WATER QUALITY MODEL FOR CARBON AND PCB (Polychlorinated biphenyl) HOMOLOGS FOR ZONES 2 - 6 OF THE DELAWARE RIVER ESTUARY

Delaware River Basin Commission
DELAWARE • NEW JERSEY
PENNSYLVANIA • NEW YORK
UNITED STATES OF AMERICA

DELAWARE RIVER BASIN COMMISSION
WEST TRENTON, NEW JERSEY

May 2011

Acknowledgements

This report was prepared by the Delaware River Basin Commission staff: Carol R. Collier, Executive Director. Dr. Namsoo Suk and Dr. Thomas J. Fikslin were the principal authors of the report. Dr. Fikslin is the Manager of the Commission's Modeling, Monitoring and Assessment Branch. Dr. Suk is the Supervisor of the Modeling Section in the Branch. Other contributing authors include Gregory J. Cavallo, Dr. Daniel Liao, Dr. Ronald A. MacGillivray, Dr. Feng Shi and John R. Yagecic. Technical recommendations and modeling support were provided by Dr. Victor Bierman and Scott Hinz of Limno-Tech, the Commission's consultant for PCB modeling efforts.

Special acknowledgment is made to the following organizations for their support in development of the report and the studies leading up to it:

Delaware Department of Natural Resources & Environmental Control
New Jersey Department of Environmental Protection
Pennsylvania Department of Environmental Protection
U.S. Environmental Protection Agency, Region II
U.S. Environmental Protection Agency, Region III
Rutgers University
University of Delaware
Limno-Tech, Inc.

Suggested Citation

Suk, N.S. and T.J. Fikslin. 2011. Water quality model for carbon and PCB (polychlorinated biphenyl) homologs for Zones 2 - 6 of the Delaware River. Delaware River Basin Commission. West Trenton, NJ. May 2011.

EXECUTIVE SUMMARY

As part of the effort to establish Stage 1 TMDLs for total PCBs for Zones 2-5 of the Delaware River Estuary by December 2003, the Delaware River Basin Commission initiated development of a water quality model for organic carbon and PCB homologs (DELPCB). DELPCB has two organic carbon (biotic carbon or BIC) and particulate detrital carbon (PDC) state variables, four state variables for an individual PCB homolog, and one inorganic solid (IS) as a pseudo-state variable linked with the one-dimensional DYNHYD5 hydrodynamic model. The time-variable model includes three types of mass balances: (1) a water balance; (2) an organic carbon (OC) sorbent balance; and (3) a PCB homolog balance. The sediment processes in DELPCB are a simplified version that includes (1) depositional flux of OC (BIC and PDC), (2) degradation of such flux (BIC and PDC), (3) re-suspension of PDC, and (4) the resulting sediment (PDC) flux. The PCB mass balance tracks all sources, losses and internal transformations of PCBs in the river and consists of four state variables: truly dissolved PCB, particulate PCB, DOC-bound PCB and total PCB. During the modeling process, upon receiving the information of physical transport from DYNHYD5, DELPCB simulates the spatial and temporal distributions of the carbon and PCB in the water column and the sediment layer. PCBs are then transported and transformed by advection, dispersion, pore water diffusion, organic carbon partitioning, and gaseous exchanges. DELPCB was originally established as a penta-PCB model in view of the time constraints imposed by a court-ordered deadline of December 15, 2003 for establishment of the TMDLs for PCBs. In 2006, the penta-PCB homolog version of DELPCB was recalibrated by the Commission staff to update model loadings and forcing functions, and utilize a revised model code. Further enhancement was deemed necessary to better simulate BIC and PDC in the region of the estuarine turbidity maximum or ETM, to incorporate additional data and new analytical approaches for estimating model inputs and parameters, and to develop and calibrate three additional PCB homolog models: tetra-PCB, hexa-PCB and hepta-PCB. These four PCB homologs comprise greater than 90% of the total PCBs found in fish tissue samples collected from the tidal Delaware River and Bay. The overall objective of this effort was to assess the predictive capability of the coupled hydrodynamic, organic carbon and PCB homolog models in representing the principal environmental processes that influence the transport and fate of four PCB homologs in the Delaware River and Estuary: tetra-PCB, penta-PCB, hexa-PCB and hepta-PCB.

The model enhancements and subsequent recalibration described in this report include:

1. Externalized assignment and revised coefficients for gas phase PCB processes including the use of six different subareas,
2. Upstream water column transport for BIC and PDC in lower Zone 5 and Zone 6,
3. Masking of sediment layers based on sediment type to limit interactions between the water column and the sediment layer ,
4. Direct incorporation of dredging and its impact on removal of PCB homologs,
5. Updating of sediment initial conditions,
6. Updating of external loads from contaminated sites, point sources, minor tributaries and air deposition,
7. Updating of boundary conditions for the Delaware River at Trenton, the Schuylkill River at Philadelphia, the C&D Canal and the ocean boundary, and

8. Parameter/constant specifications for the tetra-PCB, hexa-PCB and hepta-PCB homologs.

Another significant enhancement was the use of sediment cores collected in marshes border all 5 water quality management zones (Zones 2 - 6) to provide historical loading functions for hindcast simulations.

As done with the initial and subsequent model calibration, DELPCB was calibrated using a three step process. The available data for this calibration was from the period September 2001 through March 2003 (577 days). This period is important as the tributary inflows from the two main tributaries to the estuary, the Delaware River at Trenton and the Schuylkill River at Philadelphia, and the pattern of precipitation both mimic the log-term records of river inflow and precipitation. 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 water quality model for chloride. The calibrated hydrodynamic and chloride model was then used as a "hydraulic chassis" to drive a mass balance water quality model of organic carbon sorbent dynamics (the "carbon chassis"). 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 mass balance models of four PCB homologs in the water column and sediments. As with the initial and subsequent 2006 calibrations, no further calibration of any of the PCB homolog models were necessary based upon the fit of model predictions to ambient water quality data.

Comparisons of simulated to measured water quality concentrations indicate generally good agreement and no consistent bias of the estimates for organic carbon and the four PCB homologs during the model calibration period. Spatial, bivariate and CFD plots indicated that the model was in reasonable agreement with the observed data for dissolved PCB phase of all four homologs in all Zones. Particulate PCBs were generally in agreement with observed values for the hexa- and hepta-PCB homologs, but the tetra- and penta-PCB homolog models appear to underestimate particulate PCB concentrations. Total PCB concentrations for three homologs, penta-, hexa- and hepta-PCBs, exhibited good agreement with observed values.

