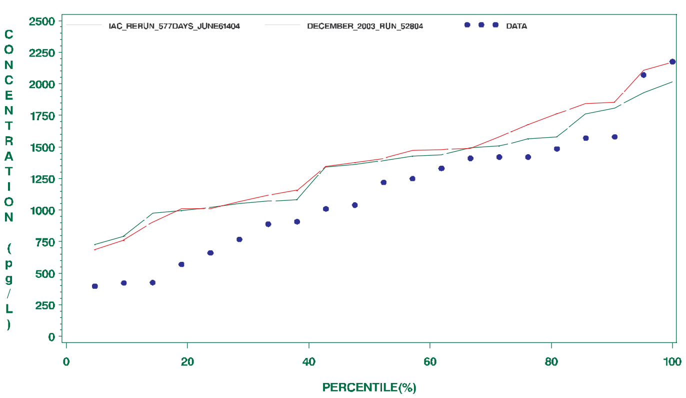
CFD PLOTS OF TPCB – OBSERVED VS SIMULATED FOR ZONE 6



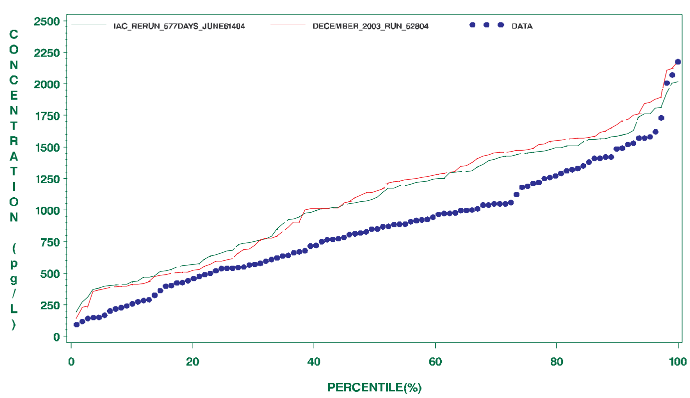
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF TPCB – OBSERVED VS SIMULATED FOR ZONE 3



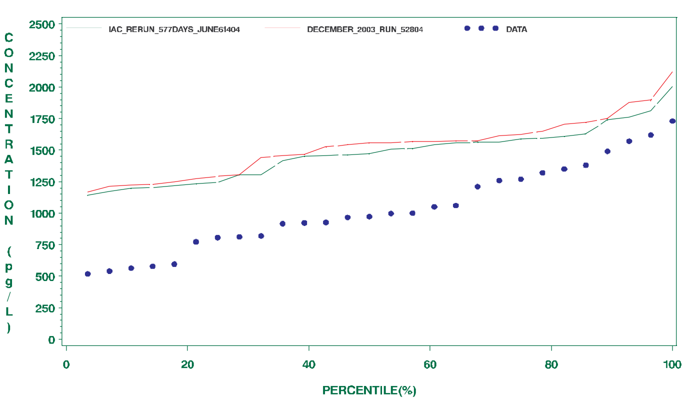
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF TPCB – OBSERVED VS SIMULATED FOR ZONE 2 – 5



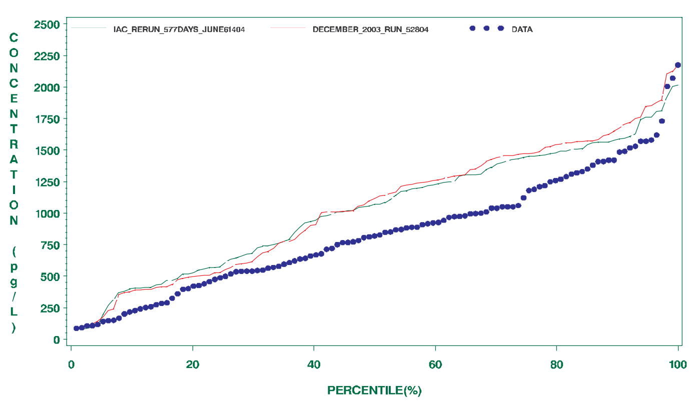
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF TPCB – OBSERVED VS SIMULATED FOR ZONE 4



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF TPCB – OBSERVED VS SIMULATED FOR ALL ZONES



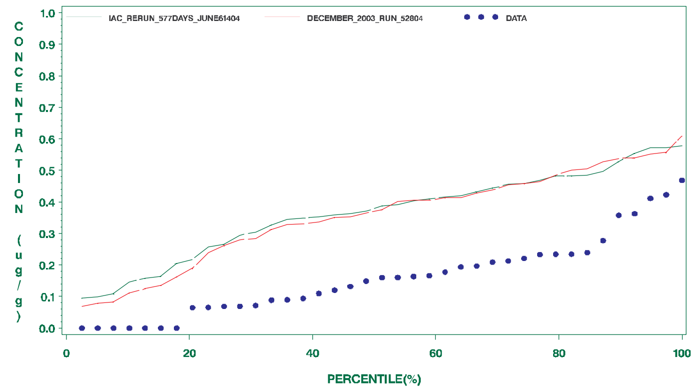
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

FIGURE 4. 19

CFD PLOTS OF WATER COLUMN ZONE COMPARISONS FOR R1

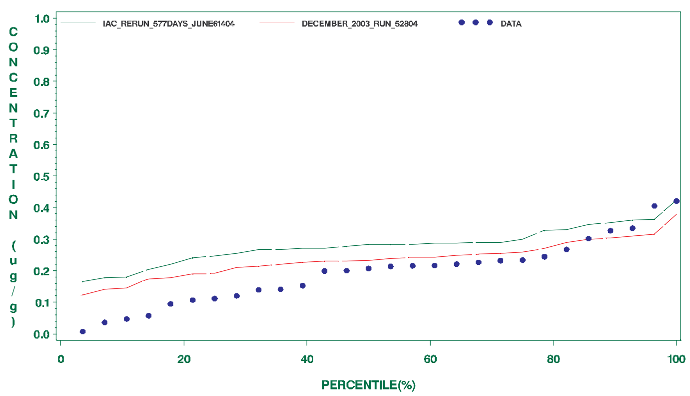
SHORT TERM CALIBRATION RESULTS

CFD PLOTS OF R1 – OBSERVED VS SIMULATED FOR ZONE 5



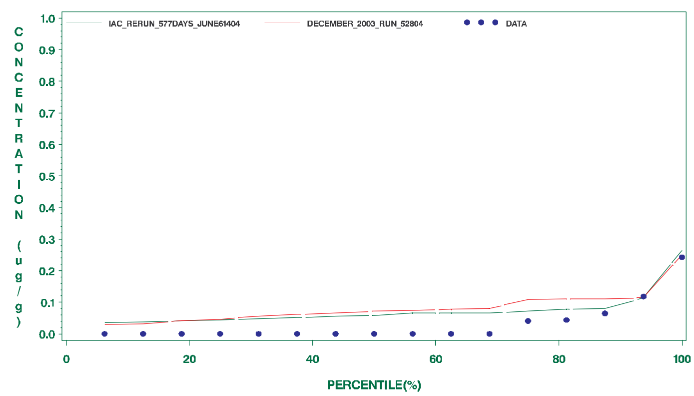
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF R1 – OBSERVED VS SIMULATED FOR ZONE 2



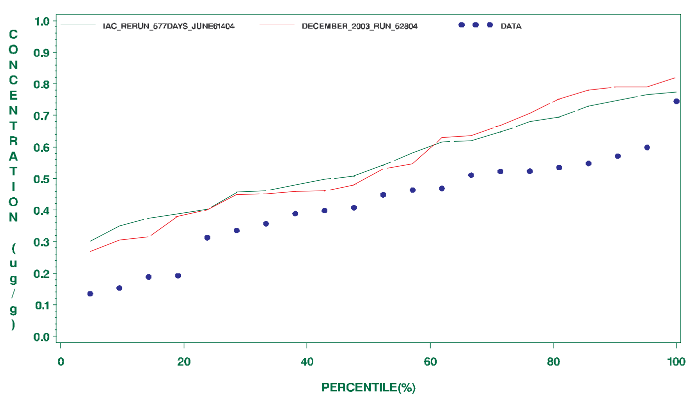
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF R1 – OBSERVED VS SIMULATED FOR ZONE 6



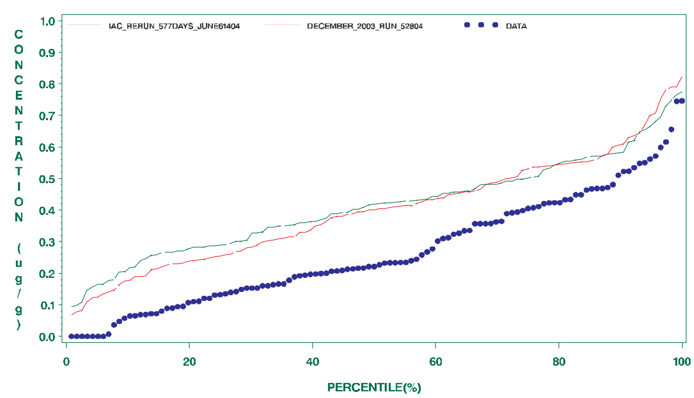
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF R1 – OBSERVED VS SIMULATED FOR ZONE 3



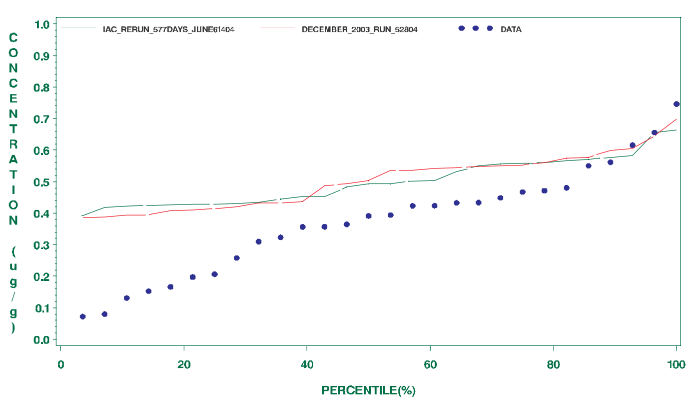
21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF R1 – OBSERVED VS SIMULATED FOR ZONE 2–5



21JUL06 17:47 FILE NUMBER IAC_RERUN_577DAYS_JUNE61404_VS_DECEMBER_2003_RUN_52804

CFD PLOTS OF R1 – OBSERVED VS SIMULATED FOR ZONE 4



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CFD PLOTS OF R1 – OBSERVED VS SIMULATED FOR ALL ZONES

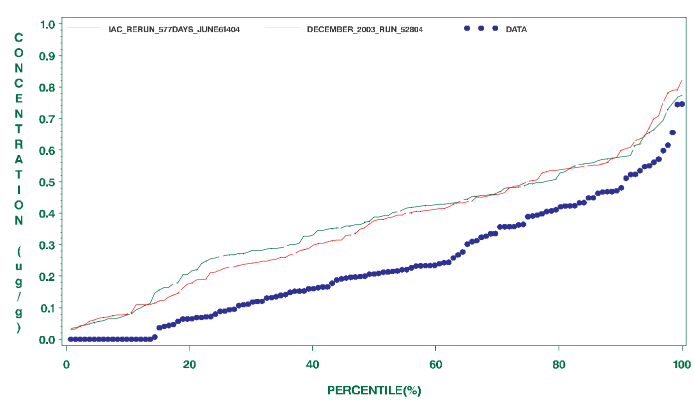

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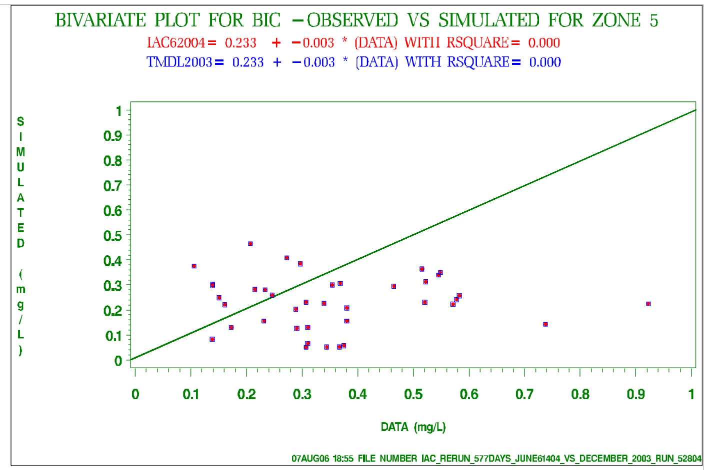
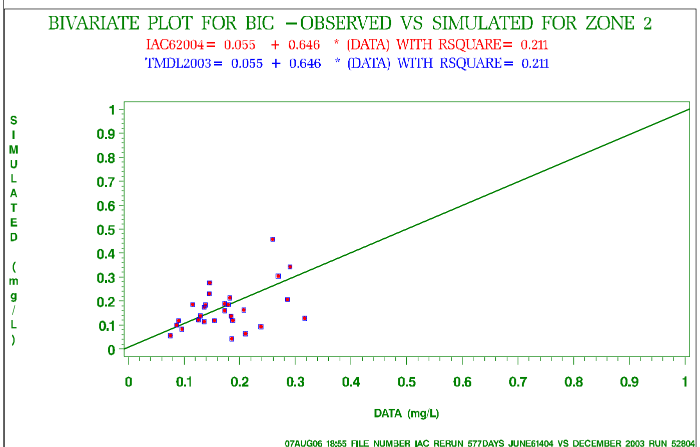
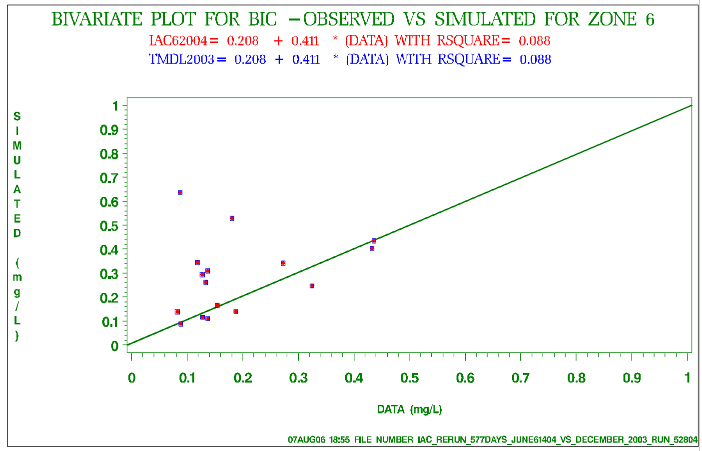
FIGURE 4. 20

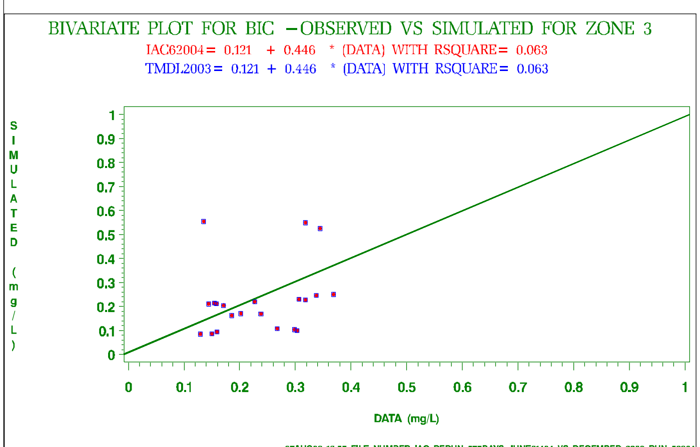
BIVARIATE PLOTS OF WATER COLUMN ZONE COMPARISONS FOR BIC

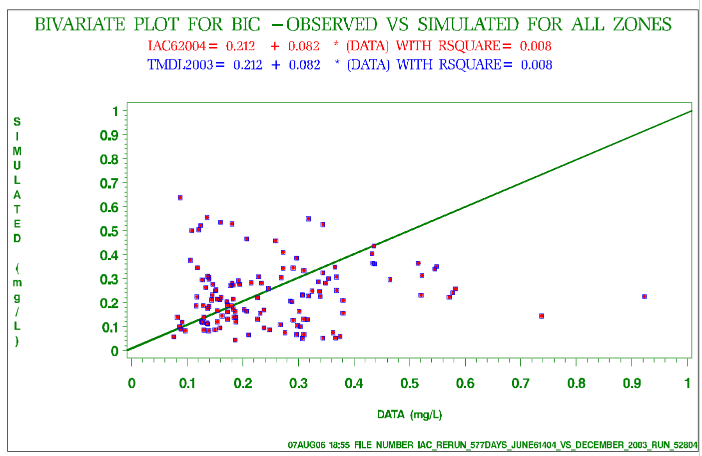
SHORT TERM CALIBRATION RESULTS

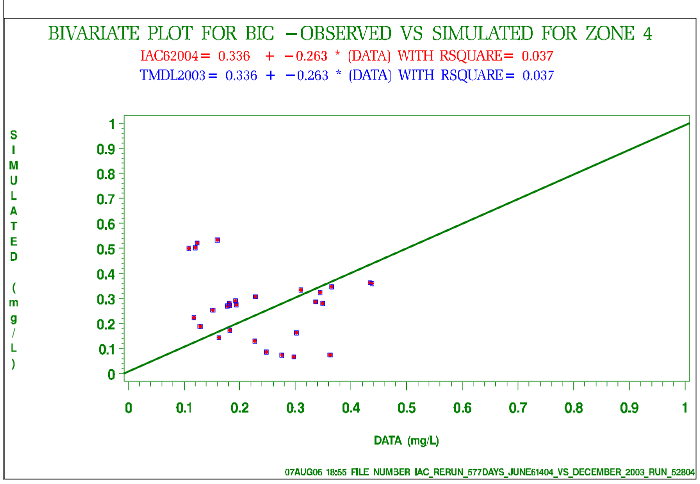












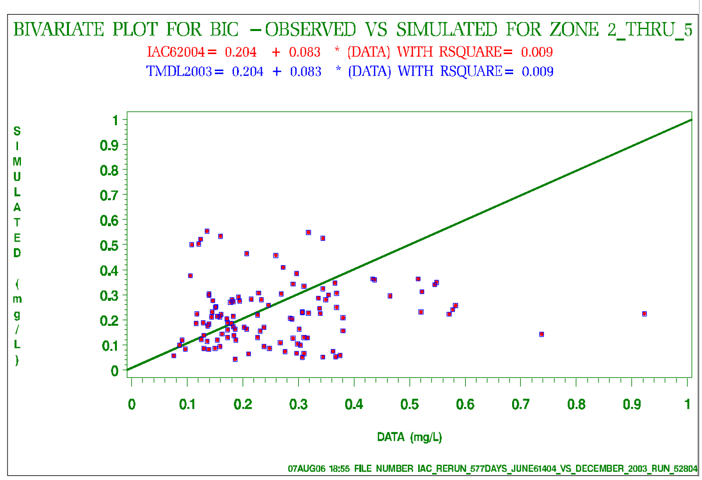
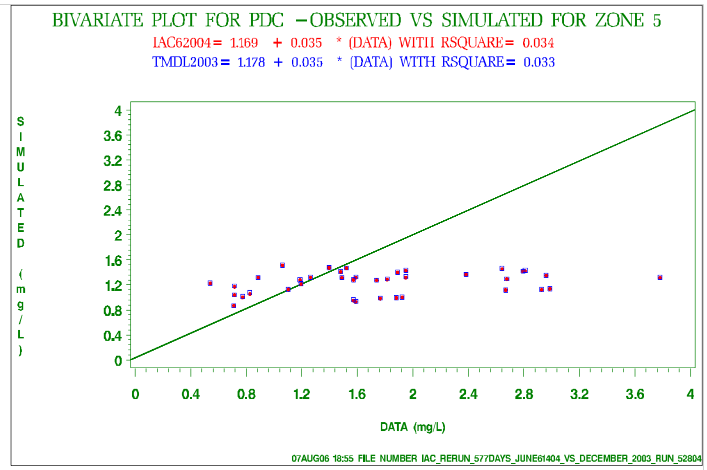
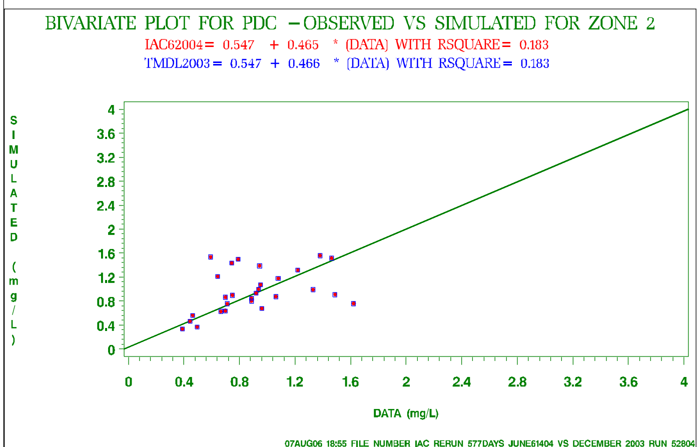


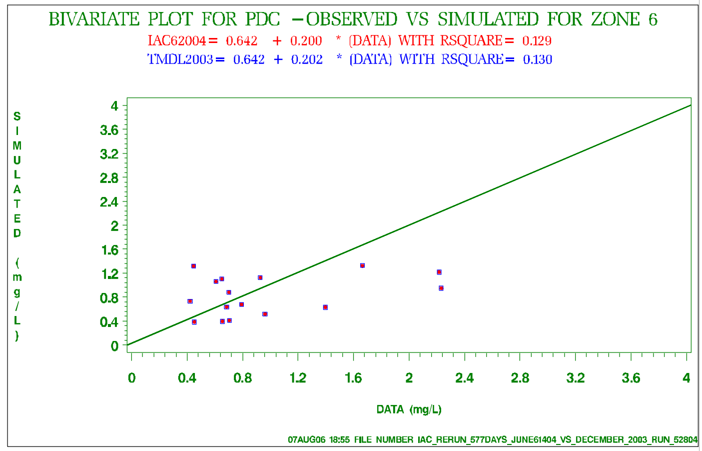
FIGURE 4. 21

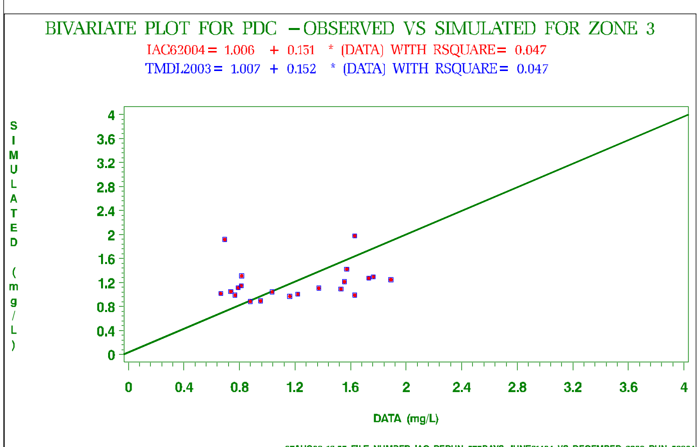
BIVARIATE PLOTS OF WATER COLUMN ZONE COMPARISONS FOR PDC

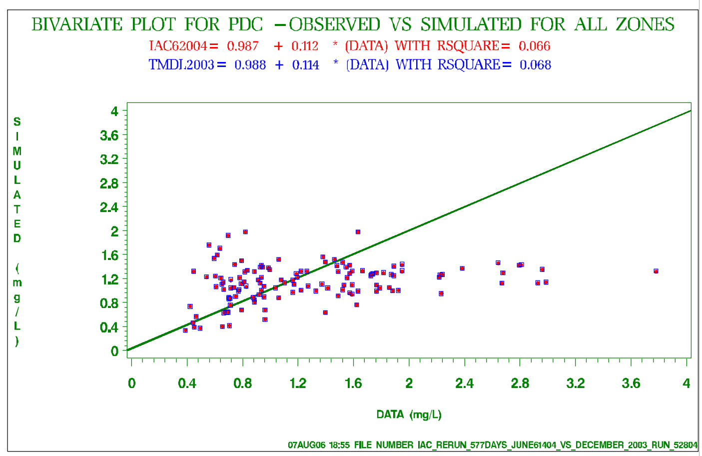
SHORT TERM CALIBRATION RESULTS

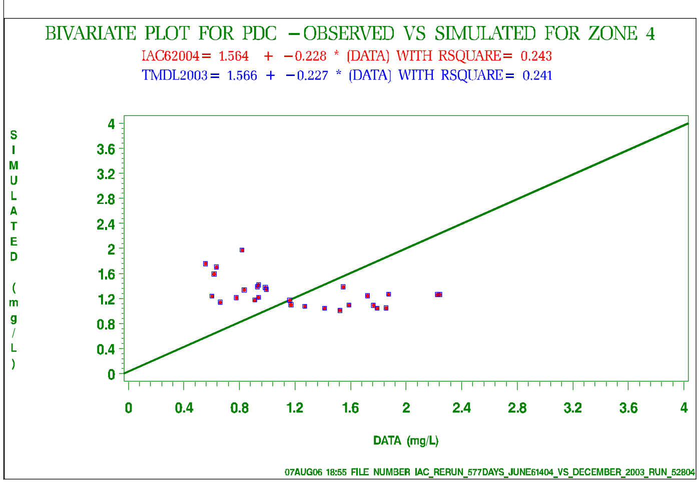












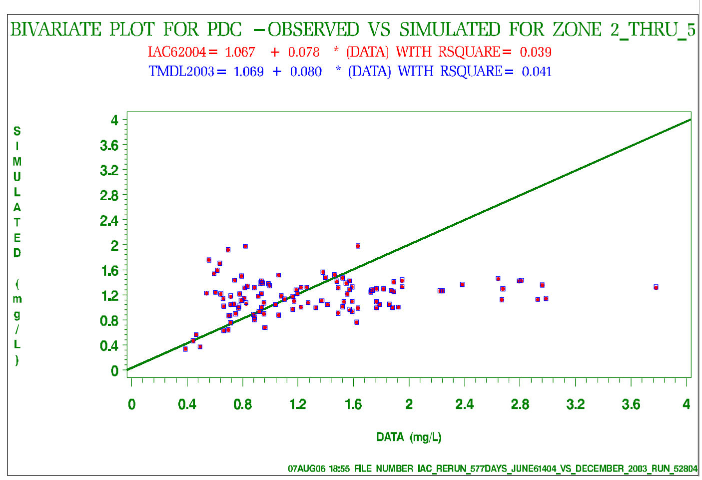
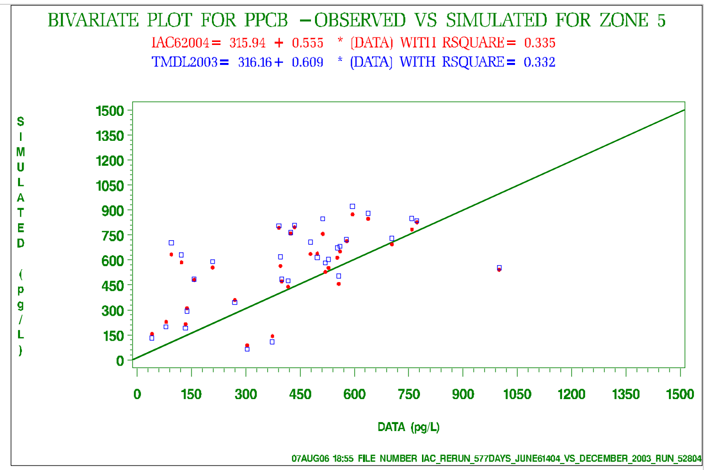
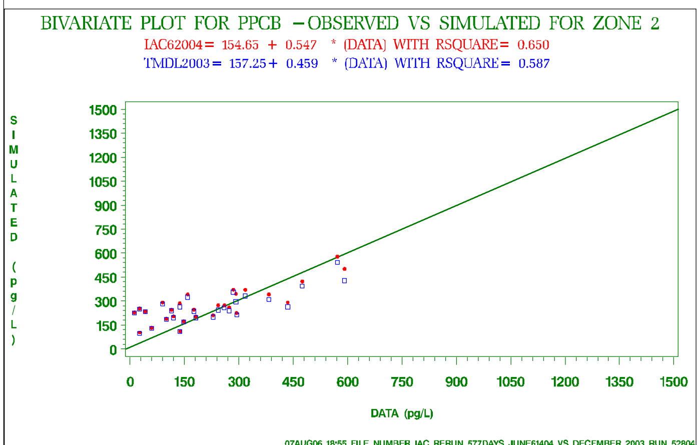