The hindcast model simulations demonstrate that the four homolog models reasonably predict water column, sediment and fish tissue concentrations. Given the variability inherent in measured concentrations and model predictions, the assigned kinetics of the model, especially the settling/re-suspension rates, the model reasonably predicts concentrations of tetra-, penta-, hexa- and hepta-PCBs in the Delaware Estuary and Bay. The mass balance tracking approach implemented within the model code demonstrated that the model does properly track mass transport fluxes and transformations.

The models will be used to establish the assimilative capacity provided by burial of PCBs in the sediments of the estuary, and may be used in the future to establish wasteload allocations and load allocations for specific PCB homologs. The model may also be exercised to answer hypothetical questions such as the effects of dredging hot spots of PCBs or curtailing the loading from selected point and non-point sources.

TABLE OF CONTENTS

1 Introduction

1.1 Background

In 2001, the Delaware River Basin Commission initiated technical studies to support the development of TMDLs for PCBs for the tidal portion of the Delaware River. These studies included the development of a water quality model for organic carbon and PCB homologs (DELPCB) which culminated in 2003 (DRBC, 2003a). DELPCB has two organic carbon (biotic carbon or BIC) and particulate detrital carbon (PDC) state variables and one inorganic solid (IS) as a pseudo-state variable linked with the one-dimensional DYNHYD5 hydrodynamic model. The time-variable model includes three types of mass balances: (1) a water balance; (2) an organic carbon (OC) balance; and (3) a PCB homolog balance. The two organic carbon variables are advected and dispersed among water segments, settle to and erode from benthic segments, and move between benthic segments through net sedimentation or erosion. The sediment process of DELPCB is a simplified version of the sediment process model that includes (1) depositional flux of OC (BIC and PDC), (2) degradation of such flux (BIC and PDC), (3) re-suspension of PDC, and (4) the resulting sediment (PDC) flux. As BIC settled to the sediment layer, BIC converted to PDC. The PCB mass balance tracks all sources, losses and internal transformations of PCBs in the river. During the modeling process, upon receiving the information of physical transport from DYNHYD5, DELPCB simulates the spatial and temporal distributions of water quality parameters such as BIC, PDC, total PCB, particulate PCB, and truly dissolved PCB, and DOC-bound PCB. PCBs are then transported and transformed by advection, dispersion, pore water diffusion, organic carbon partitioning, and gaseous exchanges. DELPCB was originally established as a penta-PCB model in view of the time constraints imposed by a court-ordered deadline of December 15, 2003 for establishment of the TMDLs for PCBs.

DELPCB was originally calibrated in the same time period using a three step process (DRBC, 2003b and c). The available data for this calibration was from the period September 2001 through March 2003. 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 water quality model for chloride. The calibrated hydrodynamic and chloride model was then used as a “hydraulic chassis” to drive a mass balance water quality 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. No further calibration of the penta-PCB model was necessary based upon the fit of model predictions to ambient water quality data.

For hydrophobic organic chemicals like PCBs, this short-term calibration approach is necessary but not sufficient to constrain all of the processes controlling the fate and transport of this chemical in an aquatic ecosystem. 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 in sediments are much slower to interact with the overlying water column. 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. To address this issue, a decadal-scale consistency check was conducted on the short-term 19-month calibration to assess its long-term performance. This check involved a 74-year hindcast simulation for penta-PCBs from 1930 through 2003 for the Stage 1 modeling effort. In this modeling effort 61 year, from 1950 to 2010, hindcast simulations were performed for four PCB homologs. This check was constrained by the limited amount of historical data on ambient water, sediment and fish tissue, and resulted in the use of many assumptions. Interpretations of these long-term simulations relied upon 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.

In 2006, the Commission staff completed a recalibration of DELPCB that involved updates to model loadings and forcing functions and utilized a revised model code (Fikslin et al, 2006). Updates included corrections in an error in loadings for some of the contaminated sites, additional data for boundary concentrations at the C&D Canal and ocean boundary, and additional and updated ambient data from three ambient surveys in the estuary. Revised model coding included minor modification to the air-water exchange subroutine. Model input changes were also made to the value for parameter VELFM and to PDC resuspension rates.

1.2 Model Enhancements

Since 2006, the Commission staff continued to refine the DELPCB model for penta-PCBs and extend the model to three other PCB homologs: tetra-PCBs, hexa-PCBs and hepta-PCBs. These refinements/extensions include:

A. Externalized gaseous PCB assignment
   - Issue: In the Stage 1 DELPCB model, Clausius-Clapeyron (C-T) equation was hard-wired in the model code to calculate the gaseous PCB concentrations for seven air-sheds in the Delaware Estuary. The basis for this assignment was data collected at three sites that comprise the regional active air monitoring program. However, data collected at Swarthmore University station was somewhat questionable. Recently, air data collected during two passive air surveys provided spatial coverage to supplement the active air monitoring data.
   - Implementation: Modify the code to externalize the input parameters and conduct data analysis to establish appropriate input parameters.
   - Results:
     a) Daily, segment by segment gaseous PCB concentrations are directly assigned in the input file through external calculations using the revised C-T equations.
     b) Stage 1 air sheds are redefined into six air sheds in the model.

c) C-T functions for six air-sheds have been revised based on active and passive air monitoring data. Generally, the revised gaseous PCB concentrations are lower compared to values calculated in the Stage 1.

B. Upstream water column transport for BIC and PDC

- Issue: Stage 1 DELPCB model was not able to accurately simulate the spatial structure of PDC and BIC in water column, especially higher PDC and BIC concentrations near the Estuarine Turbidity Maximum or ETM area.
- Implementation: Based upon the study conducted by Dr. Sommerfield at the University of Delaware (Sommerfield, 2009), two directional net flows (seaward and landward) were observed in the water column in the lower portion of the Estuary (See Sommerfield Report/Presentation). The current DELPCB model cannot account for the impact of net upstream flow since the DELPCB model is one dimensional. Net upstream transport of BIC and PDC are incorporated by assigning a constant upstream transport velocity of 0.1 m/sec for 20 percent of the cross-sectional area for the model segments in the lower portion of the Estuary (from River Mile 8 to River Mile 63 or model segment 22)
- Results: Model was able to better simulate the observed data for BIC and PDC near the ETM area.

C. Masking of sediment layer based on sediment type

- Issue: Based upon sediment studies (DRBC, 2003c; Sommerfield and Madsen, 2003 and PDE, 2008) in recent years, some portions of the estuary bottom are composed mainly of sand and gravel. Data indicates that the carbon content in those areas is very low and consequently, the PCBs in those areas will have low concentration since they preferentially sorb to organic carbon. Stage 2 model implements "masking" to reduce the area of exchange in model segments with between water column and sediments based upon the percentage of clay in samples collected in each segment or adjacent segments.
- Implementation: Using percent clay in the surface sediment layer as a guideline, the inverse of the percent clay per model segments was used to establish the area masked. For example, if the bottom is zero percent clay content (i.e., 100 percent sand or gravel), the entire model segment is masked. There will be no interaction with water column (zero settling, zero resuspension, and zero pore water diffusion) in that model segment.

D. Data Assessment and Reassignment of Loads, Dredging Impacts, and Boundary and initial conditions

Boundary conditions:

- PCB concentrations for two downstream boundaries (the C&D Canal and the ocean) are re-assigned based upon additional data obtained after Stage 1 model development.
- Originally developed by HydroQual, Inc., a POC-normalized method is used to derive the daily PCB concentrations for two upstream boundaries: the Delaware River at Trenton and the Schuylkill River.

Initial sediment conditions:

- Issue: A 13 bin rolling average algorithm was used for the assignment of initial PDC, ISS, and PCB concentrations in sediment layers in the Stage 1 model development. This algorithm resulted in a step function of sediment PCB concentrations which is not realistic. An alternative approach was necessary.
- Implementation: The new sediment data set was analyzed using a statistical procedure called locally weighted scatterplot smoothing or LOWESS. This procedure fits regression surfaces to data through multivariate smoothing. The fitting is done to selected reaches in the tidal river or bay to obtain predicted concentrations of the parameter of interest for each reach. This value is then assigned to the model segments within that reach.

Dredging impact

- Issue: Carbon chassis Stage 1 model was calibrated to uniform net burial target of less than 1 cm/year to match roughly with the burial rates extracted from a limited set of sediment core data. Dredging information was compared to estimated mass buried in the Stage 2 model as a consistency check.
- Implementation: The Delaware Estuary is dredged annually of approximately 5 million cubic yards to maintain shipping channel. Data for annual dredged volume, porosity, grain size analysis, and carbon content is used to develop segment by segment net burial target for carbon mass to guide the net burial rates in calibration of Stage 2 carbon chassis model.
- Results: Carbon chassis model is calibrated using the PDC gross settling velocity of 1.5 m/day (all but segments 33 and 34 for 3.0 m/day) and corresponding resuspension rates are determined to match with the dredging volume removed in each segment.
- Incorporate explicit loss of PCBs to account for maintenance dredging. The dredging mass is also added as a component in the mass balance component analysis.

External loads

- Contaminated sites: loads from all contaminated sites are developed using one consistent method, the Revised Universal Soil Loss Equation (RUSLE) Version 2.
- Point sources: Point source PCB concentrations for the Stage 1 PCB TMDL were revised to better characterize PCB loads. Effluent data from dischargers which were not original included in the Stage 1 efforts were captured, and more accurate Stage 1 PCB concentrations for existing dischargers were extrapolated using PCB data from the Stage 2 efforts.
- Minor tributaries: add tributaries in Zone 6 which were counted in the NPS category in the Stage 1 model.
- Air deposition: use of the revised C-T equation to calculate revised loadings

E. PCB homolog specifications

- Issue: DELPCB model requires specifications of the chemical properties for each PCB homolog. Chemical properties include molecular weight, partition coefficients ($\log K_{oc}$ and $\log K_{doc}$) and unitless Henry's Law constant.
- Implementation: Molecular weights and partition coefficients were assigned for four homologs in separate input files. Algorithms to calculate unitless Henry's Law constants

for four homologs, tetra, penta, hexa, and hepta were incorporated in the model code. The homolog-specific executable file needs to be run with the corresponding homolog input file.
- Results: Weighted average unitless Henry's Law constants for four homolog can be calculated internally. Homolog specific input files for tetra, penta, hexa, and hepta PCBs were prepared.

F. Miscellaneous revisions:

Code changes
- Issue: To link the homolog-specific DELPCB model with the hydrodynamic model outputs, it is necessary to assign boundary conditions for all water column segments in DELPCB model.
- Implementation: Dimension for boundary conditions are increased from 20 to 100 in "WASP.CMN" file.
- Result: Boundary input conditions are required for all segments receiving inflows. Up to 180 boundary conditions can be assigned in the current model input file.

G. Hydrodynamic Model

- Issue: A minor portion of the PCB mass was lost through upstream boundaries in the Stage 1 model. In addition, the computational speed and accuracy of the model can be improved by using the binary output of hydrodynamic model.
- Implementation: Code and input file modification.
- Result: Extra junctions for upstream boundaries were eliminated resulting in direct one to one mapping with the DELPCB (TOXIWASP5) model. This eliminates the loss of mass through the upstream boundaries. Use of binary output enhances the computational speed and allows the specification of additional significant digits.

1.3 Report Objective and Use

The objective of this report is to describe in detail the model enhancements listed above, and present the results of short calibration and hindcast simulations for four DELPCB homolog models: tetra-PCB, penta-PCB, hexa-PCB and hepta-PCB. The updated carbon and penta-PCB homolog models will be used in the development of Stage 2 TMDLs for total PCBs for Water Quality Management Zones 2 through 6 of the Delaware River.

2 Carbon Chassis Enhancement

2.1 Background

As discussed in previous reports on the development and calibration of the DELPCB water quality model, the DELPCB is composed of three submodels: a hydrodynamic and chloride model, an organic carbon submodel and a PCB homolog-specific submodel (DRBC, 2003a, 2003b, and 2003c; Fikslin et al, 2006). A key component of this model system is the organic carbon submodel or carbon chassis. This latter term refers to the potential use of this submodel with other hydrophobic pollutants such as metals and chlorinated pesticides.