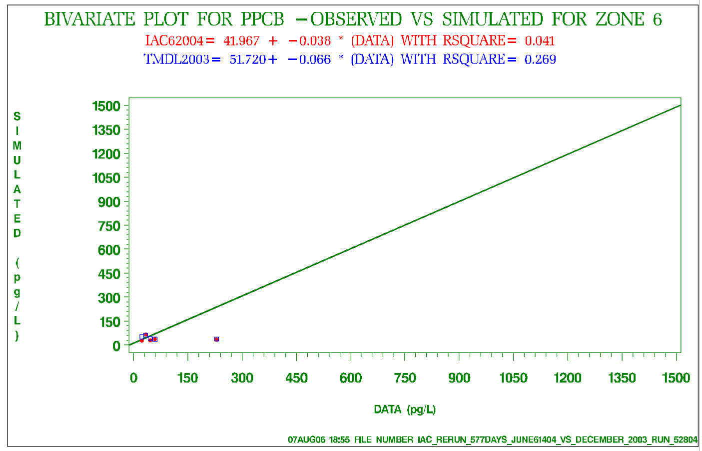
FIGURE 4. 22

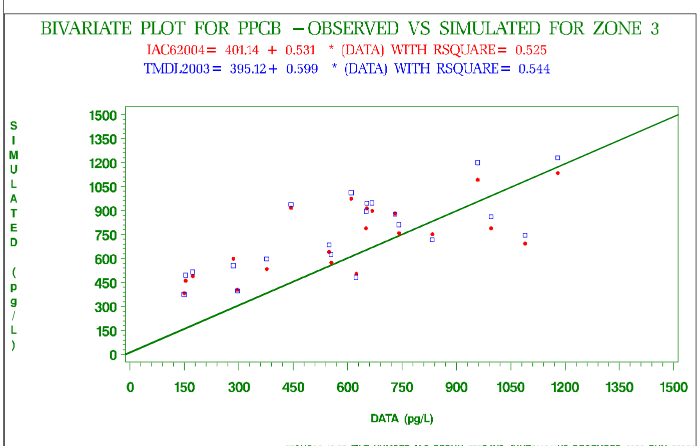
BIVARIATE PLOTS OF WATER COLUMN ZONE COMPARISONS FOR PPCB

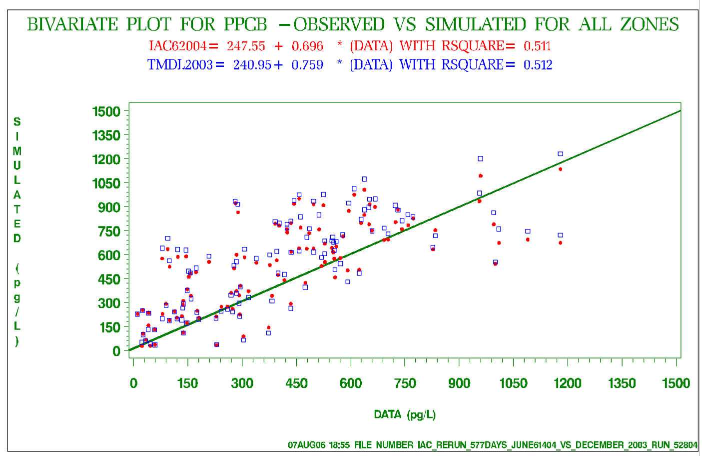
SHORT TERM CALIBRATION RESULTS

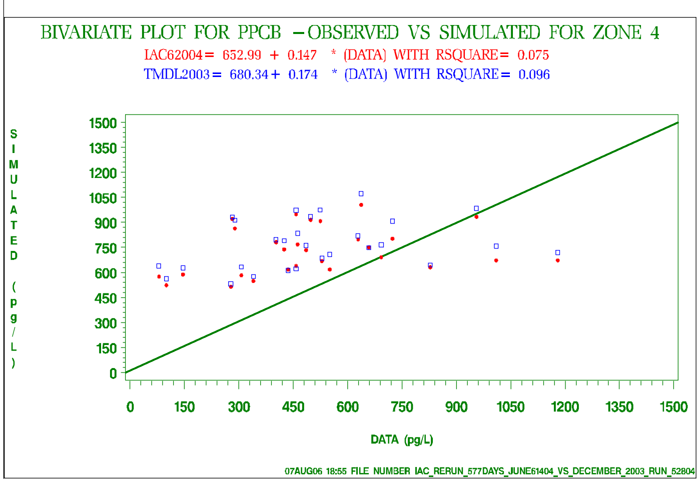












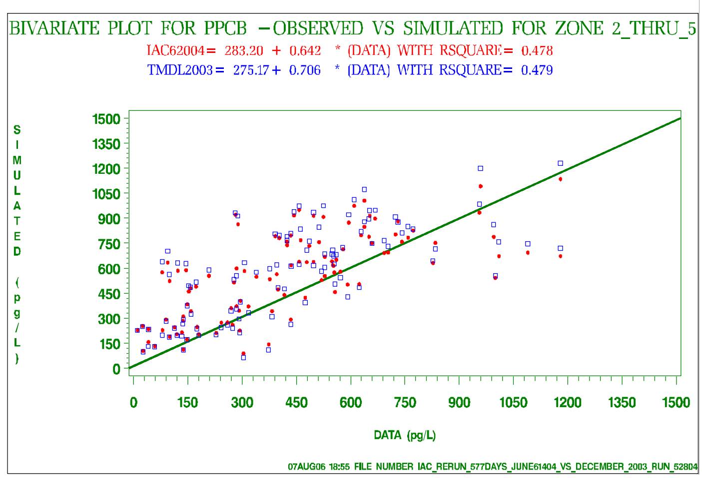
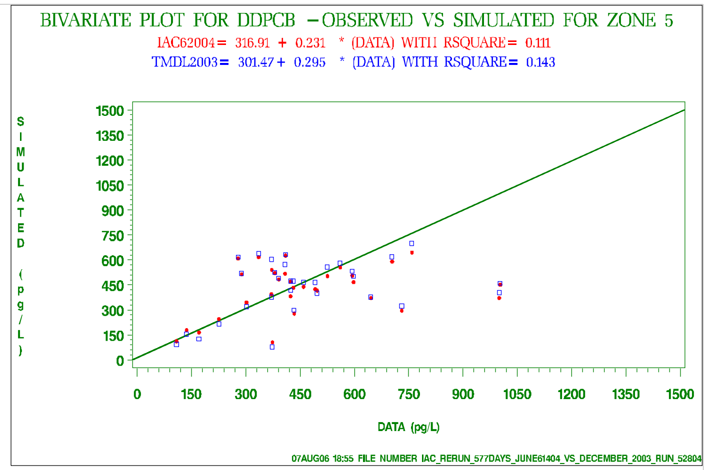
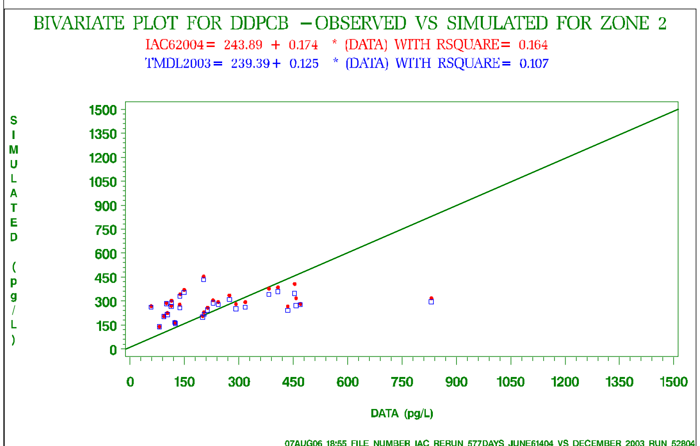


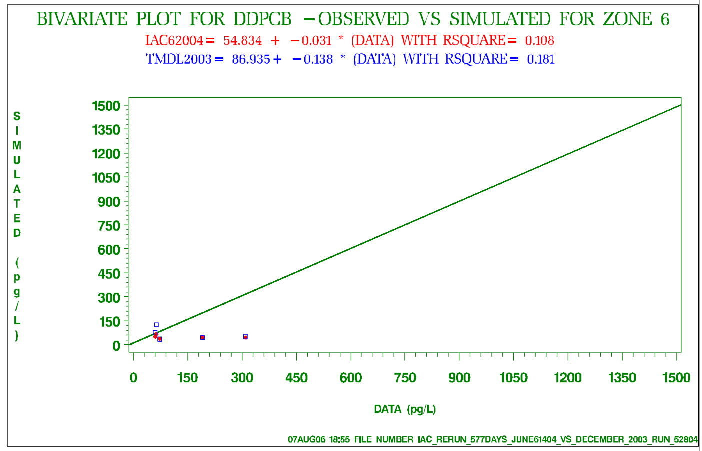
FIGURE 4. 23

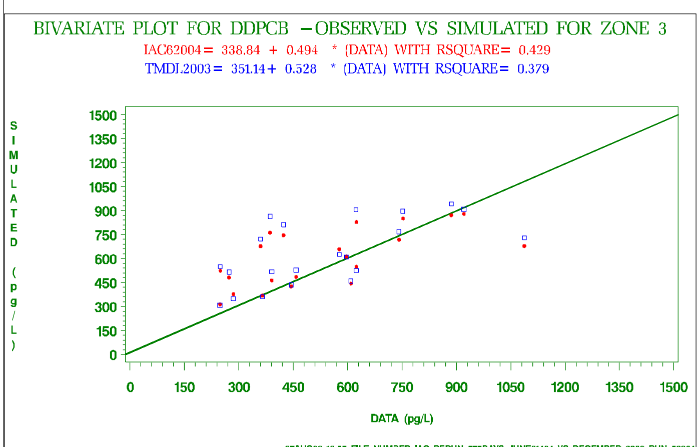
BIVARIATE PLOTS OF WATER COLUMN ZONE COMPARISONS FOR DDPCB

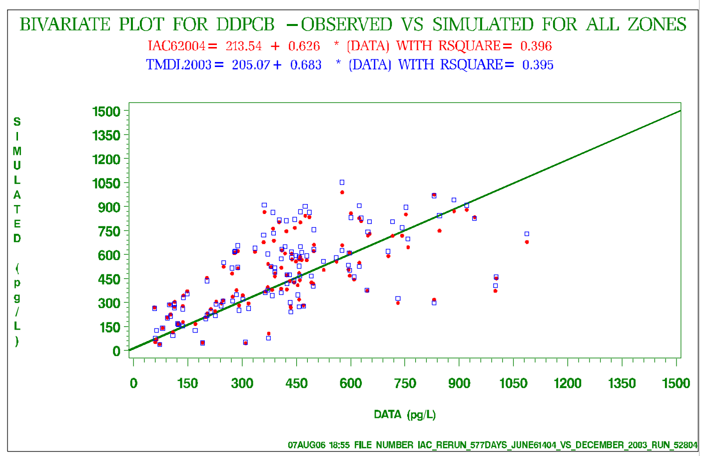
SHORT TERM CALIBRATION RESULTS

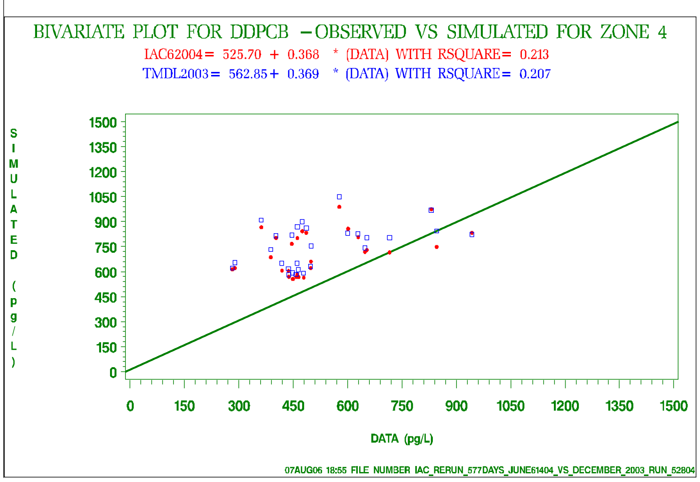












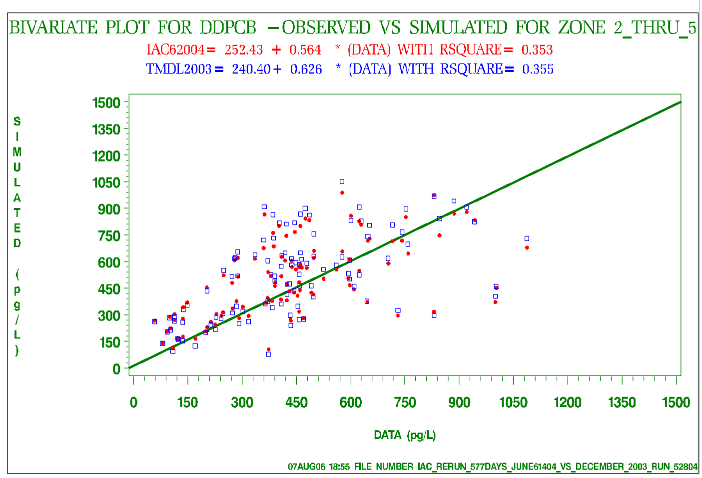
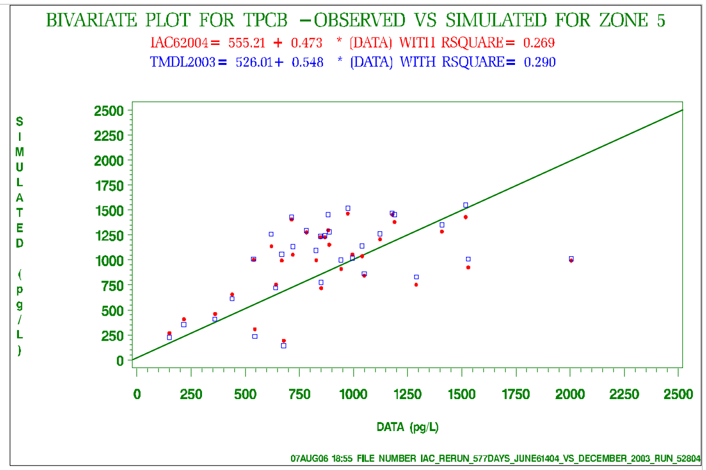
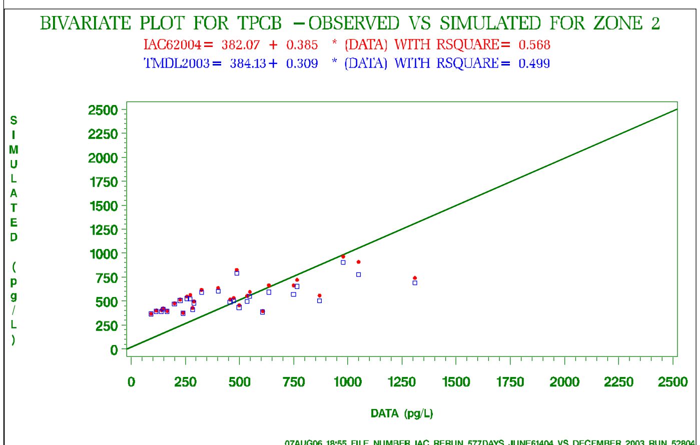


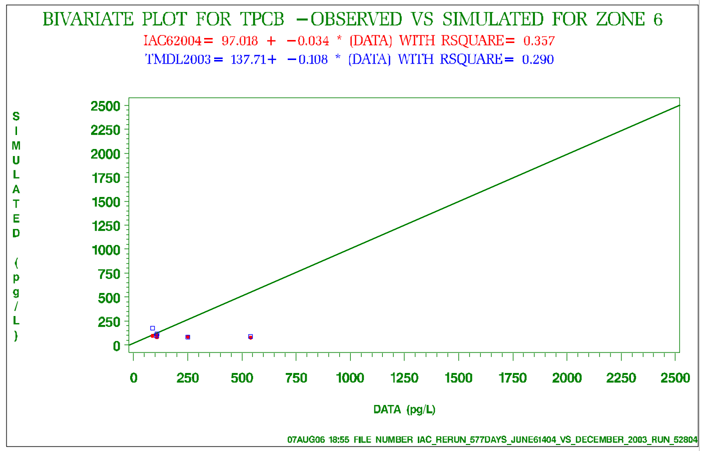
FIGURE 4. 24

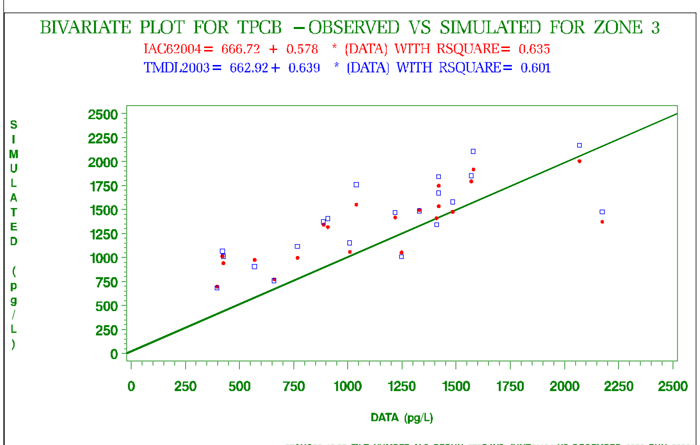
BIVARIATE PLOTS OF WATER COLUMN ZONE COMPARISONS FOR TPCB

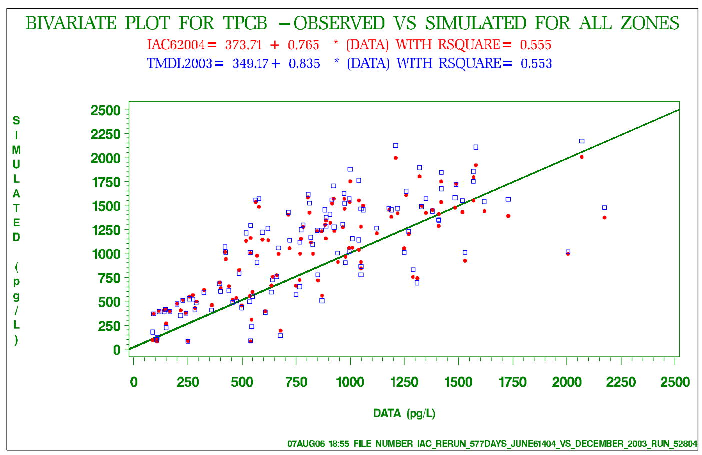
SHORT TERM CALIBRATION RESULTS

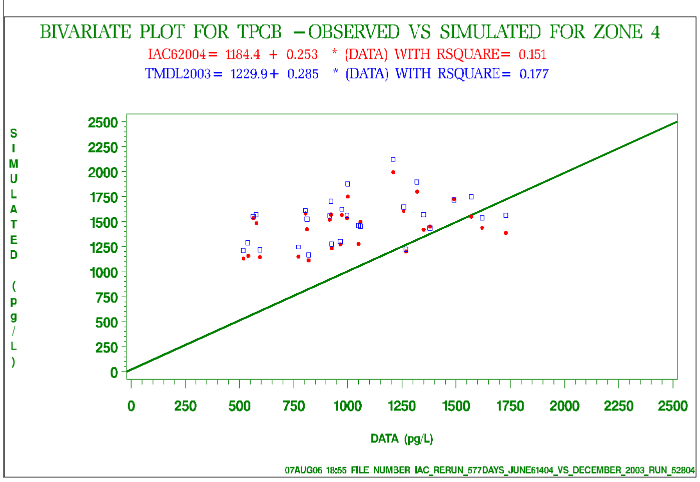


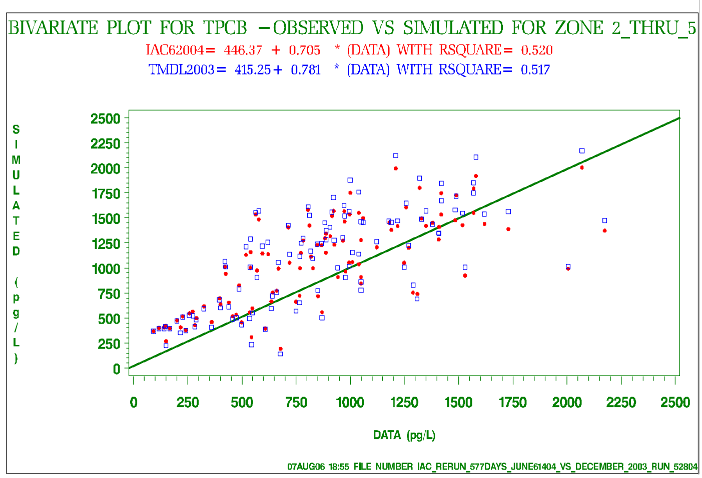












5 Model Sensitivity Analyses

Sensitivity analyses were performed to evaluate and understand the responses and behaviors of the Delaware Estuary PCB Model (DELPCB). Two sets of short-term sensitivity analyses were performed and the results are presented in the following two subsections. Subsection 5.1 - Two-Year Short Term Sensitivity Analysis describes the parameter perturbation sensitivity analyses. Results are expressed in dimensionless relative sensitivity terms. Subsection 5.2 - 575-day Calibration Period Sensitivity Analysis presents the relative influence from four source categories through what-if scenario simulations during the calibration period. The results from both parameter perturbation and scenario simulation results can be used to identify the most sensitive input parameters for each of the model state variables and to efficiently guide efforts for potential model enhancement and resource allocation as a part of Stage 2 PCB TMDL.

5.1 Two-Year Short Term Sensitivity Analysis

5.1.1 Approach

A major purpose of these sensitivity analyses is to evaluate and understand the responses and behaviors of the Delaware Estuary PCB Model (DELPCB) by systematically varying input conditions. The approach is designed to reveal the sensitivity of the model to the individual input conditions that were assigned for the calibration period of the DELPCB model. Sensitivities of parameters can be compared across the numerous simulations that were conducted by expressing the results in dimensionless relative sensitivities. The results of this study may be useful in more efficiently allocating efforts in future modeling work that will support the development of the Stage-2 PCB TMDLs by focusing on more critical or sensitive parameters.

A total of fifty-three (53) short term sensitivity simulations (STSS) were performed. A detailed description of the individual scenarios and tracking numbers for those scenarios are described in Table 5-1. Model input conditions for parameters, constants, coefficients, PCB and carbon loads, initial concentrations, and boundaries were varied. During each simulation one input condition was changed with a fixed rate of +/- 30 percent of its baseline value while retaining the remaining input conditions at the same value as in the baseline simulation conditions. Sensitivity simulations in 2 out of 53 cases, STSS_3040 and 3042, are not qualified to make comparisons because input conditions were not changed with a rate of +/- 30 percent. Responses of five state variables of model outputs and carbon-normalized particulate PCB concentrations (R1) were examined to assess the impacts of the output results from the input condition perturbation. These state variables are Biotic Carbon (BIC), Particulate Detrital Carbon (PDC), total pentachlorobiphenyls (TPCBs), truly dissolved plus dissolved organic carbon-bound penta-PCBs (DDPCBs), and particulate organic carbon-bound penta-PCBs (PPCBs).

Prior to performing the sensitivity analysis, initial baseline conditions were reassigned to their equilibrium conditions with the external loads for 348 water column and sediment segments for PCBs and 87 water column segments for both PDC and BIC. This was done to minimize the influence of initial conditions during the sensitivity simulations. The sensitivity analyses are focused on a short term period impact even though the true impact from any input condition changes may require a decade-long simulation to obtain the equilibrium condition.

Table 5.1 - Scenario tracking numbers and description of scenarios

Scenario Tracking number	Change in Input Condition
3001	PCB from 'Contaminated Site Load'
3002	PCB from 'Non-point Source Load'
3003	PCB from 'Point Source Load'
3004	PCB from 'CSOs Load'
3005	PCB from' Other Tributaries' Load'
3006	PCB from 'Wet and Dry Air Deposition'
3007	PCB from All_six_ Load_Categor ies
3008	PDC 'Non-point Source Load'
3009	PDC 'Point Source Load'
3010	PDC' CSOs Load'
3011	PDC' other Tributaries' Load'
3012	PDC 'Wet and Dry Air Deposition'
3013	PDC 'Marsh Load'
3014	PDC All_six_Load_Categor ies
3015	BIC 'other Tributaries' Load'
3016	BIC Primary production rate
3017	BIC two_Loads (Primary production rate plus loads from tribu taries)
3018	PCB at Delaware R. at Trenton Boundary
3019	PCB at Schuylkill River Boundary
3020	PCB at C&D Canal Boundary
3021	PCB at Atlantic Ocean Boundary
3022	PDC at Delaware R. at Trenton Boundary
3023	PDC at Schuylkill River Boundary
3024	PDC at C&D Canal Boundary
3025	PDC at Atlantic Ocean Boundary
3026	BIC at Delaware R. at Trenton Boundary
3027	BIC at Schuylkill River Boundary
3028	BIC at C&D Canal Boundary
3029	BIC at Atlantic Ocean Boundary
3030	PCB for all four boundaries
3031	PDC for all four boundaries
3032	BIC for all four boundaries
3033	Gaseous phase atmospheric PCBs
3034	Partition coefficient to organic carbon (Log (K_{oc}))
3035	Partition coefficient to dissolved organic carbon (Log (K_{doc}))
3036	BIC decay rate to PDC in wa ter column
3037	PDC decay rate to DOC in sediment layer
3038	PDC decay rate to DOC in water column
3039	Water temperature with +/ - 30 percent
3040 *	Water temperature with +/ - 5 degrees
3041	Wind speed
3042 *	Zeroed out initial PCB conditions in wate r column and sediment layers
3043	Air temperature
3044	Molecular weight
3045	DOC in Water column and Sediment
3046	BIC net settling rate
3047	PDC Gross settling rate
3048	PDC Gross resuspension rate
3049	Enhanced diffusion rate across sediment -water interface
3050	Molecular diffusion rate between surface and deep sediment layers
3051	Initial PCB concentrations in sediment layer
3052	Initial PCB concentrations in water column
3053	Depth of the surface sediment layers

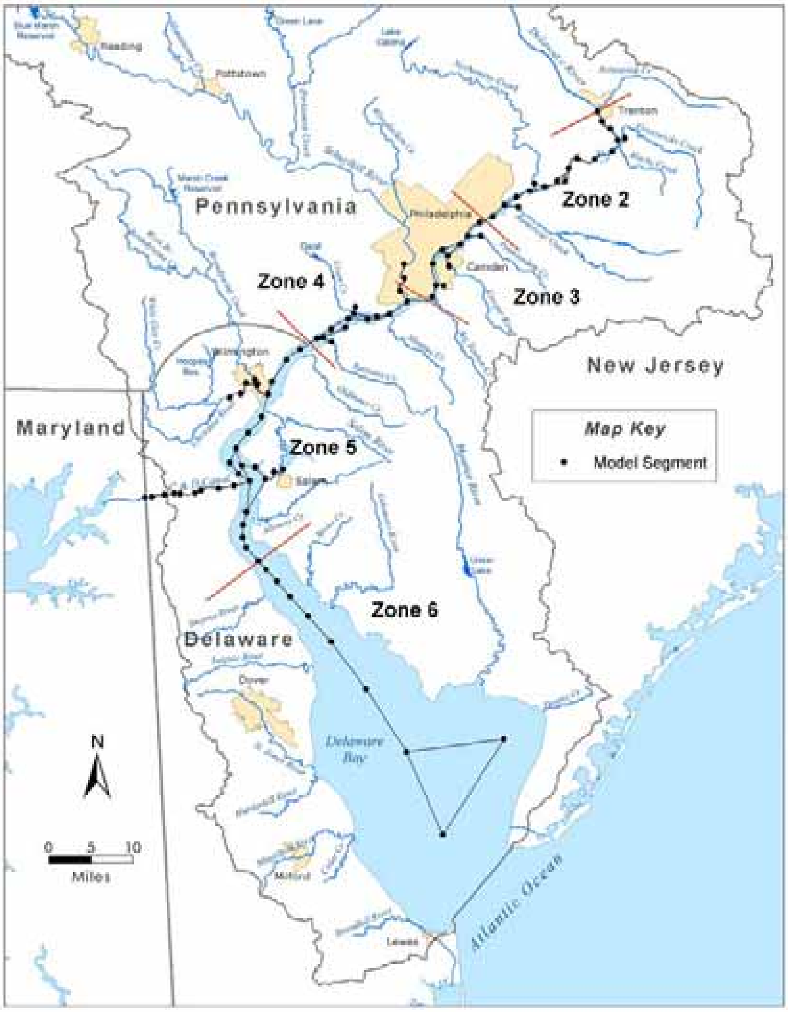
* Simulation conditions are not qualified to calculate the relative sensitivity

The sensitivity simulations were performed for a two year period by cycling a representative annual set of hydrologic conditions. The period of February 2002 to January 2003, a subset of the 575 day calibration period, was selected as the representative annual set of hydrologic conditions. The relative sensitivities were computed using model outputs from the 2nd year of the simulation results.

5.1.2 Results and Discussion

Five state variables, BIC, PDC, TPCB, DDPCB and PPCB, and particulate carbon-normalized penta-PCBs (R1) were of concern in these sensitivity analyses. All evaluations focused on concentration changes in the water column for the 2nd year of the model simulation results. Model simulations were not conducted for longer durations due to extensive model executions times. Therefore, the ultimate (or the absolute) impacts were not quantified in this study. Rather, the sensitivity simulations were performed for two years and the relative influences were evaluated by comparing the model outputs between the baseline and the sensitivity simulation in the 2nd year.

Figure 5.1 - Delaware Estuary water quality management zones and model segmentation



The relative sensitivities are varied spatially and temporally. The short term sensitivity simulation results are organized and summarized for five locations in the Estuary representing five water quality management zones (Zones 2-6) in the Delaware River Estuary (Figure 5-1). The selected locations are listed below.

1. Zone 6: Segment number 83 = River Mile 29
2. Zone 5: Segment number 24 = River Mile 68
3. Zone 4: Segment number 38 = River Mile 85
4. Zone 3: Segment number 51 = River Mile 99
5. Zone 2: Segment number 69 = River Mile 123

The criteria used in selecting the above locations are: (1) locations should represent variable air concentrations, (2) one location should represent each water quality management zone, (3) the location should be near the mid-point of the zone, and (4) the locations should have similar burial rates. Any branched segment was not considered. Median values from the results of the second year of model simulations are used in sensitivity calculation to simplify the temporal variation.

Relative Sensitivity (S_R)

The resulting scenario simulations are summarized in Tables 5-2 to 5-4. Relative sensitivities are calculated to evaluate relative importance among scenarios using the following equation:

$$S_R = \left(\frac{Input_{Baseline}}{Output_{Baseline}}\right)\left(\frac{\Delta Output}{\Delta Input}\right) = \frac{\left(\dfrac{\Delta Output}{Output_{Baseline}}\right)}{\left(\dfrac{\Delta Input}{Input_{Baseline}}\right)} \qquad \text{(Equation 1)}$$

The relative sensitivities can be compared across scenarios since they are dimensionless. The relative sensitivities are calculated using the median values from the second year of model simulations. The relative sensitivity (S_R) is the ratio of the rate change in output from 0.6 (60 percent overall or +/- 30 percent) changes in input (Equation 1). The relative sensitivity can be either positive or negative. A positive relative sensitivity indicates an increase in an output from increase in an input parameter. The magnitude of change indicates the sensitivity of the parameter to the output variable. When a relative sensitivity equals to 1.0 then the rate of change in the output variable is equal to the change in the input parameter. Because we used an input change rate of +/-30 percent, the changes in the output variable would be +/-30 percent for the case with S_R of 1.0. If a relative sensitivity is 0.5 then 30 percent change of input condition results in a 15 percent change in an output variable.

Four types of sensitivities can be described from the results of this sensitivity analysis. Those are (1) no impact; (2) minor impact; (3) localized impact; and (4) global impact. An example of the 'No Impact' scenario occurs when changes in external PCB loads do not affect the carbon concentrations in the water column. Carbons (either BIC or PDC) are independent state variables from the changes in PCB loads as shown in STSS_3001 to 3007 in Table 5-2. A 'Minor Impact' scenario is defined when the relative sensitivity is less than 0.20, which causes less than +/- 6 percent (or 12 percent changes overall) in the output. For example, this case occurs for total PCBs (TPCB) from changes in 'BIC decay rate to PDC in water column (STSS_3036)'.