The organic carbon submodel involves two state variables: biotic carbon or BIC and particulate detrital carbon or PDC. This dynamic transport submodel includes water column gross settling and decay functions for BIC and PDC. Within the water column, BIC is converted to PDC at the rate of 0.2/day and PDC decayed at the rate of 0.05/day. Upon settling to the sediment, all BIC turns into PDC and PDC is then resususpended or buried. PDC in the sediment has a decay rate of 0.00026/day. All of these decay rates are temperature-dependent, and this dependence is incorporated in the model algorithms.

There are three sediment layers in this submodel: a surface layer (layer 1), an intermediate layer (layer 2), and a bottom layer (layer 3). The first two layers are 5 cm deep and the third layer 30 cm deep. The selection of surface layer depth of 5 cm is based on: (1) available sediment data, mostly surface grabs representing a 5 cm surface layer; and (2) interpretation of dated sediment core profiles. An inorganic solid (ISS) is coexistent with PDC for all three sediment layers. IS does not exist in the water column and is not resuspended with PDC from the sediment, but is buried with PDC in the DELPCB modeling frame work.

As described in the 2006 model recalibration report, updated loadings, model functions and a revised model code were utilized (Fikslin et al, 2006). For this report, carbon submodel enhancements included updated initial conditions for organic carbon and ISS, updated model boundaries for particulate organic carbon (POC) at the Delaware River at Trenton and the Schuylkill River at Philadelphia, additional carbon water column data from ambient surveys for model hindcast simulations, use of masking of portions of the water column-sediment interface to better describe interactions with sediment, incorporation of upstream transport of BIC and PDC from Delaware Bay to lower Zone 5, and direct incorporation of the removal of PDC and PCB mass through dredging of the navigational channel and anchorages.

2.2 Enhancements

2.2.1 LOWESS Analysis of Sediment Data

In the original calibration of the Penta-PCB Model, data sources for establishing initial sediment conditions included a survey conducted by DRBC in the fall of 2001 at 51 stations in Zones 2 through 5, a survey conducted by A.D. Little for the Delaware Estuary Program in 1993, samples collected by NOAA in 1997 (NOAA, 2001), and data from the Corps of Engineers and NOAA. Extrapolation from the last three data sets was necessary since the samples were not analyzed for the same number of PCB congeners as the DRBC samples. In this report, a total of 73 samples were used to establish the initial sediment conditions for each of the PCB homologs. These included the 51 DRBC samples analyzed by Axys Analytical Laboratories for 148 congeners, and 22 of the samples collected as part of the U.S. EPA's National Coastal Assessment Program in 2001 and reanalyzed by Axys Analytical Laboratories for 209 congeners. The parameters included in this data set include PCBs, Total Organic Carbon (TOC) and Inorganic Solids (ISS). This data set was believed to better represent the sediment quality of the Delaware Estuary and Bay for the calibration period.

This data set was analyzed using a statistical procedure called locally weighted scatterplot smoothing or LOWESS (Cleveland, 1979; Cleveland and Devlin, 1988). This procedure fits regression surfaces to data through multivariate smoothing. That is, the dependent variable (e.g., sediment PCB concentration) is smoothed as a function of the independent variable(s) in a moving fashion. This procedure is more useful that traditional parametric models because you can use it when the underlying parametric surface is not known and when the data contains outliers (Cohen, 1999). The procedure fits quadratic functions of the predictors at the centers of neighborhoods. The neighborhoods of data points are selected so that they include a specified percentage of the data points in each neighborhood (called the smoothing parameter). The data points are also weighted as a function of their distance from the center of the neighborhood.

In this application of LOWESS, fitting is done to selected reaches in the tidal river or bay to obtain predicted concentrations of the parameter of interest for each reach. This value is then assigned to the model segments within that reach.

Prior to application of this procedure, the data set was assigned to bins representing river reaches and model segments. Data were binned according to the following criteria:

1. All samples were within one model segment.
2. Samples were generally within 2 miles of each other.
3. TOC concentrations were similar.

The values within each bin were then averaged to obtain the bin value. Following the assignment of samples to bins, the bined data set consisted of 31 data values.

A key element in applying this procedure is the selection of the smoothing parameter. A smoothing parameter should be selected that produces a smoothed regression line through the data without overly smoothing the data. An automated method called the bias corrected Akaike criteria was used to select an appropriate smoothing factor for each parameter (Hurvich and Simonoff, 1998). This criteria was selected to both minimize the error about the regression line (residual sums of squares or RSS) while avoiding the undersmoothing that often occurs with the classical Akaike criterion. The smoothing factor that results in the minimum value of the bias corrected Akaike criteria was identified by plotting the Akaike criteria versus the smoothing parameter (Figure 2.2.1-1).