Sensitive parameters are defined as having a relative sensitivity larger than 0.2 and can result in localized or global impact. Sensitive parameters are indicated in bold in Tables 5-2 to 5-4. Influences from a certain scenario can be spatially variable because of unequal physical conditions or the nature of the parameter. An example of a 'localized impact' is observed in sensitivity analysis of the total PCB (TPCB) state variable (STSS_3018) from the loading of PCBs at the Trenton boundary. The relative sensitivity of PCBs from the Trenton boundary on TPCB in Zone 2 is 0.67 while the relative sensitivities in other zones are less than 0.20. The 'global impact' case can be observed in the scenario run that varies partition coefficients to organic carbon (STSS_3034) on DDPCB state variable. The relative sensitivities vary from -0.52 to -0.71 throughout the Estuary. The relative sensitivity can be used to identify the most sensitive input parameters for each of the model state variables. Perturbation simulation results on individual state variables are discussed below.

The Biotic Carbon (or BIC) concentrations in the Delaware Estuary are predominantly governed by the internal carbon production through photosynthesis, also known as primary productivity rate (STSS 3016). The relative sensitivities to this rate (S_R) range from 0.57 to 0.98 in Zones 3 to 6. It is notable that the upper portion of the Estuary, Zone 2, is more sensitive to the BIC concentration assignment at the upstream boundary condition at Trenton, NJ (STSS 3026), showing the localized impact with S_R of 0.80. Conversely, Zone 6 or the Bay is not sensitive (STSS 3029) to the assignment of the downstream boundary condition since downstream concentrations of BIC are low, 0.07 mg/L, for the baseline simulation case. BIC decay rate to PDC (STSS 3036) and water temperature (STSS 3039) were found to be globally sensitive parameters to the BIC state variable. Even though water temperatures are a sensitive parameter for BIC, water temperature input conditions would not be manipulated to improve the model calibration since observed water temperatures for the Estuary are already used. Accurate specification of the ambient water temperature during the model simulation period is required however.

Particulate Detrital Carbon (PDC):

Particulate Detrital Carbon (or PDC) concentrations are positively sensitive to the PDC resuspension rates (STSS 3048) and inversely related to the PDC gross settling rates (STSS 3047), globally. BIC primary production has a marginal impact on PDC (STSS 3016) for Zones 3, 4 and 6. BIC decay rate to PDC (STSS_3036) is one of the most sensitive parameters to predicted BIC concentrations with relative sensitivity of about -0.75 however PDC concentrations are insensitive to changes in this rate. A possible explanation is that, the PDC portion derived from BIC in Zones 2 to 5 is minimal when compared to the other sources of PDC. Thus, influence of the ‘BIC decay rate to PDC’ on PDC concentrations is minimal for Zones 2 – 5 while a S_R of 0.17 (or +/- 5.1 percent) of impact is shown in Zone 6 where the biggest carbon source is the primary production of BIC.

Table 5.2 - Summary of the relative sensitivity for BIC and PDC

Variable Scenario	BIC RM 29	BIC RM 68	BIC RM 85	BIC RM 99	BIC RM 123	PDC RM 29	PDC RM 68	PDC RM 85	PDC RM 99	PDC RM 123
STSS_3001	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3002	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3003	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3004	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3005	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3006	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3007	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3008	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.04	0.05	0.10
STSS_3009	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.05	0.06
STSS_3010	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.04	0.00
STSS_3011	0.00	0.00	0.00	0.00	0.00	0.04	0.02	0.02	0.02	0.04
STSS_3012	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3013	0.00	0.00	0.00	0.00	0.00	0.04	0.09	0.09	0.14	0.17
STSS_3014	0.00	0.00	0.00	0.00	0.00	0.09	0.18	**0.24**	**0.29**	**0.31**
STSS_3015	0.00	0.01	0.02	0.08	0.12	0.00	0.00	0.00	0.00	0.00
STSS_3016	**0.98**	**0.89**	**0.72**	**0.57**	0.17	**0.32**	0.11	**0.20**	**0.21**	0.11
STSS_3017	**0.98**	**0.92**	**0.75**	**0.65**	**0.20**	**0.33**	0.11	**0.20**	**0.21**	0.11
STSS_3018	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3019	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3020	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3021	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3022	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.13	**0.37**
STSS_3023	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.01	0.00
STSS_3024	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00
STSS_3025	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00
STSS_3026	0.00	0.00	0.08	**0.35**	**0.80**	0.00	0.01	0.01	0.01	0.02
STSS_3027	0.00	0.03	0.15	0.00	0.00	0.00	0.01	0.01	0.00	0.00
STSS_3028	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3029	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
STSS_3030	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3031	0.00	0.00	0.00	0.00	0.00	0.11	0.09	0.08	0.14	**0.37**
STSS_3032	0.02	0.08	**0.25**	**0.37**	**0.80**	0.01	0.02	0.02	0.01	0.02
STSS_3033	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3034	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3035	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3036	**-0.74**	**-1.01**	**-0.62**	**-0.50**	-0.15	0.17	0.02	0.04	0.04	0.05
STSS_3037	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3038	0.00	0.00	0.00	0.00	0.00	-0.09	-0.19	**-0.21**	**-0.21**	-0.10
STSS_3039	**-1.13**	**-1.07**	**-0.58**	**-0.41**	-0.12	0.01	-0.19	**-0.23**	**-0.24**	-0.06
*STSS_3040 **	***-0.69***	***-0.93***	***-0.57***	***-0.48***	*-0.16*	*0.06*	*-0.16*	*-0.17*	*-0.15*	*-0.04*
STSS_3041	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3042 *	***0.00***	***0.00***	***0.00***	***0.00***	***0.00***	***0.00***	***0.00***	***0.00***	***0.00***	***0.00***
STSS_3043	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3044	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3045	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3046	-0.05	-0.08	-0.06	-0.05	-0.02	-0.03	-0.01	-0.01	-0.01	0.00
STSS_3047	0.00	0.00	0.00	0.00	0.00	**-0.66**	**-0.78**	**-0.67**	**-0.57**	**-0.28**
STSS_3048	0.00	0.00	0.00	0.00	0.00	**0.51**	**0.60**	**0.46**	**0.37**	0.16
STSS_3049	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3050	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3051	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3052	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3053	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Simulation conditions are not qualified to calculate the relative sensitivity

Table 5.3 - Summary of the relative sensitivity for TPCB and DDPCB.

Variable	TPCB	TPCB	TPCB	TPCB	TPCB	DDPCB	DDPCB	DDPCB	DDPCB	DDPCB
Scenario	RM 29	RM 68	RM 85	RM 99	RM 123	RM 29	RM 68	RM 85	RM 99	RM 123
STSS_3001	0.01	0.11	0.03	0.03	0.00	0.02	0.10	0.03	0.03	0.00
STSS_3002	0.07	0.06	0.13	0.14	0.07	0.06	0.08	0.08	0.13	0.09
STSS_3003	0.02	0.10	0.10	0.12	0.09	0.03	0.10	0.12	0.11	0.06
STSS_3004	0.01	0.03	0.08	0.05	0.00	0.01	0.03	0.06	0.05	0.00
STSS_3005	0.01	0.03	0.05	0.07	0.04	0.01	0.05	0.05	0.07	0.04
STSS_3006	0.02	0.01	0.01	0.01	0.00	0.02	0.01	0.01	0.01	0.00
STSS_3007	0.15	**0.35**	**0.40**	**0.43**	**0.20**	0.13	**0.37**	**0.37**	**0.43**	**0.20**
STSS_3008	0.00	-0.01	-0.01	-0.01	0.00	-0.01	-0.03	-0.02	-0.04	-0.02
STSS_3009	0.00	-0.01	-0.01	-0.01	0.00	-0.01	-0.02	-0.03	-0.03	-0.01
STSS_3010	0.00	-0.01	-0.01	-0.01	0.00	0.00	-0.02	-0.04	-0.06	0.00
STSS_3011	-0.01	-0.01	0.00	-0.01	0.00	-0.01	-0.02	-0.01	-0.04	-0.01
STSS_3012	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3013	-0.02	-0.02	-0.02	-0.03	-0.01	-0.04	-0.07	-0.06	-0.07	-0.08
STSS_3014	-0.04	-0.06	-0.06	-0.06	-0.02	-0.06	-0.15	-0.16	**-0.21**	-0.12
STSS_3015	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00
STSS_3016	0.00	0.02	0.00	0.00	0.01	**-0.35**	-0.09	-0.11	-0.12	-0.04
STSS_3017	0.00	0.02	0.00	0.01	0.01	**-0.35**	-0.10	-0.11	-0.12	-0.04
STSS_3018	0.01	0.06	0.10	0.19	**0.67**	0.01	0.06	0.09	**0.22**	**0.72**
STSS_3019	0.01	0.06	0.11	0.01	0.00	0.01	0.08	0.10	0.02	0.00
STSS_3020	0.03	0.04	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.00
STSS_3021	**0.35**	0.00	0.00	0.00	0.00	**0.36**	0.00	0.00	0.00	0.00
STSS_3022	0.00	-0.02	-0.01	-0.03	-0.04	0.00	-0.03	-0.04	-0.08	**-0.26**
STSS_3023	0.00	-0.01	-0.01	0.00	0.00	0.00	-0.04	-0.04	-0.01	0.00
STSS_3024	-0.01	-0.01	0.00	0.00	0.00	-0.01	-0.02	0.00	0.00	0.00
STSS_3025	-0.03	0.00	0.00	0.00	0.00	-0.05	0.00	0.00	0.00	0.00
STSS_3026	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01	-0.03	-0.06
STSS_3027	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01	0.00	0.00
STSS_3028	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00
STSS_3029	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00
STSS_3030	**0.40**	0.14	0.18	**0.20**	**0.67**	**0.42**	0.16	0.18	**0.24**	**0.72**
STSS_3031	-0.05	-0.04	-0.03	-0.03	-0.04	-0.07	-0.10	-0.07	-0.09	**-0.26**
STSS_3032	0.00	0.00	0.00	0.00	0.00	-0.01	-0.02	-0.02	-0.03	-0.06
STSS_3033	0.03	0.13	0.14	0.11	0.00	0.03	0.09	0.10	0.07	0.00
STSS_3034	-0.12	-0.09	-0.11	-0.07	-0.06	**-0.71**	**-0.68**	**-0.66**	**-0.69**	**-0.52**
STSS_3035	**0.23**	0.19	0.15	0.13	0.09	**0.52**	**0.48**	**0.49**	**0.43**	**0.30**
STSS_3036	-0.09	-0.06	-0.04	-0.03	-0.01	-0.02	0.01	0.01	0.00	0.00
STSS_3037	0.02	0.02	0.02	0.01	0.01	0.03	0.03	0.02	0.02	0.00
STSS_3038	0.05	0.05	0.03	0.02	0.00	0.09	0.12	0.10	0.09	0.02
STSS_3039	**-0.21**	-0.18	-0.13	-0.15	-0.09	-0.18	-0.04	0.03	0.04	-0.01
*STSS_3040 **	***-0.28***	*-0.19*	*-0.11*	*-0.12*	*-0.08*	***-0.20***	*-0.05*	*0.01*	*0.03*	*-0.02*
STSS_3041	-0.12	-0.05	-0.02	-0.03	-0.05	-0.14	-0.07	-0.04	-0.03	-0.02
*STSS_3042 **	*0.70*	*0.62*	*0.45*	*0.46*	*0.17*	*0.68*	*0.64*	*0.48*	*0.46*	*0.10*
STSS_3043	0.06	**0.33**	**0.37**	0.18	0.01	0.05	**0.29**	**0.29**	0.19	0.00
STSS_3044	0.06	0.03	0.02	0.01	0.03	0.07	0.03	0.01	0.01	0.01
STSS_3045	**0.23**	0.19	0.15	0.13	0.09	**0.52**	**0.48**	**0.49**	**0.43**	**0.30**
STSS_3046	-0.04	-0.02	-0.02	-0.01	0.00	-0.01	0.00	0.00	0.00	0.00
STSS_3047	**-0.48**	**-0.44**	**-0.34**	**-0.33**	-0.14	**-0.24**	-0.06	-0.04	-0.03	-0.01
STSS_3048	**0.35**	**0.37**	**0.26**	**0.26**	0.12	**0.21**	0.07	0.06	0.04	0.01
STSS_3049	0.03	0.03	0.02	0.01	0.01	0.03	0.02	0.02	0.01	0.01
STSS_3050	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3051	**0.41**	**0.38**	**0.29**	**0.26**	0.13	**0.42**	**0.37**	**0.36**	**0.26**	0.08
STSS_3052	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3053	-0.03	-0.03	-0.02	-0.02	-0.01	-0.04	-0.02	-0.02	-0.01	-0.01

Simulation conditions are not qualified to calculate the relative sensitivity

Table 5.4 - Summary of the relative sensitivity for PPCB and R1.

Variable	PPCB	PPCB	PPCB	PPCB	PPCB	R1	R1	R1	R1	R1
Scenario	**RM 29**	**RM 68**	**RM 85**	**RM 99**	**RM 123**	**RM 29**	**RM 68**	**RM 85**	**RM 99**	**RM 123**
STSS_3001	0.02	0.10	0.03	0.05	0.00	0.02	0.10	0.03	0.03	0.00
STSS_3002	0.08	0.08	0.13	0.14	0.07	0.06	0.08	0.08	0.13	0.09
STSS_3003	0.03	0.11	0.11	0.15	0.08	0.03	0.10	0.12	0.11	0.06
STSS_3004	0.01	0.03	0.08	0.05	0.00	0.01	0.03	0.06	0.05	0.00
STSS_3005	0.01	0.03	0.06	0.06	0.05	0.01	0.05	0.05	0.07	0.04
STSS_3006	0.02	0.01	0.01	0.01	0.00	0.02	0.01	0.01	0.01	0.00
STSS_3007	0.18	**0.35**	**0.42**	**0.46**	0.19	0.13	**0.37**	**0.37**	**0.43**	**0.20**
STSS_3008	0.00	0.00	0.01	0.00	0.02	-0.01	-0.03	-0.02	-0.04	-0.02
STSS_3009	0.00	0.00	0.01	0.01	0.01	-0.01	-0.02	-0.03	-0.03	-0.01
STSS_3010	0.00	0.00	0.01	0.02	0.00	0.00	-0.02	-0.04	-0.06	0.00
STSS_3011	0.00	0.00	0.00	0.00	0.01	-0.01	-0.02	-0.01	-0.04	-0.01
STSS_3012	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3013	-0.01	0.00	0.02	0.02	0.06	-0.04	-0.07	-0.06	-0.07	-0.08
STSS_3014	-0.02	0.00	0.05	0.04	0.08	-0.06	-0.15	-0.16	**-0.21**	-0.12
STSS_3015	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00	-0.01	0.00
STSS_3016	0.18	0.11	0.10	0.10	0.07	**-0.35**	-0.09	-0.11	-0.12	-0.04
STSS_3017	0.19	0.11	0.11	0.10	0.07	**-0.35**	-0.10	-0.11	-0.12	-0.04
STSS_3018	0.01	0.05	0.11	0.17	**0.72**	0.01	0.06	0.09	**0.22**	**0.72**
STSS_3019	0.02	0.05	0.12	0.02	0.00	0.01	0.08	0.10	0.02	0.00
STSS_3020	0.02	0.06	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.00
STSS_3021	**0.35**	0.00	0.00	0.00	0.00	**0.36**	0.00	0.00	0.00	0.00
STSS_3022	0.00	-0.01	0.01	-0.02	0.13	0.00	-0.03	-0.04	-0.08	**-0.26**
STSS_3023	0.00	-0.01	0.02	0.00	0.00	0.00	-0.04	-0.04	-0.01	0.00
STSS_3024	-0.01	0.02	0.00	0.00	0.00	-0.01	-0.02	0.00	0.00	0.00
STSS_3025	0.01	0.00	0.00	0.00	0.00	-0.05	0.00	0.00	0.00	0.00
STSS_3026	0.00	0.00	0.01	0.00	0.04	0.00	-0.01	-0.01	-0.03	-0.06
STSS_3027	0.00	0.00	0.01	0.00	0.00	0.00	-0.01	-0.01	0.00	0.00
STSS_3028	0.00	0.01	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00
STSS_3029	0.01	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00
STSS_3030	**0.41**	0.14	**0.23**	0.19	**0.72**	**0.42**	0.16	0.18	**0.24**	**0.72**
STSS_3031	-0.02	0.00	0.02	-0.02	0.13	-0.07	-0.10	-0.07	-0.09	**-0.26**
STSS_3032	0.02	0.02	0.03	0.01	0.04	-0.01	-0.02	-0.02	-0.03	-0.06
STSS_3033	0.02	0.12	0.11	0.09	0.00	0.03	0.09	0.10	0.07	0.00
STSS_3034	**0.35**	**0.36**	**0.39**	**0.30**	**0.47**	**0.34**	**0.36**	**0.38**	**0.36**	**0.51**
STSS_3035	-0.01	-0.03	-0.16	-0.07	-0.19	0.00	-0.04	-0.15	-0.09	**-0.23**
STSS_3036	-0.14	-0.11	-0.06	-0.08	-0.02	-0.02	0.01	0.01	0.00	0.00
STSS_3037	0.03	0.03	0.02	0.02	0.01	0.03	0.03	0.02	0.02	0.00
STSS_3038	0.03	0.00	-0.03	-0.02	-0.03	0.09	0.12	0.10	0.09	0.02
STSS_3039	**-0.30**	**-0.33**	**-0.23**	**-0.24**	-0.18	-0.18	-0.04	0.03	0.04	-0.01
STSS_3040 *	-0.37	-0.30	-0.19	-0.19	-0.13	-0.20	-0.05	0.01	0.03	-0.02
STSS_3041	-0.12	-0.08	-0.03	-0.05	-0.04	-0.14	-0.07	-0.04	-0.03	-0.02
STSS_3042 *	0.63	0.62	0.44	0.44	0.15	0.68	0.64	0.48	0.46	0.10
STSS_3043	0.06	**0.34**	**0.34**	0.16	0.00	0.05	**0.29**	**0.29**	0.19	0.00
STSS_3044	0.06	0.04	0.02	0.02	0.02	0.07	0.03	0.01	0.01	0.01
STSS_3045	-0.01	-0.03	-0.16	-0.07	-0.19	0.00	-0.04	-0.15	-0.09	**-0.23**
STSS_3046	-0.04	-0.03	-0.01	-0.01	-0.01	-0.01	0.00	0.00	0.00	0.00
STSS_3047	**-0.76**	**-0.75**	**-0.59**	**-0.60**	**-0.24**	**-0.24**	-0.06	-0.04	-0.03	-0.01
STSS_3048	**0.54**	**0.58**	**0.42**	**0.43**	0.16	**0.21**	0.07	0.06	0.04	0.01
STSS_3049	0.02	0.02	0.01	0.02	0.01	0.03	0.02	0.02	0.01	0.01
STSS_3050	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3051	**0.38**	**0.39**	**0.24**	**0.29**	0.10	**0.42**	**0.37**	**0.36**	**0.26**	0.08
STSS_3052	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STSS_3053	-0.03	-0.03	-0.01	-0.02	-0.01	-0.04	-0.02	-0.02	-0.01	-0.01

* Simulation conditions are not qualified to calculate the relative sensitivity.

Total pentachlorobiphenyls (Total penta-PCBs or TPCBs):

Total pentachlorobiphenyls concentrations in the water column are globally and locally affected by the external PCB loads and boundary conditions (Table 5-3). It should also be noted that the interaction with sediment layer plays an important role in TPCB concentrations in water column. Therefore, PDC gross settling, resuspension rates and initial PCB concentrations in sediment layers become relatively important parameters in all the zones with relative sensitivities of -0.48 to 0.41 except in Zone 2. Air temperature shows localized sensitivity to TPCB concentrations since the assignment of gaseous atmospheric PCB concentrations are positively related to the air temperature (STSS_3043).

Truly Dissolved plus Dissolved Organic Carbon-bound Pentachlorobiphenyls (DDPCB):

DDPCBs are globally sensitive to the partition coefficients to dissolved organic carbon (K_{doc}; STSS 3035) and the particulate organic carbon (K_{oc}; STSS_ 3034). DDPCB concentrations show the exact same responses to the changes in DOC concentrations (STSS_3045) as to the changes in K_{doc} (STSS_3035) input conditions. Changes in external PCB loadings (STSS_3007), PCB boundary assignments (STSS_3030), or initial PCB concentrations in sediment layers (STSS_3051), result in a positive change with DDPCB in water column. In general, increases in BIC or PDC concentrations (or particulate carbon concentrations) result in a reduction of DDPCB concentrations in the water column because more PCBs are partitioned to those additional carbon molecules and particulate-sorbed PCBs settle out of the water column (STSS_3008 to 3017 in Table 5-3).

Particulate Organic Carbon-bound Pentachlorobiphenyls (PPCB):

PPCBs in the water column show a similar response pattern as TPCBs. External PCB loadings (STSS_3007) and PCB boundary assignment (STSS_3030) have a localized impact on PPCB. PPCBs are globally sensitive to PDC gross settling, resuspension rates and initial PCB concentrations in sediment layers (STSS_3047, 3048, and 3051) with relative sensitivities ranging from -0.76 to 0.54. PPCBs also show global sensitivity to the partition coefficient to particulate organic carbon (STSS_3034) and water temperature (STSS_3039). The largest global sensitivity on PPCB variable is the ‘PDC gross settling rate (STSS_3047) with a relative sensitivity of -0.59 or larger for Zones 3 to 6. The results are summarized in Table 5-4.

Carbon-normalized Particulate PCBs in Water Column (R1):

Carbon-normalized particulate PCBs in water column (R1) are globally sensitive to the external PCB loads (STSS_3007), the partition coefficient for particulate organic carbon (LK_{oc}, STSS_3034), and initial sediment PCB concentrations (STSS_3051). Localized impacts are shown from boundary or loading condition changes (STSS_ 3014; 3018; 3031, in Table 5-4, for example).

5.2 575-day Calibration Period Sensitivity Analysis

5.2.1 Approach

Four sensitivity scenarios were performed to evaluate the relative importance of sources of PCBs during the 575-day calibration period. Sources of PCBs are grouped into four categories and the details are described below.

(1) Six external PCB loads: loads from non-point, point sources, contaminated sites, other tributaries, atmospheric deposition, and CSOs.
(2) Assigned PCB concentrations at four major boundaries
(3) Initial PCB concentrations in sediment layers
(4) Assigned gaseous PCB concentrations.

Results from the two-year short term sensitivity analyses discussed in the previous sub-section indicated that external PCB loadings, boundary PCB concentrations and initial PCB sediment conditions are locally and globally important to PCB variables (PPCB, DDPCB, and TPCB). However, it is somewhat difficult to quantify and to compare the influences among four source categories because the four categories have different types of PCB sources. The first two categories are the external sources to the Estuary expressed in units of loads and concentrations. The latter two categorical sources are expressed in concentrations but both could be either internal sources or sinks, determined by concentration gradients or the direction of net flux exchanges. The impacts of the four different sources on total PCBs during the calibration period were examined by zeroing out individual categories of PCB sources, and comparing the simulation results with the baseline calibration results.

5.2.2 Results and Discussion

The four sensitivity simulation results are compared graphically with baseline simulations. Temporal simulation results are compared for Zones 2 through 5 in Figures 5-2 to 5-5. The greater the difference between the baseline and the scenario simulations can be interpreted as indicating a more sensitive source of TPCB during the calibration period. In general, initial PCB concentrations in sediment layers seem to be the most influential source category in all four zones. The least influential category among the four is the assignment of atmospheric gaseous PCB concentrations where little differences, when compared against the baseline simulation results, are observed with exception for the period of summer months.

<u>Zone 2:</u>

The relative influences of the four scenarios in Zone 2 are graphically compared in Figure 5-2. Influences from the boundary conditions are relatively substantial compared to the other zones. This implies that the boundary at Trenton, NJ is a dominant source of PCBs in Zone 2. The inflows from the Delaware River at Trenton during the model calibration period are depicted in Figure 5-6. Relatively high inflows occurred from October 2002 to the end of calibration period. For example, a larger influence from the boundary at Trenton, NJ is observed during this high inflow period shown in lower left panel in Figure 5-2.

Figure 5.2 - Temporal plots of sensitivity simulations for the calibration period for Zone 2

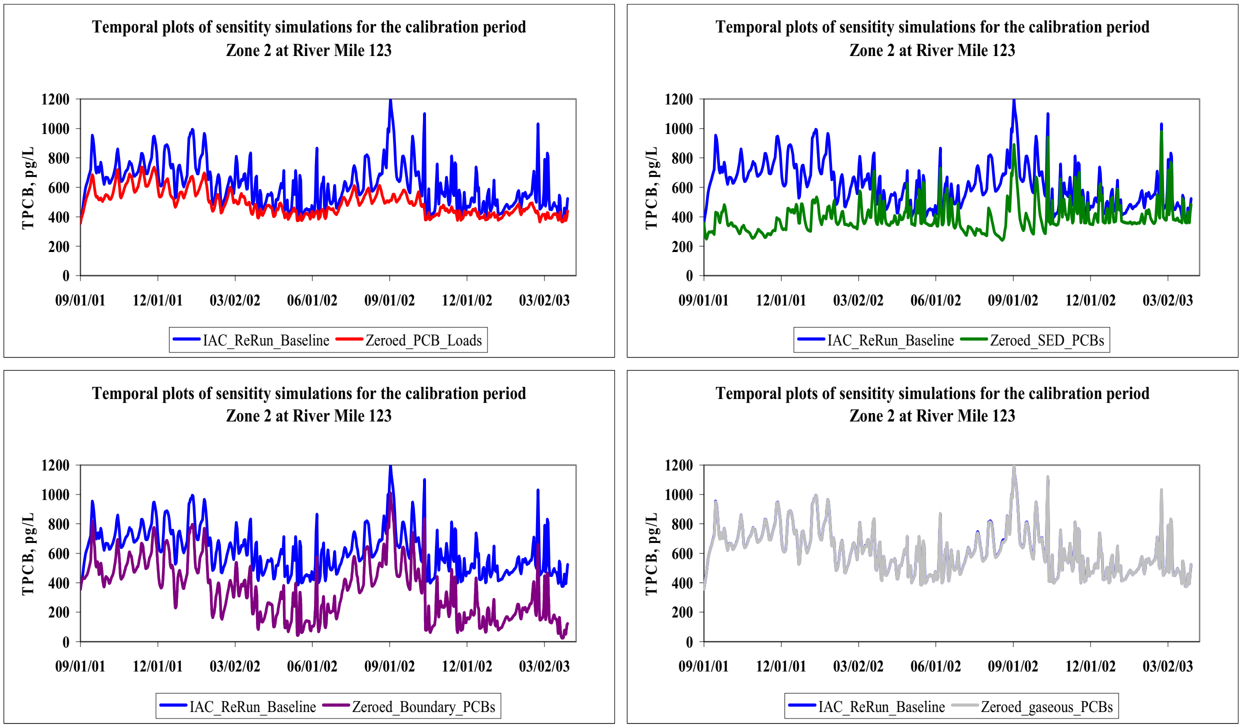


Figure 5.3 -Temporal plots of sensitivity simulations for the calibration period for Zone

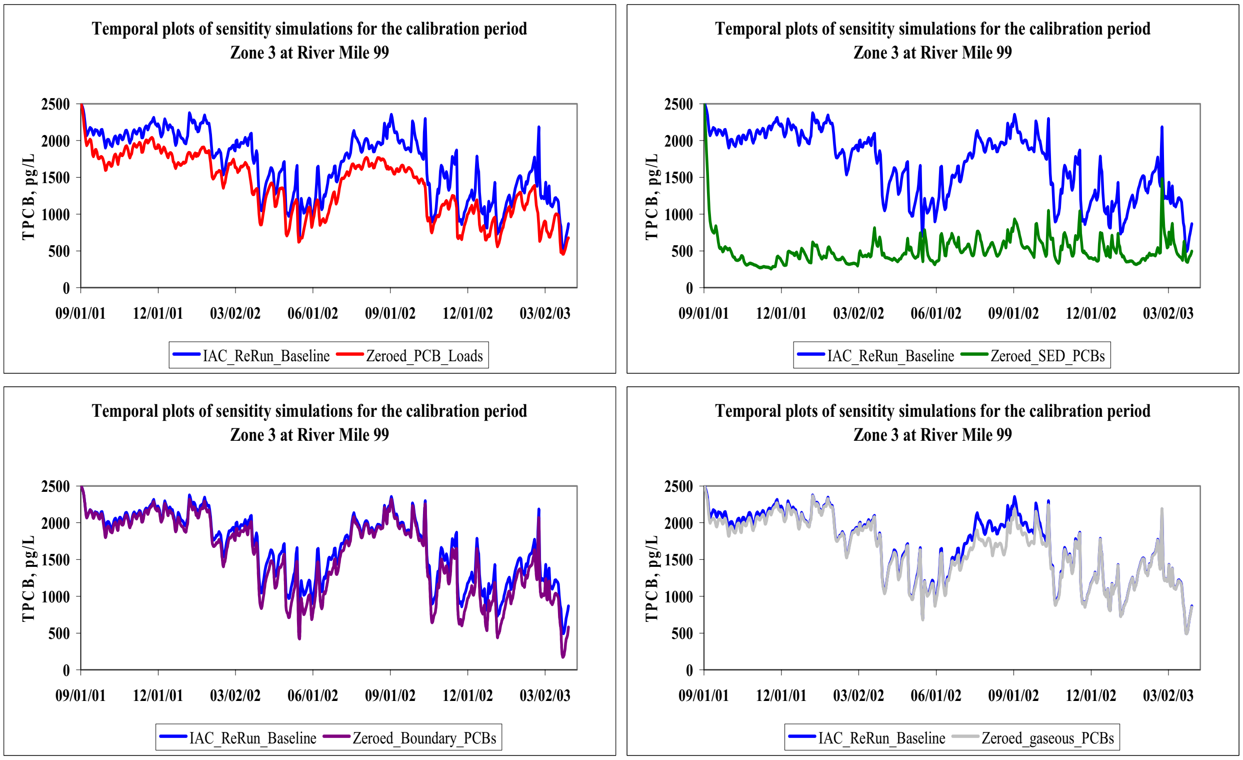
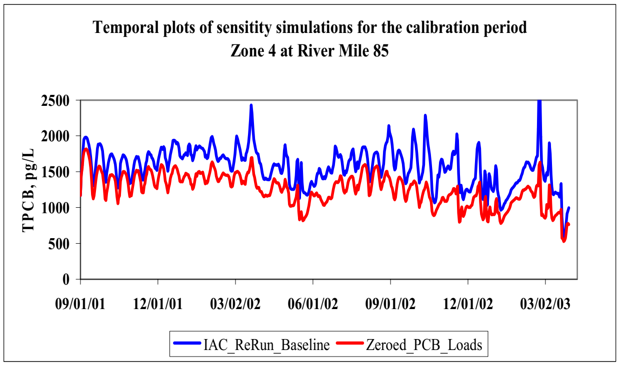
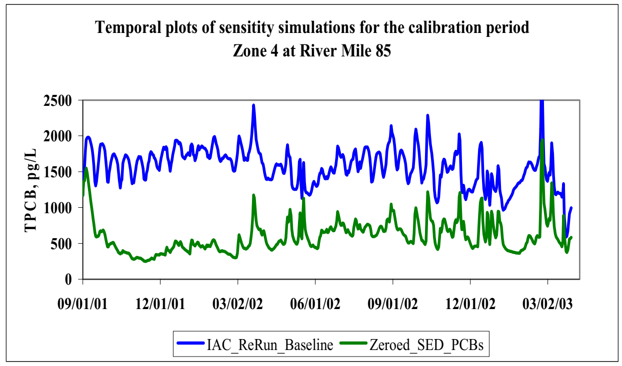
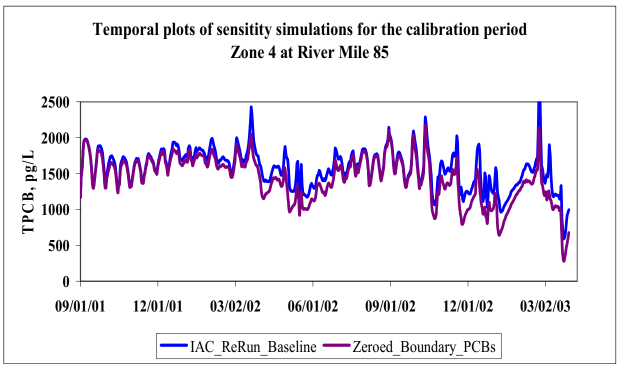


Figure 5.4 - Temporal plots of sensitivity simulations for the calibration period for Zone







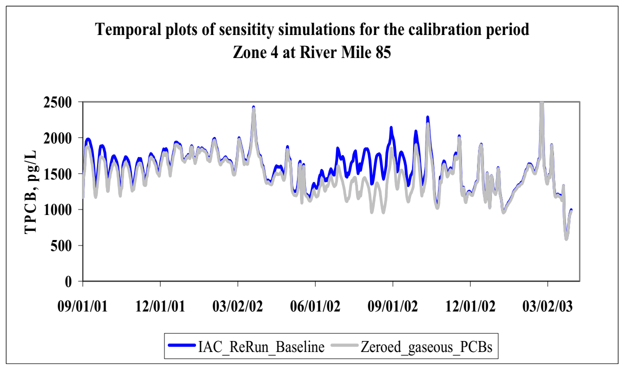
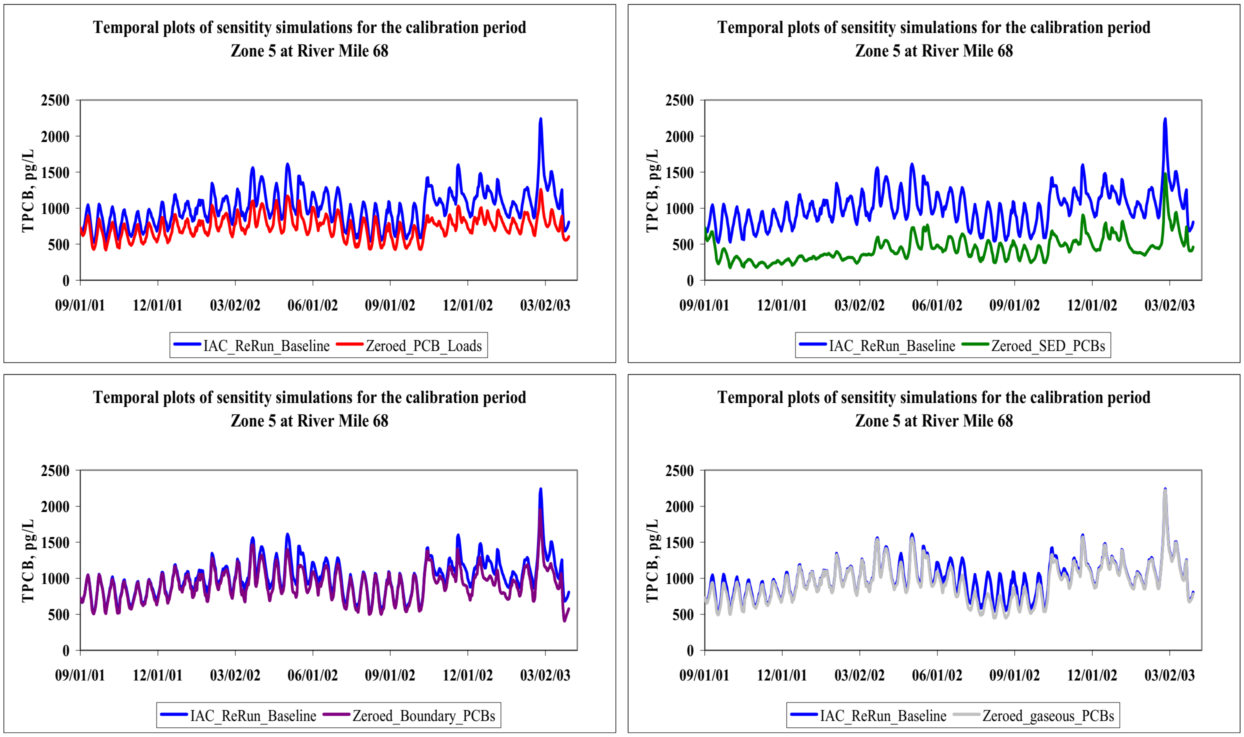


Figure 5.5 - Temporal plots of sensitivity simulations for the calibration period for Zone



Zone 3:

The relative influences of the four categories in Zone 3 are graphically compared in Figure 5-3 (Note that the y-axis scales in Figure 5-3 differ from the ones in Figure 5-2). Influences from the initial PCB concentrations in sediment layer appear to be the largest in Zone 3. Since there are no upstream or downstream boundaries in Zone 3, the influences from the boundaries are very minimal.

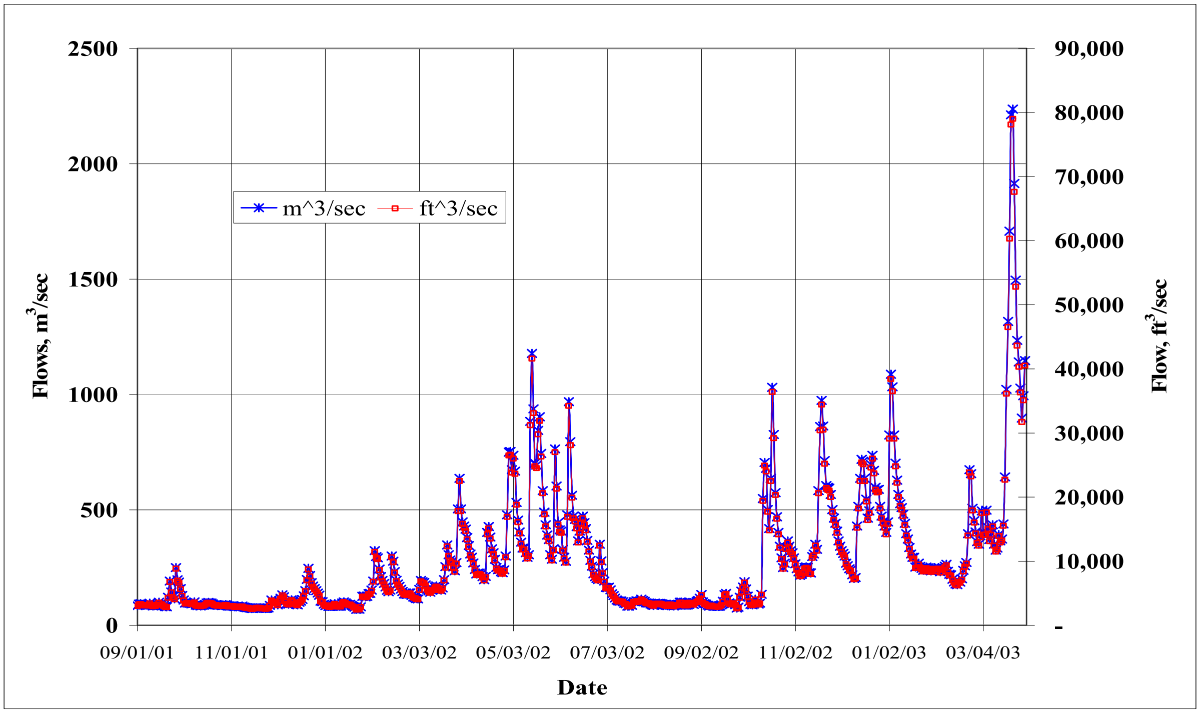
Zone 4:

Even though the Schuylkill River flows into the Delaware River in Zone 4, the influences from the boundary conditions are minor during low flow period (Figure 5-4). Initial sediment PCB conditions are the predominant influence in Zone 4. The influence of the assignment of atmospheric gaseous PCB concentrations is only minimally important during the warmer season.

Zone 5:

The relative influences of the scenarios from all four categories appear to be less than th other zones since the simulated baseline concentrations for all are lower than those in Zones 3 and 4. A strong impact is still observed when the initial sediment PCB conditions are changed (Figure 5-5).

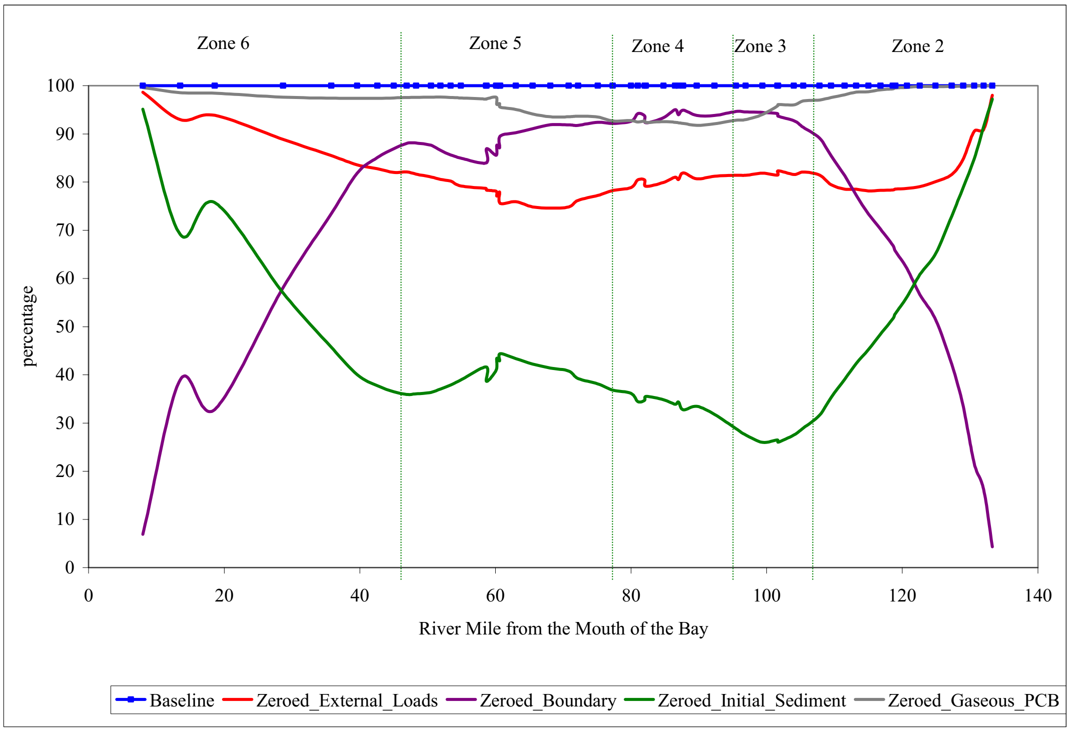
Figure 5.6 - Observed daily average flow for Delaware River at Trenton during the model calibration period from September 2001 to March 2003.



The sensitivity of the four scenario simulations is summarized in a single spatial plot (Figure 5-7). The median values of the simulated results during the calibration period were obtained. Then, percentages of relative PCB concentrations compared with baseline simulation results were calculated using median values and plotted against the River Mile system of the Delaware Estuary. A point at the 100 percent level indicates the scenario simulation results have the same PCB concentrations in the water column as the baseline results. A 50 percent level indicates that 50 percent of baseline PCB concentrations are observed in the scenario simulation, or that the concentrations of PCBs are 50 percent lower than concentrations in the baseline case.

In the mid portion of the Delaware Estuary, the impact of zeroing out the initial PCB concentrations in sediment layers has almost three times more influence on water column PCB concentrations than zeroing out the six external PCB loadings. The impact of zeroing out the initial PCB sediment concentrations could result in a more than 70 percent reduction in Zone 3. The reason for this is that the sediment layers become an immense sink for PCBs. A calibration period of 575 days is not long enough to equilibrate with other PCB sources, and thus the sediment layers remain as a sink for PCBs during the calibration period. The scenario which zeros out the ‘six external PCB loadings’ indicates that the impact can result in about a 20 percent reduction in PCB concentrations in water column in mid-Estuary. Zeroing out the ‘Gaseous PCB’ concentrations results in about a 10 percent reduction of PCB concentrations in Zones 3, 4 and portions of 5. Substantial influences from boundary conditions are observed at the extreme ends of the Estuary. The four sensitivity scenario simulation results point to importance of the initial sediment conditions during the short term model calibration period.

Figure 5.7 - Percentages of relative PCB concentrations in the water column by four scenario simulations



6 Mass Balance Components Analysis

6.1 Approach

The capability to track mass transport and fate fluxes within a water quality model provides a valuable means by which a modeler can:

1. Quantify the relative importance of sources, sinks and environmental processes in controlling the state variables in the model; and,
2. Help confirm the integrity of the model computer code by demonstrating that it maintains mass balance over space and time.

These are two important objectives towards understanding the primary factors which control sediment and water quality responses, and insuring that the model framework is scientifically credible and has utility for water quality management purposes.

The WASP5 model code, as distributed by the U.S. EPA, tracks mass fluxes, but only over the entire model spatial domain. The standard WASP5 model code also aggregates individual processes (e.g., solids settling and resuspension fluxes are lumped), so it is insufficient to support the first objective listed above with regard to conducting a mass balance components analysis. Additionally, since the mass balance is tracked over the entire spatial domain, processes affecting different compartments (e.g., water column and sediments) cannot be individually tracked.

Despite the limitations of the mass balance tracking in standard WASP5, the approach implemented within the model code does properly track mass transport fluxes and transformations. Therefore, the approach taken for DELPCB builds upon the existing WASP5 mass balance coding by enhancing the mass tracking in two ways:

1. Instead of tracking mass over the entire spatial domain, the code was modified to track mass fluxes and transformations through every model segment, including both water column and sediment segments.
2. Model processes that would normally be aggregated in WASP5 (e.g., kinetic transformations, gross settling and resuspension, etc.) were identified and coding was implemented to track these separately to the degree needed for the Delaware TMDL modeling effort.

These enhancements meet the primary mass balance analysis objectives for conducting the PCB modeling required for this TMDL study. The following sections describe the components of the PCB and carbon mass balance tracking implemented in the DELPCB model and summarize the mass balance results on an annual basis.

6.2 Components of the DELPCB Model Mass Balance

The DELPCB model framework incorporates the principal organic carbon sorbents that are found in the water column and sediments, and simulates the net burial of solids and ultimate fate of organic carbon in the sediments in the simplified manner (DRBC, 2003a). Mass balances are conducted for biotic carbon (BIC) and particulate detrital carbon (PDC) in the water column and the sediment layers simulated by the model. The DELPCB model employs equilibrium partitioning to separate the total PCB concentration into four components: a truly dissolved aqueous phase and three sorbed phases corresponding, respectively, to BIC-bound, PDC-bound and DOC-bound. The process mechanisms for the three sorbed PCB phases are the same as those in the organic carbon sorbents model. Additional PCB process mechanisms include the flux of gas phase PCBs across the air-water interface and diffusion of PCBs across the sediment-water interface and between sediment layers. Diffusion of PCB can occur for both the truly dissolved phase and DOC-bound phases. The mass balance tracking capability incorporated in DELPCB allows each of these mass transfer processes to be tracked and accumulated for every cell in the model grid over each model time step. These accumulated mass fluxes are then written to an output file at a user-specified time interval over the course of a model simulation.

Once a model simulation is complete, the mass balance output generated by DELPCB is externally post-processed using an Excel-based spreadsheet template so that the results may be analyzed over appropriate, user-defined, space and time scales. For example, the model cells may be aggregated according to ecosystem compartments (i.e., water, biologically-active surface sediments, and deep sediments) and over spatial regions, such as water quality Zones 2 through 6 of the Delaware River Estuary. These water quality zones, and their corresponding water, surface sediment and deep sediment compartments were selected for presenting the mass balance components results for the DELPCB model.

Although the model tracks total external mass loads delivered to individual model spatial segments, external mass loads from different source categories can not be easily tracked within the WASP5 and DELPCB model codes. In the present study, external mass loads from different source categories were taken directly from the model input file, after confirming that the total mass loads computed by the model were consistent with those specified in the input file.

6.3 Results

The one year (365-day) cycling period utilized for TMDL development was selected as the timeframe for the mass balance components analysis of the DELPCB model short-term calibration. Analysis of results on a standard annual basis ensures proper representation of seasonal cycles for hydrologic, temperature, and internal primary productivity conditions in the Delaware River Estuary. The annualized model calibration mass balance results for biotic carbon (BIC), particulate detrital carbon (PDC) and Penta PCBs were developed for the individual water quality zones (Zones 2 though 6) to include the entire spatial domain of the model, and for the sum of Zones 2 through 5 to represent the aggregated spatial domain for the PCB TMDL. The mass balance results for the carbon and PCB state variables are presented in the following sections.

6.3.1 Mass Balance for Biotic Carbon (BIC):

Figure 6.1 depicts the direction and magnitude of the BIC mass flux components across the water quality zones of the Delaware River Estuary with a box and arrow diagram. The detailed BIC mass balance results for each of the sources and sinks are presented in Tables 6.1a and 6.1b for the water column and the sediment layers, respectively, while the stacked bar charts in Figures 6.2a and 6.2b demonstrate that the individual mass flux components maintain mass balance within the water column and the surface sediment layer.

The primary source of BIC to the water column is internal primary production, contributing greater than 99% of the loading for BIC over Zones 2 through 6 and about 82% over Zones 2 through 5. This loading source category is represented in the model as an external load and was estimated using a long-term historical data set for primary production in the Delaware River Estuary that was provided by Dr. Jonathan Sharp, of the University of Delaware. Upstream loads (5%) represent the next largest contribution of BIC to the water column overall for Zones 2 through 5, followed closely by the C&D Canal (5%) and the Schuylkill River (4%). Together, these secondary contributions represent less than 1% of the BIC loading over Zones 2 though 6, but they are relatively more significant to the BIC mass balance within each of their respective zones upstream of Delaware Bay. It is also worth noting that gross primary production in Zone 5 represents nearly half (49%) of the internally generated BIC loading to Zones 2 through 5, highlighting the relative significance of this carbon source in the lower zones of the Delaware Estuary.

The primary fate pathways which result in BIC loss from the water column include decay to PDC and net settling. Advection, of course, also moves BIC between model segments, and eventually out of the Estuary. For Zones 2 through 5, BIC decay is, by far, the largest loss mechanism (79%), followed by advection (11%) and net settling (7%). The variation in the magnitude of BIC losses or gains across the water quality zones is primarily attributable to the spatial dimensions, with Zones 5 and 6 representing a significantly larger region of the Estuary than Zone 2 through 4. Gross primary production in Delaware Bay (Zone 6) is nearly three times greater than in Zones 2 through 5 on a per unit area basis, significantly enhancing the cycling rate of organic carbon in the Bay relative to the rest of the Estuary. Much of the BIC generated in the Bay through primary production either decays in the water column or is lost across the ocean boundary, but the enhanced production rate also results in significantly increased BIC settling to the surficial sediment layer where it degrades to PDC which can be resuspended into the water column and thus enhance the overall cycling rate of particulate organic carbon across the sediment-water interface relative to upstream reaches of the Delaware.

6.3.2 Mass Balance for Particulate Detrital Carbon (PDC):

Figure 6.3 graphically depicts the direction and magnitude of the PDC mass flux components across the water quality zones of the Delaware River Estuary. The detailed PDC mass balance results for each of the sources and sinks are presented in Tables 6.2a and 6.2b for the water column and the sediment layers, respectively, while the stacked bar charts in Figures 6.4a and 6.4b demonstrate that the individual mass flux components maintain mass balance within the water column and the surface sediment layer.

The significance of BIC decay as a source of PDC is offset by PDC decay in Zones 2 through 5 as a whole, even though over the estuary as a whole (Zones 2 though 6) BIC decay is the largest source (internal or external) of PDC to the water column due to the large amount of gross primary production (and subsequent algal die-off) which occurs in Delaware Bay (Zone 6). For Zones 2 through 5, the largest contributions of PDC derive from external sources and the incoming upstream load to Zone 2. In general, the fate pathways for water column PDC are relatively similar in magnitude. Most of the PDC leaves the upper zones of the estuary through decay (36%), net settling (35%) and advection (24%). For Zones 2 through 6 as a whole, the balance of the PDC losses alters slightly with downstream advection to the ocean (31%) increasing to a level that is nearly equal to the losses resulting from net settling (35%) and decay (33%). Within the surficial sediment layer approximately half the settling PDC degrades with the remaining fraction burying to the deep sediments in the estuary as whole and within just Zones 2 through 5.

It is also worth noting that while PDC accounts for nearly 90% of the particulate organic carbon (POC) in Zones 2 through 5, internal primary productivity and the subsequent decay of BIC within Delaware Bay (Zone 6) results in a reduction in the proportion of PDC mass relative to POC by nearly 20% for the estuary as a whole based upon the final mass values reported in Tables 6.1a and 6.2a. These findings highlight the need to account for both BIC and PDC as distinct particulate sorbents for describing PCB fate and transport throughout the length of the Delaware River-Estuary system.

6.3.3 Mass Balance for Penta PCBs:

The fate and transport of pent-PCB in the Delaware River Estuary is largely controlled by particulate carbon dynamics as represented by BIC and PDC, but other factors result in a very different picture for the principle mass fluxes for PCBs across the water quality zones. The magnitude and direction of the primary sources and sinks related to PCB fate and transport in the Estuary are depicted in Figure 6.5. While both PDC and BIC were assumed to result in net sedimentation of particulate carbon throughout the estuary in the model calibration process, the net direction of PCB cycling between the water column and the sediment bed shifts direction from upstream to downstream water quality zones. The sediments are a net source of PCB loading to the water in Zones 2 through 4 but a net sink for PCBs in Zones 5 and 6, largely as a result of differences in the level of PCB contamination in the sediments under short-term calibration conditions which are effectively representative of the present state of the system.

While water column PCB concentrations are influenced by ongoing watershed sources, legacy contamination in the sediments is still a major source of PCB to the water column in the upper estuary as a result of both carbon cycling and sediment-water diffusion. This disequilibrium between water column and surface sediment PCB concentrations is reversed in the lower estuary due to the effects of greater primary production on particulate carbon cycling, tidal action increasing the effective residence time and the large surface area over which the particulate bound PCB can settle from the water column. For the estuary as a whole there is a net PCB flux from the water column to the surficial sediments of 17.1 g/day, and net burial of PCB from the surficial sediments to the deep sediments of 18.7 g/day. The difference between these two vertical fluxes represents a dynamic disequilibrium condition during the short-term calibration period.

Besides the effects of legacy sediment contamination, water column PCB levels in the Delaware are also influenced by exchanges across external boundaries with the C&D Canal and Atlantic Ocean, and the air-water interface. PCB exchanges with the estuary at the C&D Canal and Atlantic Ocean boundaries depend on the combined effects of water flow, tidal mixing and the relative PCB concentrations on the opposing side of these boundaries. Based upon the information available for the short-term model calibration, the C&D Canal is a net source of PCBs to the Delaware Estuary. At the ocean boundary, it is difficult to determine whether there is net PCB transport into or out of the estuary because it was not possible to independently determine the PCB concentrations in the estuary and ocean waters on either side of the boundary with available information. Although the model calibration predicts a net influx of Penta PCB from the ocean to the bay (Zone 6), there us a high level of uncertainty with that result due to data limitations. Net volatilization of PCB occurs throughout the estuary, since truly dissolved Penta PCB levels in the water column were high relative to the observation-based atmospheric gas-phase concentrations over nearly the entire short-term calibration period in each of the water quality zones. The detailed Penta PCB mass balance results for each of the sources and sinks are presented in Tables 6.3a and 6.3b for the water column and the sediment layers, respectively, while the stacked bar charts in Figures 6.6a and 6.6b demonstrate that the individual mass flux components maintain mass balance within the water column and the surface sediment layer.

6.3.4 Summary of Mass Balance Results:

The mass balance results for the short-term calibration one year cycling period, which is representative of current conditions in the Delaware River Estuary, show that the for the water quality zones of interest for the PCB TMDL study there are three ultimate fate pathways for Penta PCB as depicted in Figure 6.7. These include: transport to the bay (53%), volatilization (44%), and net burial (3%). Juxtaposed against PCB fate, the ultimate pathways for particulate organic carbon (BIC plus PDC) losses from Zones 2 through 5 are also depicted in Figure 6.7. For POC these pathways include: decay within the water column (37%), transport to the bay (29%), decay in the sediment bed (19%), and net burial to deep sediments (15%). For the short-term calibration period, downstream transport is clearly the most significant fate pathway for Penta PCBs and that portion of POC that does not degrade within the water column in Zones 2 through 5.