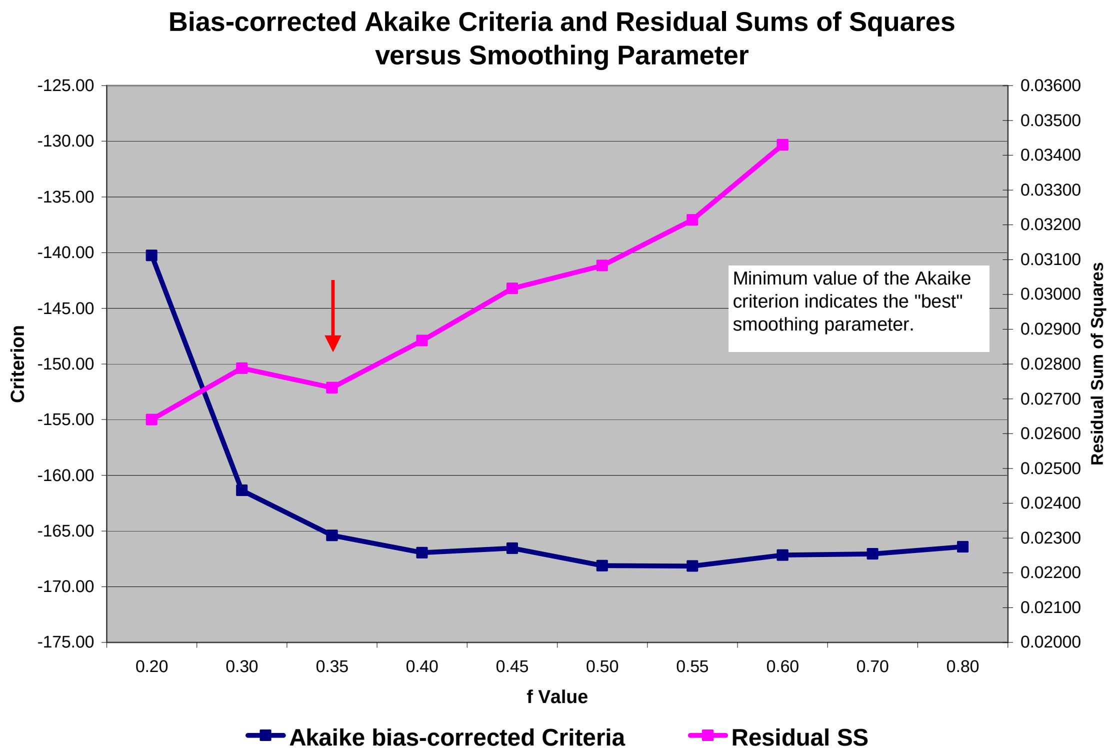


Figure 2.2.1-1: Plot of bias corrected Akaike criteria and residual sums of squares (RSS) versus smoothing parameter (f value) for penta-PCBs.

Penta-PCBs

Figure 2.2.1-1 indicates that the minimum Akaike criterion and the minimum RSS occurs at a smoothing parameter of 0.35. Figure 2.2.1-2 presents a plot of the binned data for Penta-PCBs, the smoothed regression line and confidence intervals for the line at this f value. Note the elevated concentrations of Penta-PCBs in Zone 3 (RM 95.0 to 108.4), and the low concentration in Delaware Bay (Zone 6). Figure 2.2.1-3 presents a cumulative frequency distribution (CFD) plot of the predicted versus observed Penta-PCB sediment concentrations indicating a reasonable fit of the regression line to the data.

Total Organic Carbon

Figure 2.2.1-4 indicates that both the Akaike criterion and RSS gently slope between f values of 0.3 and 0.6. Comparison of the CFD plots in Figure 2.2.1-5 indicates that an f of 0.3 results in a closer fit to the observed distribution. Since a break point occurs for both the Akaike criterion and RSS values at an f value of 0.3, a smoothing factor of 0.3 was selected for the initial conditions for TOC. Figure 2.2.1-6 presents a plot of the binned data for TOC, the smoothed regression line and confidence intervals for the line at this f value. Note the elevated concentrations of Penta-PCBs in Zone 3 (RM 95.0 to 108.4), and the low concentration in Delaware Bay (Zone 6).

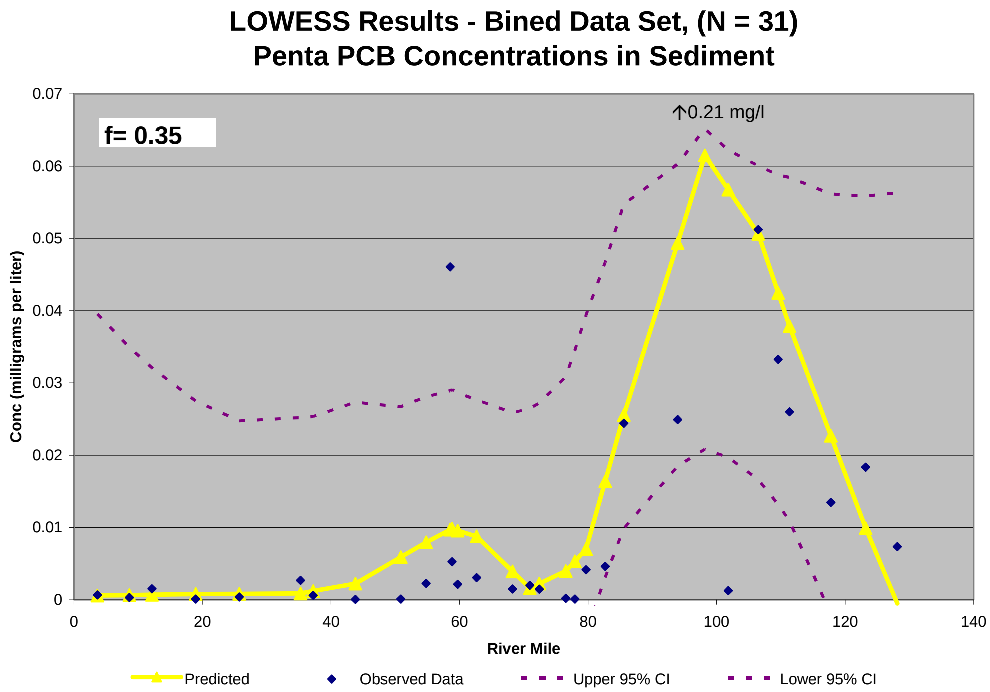


Figure 2.2.1-2: Plot of bined Penta-PCB sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay. The yellow line indicates the smoothed regression line that was fit to the data and used in the initial conditions in the PCB water quality model.

Inorganic Solids

Figure 2.2.1-7 indicates a significant change in both the Akaike criterion and RSS at f=0.2 with little change between f values of 0.3 to 0.9. The figure suggests that an f of 0.25 presents the best compromise between minimizing both the Akaike criterion and RSS. This value also imparts some structure to the LOWESS line. A smoothing factor of 0.25 was therefore selected for the initial conditions for ISS. A CFD plot in presented in Figure 2.2.1-8. Figure 2.2.1-9 presents a plot of the binned data for ISS, the smoothed regression line and confidence intervals for the line at this f value.

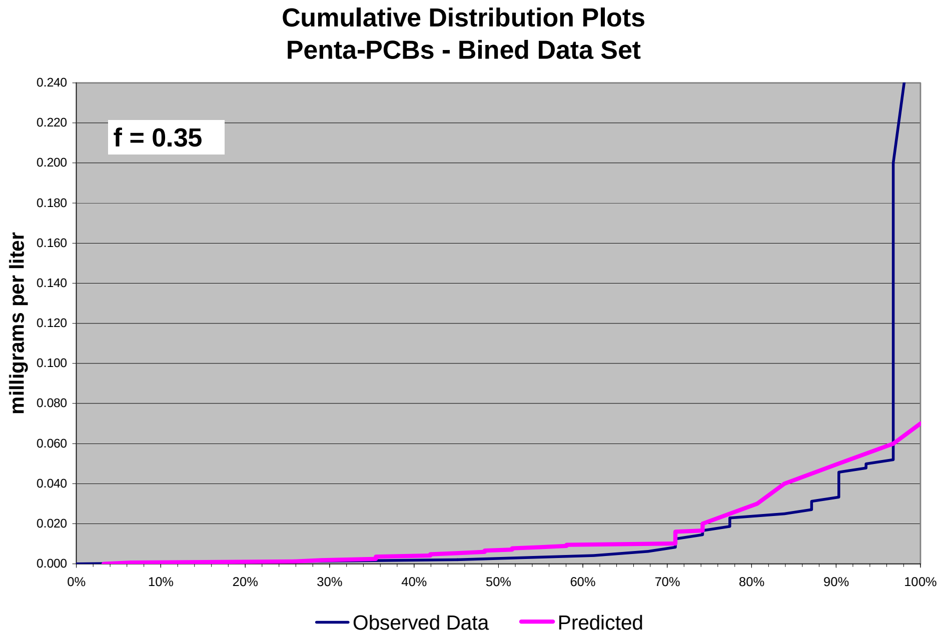


Figure 2.2.1-3: Cumulative frequency distribution (CFD) plot of the predicted versus observed Penta-PCB sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay.

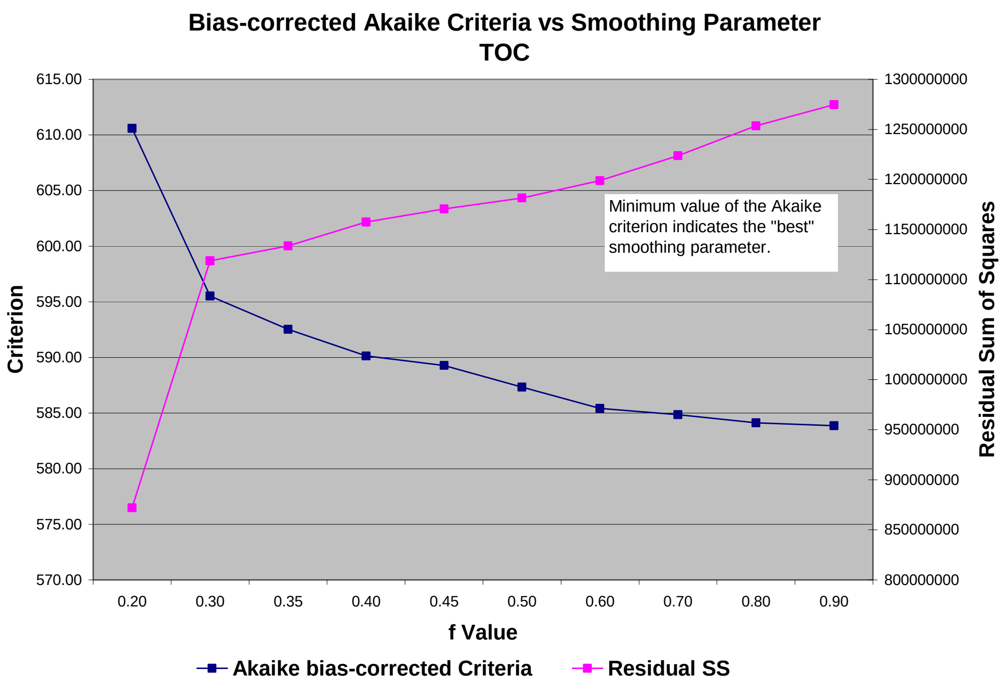


Figure 2.2.1-4: Plot of bias corrected Akaike criteria and residual sums of squares (RSS) versus smoothing parameter (f value) for total organic carbon (TOC).

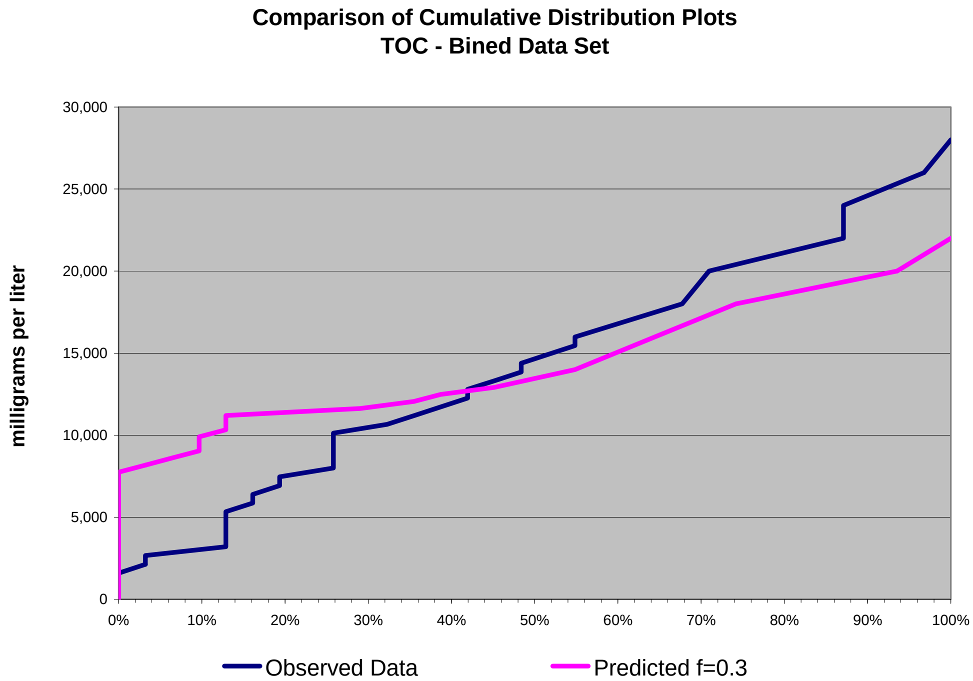


Figure 2.2.1-5: Cumulative frequency distribution (CFD) plot of the predicted versus observed total organic carbon (TOC) sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay.