Table 6.1a Water Column Mass Balance Component Analysis by Zone for BIC (kg/day) Over the Short-Term Calibration Cycling Year

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	11,213	8,537	15,221	32,996	1,410,433	1,478,400	67,968
Schuykill River	----	----	2,987	----	----	2,987	2,987
C&D Canal	----	----	----	3,938	----	3,938	3,938
Exchange at Smaller Tributary Boundaries	-6	-20	-357	-1,905	----	-2,288	-2,288
Water Withdrawls (Segs 60, 66, 69)	-230	----	----	----	----	-230	-230
Upstream Interface Advection	4,148	7,005	7,129	10,361	9,207	4,148	4,148
Upstream Interface Dispersion	----	7	-3	144	-4,137	----	----
Downstream Interface Advection	-7,005	-7,129	-10,361	-9,207	-580,408	-580,408	-9,207
Downstream Interface Dispersion	-7	3	-144	4,137	----	----	4,137
Net Sediment-Water Diffusion	0	0	0	0	0	0	0
Net of Settling and Resuspension	-540	-503	-1,070	-3,764	-84,990	-90,867	-5,877
Kinetics (BIC Decay)	-7,565	-7,892	-13,397	-36,645	-749,235	-814,734	-65,499
Model Reported Excess Mass	**0**	**0**	**-5**	**-1**	**7**	**2**	**-5**
Change in Mass (ΣFluxes - Excess)	**9**	**7**	**11**	**55**	**863**	**945**	**82**
Initial Mass	25	17	38	347	6,310	6,736	427
Final Mass	34	24	48	402	7,173	7,681	509
Change in Mass (Initial - Final)	**9**	**7**	**11**	**55**	**863**	**945**	**82**
Water Column Mass Balance Closure (kg/day)	**-0.001**	**0.001**	**-0.001**	**0.006**	**-0.003**	**0.001**	**0.004**
Percent Tracking Error	**-0.00424%**	**0.00375%**	**-0.00278%**	**0.00154%**	**-0.00004%**	**0.00002%**	**0.00085%**
Model Reported Excess Mass (kg/day)	**-0.017**	**0.003**	**-4.621**	**-0.792**	**7.250**	**1.823**	**-5.426**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-540	-503	-1,070	-3,764	-84,990	-90,867	-5,877
Gross Resuspension (kg)	0	0	0	0	0	0	0

Table 6.1b Surface Sediment Layer Mass Balance Component Analysis by Zone for BIC (kg) Over the Short-Term Calibration Cycling Year

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Surface Sediment Layer							
Net of Settling and Resuspension	540	503	1,070	3,764	84,990	90,867	5,877
Net Sediment-Water Diffusion	0	0	0	0	0	0	0
Net Particle Mixing	0	0	0	0	0	0	0
Net Porewater Diffusion	0	0	0	0	0	0	0
Burial	0	0	0	0	0	0	0
Kinetics (BIC Decay)	-540	-503	-1,070	-3,764	-84,990	-90,867	-5,877
Model Reported Excess Mass	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Change in Mass (ΣFluxes - Excess)	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Initial Mass	0	0	0	0	0	0	0
Final Mass	0	0	0	0	0	0	0
Change in Mass (Initial - Final)	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
Surface Sediment Mass Balance Closure (kg/day)	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
Percent Tracking Error	**n/a**	**n/a**	**n/a**	**n/a**	**n/a**	**n/a**	**n/a**
Model Reported Excess Mass (kilograms)	**0.000**	**0.000**	**0.000**	**0.001**	**0.009**	**0.010**	**0.000**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-540	-503	-1,070	-3,764	-84,990	-90,867	-5,877
Gross Resuspension (kg)	0	0	0	0	0	0	0

Table 6.2a Water Column Mass Balance Component Analysis by Zone for PDC (kg) Over the Short-Term Calibration Cycling Year

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	26,665	14,719	13,700	33,328	160,228	248,641	88,413
Schuykill River	----	----	15,306	----	----	15,306	15,306
C&D Canal	----	----	----	15,456	----	15,456	15,456
Exchange at Smaller Tributary Boundaries	-15	-54	-1,278	-6,276	----	-7,623	-7,623
Water Withdrawls (Segs 60, 66, 69)	-1,068	----	----	----	----	-1,068	-1,068
Upstream Interface Advection	21,252	36,719	43,899	53,342	48,653	21,252	21,252
Upstream Interface Dispersion	----	-179	110	237	3,269	----	----
Downstream Interface Advection	-36,719	-43,899	-53,342	-48,653	-346,251	-346,251	-48,653
Downstream Interface Dispersion	179	-110	-237	-3,269	----	----	-3,269
Net Sediment-Water Diffusion	0	0	0	0	0	0	0
Net of Settling and Resuspension	-10,696	-6,604	-17,109	-37,645	-317,004	-389,058	-72,054
Kinetic (Gain from BIC Decay)	7,565	7,892	13,397	36,645	749,235	814,734	65,499
Kinetic (Loss from PDC Decay)	-7,352	-8,655	-14,584	-43,505	-298,573	-372,669	-74,096
Model Reported Excess Mass	**-2**	**0**	**-11**	**-1**	**16**	**1**	**-15**
Change in Mass (ΣFluxes - Excess)	**-187**	**-172**	**-126**	**-339**	**-458**	**-1,281**	**-823**
Initial Mass	475	562	894	3,016	16,003	20,951	4,947
Final Mass	288	391	768	2,677	15,545	19,669	4,124
Change in Mass (Initial - Final)	**-187**	**-172**	**-126**	**-339**	**-458**	**-1,281**	**-823**
Water Column Mass Balance Closure (kg)	**-0.002**	**-0.013**	**0.010**	**0.017**	**-0.014**	**-0.001**	**0.013**
Percent Tracking Error	**-0.000695%**	**-0.003210%**	**0.001291%**	**0.000640%**	**-0.000087%**	**-0.000005%**	**0.000304%**
Model Reported Excess Mass (kilograms)	**-2.488**	**0.054**	**-10.912**	**-1.431**	**15.701**	**0.924**	**-14.777**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-24,623	-25,349	-53,036	-191,737	-1,262,423	-1,557,168	-294,745
Gross Resuspension (kg)	13,926	18,745	35,928	154,092	945,419	1,168,110	222,692

Table 6.2b Surface Sediment Layer Mass Balance Component Analysis by Zone for PDC (kg) Over the Short-Term Calibration Cycling Year

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Surface Sediment Layer							
Net of Settling and Resuspension	10,696	6,604	17,109	37,645	317,004	389,058	72,054
Net Sediment-Water Diffusion	0	0	0	0	0	0	0
Net Particle Mixing	4	3	5	13	97	123	26
Net Porewater Diffusion	0	0	0	0	0	0	0
Burial	-5,152	-2,562	-7,488	-15,062	-230,618	-260,882	-30,264
Kinetic (Gain from BIC Decay)	540	503	1,070	3,764	84,990	90,867	5,877
Kinetic (Loss from PDC Decay)	-4,671	-4,102	-7,307	-21,234	-156,499	-193,813	-37,314
Model Reported Excess Mass	**2**	**1**	**2**	**4**	**24**	**33**	**9**
Change in Mass (ΣFluxes - Excess)	**1,416**	**445**	**3,387**	**5,122**	**14,950**	**25,320**	**10,369**
Initial Mass	56,709	50,011	88,740	259,769	1,891,524	2,346,753	455,229
Final Mass	58,125	50,456	92,127	264,891	1,906,474	2,372,072	465,598
Change in Mass (Initial - Final)	**1,416**	**445**	**3,387**	**5,122**	**14,950**	**25,320**	**10,369**
Surface Sediment Mass Balance Closure (kg)	**0.000**	**0.000**	**0.000**	**0.001**	**0.013**	**0.013**	**0.000**
Percent Tracking Error	**-0.000001%**	**0.000000%**	**0.000000%**	**0.000000%**	**0.000001%**	**0.000001%**	**0.000000%**
Model Reported Excess Mass (kilograms)	**1.509**	**1.065**	**2.281**	**4.372**	**23.997**	**33.224**	**9.227**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-24,623	-25,349	-53,036	-191,737	-1,262,423	-1,557,168	-294,745
Gross Resuspension (kg)	13,926	18,745	35,928	154,092	945,419	1,168,110	222,692

Table 6.3a Water Column Mass Balance Components by Zone for Penta PCB (mg/day) Over the Short-Term Calibration Cycling Year

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	7,387	7,375	11,552	14,199	9,290	49,804	40,513
Schuykill River	----	----	7,545	----	----	7,545	7,545
C&D Canal		----	----	1,305	----	1,305	1,305
Exchange at Smaller Tributary Boundaries	-13	-75	-1,413	-3,366	----	-4,867	-4,867
Water Withdrawls (Segs 60, 66, 69)	-725	----	----	----	----	-725	-725
Upstream Interface Advection	9,991	21,516	45,279	59,416	26,553	9,991	9,991
Upstream Interface Dispersion	----	-829	30	1,038	9,073	----	----
Downstream Interface Advection	-21,516	-45,279	-59,416	-26,553	12,858	12,858	-26,553
Downstream Interface Dispersion	829	-30	-1,038	-9,073	----	----	-9,073
Air-Water Exchange	-2,386	-2,785	-3,926	-20,883	-29,567	-59,546	-29,980
Net Sediment-Water Diffusion	1,913	2,953	1,702	2,080	2,758	11,407	8,649
Net of Settling and Resuspension	4,437	16,989	-756	-18,402	-30,818	-28,551	2,267
Model Reported Excess Mass	**-4**	**0**	**-17**	**0**	**0**	**-21**	**-21**
Change in Mass (ΣFluxes - Excess)	**-79**	**-165**	**-424**	**-238**	**149**	**-757**	**-905**
Initial Mass	367	747	1,491	1,966	3,277	7,848	4,570
Final Mass	288	582	1,067	1,728	3,426	7,091	3,665
Change in Mass (Initial - Final)	**-79**	**-165**	**-424**	**-237**	**148**	**-757**	**-905**
Water Column Mass Balance Closure (mg/d)	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Percent Tracking Error	**0.0001877%**	**0.0005142%**	**0.0002254%**	**0.0013943%**	**-0.0009752%**	**-0.0000475%**	**0.0008196%**
Model Reported Excess Mass (mg/day)	**-3.980**	**0.000**	**-17.223**	**0.006**	**-0.024**	**-21.222**	**-21.198**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-7,207	-13,257	-26,360	-60,354	-66,598	-173,776	-107,178
Gross Resuspension (mg/day)	11,643	30,245	25,604	41,952	35,781	145,226	109,445

Table 6.3b Surface Sediment Layer Mass Balance Components by Zone for Penta PCB (mg/day) Over the Short-Term Calibration Year

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Surface Sediment Layer							
Net of Settling and Resuspension	-4,437	-16,989	756	18,402	30,818	28,551	-2,267
Net Sediment-Water Diffusion	-1,913	-2,953	-1,702	-2,080	-2,758	-11,407	-8,649
Net Particle Mixing	5,427	11,567	3,746	-4,938	-8,224	7,578	15,802
Net Porewater Diffusion	0	1	0	-1	-1	-1	1
Burial	-4,255	-4,149	-5,233	-4,082	-8,565	-26,284	-17,719
Model Reported Excess Mass	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Change in Mass (ΣFluxes - Excess)	**-5,178**	**-12,523**	**-2,432**	**7,301**	**11,269**	**-1,564**	**-12,832**
Initial Mass	50,556	87,716	63,065	67,656	66,688	335,680	268,992
Final Mass	45,378	75,192	60,633	74,957	77,957	334,117	256,160
Change in Mass (Initial - Final)	**-5,178**	**-12,523**	**-2,432**	**7,301**	**11,269**	**-1,563**	**-12,832**
Surface Sediment Mass Balance Closure (kg)	**0**	**0**	**0**	**0**	**0**	**1**	**0**
Percent Tracking Error	**0.0010956%**	**0.0000020%**	**-0.0000027%**	**0.0000024%**	**0.0000017%**	**0.0001497%**	**0.0001947%**
Model Reported Excess Mass (mg/day)	**0.032**	**0.225**	**-0.075**	**0.027**	**-0.056**	**0.154**	**0.209**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-7,207	-13,257	-26,360	-60,354	-66,598	-173,776	-107,178
Gross Resuspension (mg/day)	11,643	30,245	25,604	41,952	35,781	145,226	109,445

Figure 6.1 Magnitude and Direction of BIC Mass Loads, Transfers and Fluxes for the Short-term Calibration

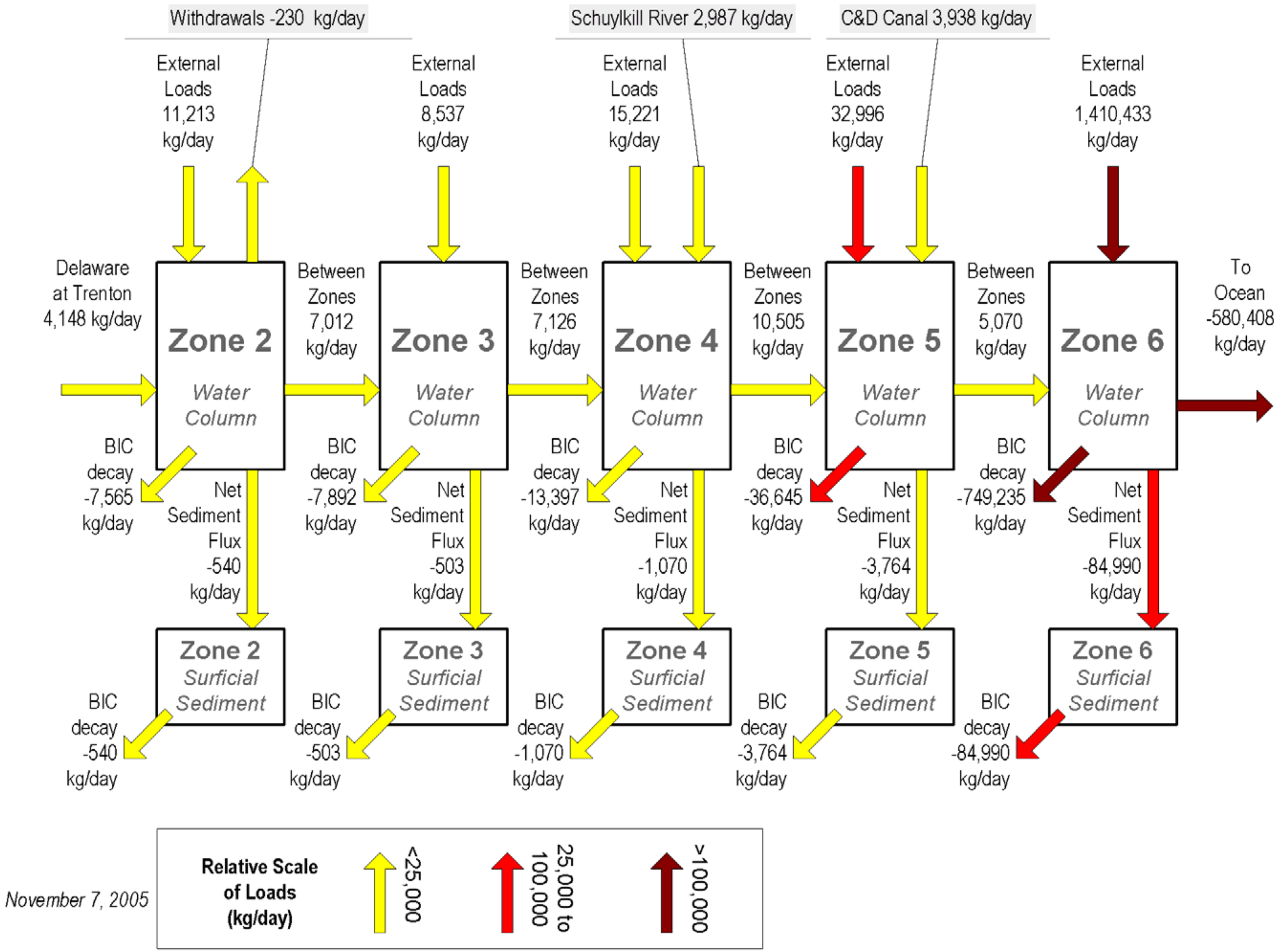


Figure 6.2a Water Column BIC Mass Balance Fluxes by Zone for the Short-Term Calibration Year

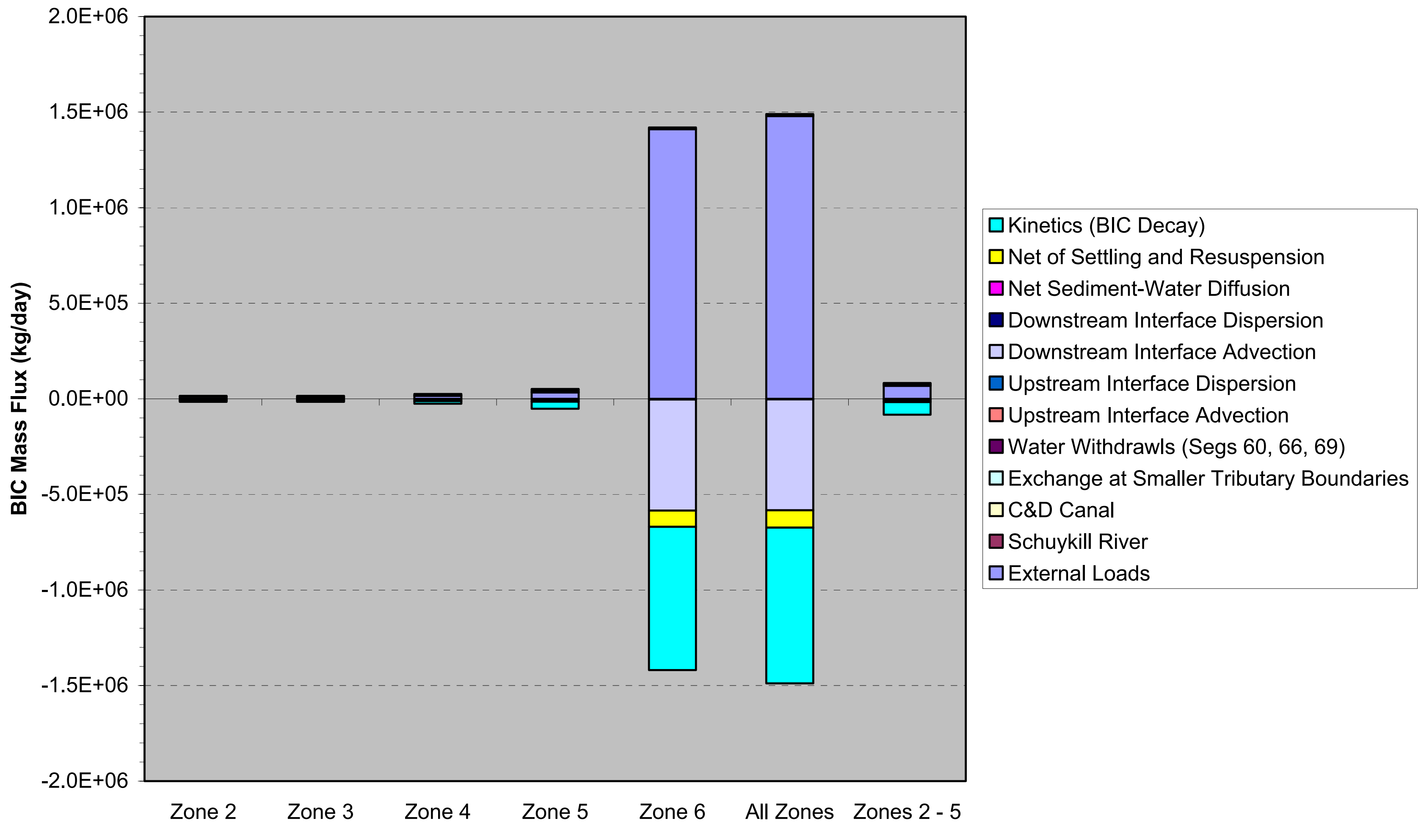


Figure 6.2b Surface Sediment Layer BIC Mass Balance Fluxes by Zone for the Short-Term Calibration Year

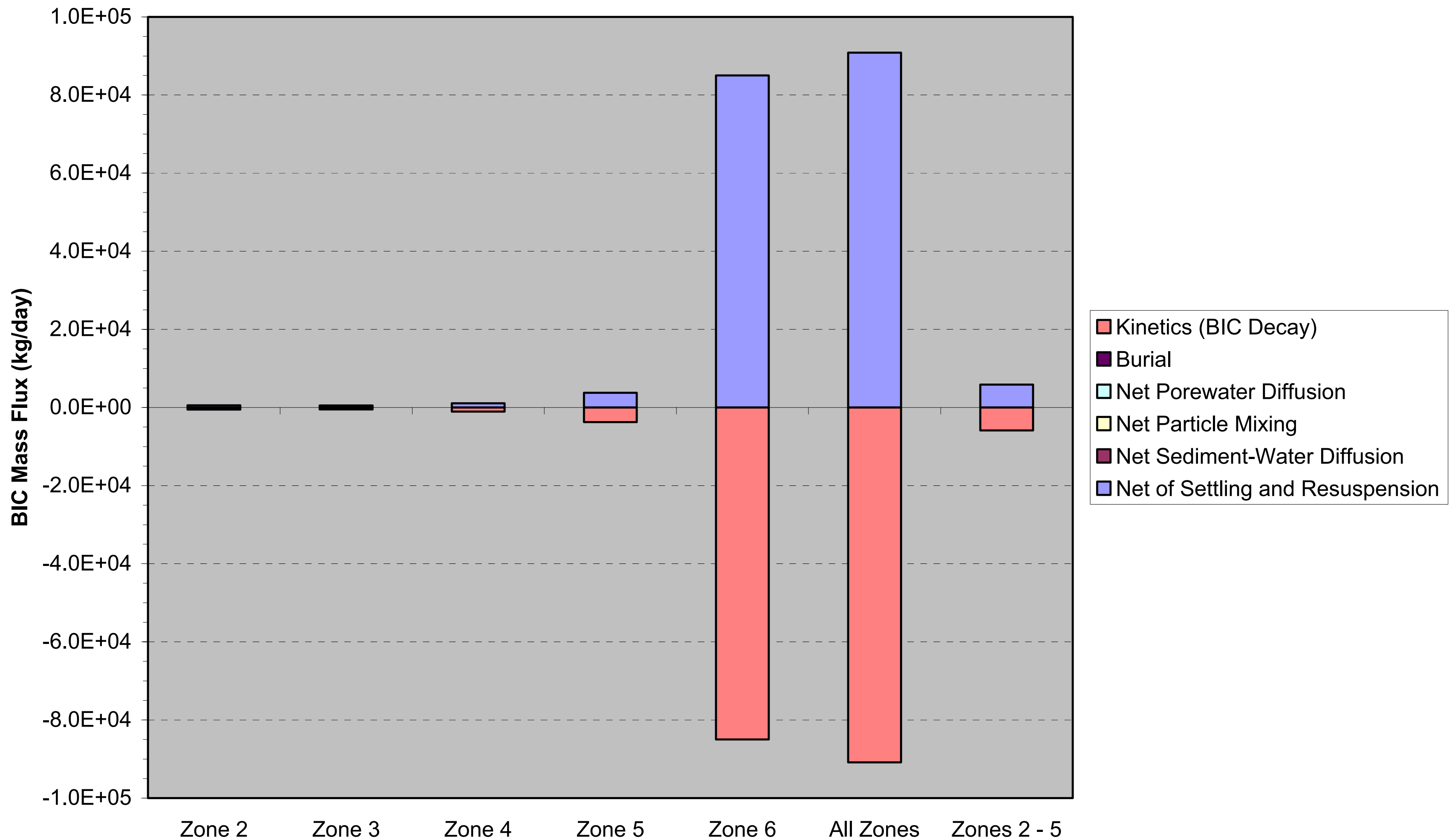


Figure 6.3 Magnitude and Direction of PDC Mass Loads, Transfers and Fluxes for the Short-term Calibration

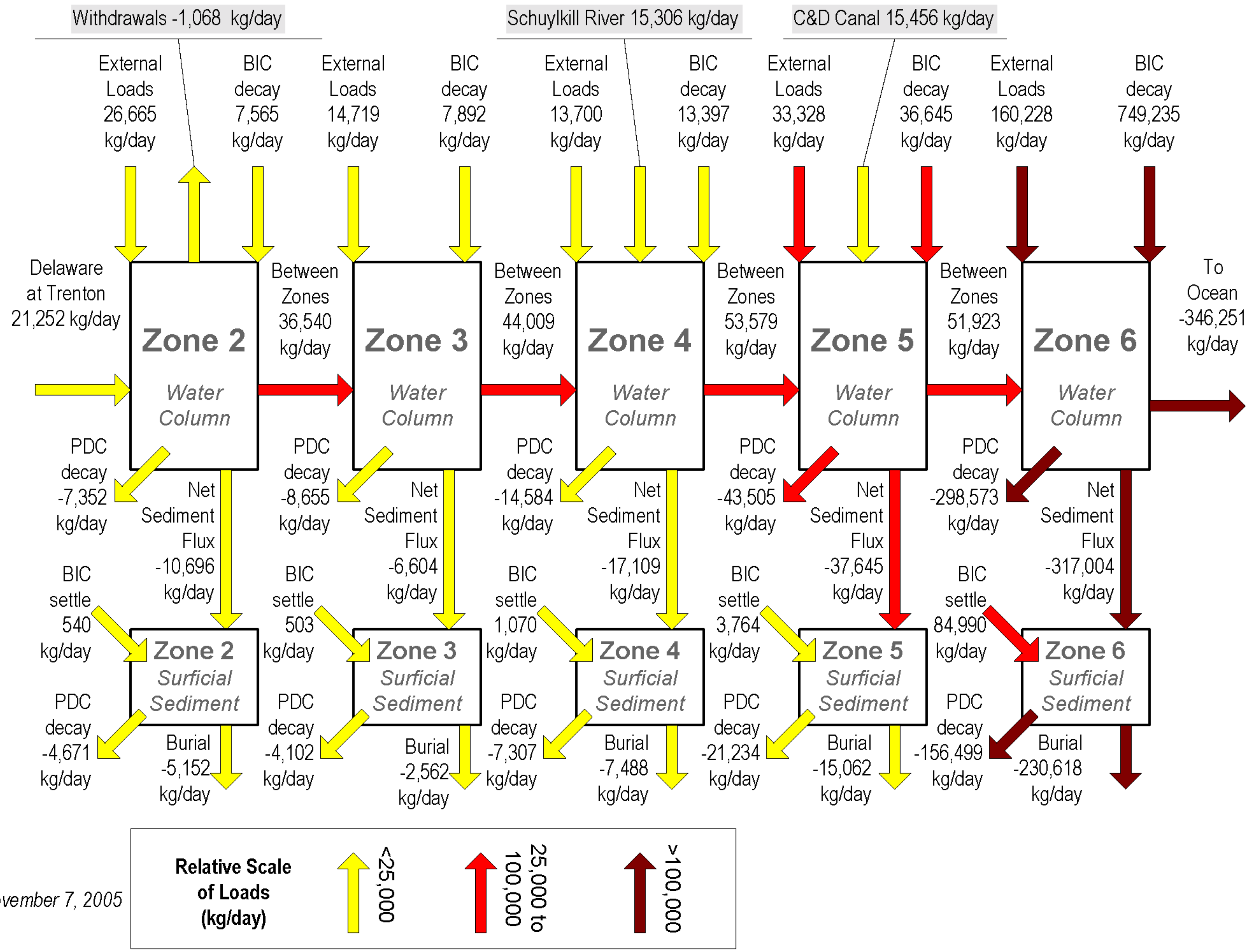


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Figure 6.4a Water Column PDC Mass Balance Fluxes by Zone for the Short-Term Calibration Year

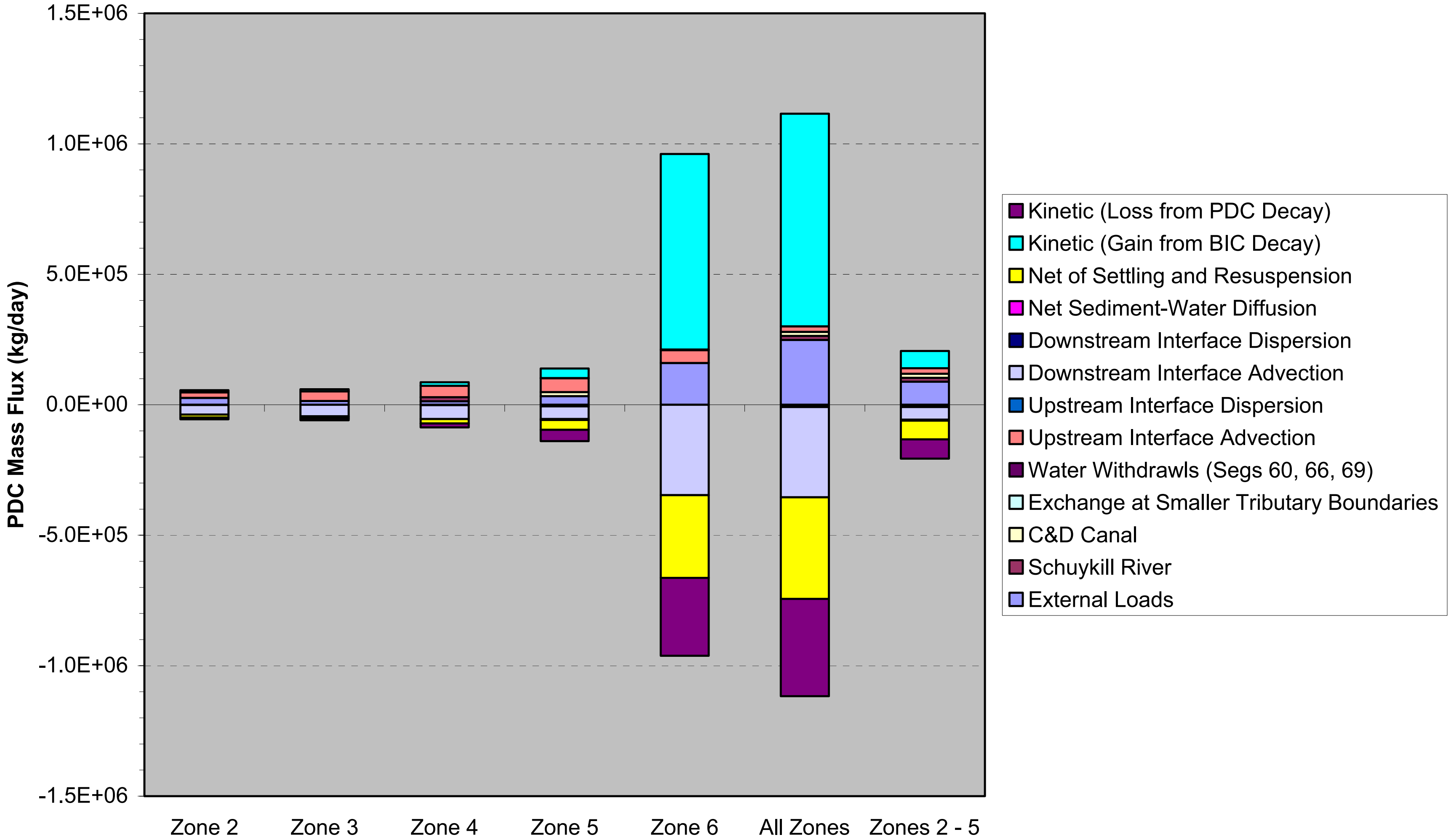


Figure 6.4b Surface Sediment Layer PDC Mass Balance Fluxes by Zone for the Short-Term Calibration Year