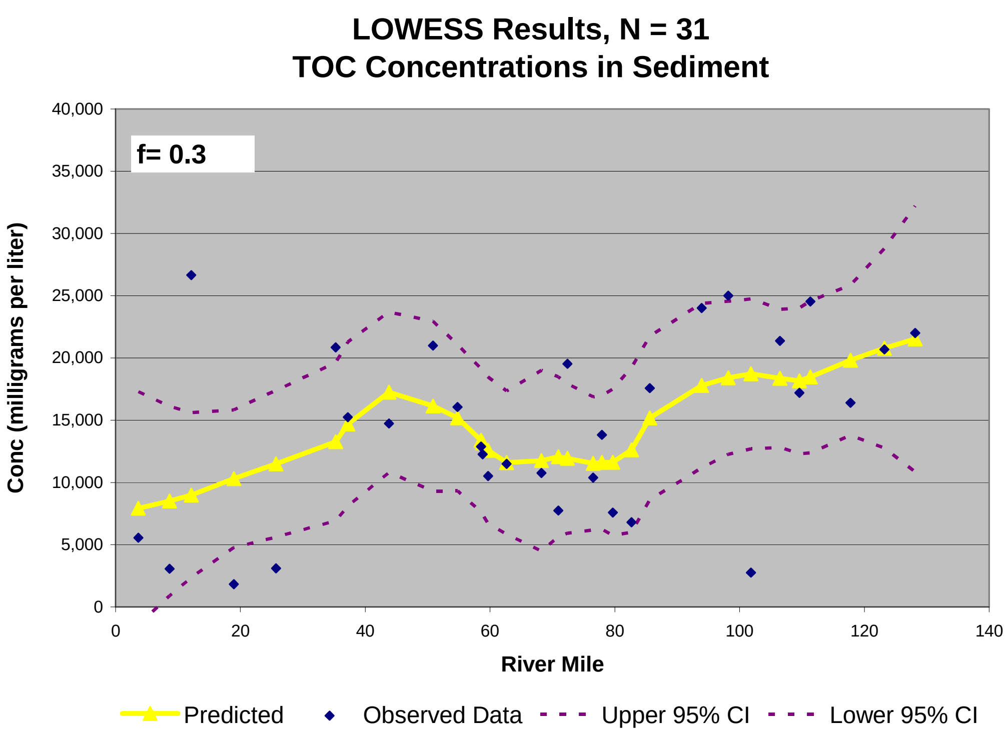


Figure 2.2.1-6: Plot of bined total organic carbon (TOC) sediment concentrations in the

Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay. The yellow line indicates the smoothed regression line that was fit to the data and used in the initial conditions in the PCB water quality model.

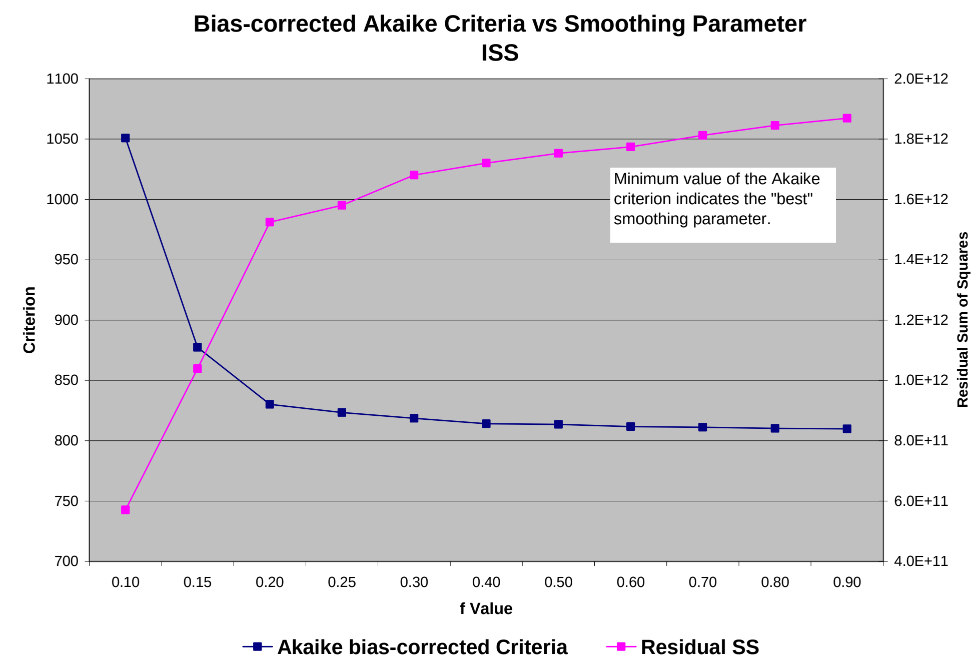


Figure 2.2.1-7: Plot of bias corrected Akaike criteria and residual sums of squares (RSS) versus smoothing parameter (f value) for inorganic solids (ISS).