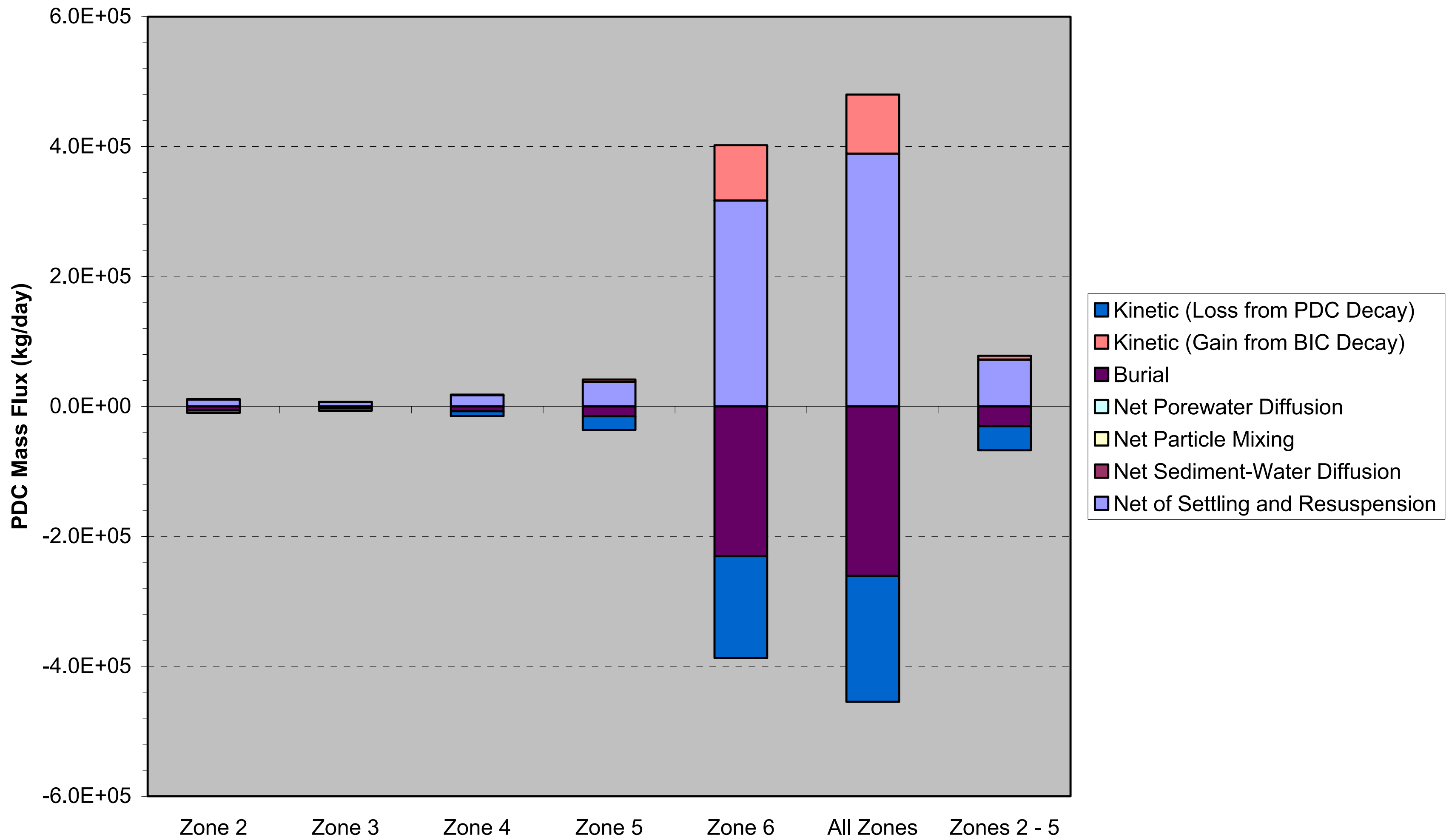
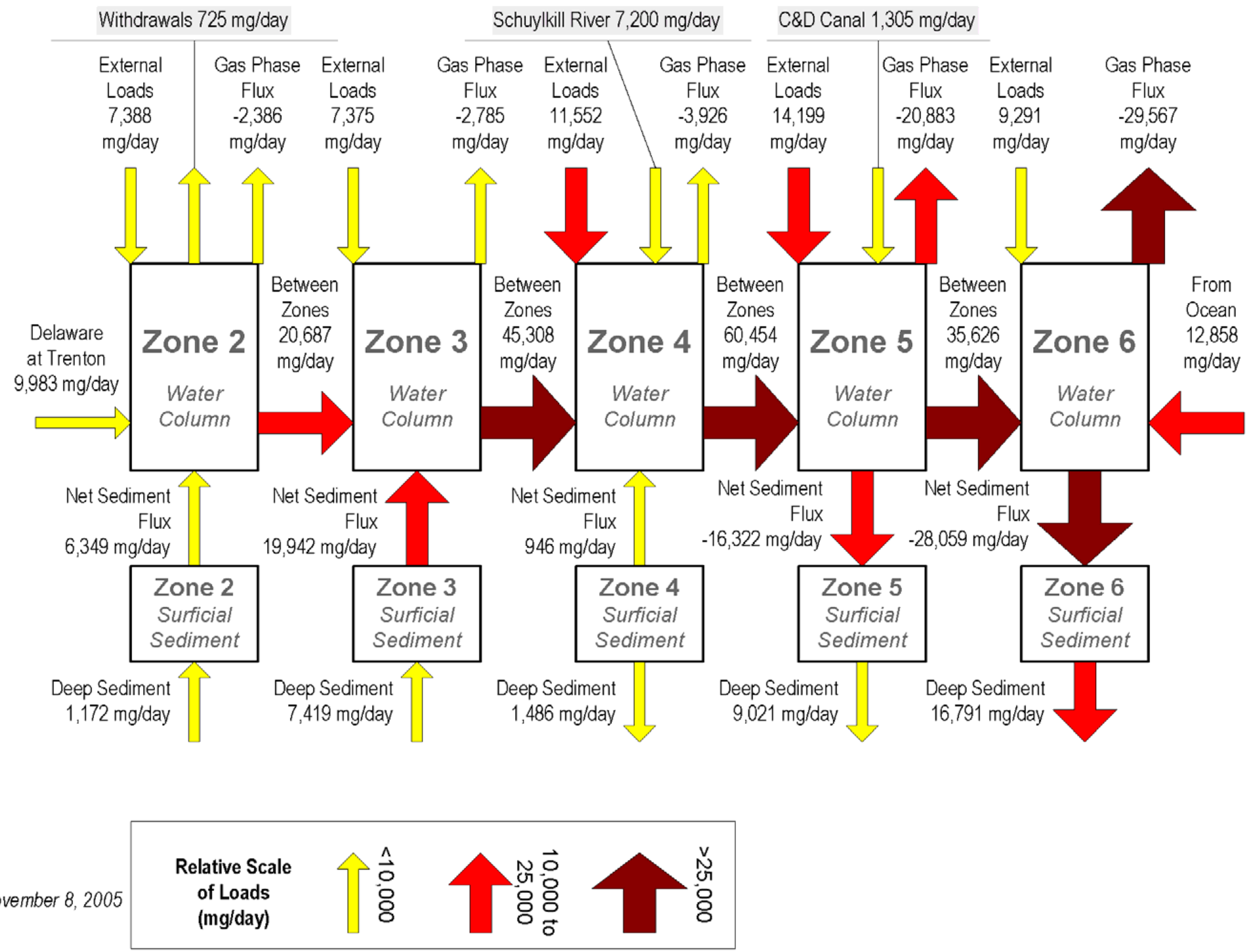


Figure 6.5 Magnitude and Direction of Penta PCB Mass Loads, Transfers and Fluxes for the Short-term Calibration



November 8, 2005

Figure 6.6a Water Column Penta PCB Mass Balance Fluxes by Zone for the Short-term Calibration Year

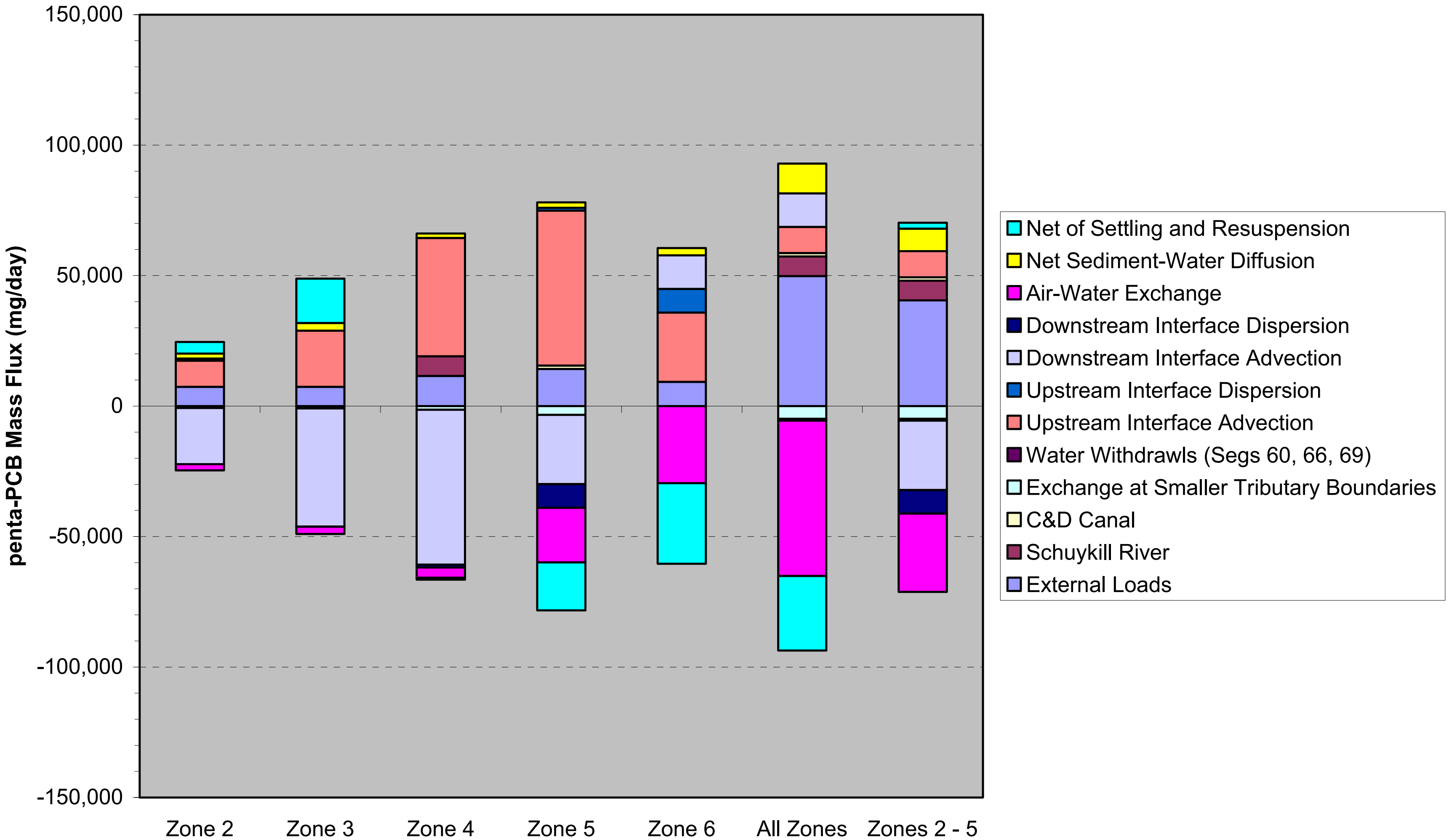


Figure 6.6b Surface Sediment Layer Penta PCB Mass Balance Fluxes by Zone for the Short-term Calibration Year

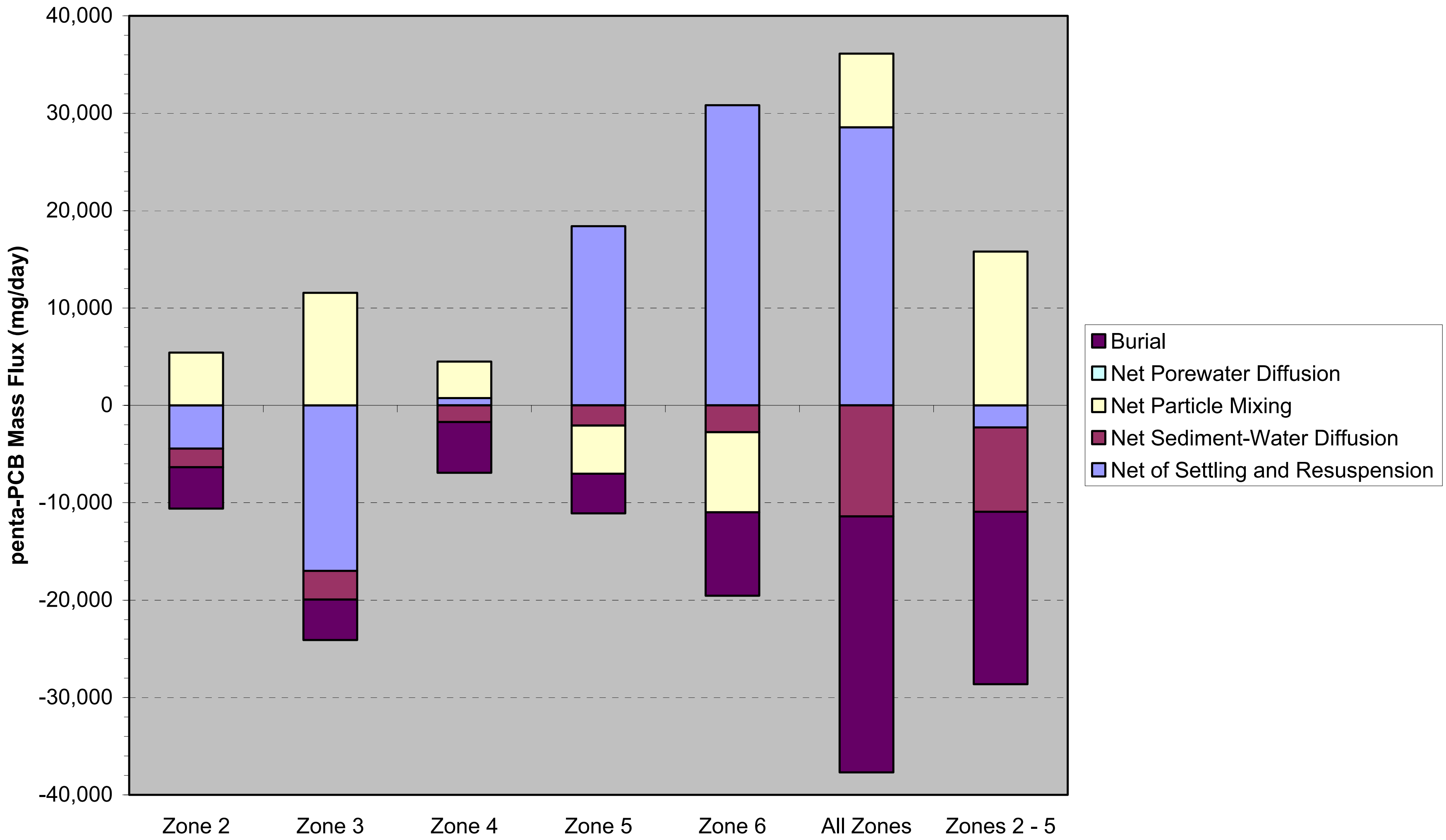
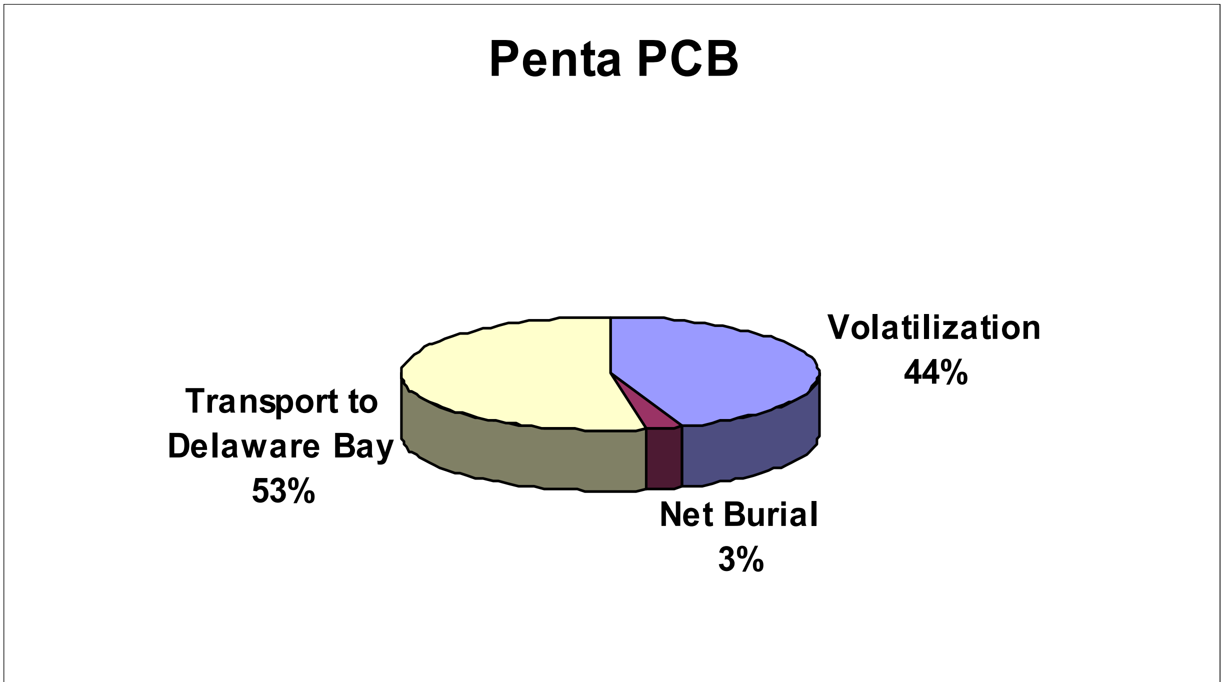
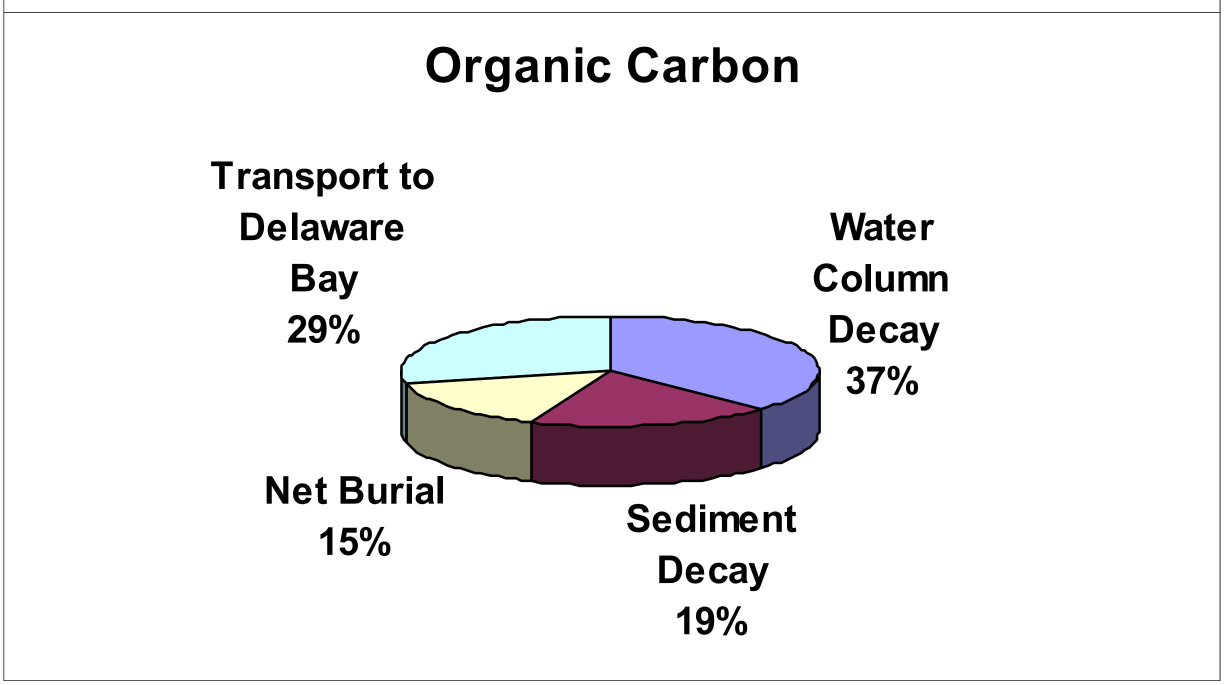


Figure 6.7 Ultimate Fate Pathways for Penta PCB and Organic Carbon in Delaware Estuary Zones 2 through 5





7 Decadal Scale Consistency Check

7.1 Introduction

7.1.1 Background

Due to their hydrophobic nature, PCBs strongly adhere to, and are transported with the organic carbon fraction of solids. The sediment bed in aquatic systems has a high solids concentration and therefore it usually is a significant storage compartment for PCBs. PCBs are moved between the water column and sediment bed by various processes, including solids deposition and resuspension, and pore water diffusion. The result is that (a) the sediment bed acts to decrease the response time of the estuary to changes in forcing functions, and (b) the "legacy" PCBs presently in the sediment bed are a current source to the water column.

The sediment bed has a slow response time (compared to the water column), which makes it difficult to constrain the model parameters that determine the water column-sediment bed interaction using short-term simulations. The net accumulation of solids in the sediment, quantified as the burial rate, can be constrained using information from sediment cores dated using various tracers (e.g. ^{137}Cs), and dredging records. However, information on the net accumulation of sediment does not constrain other sediment parameters that affect the long-term behavior of PCBs: the intensity of interaction between the water column and sediment bed via solids deposition and resuspension, and pore water diffusion; and the effective size of the sediment bed reservoir determined by the mixed layer depth. As a result, various combinations of settling and resuspension velocities and mixed layer depths can produce an adequate fit to the current water column data and net burial rate.

To illustrate the buffering effect of the sediment bed and the effect of the sediment parameters, several "washout" simulations with various combinations of settling and resuspension velocities and mixed layer depths were performed. Either high settling (1 m/day) and the correspondingly appropriate resuspension velocities, or low settling (0.5 m/day) and the smaller resuspension velocities, denoted as high/low interaction were used. Also two sediment mixed layer depths: 5 cm and 10 cm (small/large reservoir) were employed. These depths were assigned by DRBC/LTI based on observed ^{137}Cs and PCB profiles in sediment cores. The simulations were started at present conditions and all forcing functions (e.g. point source loads, tributaries, atmospheric gas phase concentration, etc.) were set to zero. It should be pointed out that this is not a realistic scenario because it is impossible to completely eliminate all inputs to the estuary. The results are presented in Figure 5.1. As a point of comparison, the present total PCB water quality criterion of 44 pg/L is also presented. Without sediment bed interaction the estuary would reach the water quality criterion in a very short time (~2 months–the almost vertical line in Figure 5.1). However, with sediment bed interaction the response time is much longer and, depending on the sediment transport scenario, it would take 15-40 years to reach the criterion (for this future zero-load scenario).

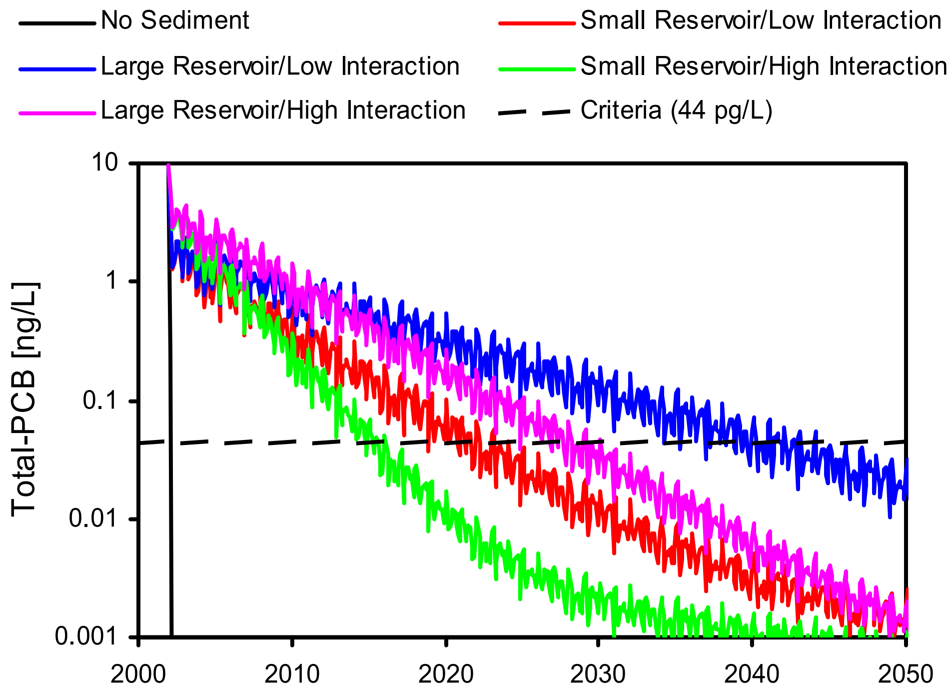


Figure 7.1 – Washout simulations for various sediment transport scenarios

Results are for model segment 44 near the Schuylkill River in Zone 4.

The washout simulations also illustrate that the PCBs presently in the sediment bed are a current source to the water column. At the beginning of the simulations, after the water column has equilibrated with the sediment bed (~2 months), the water column concentration is about 3 ng/L (depending on the scenario), which is close to the ambient concentrations currently measured. With all the loads set to zero, sediment interaction results in a water column concentration that is close to present levels.

To further illustrate the contribution of the PCBs currently in the sediment bed to the PCB concentration in the water column another diagnostic simulation was performed. The short-term simulation was run with initial PCB concentrations in the sediment bed set to zero. For this simulation the “large reservoir/high interaction” sediment transport scenario, which is the final one selected for the short-term simulation, is used. The results of the simulation, presented in Figure 5.2, show that about half of the PCB mass in the water column can be attributed to the PCBs currently in the sediment bed. It should be noted that the sediment bed is also a sink of PCBs, and depending on the time and location, the sediment bed can be a net source or sink.

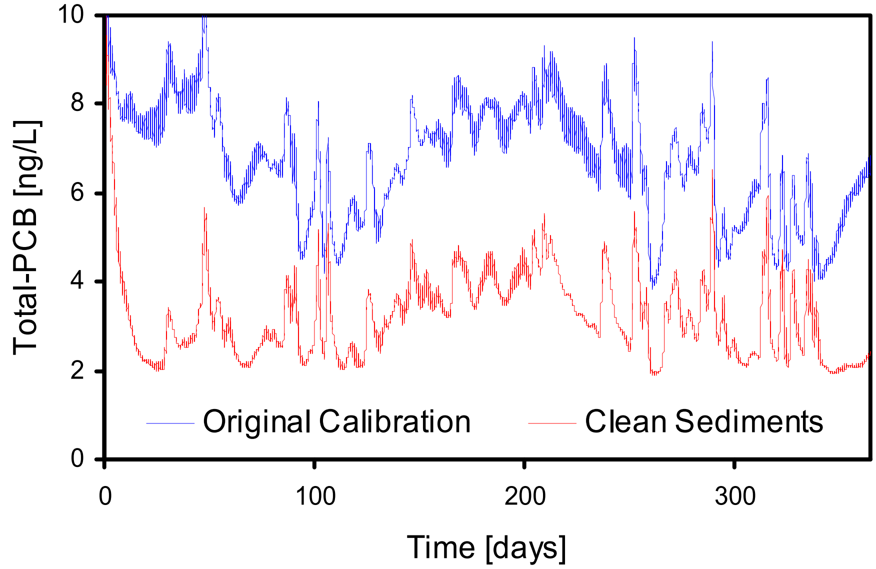


Figure 7.2 – Short-term simulation with and without PCBs in the sediment

Results are for model segment 44 near the Schuylkill River in Zone 4.

One way to constrain the sediment parameters (settling and resuspension velocities, mixed layer depth) is to perform a long-term simulation of a tracer for which the historical loading is known, for example ^{137}Cs (Lower Hudson River, Thomann et al., 1989; Green Bay, DePinto et al., 1993). Another approach is to reconstruct the historical loading of PCBs and to check the model's performance using this loading. This approach is adopted for the Delaware Estuary PCB model.

7.1.2 Objective and scope

Due to the importance of the sediment bed in influencing the fate and transport of PCBs in the estuary, the PCB Model Expert Panel recommended DRBC perform a long-term (decadal scale) simulation. Significant time constraints prevented DRBC from diverting attention from the short-term simulation. In order to contribute to the overall TMDL process, the Delaware Estuary TMDL Coalition agreed to fund this analysis and retained HydroQual to perform this task. The work consisted of using the DRBC model as constructed by DRBC and performing long-term simulations. No other parts of the DRBC model were evaluated as part of this effort.

The purpose of this section is to present the results of the long-term simulation of PCBs in the Delaware Estuary. The objective of the analysis was to determine if the long-term behavior of the model is consistent with the available data. The strategy used was to simulate the period from the beginning of PCB production to the present. That is, to perform a hindcast, and compare the model computed PCB concentrations to historical and contemporary data.

The remainder of this section documents the data sources (Section 5.2), PCB loading development (Section 5.3), hindcast results (Section 5.4), and the conclusions and recommendations (Section 5.5).

7.2 Data Sources

To evaluate the model's long-term behavior requires historical PCB data. An extensive data search for historical PCB concentrations in various media (water column, sediment bed, fish and birds) was performed. All data found were included. A special effort was made to locate data as far into the past as possible since a long time span is often required to identify a time trend when other sources of unaccounted variability are present, such as spatial variations where samples were taken. The data sources are summarized in Table 5.1, and the data are presented and discussed along with the model results in Section 5.4.

Table 7.1 - Sources of Historical PCB data

Source	Year	N	D
Water column			
Crump-Wiesner et al. (1973)	71-72	11	3
Kurtz (1978), PADER (1980)	74-75	10	3
USACOE (unknown date)	~80	11	2
Collier (1980)	80	4	0
Stamer et al. (1985)	79-80	12	10
Taylor (1996)	95	1	0
Versar (1999)	98	4	4
Versar (2000)	99	4	4
DRBC (2002)	01	12	12
Sediment bed			
Crump-Wiesner et al. (1973)	71-72	12	10
PADER (1980)	76-77	37	16
Collier (1980)	80	10	5
USACOE (unknown date)	~80	36	7
USACOE (1981)	81	4	0
Hochreiter (1982)	79-81	18	17
NOAA (2003)	86-97	46	46
USACOE (1997, 2003)	91,92,94	84	2
Costa and Sauer (1994)	93	16	16
Block (1991)	89	4	0
Hardy et al. (1995)	85-87	40	25
DRBC (1994)	91	22	0
Taylor (1996)	95	17	7
Burton (1997)	96	15	15
McCoy et al. (2002)	97	64	64
DeLuca et al. (1999)	98-00	42	9
Sommerfield and Madsen (2003), Eisenreich (2003)	48-01	27	27
EPA (2002a)	81-93	54	43
DRBC (2002)	01	51	51
Fish			

Greene (2002)	69-00		
Birds			
Clark et al. (2001)	98	6	6
Steidl et al. (1991)	89	7	7
Rattner et al. (2000)	97	15	15

N = number of samples; D = number of detects.

Due to different sampling and analytical techniques (e.g. packed vs. capillary column) the quality of historical contamination data is generally uncertain. An effort was made to quantify the accuracy of the historical data. In 1977 and 1979 White Perch collected from Zone 2 were analyzed using packed column Aroclor analysis techniques. The results are presented in Figure 5.3. Portions of the fish fillet were archived (frozen) and re-analyzed in 2003 using modern capillary column congener techniques. The total PCB concentrations computed by summing the Aroclors from the historical analysis and congeners from the contemporary analysis differ by 14% and 20% for the 1977 and 1979 fish, respectively, and no bias is evident. Although, this provides some reassurance in the accuracy of the historical data, it should be noted that these results are not necessarily representative of all historical data and larger errors and biases could be present for data in other media.

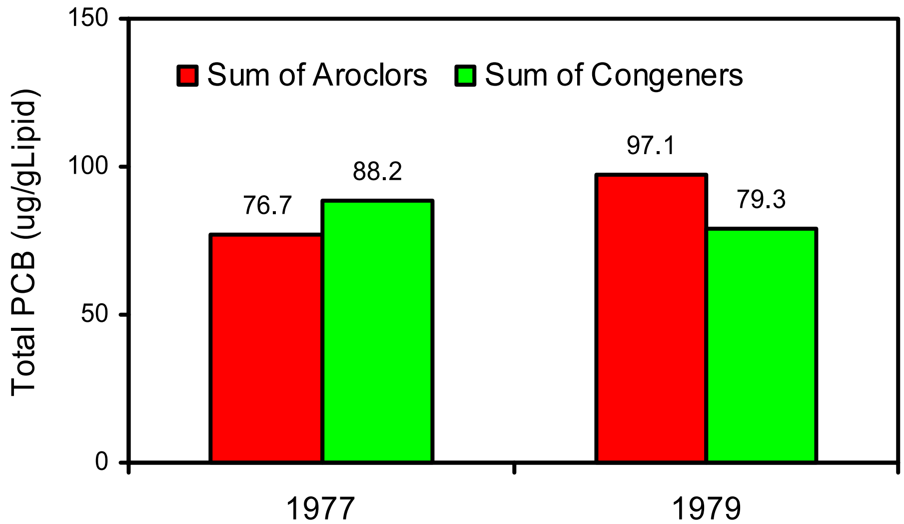


Figure 7.3 – Total PCB concentration in White Perch collected from Zone 2

The same two fish were analyzed in 1977 and 1979 using packed column Aroclor analysis and in 2003 using capillary column congener analysis.

7.3 PCB Loading Development

7.3.1 Strategy

The hindcast simulations are started in 1930, the approximate beginning of commercial production of PCBs (see Figure 5.4a), and ended in 2002, the time of the short-term simulation. This required developing historical time trends for PCB loads (point and non-point sources) and boundary concentrations (Delaware River at Trenton, Schuylkill River at Philadelphia, other tributaries, open boundaries at the Atlantic Ocean and C&D Canal, atmospheric boundary conditions). A back-scaling methodology is used to develop these inputs. This consists of developing a time trend of historical PCB forcing functions using various sources as discussed below. The PCB forcing functions for the hindcast are constructed by scaling the time trend using the present day values that are part of the short-term simulation. For example, the input associated with the Schuylkill River is assigned an average penta-PCB concentration of 1.1 ng/L in the short-term simulation. If the ratio of loads from 1970 to 2002 in the loading trend is 200, then a value of 1.1 x 200 = 220 ng/L is used for the Schuylkill River in 1970.

The loading trend is applied uniformly to all PCB forcing functions: e.g. point sources, open boundary concentrations, atmospheric gas phase concentrations, assuming they all followed the same historical time trend. Although this might not be a good assumption for some forcing functions, and evidence presented below suggests that this is the case for the Atlantic Ocean boundary condition, it greatly simplifies the analysis and facilitates the interpretation of the results.

There are two sources of uncertainty in the historical loading sequence constructed using the back-scaling methodology. The first is the shape of long-term loading time trend itself. The second is the current loadings, because the historical loadings are directly proportional to them. This means that any errors in the current loadings translate directly into errors in the historical loadings. Since there are large uncertainties in the current loadings there are also large uncertainties in the historical loadings.

Other, non-PCB, forcing functions: the hydrodynamic transport and organic carbon fate and transport, were cycled using the time series for the period 2/1/2002-1/31/2003. That is, these time series were repeated for each year in the long-term simulation. This period was identified by DRBC as a typical hydrologic year and therefore does not account for any inter-annual episodic events (e.g. hurricane, 50-year flood). Also, by cycling the organic carbon forcing functions the simulation does not account for any long-term changes in the organic carbon discharge from municipal wastewater treatment plants and non-point sources (erosion control practices).

To develop the historical forcing functions several trends were considered. Some trends were rejected after initial investigation of the loadings that resulted after back-scaling for various reasons: They produced loading trends inconsistent with the magnitude of PCBs produced during the simulation period. They produced a peak loading at a time inconsistent with the dated core data. Based on the ^{137}Cs dated core (PC-15, Woodbury Creek) it is known that the peak concentration in the estuary occurred at approximately 1970. Therefore, any loading trend would have to peak at approximately that time as well. Two loading trends were selected for simulation: one based on the estimated US penta-PCB air emission, and one based on the estimated Lower Hudson River total PCB emission, as discussed in the following sections.

7.3.2 US air penta-PCB emission trend (“Air Trend”)

An historical (1930-2000) emission inventory for 22 PCB congeners and 113 countries was developed by Breivik et al. (2002a,b). Briefly, the methodology consisted of estimating production and consumption (production + import – export) for each country. The consumption was divided amongst various usage categories (open, small capacitors, nominally closed, closed). Emissions then occur directly as a result of the usage (i.e. open usage), accidental release, or after the lifetime of the usage category (e.g. small capacitors) when it is disposed of in some way (landfills, open burning, waste incineration, destruction). The purpose of the model by Breivik et al. was to produce input to a global PCB fate and transport model (Globo-POP, Wania and Daly, 2002). On a global scale, transport via the atmosphere is most important and because of that Breivik et al. estimated emissions to air only. Figure 5.4b shows the time trend they developed.

Breivik et al. developed three emission trends designated as low, mid and high based on the uncertainties in the model input parameters (e.g. lifetime of small capacitors). The absolute magnitude of the estimates vary by up to three orders of magnitude and the time trends have different shapes as well. Differences in the absolute magnitude are not important in this analysis, because the absolute magnitude is normalized out in the back-scaling procedure. In other words, if the emission rate for every year were higher by a factor of 10 (e.g. 170 instead of 17 t/year in 1970, Figure 5.4b) the output of this analysis would be identical. However, differences in the shape of the time trend are important in this analysis. As an example, if the emission rate for just 2002 were higher by a factor of 10 (0.85 instead of 0.085 t/year, Figure 5.4b) then the mass discharged in the hindcast simulation would change by a factor of 10 for every year (except 2002). Here we use the mid estimate of Breivik et al. as being representative of their best estimate. The analysis by Breivik et al. was limited to 22 congeners, 6 of which are penta-PCBs. Since the DRBC model is for penta-PCBs we use the sum of the 6 penta-PCB congeners. This assumes the time trend of the sum of the 6 penta-PCB congeners is representative of the time trend of the sum of all penta-PCB congeners.

In this study the Breivik et al. trend is used for emissions to the Delaware Estuary. Although air and water are different emission pathways, it is reasonable to assume that their time trends are similar. Consider, for example, the disposal of capacitors to landfills. As emissions to the air occur by volatilization, emissions to water occur by rainfall runoff. Since both are related to the same landfill source, it is not unreasonable to assume that the time trend of PCBs attributable to that source would be the same. However, some emission scenarios, like fires, are clearly different and a future analysis might refine the work of Breivik et al. to estimate emissions to water. It should be emphasized that it is not assumed that the air emission estimate from Breivik et al. is applicable to the water emission to the Delaware Estuary, but rather that the time trends have the same shape. The Breivik et al emission time trend ended in 2000. The trend was extended from 2000 to 2002 using an exponential curve fit (see Figure 5.4b).

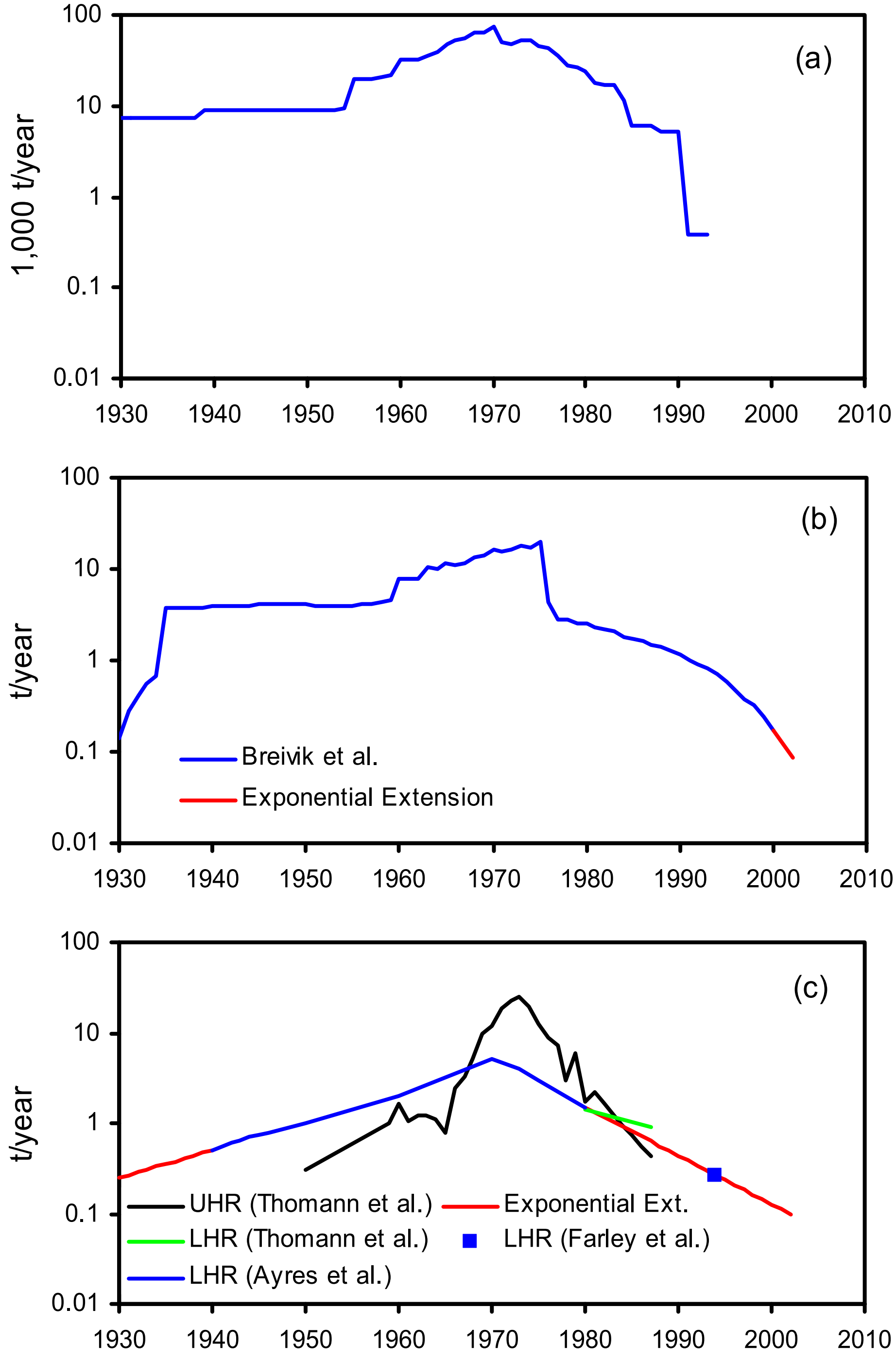


Figure 7.4 – Production and Emission Trends

(a) Global total PCB production (from Breivik et al. 2002a). (b) US penta-PCB air emission (sum of 6 congeners, mid estimate from Breivik et al. 2002b) and exponential extension to 2002. (c) Hudson River load estimates (UHR = Upper Hudson River, LHR = Lower Hudson River, Ayres et al. 1985, Thomann et al. 1989, Farley et al. 1999).

7.3.3 Lower Hudson River total-PCB emission trend (“Hudson Trend”)

Thomann et al. (1989) performed a historical simulation of PCB fate and transport in the Lower Hudson River. PCB mass entering the Lower Hudson River can be broken down into that from the Upper Hudson River, which is significantly influenced by discharges from two General Electric (GE) plants, and that from other sources. The following discussion refers to inputs entering the Lower Hudson River from sources other than the Upper Hudson River. Thomann et al. developed a loading function using a similar strategy as done here. Using various information sources they estimated the PCB loads for one year (1980) and then applied the time trend of historical PCB discharges developed by Ayres et al. (1985) (Figure 5.4c). The loads calculated by Thomann et al. are close to the estimates of Ayres et al. (1.46 vs. 1.5 t/yr in 1980). To extend the trend from the end of the Ayres et al. estimate (1980), to the end of their model period (1987) Thomann et al. applied the rate of decrease of PCBs in striped bass. The extension is shown in Figure 5.4c. In a subsequent analysis Farley et al. (1999) estimated the PCB loads to the Lower Hudson River for 1994. This analysis was done based on measurements, independently of the Thomann et al. extension. That estimate indicates a significantly faster rate of decrease from 1980 than estimated by Thomann et al. This is not surprising as it is expected that the decrease in striped bass lags the decrease in loads. The load estimate of Farley et al. corresponds to an exponential decrease from 1980 at about the same rate as the decrease from 1970 to 1980 in the Ayres et al. estimate (Figure 5.4c). The trend used in this study consists of the Ayres et al. estimate, with extensions for the periods 1930-1940 and 1980-2002 (Figure 5.4c). The extension for 1930-1940 was assumed to be exponential based on the rate of increase from 1940 to 1950 in the Ayres et al. estimate. For the extension for 1980-2002 an exponential decreases was assumed based on the rate of decrease from the 1980 Ayres et al. to the 1994 Farley et al. estimates. The rate of decrease thus obtained is similar to the rate of decrease from 1970 to 1980 in the Ayres et al. estimate.

7.3.4 Trend evaluation

Only limited data are available to evaluate the resulting loading trends. Water column PCB concentrations from two tributaries (Schuylkill River and Rancocas Creek) are overlaid with the loading trends in Figure 5.5a. The data were scaled so that the recent data (~2000) are in agreement with the loadings trends. Note that since data are not necessarily available for 2002 this adjustment involved some judgment. If the loading trends are appropriate for those tributaries then the historical data (1970-1980) should be close to the loading trends as well. The same test was done for PCB concentrations in sludges from municipal wastewater treatment plants (Figure 5.5b). The comparison suggests that the loading trends might underestimate the peak concentration in the Schuylkill River. The comparison for Rancocas Creek is good, with the data point in 1971 lying between the two loading trends. The trend of PCB concentrations in sludges observed is in reasonable agreement with the loadings trends. It should be pointed out that these comparisons only provide support for portions of the historical time trends (i.e. the marked decline from the 1970s to ~2000 for the tributaries, the marked decline from the 1950s to 1990s for the sludge). Other parts of the time trends (e.g. continued decrease during the 1990s in the tributaries or sludge) cannot be evaluated in this manner due to the lack of data.

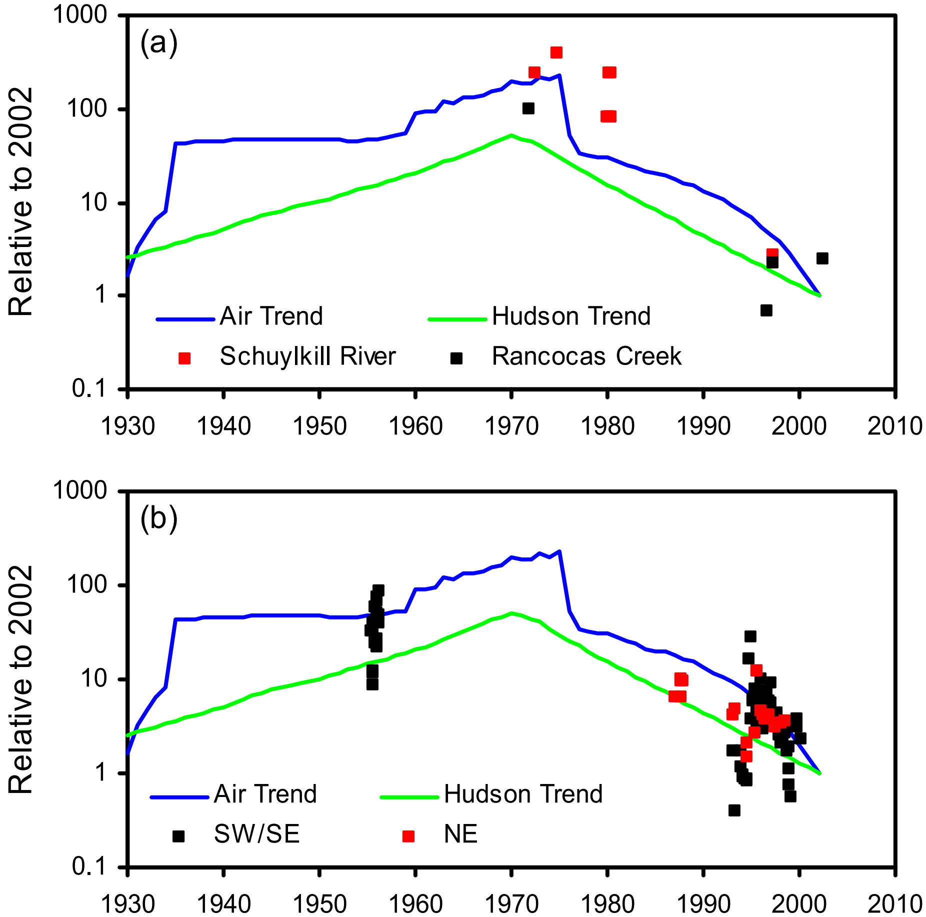


Figure 7.5 – Comparison of loadings trends with (a) tributary concentrations and (b) municipal wastewater treatment plant sludge concentrations

SW/SE and NE refer to different treatment plants of the Philadelphia Water Department. Data were provided by D. Blair (personal communication).

Another check is to compare the total mass discharged to the Delaware Estuary to other water bodies. The total PCB mass discharged to the estuary calculated by back-scaling and integrating the loading trends are compared to other mass estimates in Table 5.2. This check is useful, because the present analysis is not constrained by the total mass discharged. Some time trends produced a total PCB mass in excess of the global production and this check served as a basis for dismissing those trends. The total global production exceeds 1 million tons of which approximately 650,000 tons were produced in the US. The US air emissions were approximately 8,500 tons. Discharges to major waterbodies (Hudson and Fox Rivers) are in the range of approximately 100 to 600 tons. The two trends used for the Delaware Estuary are in the same range suggesting the time trends are not unreasonable.

Table 7.2: PCB Mass Inventories

Description	Total PCB (tons)
Production	
Global (a)	1,324,131
US (a)	641,700
Emissions	
Global to air (a)	18,538
US to air (a)	8,509
Upper Hudson River (GE plants) (b)	95-590
Lower Hudson River (c)	78
Lower Fox River (paper mills) (d)	314
Delaware Estuary	
"Air Trend"	512
"Hudson Trend"	128

(a) Breivik et al. (2002), (b) EPA (2002b), (c) 1946-1987, excluding Upper Hudson River, Thomann et al. (1989), (d) WDNR (1999).

7.4 Hindcast Results

This section presents the results of the hindcast simulations. For many historical data only total PCB concentrations are available and to allow for a comparison the model computed penta-PCB concentrations were multiplied by a factor of 4. This approximates the ratio of total PCBs to penta-PCBs found in the present forcing functions and present and historical (dated core) ambient data. It should be pointed out that the ratio of total to penta-PCBs can vary significantly (3 to 400 in the DRBC surficial sediment data). When model results are presented by zone they correspond to the average of the model segments for the mainstem estuary (e.g. segments 49, 51, 52, 53, 55, 56, 58 for Zone 3). Data reported as below detection limit are not included in the figures. When only a subset of Aroclors or congeners analyzed for were detected the data point is plotted at the logarithmic midpoint of the range obtained by setting non-detects to zero and the detection limit (see example in Section 5.4.1).

Various combinations of sediment transport parameters (settling and resuspension velocities, mixed layer depth, see Figure 5.1) were simulated. There are significant differences for the various scenarios. However, without more confidence in the historical data and historical and current forcing functions the hindcast simulations are unable to constrain the sediment parameters further. Here only the results of the final sediment transport scenario (high interaction/large reservoir) are presented, consistent with the presentation of the short-term simulation results. The results for the other three simulations are presented in Appendix G.

7.4.1 Historical water column data

The historical water column data for Zone 3 are presented in Figure 5.6. Data in other zones are insufficient for a useful model-data comparison. The 1980 data point represents two samples. Each sample was analyzed for 7 Aroclor mixtures (e.g. Aroclor1242). One Aroclor mixture was detected and quantified as "1-9 μg/l" and 6 Aroclor mixtures were reported as not detected (USACOE, unknown date). Based on the reported values, the estimated total PCB concentration of the samples ranges from 1,000 (1×1,000+6×0) to 15,000 (1×9,000+6×1,000) ng/L. This data point is plotted at the logarithmic midpoint of that range (4,000 ng/L) in Figure 5.6. The model results for the Air Trend fall within the range of data (assuming the 1980 data are representative of actual conditions). The results for the Hudson Trend are below the data in the late 1970s. Both trends are in good agreement with the contemporary data in 2001.

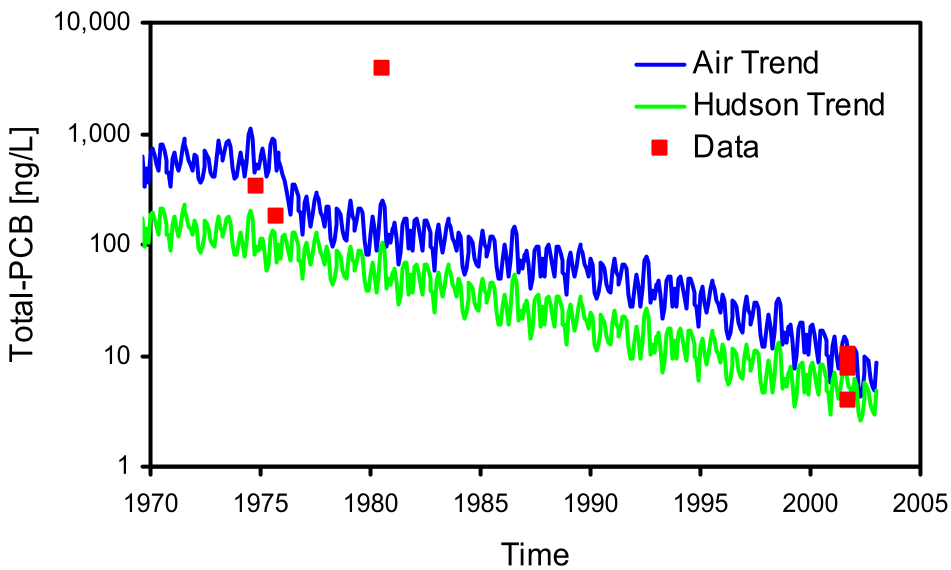


Figure 7.6 – Historical water column total-PCB concentrations in Zone 3

Historical sediment data

Historical sediment concentrations for Zones 2- 6 are presented in Figure 5.7. The data are highly variable, presumably a result of high spatial variability. Here all samples were lumped by zone. It is possible that a more careful analysis that accounts for differences in sample location (e.g. main channel, nearshore, near tributary mouths, etc.) would reduce some of that variability. The data in all zones are relatively constant in time and a trend of decreasing concentrations is not evident. By comparison the model results for both loading trends are on the high end of the data and decrease in time. Thus the model is not in agreement with the long-term trend seen in the sediment data. This could be the result of error(s) in the model, forcing functions and/or data.

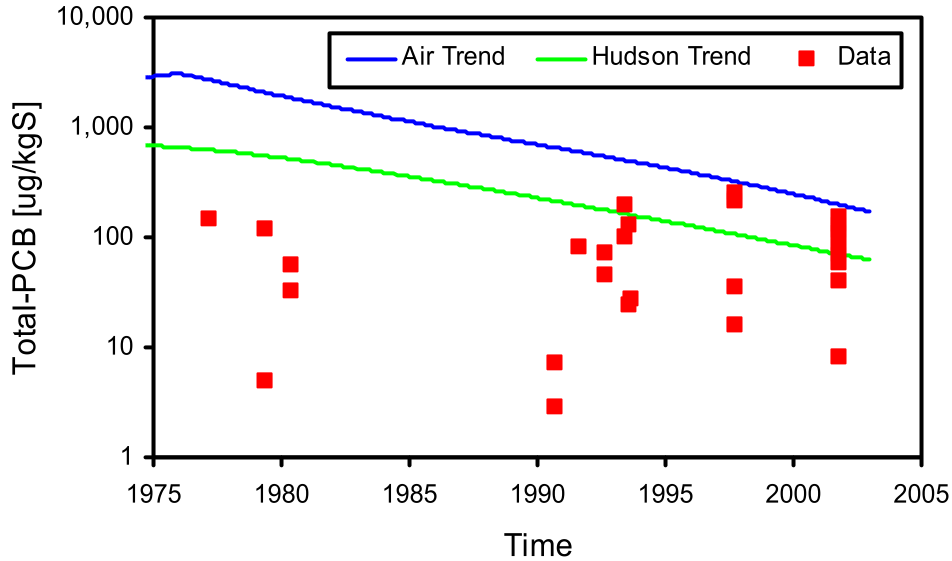


Figure 7.7(a) – Historical sediment bed total-PCB concentrations in Zone 2. Model results are average of layers 1 and 2

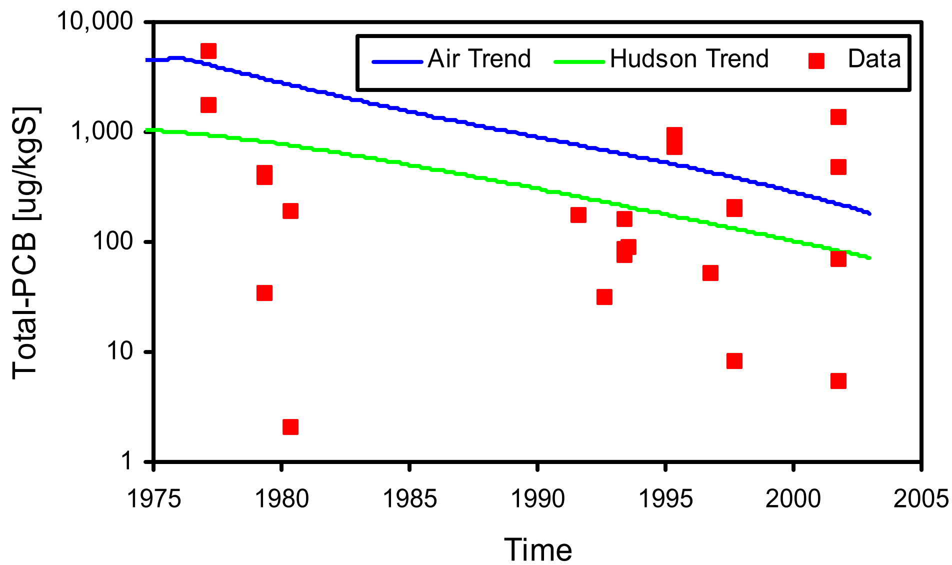


Figure 7.7(b) – Historical sediment bed total-PCB concentrations in Zone 3. Model results are average of layers 1 and 2

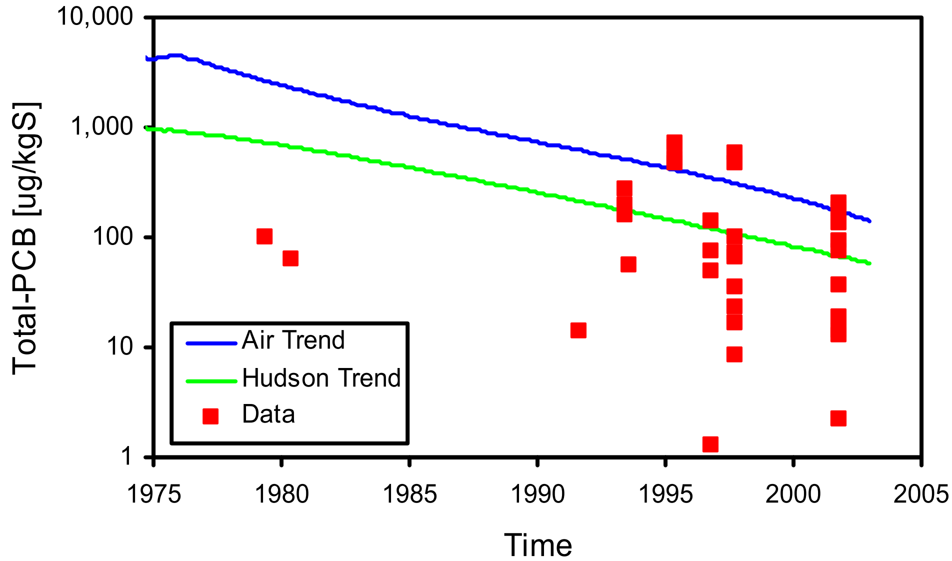


Figure 7.7(c) – Historical sediment bed total-PCB concentrations in Zone 4. Model results are average of layers 1 and 2

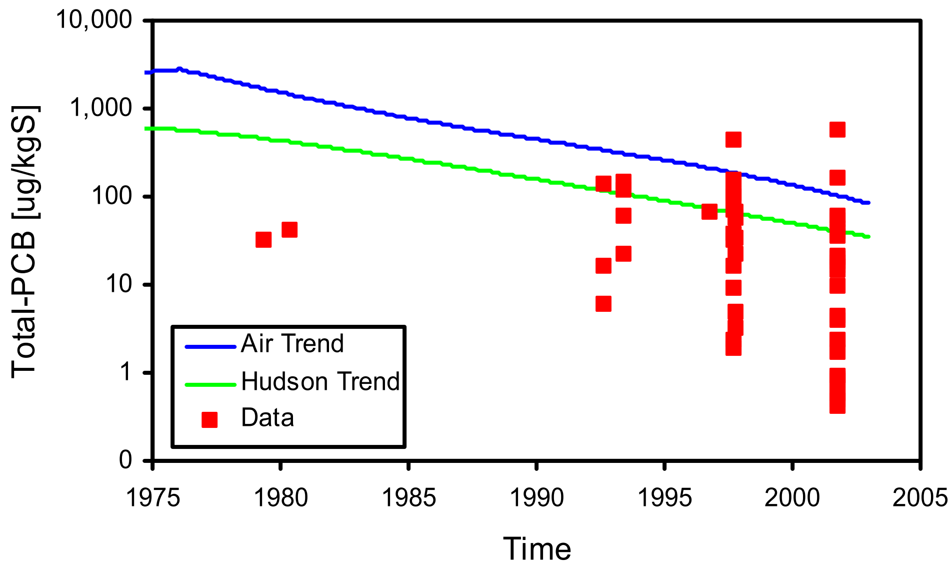


Figure 7.7(d) – Historical sediment bed total-PCB concentrations in Zone 5. Model results are average of layers 1 and 2

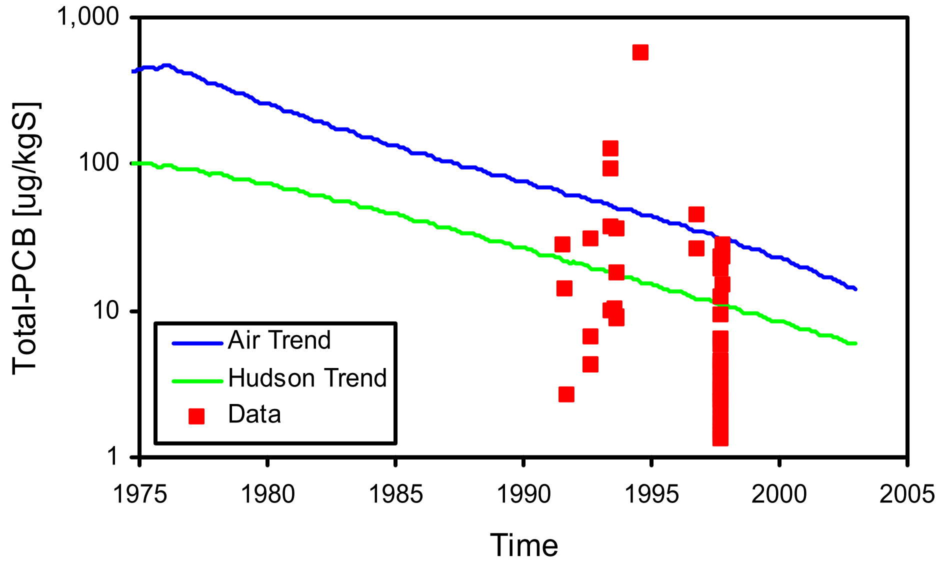


Figure 7.7(e) – Historical sediment bed total-PCB concentrations in Zone 6. Model results are average of layers 1 and 2

7.4.2 Historical fish data

Observed PCB concentrations in fish, compiled by Greene (2002), are presented in Figure 5.8 for Zones 2-6. For this comparison fillet and whole body results are not differentiated and when no lipid data are available it is assumed the lipid content is the average of the samples in the database (fillet = 2.7%, whole body = 6.8%, White Perch). Those data points are represented by different symbols on the plots.

The model does not include a fish compartment and a direct model-data comparison is therefore not possible. Fish concentrations on a µg/gLipid basis are compared to water column and sediment bed concentrations on a µg/gOC basis. The validity of this method depends on the assumptions that the partitioning of PCBs between water and organic carbon, and water and fish lipid is similar. For hydrophobic chemicals (like PCBs), this is known to be the case (Di Toro et al., 2000). The comparison is complicated by biomagnification, however, which will tend to increase the fish concentrations relative to the water column and sediment concentrations. Also, it is expected that the time trend of fish tissue concentration lags that of the water column and/or sediment bed concentrations, because it takes some time for the PCBs to move up the food chain. Whether the fish concentrations should reflect the water column or sediment bed concentration depends on the source of PCBs for the fish. The reasoning for presenting model results for both compartments is that depending on the base of the food web (benthic or pelagic) the fish concentration should equilibrate with the water column or sediment bed or some combination of them. The data shown in Figure 5.8 are for White Perch whose feeding habits vary with age and are not well defined (opportunistic). Data for other biota (American Eel, Striped Bass, Channel/White Catfish, Weakfish, Osprey eggs) are presented in Appendix G.

The data show a decrease in fish tissue concentration from ~1970 to ~1990. However, over the past ~10 years, from 1990 to 2002 no decrease in concentration is evident. This is roughly consistent with the relatively constant sediment concentrations (Figure 5.7). The last two years show an increasing trend in fish tissue concentrations. This recent increase is seen in the White/Channel Catfish data as well (Appendix G). The model sediment concentrations for the Air Trend are at the high end of the data. If any biomagnification is accounted for the agreement worsens. The sediment concentrations for the Hudson Trend are at the low end of the data, which is more consistent when biomagnification is assumed to occur. Neither trend captures the constant concentration over the past ~10 years or increase over the last two years. This is an important discrepancy between the model and historical data. This could be the result of error(s) in the model, forcing functions and/or data.

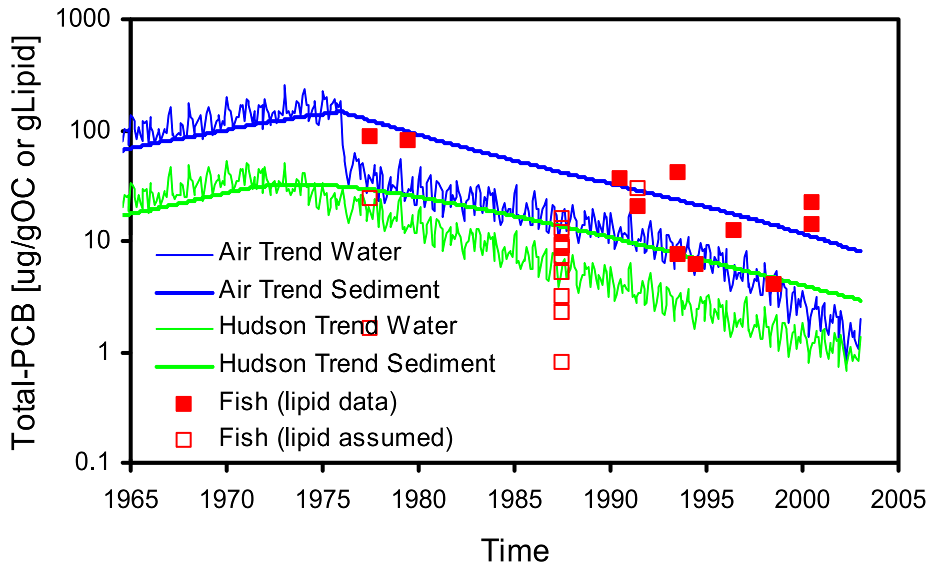


Figure 7.8(a) – Historical fish total-PCB concentration in Zone 2. Data are for White Perch. Model sediment results are for layer 1

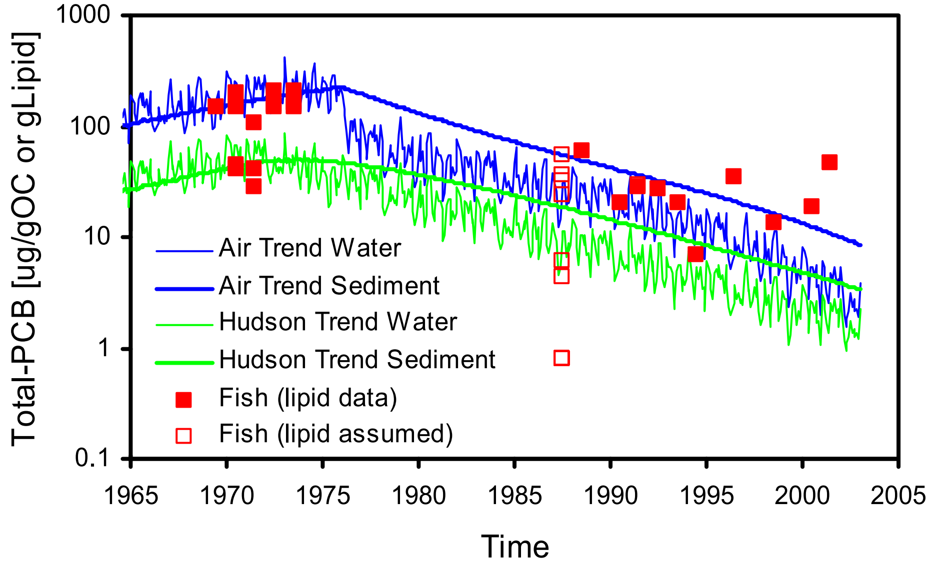


Figure 7.8(b) – Historical fish total-PCB coFncentration in Zone 3. Data are for White Perch. Model sediment results are for layer 1

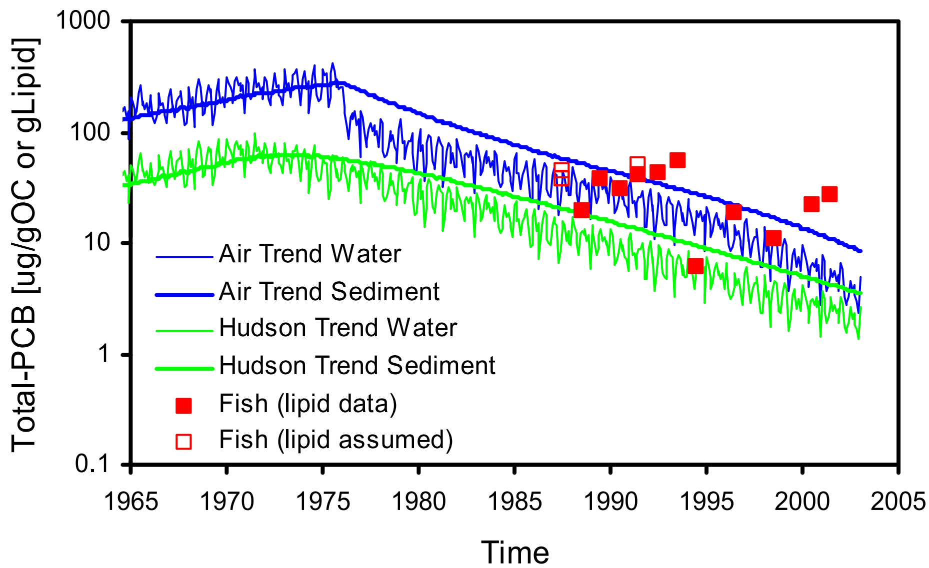
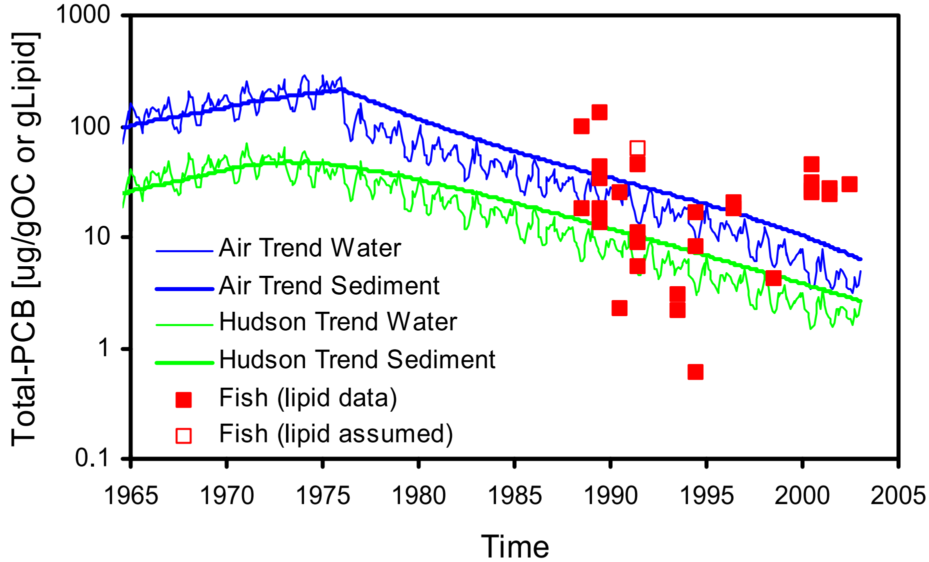


Figure 7.8(c) – Historical fish total-PCB concentration in Zone 4. Data are for White Perch. Model sediment results are for layer 1



7.8(d) – Historical fish total-PCB concentration in Zone 5. Data are for White Perch. Model Figure sediment results are for layer 1

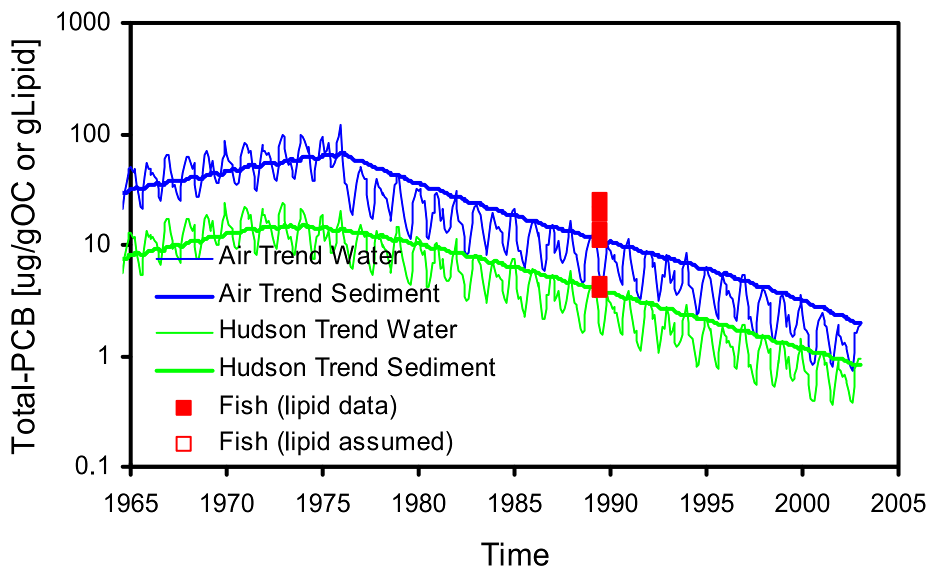


Figure 7.8(e) – Historical fish total-PCB concentration in Zone 6. Data are for White Perch. Model sediment results are for layer 1

7.4.3 Contemporary sediment data

A stringent test of the model is its ability to predict the presently observed PCB concentrations, using the historical loading. Contemporary sediment data are presented in Figure 5.9. The data were processed by DRBC by averaging the dry-weight PCB concentrations (μg/kg) by zone. However, sediment bed fraction organic carbon (foc) data were not averaged and therefore the organic carbon-based PCB concentrations (μg/gOC) vary somewhat within each zone.

The model-simulated concentrations for the two loading trends bracket the data in the upstream portion of the estuary (Zones 2 and 3). Below that the agreement is worse with the model progressively overpredicting concentrations with distance downstream. At the downstream end (Delaware Bay, Zone 6) the model overpredicts PCB concentrations for both loading trends by almost an order of magnitude. This is consistent with the model-data comparison for historical sediment concentrations presented in Section 5.4.2. Although the model is within the range of the historic sediment data (which has ~2-order of magnitude variability) at the end of the simulation period, it clearly tends to overpredict the observed sediment concentrations. This could be related to the inability of the model to simulate the estuarine turbidity maximum and associated effect on PCB fate and transport. On the other hand, a unit load simulation (results not presented here) demonstrated that the PCB mass in that part of the estuary is predominantly from the Atlantic Ocean. It is possible that the loading trends are not applicable to the Atlantic Ocean concentration. Due to the large volume the Atlantic Ocean responds slowly to changes in input. It is expected that applying the loading trend to the Atlantic Ocean resulted in an overestimation of the historical boundary concentration. The inability of the model to reproduce the data is therefore not necessarily a shortcoming of the model, but could be a shortcoming of the method used to develop the historical ocean boundary condition.

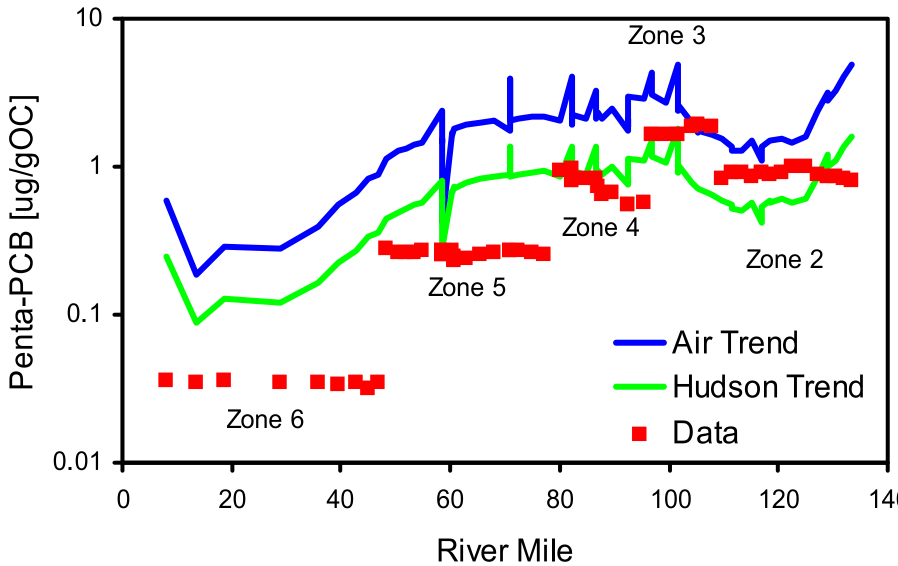


Figure 7.9 – Contemporary surface sediment penta-PCB concentrations. Model results are for sediment layer 1

7.4.4 Dated core data

The concentrations from the dated core are presented in Figure 5.10. Measured sediment concentrations on an organic carbon basis are compared to modeled water column concentrations on a particulate organic carbon basis. At first glance it might seem more appropriate to compare the data to sediment concentrations, but that would not be correct. That is because the sediment bed simulated by the model corresponds to the bioturbated sediments present throughout most of the estuary. However, the dated sediment core was collected from a location where there was apparently no significant bioturbation. The concentrations in the dated core are a record of the PCB concentration of depositing solids, and therefore the data are compared to PCB concentrations on organic carbon in the water column corresponding to the time of deposition.

The data show a relatively rapid increase in concentrations over the period 1950-60, followed by a smooth peak (1960-1980) and then decreasing concentrations from 1980 to the present. Neither loading trend predicts the rapid increase from 1950-1960. It is possible that this is a result of an error in the loading trend, model or data. To answer that question addition sediment cores should be examined. Post 1960 the Air Trend is in good agreement with the data (besides overpredicting the peak in 1970). The Hudson Trend clearly underpredicts concentrations after 1960.

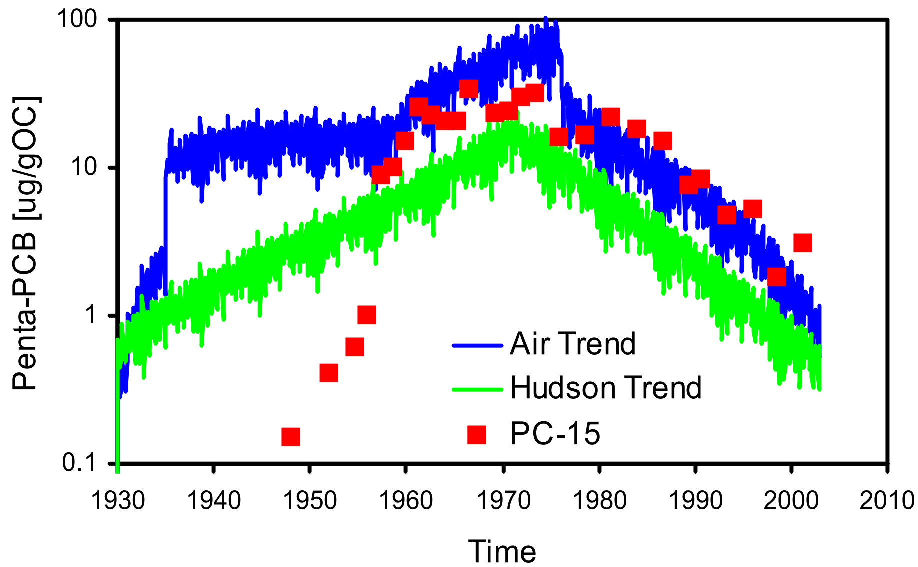


Figure 7.10 – Historical water column penta-PCB concentrations. Data are from Woodbury Creek core (PC-15; Sommerfield and Madsen, 2003; Eisenreich, 2003)

Depth was converted to time using 1.5 cm/yr net deposition rate. Model results are for Segment 44.

7.5 Conclusions and Recommendations

7.5.1 General conclusions

Historical hindcast simulations (1930-2002) were performed to check the long-term (decadal scale) behavior of the model. There are large uncertainties in the PCB forcing functions (current loads, historical loading trend) and ambient concentration data. Also, the present analysis neglects episodic events (e.g. hurricanes, 50-year flood) and long-term changes in non-PCB forcing functions (e.g. POC loads from municipal wastewater treatment plants, non-point sources) that could be important in the fate and transport of PCBs on the decadal scale. Therefore a meaningful quantitative statistical model-data comparison can not be performed and only a qualitative appraisal is made.

Based on our review of the hindcast simulation results with the current model: (1) The model is in reasonable agreement with the historical water column concentrations, both observed and deduced from the dated core for the period following the 1980s; (2) The model is in reasonable agreement with the contemporary sediment data in the upper estuary (Zones 2-3); (3) The model appears to be inconsistent with the historical sediment data. The model predicts a relatively fast rate of decrease in sediment concentrations which is not seen in the data, although that comparison is limited by the high variability in the sediment data; (4) The model predicted time course of water column and sediment bed concentrations also appear to be inconsistent with the fish tissue concentrations. The PCB concentrations in the fish have remained relatively constant over the past 10 years and increased over the past 2 years, which is not reproduced by the model. Thus there appears to be an important inconsistency between the historical sediment and fish tissue data and the model predictions. At present it is not clear what the source(s) of the problem is. Possible causes include error(s) in (1) forcing functions (current and/or historical), (2) the model (e.g. mixed layer depth) and/or (3) the data or how they are interpreted.

Recommendations are presented for model improvements in three areas: (1) PCB forcing functions, (2) the effect of episodic events and long-term changes in non-PCB forcing functions, and (3) sediments, bioaccumulation and fish tissue concentrations. It is important to resolve these discrepancies for the next phase of the TMDL process.

7.5.2 PCB Forcing Functions

Background

There are large uncertainties in the PCB forcing functions for the major source categories, especially the Contaminated Sites, non-point sources and possibly the gas phase source. These large uncertainties are the result of limitations in field sampling and analytical programs (number of samples, spatial and temporal resolution) and data analysis techniques (how these measurement are used to compute annual loading sequences). The uncertainty in the current forcing functions translates directly into uncertainties in the historical forcing functions, because a back-scaling methodology is used to derive the historical loadings. This limits the accuracy of the hindcast simulation.

The uncertainty in forcing functions also affects the model calibration. Suppose the Contaminated Sites loadings were underestimated. Then the model would be predicting lower water column PCBs than are actually measured. The only possible source would be the sediment, assuming all other sources are known. Therefore the sediment-water exchange would need to be increased. Conversely if the loading were overestimated, then removal processes (i.e. burial) would need to be increased. Therefore, the uncertainty in PCB forcing functions is directly relevant to assimilative capacity of the estuary and the TMDL calculation.

Understanding current loadings is also important for management. Targeting what might turn out to be minor sources will be costly and fail to achieve the desired reduction in PCB concentrations. It is necessary to properly identify and quantify the sources of PCBs in order to develop appropriate measures to address those sources.

Suggested tasks

It is recommended to reduce the uncertainty in the following loading categories:

- *Contaminated Sites.* It is possible that the mass flux from the Contaminated Sites varies over a wide range and that a small number of sites contribute a large fraction of the loadings. Those sites should be identified based on the current information. Then additional data collection and load estimation should be performed using site-specific analysis. Differences in transport pathways (e.g. rainfall runoff, groundwater migration) should be taken into account.
- *Atmospheric Loading & Boundary.* The model predicts that gas transfer of PCBs across the atmosphere-water interface is an important process. Depending on the concentration gradient across this surface, which varies in space, time and scenario (i.e. TMDL condition), the atmosphere can be a significant source or sink of PCBs to/from the estuary. It is expected that the temporal and spatial variability in the atmospheric gas-phase concentration is large. Additional data collection should be performed to characterize the gas phase concentration. The use of global models (i.e. Globo-POP, Wania and Daly, 2002) to predict the historic atmospheric gas phase concentration should be investigated. Also, cores from areas that are not hydrologically connected to the estuary and do not receive any significant non-atmospheric load of PCBs (i.e. pristine areas) should be collected, since they would record atmospheric loading. This is particularly important in the Camden region since a large present day source appears to be active. It would be important to know if this source was present in the past.
- *Unidentified historical deposits.* It is possible that historical deposits of PCBs are contributing to the present concentrations, but have not yet been identified. Shoaling areas and marsh sources may also be important. Additional sediment sampling in these locations should be performed.
- *Tributaries.* Loadings from tributaries should be calculated using standard regression techniques (rating curves) applied to flow, organic carbon and PCBs. This will require additional data collection to define the relationship between these parameters. Sediment cores should be collected upstream of the head of tides to determine the historical loadings from tributaries.
- *Tidewater.* Present estimates of PCB loadings from the "tidewater" area (direct ungaged runoff) are based on literature values. Site specific data should be collected and analyzed to confirm those estimates are representative of the Delaware Estuary area.
- *Atlantic Ocean.* The historical time trend of PCB concentrations in the Atlantic Ocean should be refined by collecting sediment cores on the shelf. Also, the use of global models (i.e. Globo-POP, Wania and Daly, 2002) to define the historical concentration should be investigated.
- *Historical time trend.* The shape and uncertainty of the historical loading time trend and the applicability to each loading category (e.g. Atlantic Ocean boundary) should be investigated. For significant individual sources (e.g. Contaminated Sites) this analysis should be done on a site-specific basis. Alternate methods for extending the Breivik et al. estimate from 2000 to 2002 and the Thomann/Farley estimate from 1994 to 2002 should be investigated.

7.5.3 Effect of Episodic Events and Long-term Changes in Non-PCB Forcing Functions

Background

The current version of the model is based on a simulation period with forcing functions representative of average conditions. The hindcast simulation was performed by cycling a 1-year period representative of average conditions. However, the transport of solids and therefore organic carbon and associated PCBs is highly event driven. On a long-term average, episodic events (e.g. hurricanes, 50-year flood) could constitute a significant import and/or export of PCBs from the estuary. Also, it is expected that the organic carbon input from point (municipal wastewater treatment plants) and non-point (erosion control practices) sources has changed significantly over the hindcast simulation period. The effects of changes in organic carbon input can be relatively direct (e.g. more POC → more POC settling → more PCBs settling) or more indirect (e.g. more DOC → less dissolved oxygen → less bioturbation → less sediment bed PCB flux).

Suggested tasks

- The effect of episodic events should be investigated by estimating the response of the forcing functions (i.e. tributary loadings) and model transport processes (e.g. sediment resuspension) to such events.
- The sensitivity of the hindcast simulation to changes in historical organic carbon discharges from municipal wastewater treatment plants and non-point sources should be investigated.

7.5.4 Sediments, bioaccumulation & fish tissue concentrations

Background

The model predicts a decline in the water column and sediments in the last ten years that has not been observed in sediment and fish tissue concentration data. This points to an important problem in the model and/or PCB forcing functions. This is an important issue, because reducing PCB concentrations in fish tissue is the ultimate goal of the overall TMDL process. If the model can not be used to predict the response of the fish tissue concentration under various management alternatives its utility is severely limited.

Suggested tasks

- A careful analysis of the fish tissue data should be performed. Differences in sampling (e.g. time of year, size of fish) and data analysis techniques (e.g. how non-detects are handled) can introduce biases, which could be responsible for the recent increase seen in the fish tissue data.
- A similar analysis should be performed for the historical surface sediment data. For sediment data, spatial variability (e.g. channel vs. bank) can introduce biases into the database.
- Additional sediment cores should be collected in order to validate the temporal trend seen in the Woodbury core
- A food chain bioaccumulation model for the Delaware Estuary should be developed. The model should be time variable, account for all major trophic levels (e.g. benthic invertebrates, small fish, large fish), various age classes and migratory behavior (if applicable). The model should be coupled to the present Delaware Estuary PCB fate and transport model and should include both water column and sediment food chains.

8 Conclusions

The overall objective of the model calibration was to assess the predictive capability of the model in representing the principal environmental processes that influence the transport and fate of penta-PCBs in the Delaware River and Estuary. These processes include hydrodynamics, sorbent (organic carbon) dynamics and partitioning of PCBs to organic carbon in the water column and bedded sediments. The model was calibrated to ambient data for biotic carbon (BIC) and particulate detrital carbon (PDC) in the water column, and to available data for net solids burial in the sediments. Finally, the calibrated sorbent dynamics model was used to drive a mass balance model of penta-PCBs in the water column and sediments.

Daily loads of organic carbon and penta-PCB were developed for each day of the 575 day continuous simulation period spanning September 1, 2001 through March 31, 2003 for the following source categories: contaminated sites, non-point sources, point discharges, model boundaries, tributaries, atmospheric deposition; and CSOs. In order to assess the uncertainty associated with the load estimation calculations, a Monte Carlo analysis was performed for each of the PCB source categories. This analysis allowed estimation of the uncertainty for each source category, comparisons of uncertainty between categories, identification of reasonable upper and lower limits for loadings for each category and for the overall penta-PCB load, and the resultant impact on water column concentrations.

Ambient water samples were collected from the mainstem Delaware Estuary for the analysis of particulate and dissolved PCBs, total suspended solids, dissolved organic carbon (DOC), chlorophyll a, and particulate organic carbon (POC). Twenty four main stem channel sites were sampled under a range of flows. The data collected allowed initial quantitation of dissolved and particulate PCB levels as well as organic carbon in the mainstem Delaware Estuary. The resultant monitoring data were used as calibration targets for the model.

The DELPCB model simulates tidal flows, and spatial and temporal distributions of organic carbon and penta-PCB. Comparisons of simulated to measured water quality concentrations indicate generally good agreement and low bias of the estimate for organic carbon and penta-PCB for the 575 day modeling time period. The correlation coefficients for particulate and dissolved penta-PCB exceed EPA's recommended correlation coefficient acceptance criteria for water quality variables.

Short-term sensitivity analyses indicate that the impact of zeroing out the initial PCB concentrations in sediment layers has almost three times more influence on water column PCB concentrations than zeroing out the six external PCB loadings. A calibration period of 575 days is not long enough to equilibrate with other PCB sources, and thus the sediment layers remain as a source of PCBs during the calibration period. The scenario which zeros out the 'six external PCB loadings' indicates that the impact can result in about a 20 percent reduction in PCB concentrations in water column in mid-Estuary. This is consistent with model simulations that indicated that PCB loads corresponding to the 20th and 80th percentile of the overall penta-PCB loading range yielded water column concentrations within -10% to +20% of the unscaled loads, respectively. Zeroing out the 'Gaseous PCB' concentrations results in about a 10 percent reduction of PCB concentrations in Zones 3, 4 and portions of 5. Substantial influences from boundary conditions are also observed at the extreme ends of the Estuary. The sensitivity analysis results point to importance of the initial sediment conditions during the short term model calibration period.

The mass balance tracking in standard WASP5 was enhanced in order to track mass fluxes of PCBs through every model segment including water column and sediment segments, and to track model processes that would normally be aggregated (e.g., kinetic transformations, gross settling and resuspension, etc.). The approach implemented within the model code demonstrated that the model does properly track mass transport fluxes and transformations.

Historical hindcast simulations (1930-2002) were performed to check the long-term (decadal scale) behavior of the model. A review of the hindcast simulation results using the current model showed: (1) The model is in reasonable agreement with the historical water column concentrations, both observed and deduced from the dated core for the period following the 1980s; (2) The model is in reasonable agreement with the contemporary sediment data in the upper estuary (Zones 2-3); (3) The model appears to be inconsistent with the historical sediment data; (4) The model predicted time course of water column and sediment bed concentrations also appear to be inconsistent with the fish tissue concentrations. At present it is not clear what the source(s) of the two inconsistencies (sediment and fish tissue) is (are). Possible causes include error(s) in (1) forcing functions (current and/or historical), (2) the model parameters(e.g. mixed layer depth) and/or (3) the data or how they are interpreted.

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