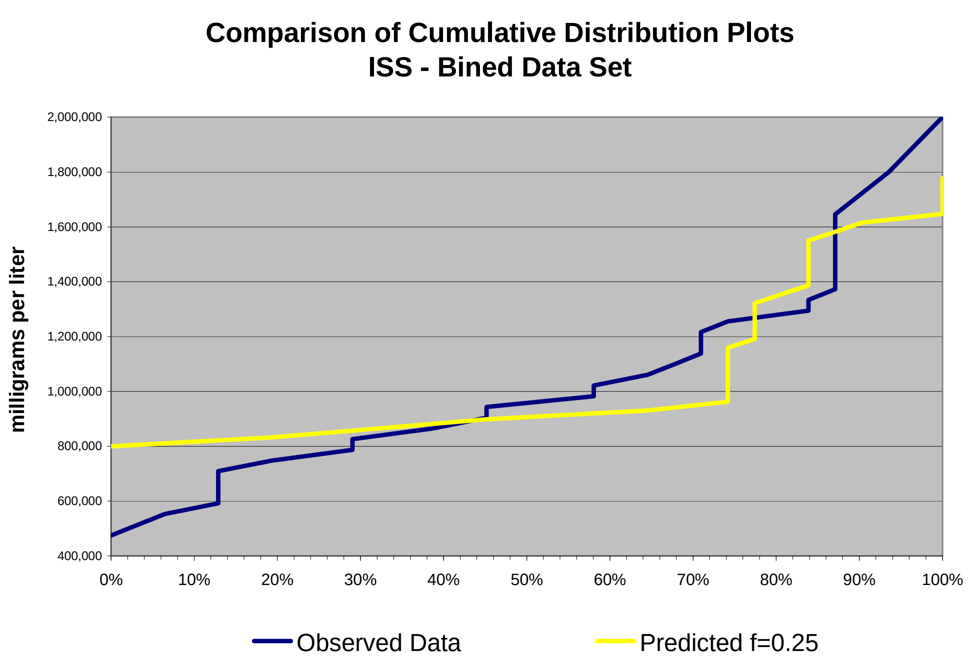


Figure 2.2.1-8: Cumulative frequency distribution (CFD) plot of the predicted versus observed

total organic carbon (TOC) sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay.

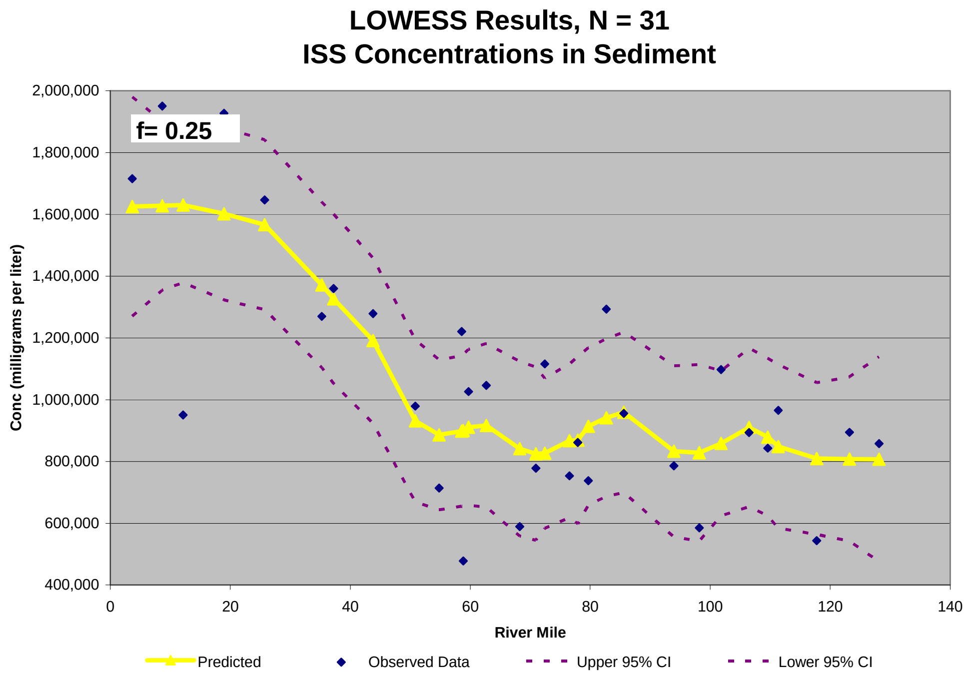


Figure 2.2.1-9: Plot of bined inorganic solids (ISS) sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay. The yellow line indicates the smoothed regression line that was fit to the data and used in the initial conditions in the PCB water quality model.

2.2.2 Sediment Masking

2.2.2.1 Introduction

Sediment interaction with the water column is a critical pathway which influences PCB concentrations in the water column. The interaction between the water column and sediments occurs through settling, resuspension, and pore water diffusion, and results in the exchange of PCBs between the water and sediment. As part of the Stage 2 TMDL we refined the interaction between sediments and water column based on the concept that interactions would occur in areas with higher mud content.

Initial sediment conditions in the Stage 1 PCB TMDL utilized Zone median PCB concentrations for the sediment data sets collected by DRBC, NOAA, the U.S. Army Corps of Engineers, and A.D. Little Associates.   For our current efforts we have redefined initial sediment conditions utilizing new sediment data which employed the same analytical method and applied a LOWESS smoothing routine to provide better spatial resolution. (See Section 2.2.1). In an effort to more accurately mimic the degree of interaction between the water column and sediment layer found in the Estuary a review of sediment types was undertaken. Sommerfield and Madsen (2003) http://www.state.nj.us/drbc/UDelsurvey/index.htm conducted a geo-physical survey of the upper portion of the Delaware Estuary in which they identified six sediment types (see Table 3 below from the survey report). They utilized sidescan and chirp sonar methods to determine the horizontal and vertical extent of subsurface sediment and their morphology. Grab sediment samples were collected and grain size analysis performed to ground-truth the interpretation of sediment types. Additional sediment data collected by the Commission as part of the Stage 1 TMDL and EPA as part of their Coastal Assessment Initiative was used to supplement Sommerfield's data set.

These supplemental data are temporally and analytically consistent with the samples collected by Sommerfield. Distinctive differences in sediment type were noted and span a full range from silt and clay to gravel and cobble. Essentially, our basic premise is that the more finer grained sediment, the greater the amount of resuspension and exchange in the water column.

Generally, the upstream composition is dominated by coarse-grained sediments, sands and gravels, and becomes progressively finer grained near the Pennsylvania-Delaware Border. However, the aerial extent of this mapping effort was limited to those areas where these techniques could be deployed, generally this required a few meters of water. Therefore, the near shore subsurface was typically unmapped.

2.2.2.2 Methods

Sommerfield and Madsen (2003) described sediment types by grain size and bottom morphology from lower Zone 2 through upper Zone 5. Sonar tracklines were used to develop Geographical Information System (GIS) coverages for the differing bottom morphologies and applied to surveyed areas in zones 2 through the upper portion of Zone 5.

Grab samples were used to help define the amount of "mud" found in each bottom type. Sommerfield and Madsen define the combined clay and silt sized fractions, as having a grain size of < 63 um as "mud", with the coarser fractions identified as either sand or cobble. Therefore, sediment types based on the amount of mud present was utilized as a surrogate for estimating the amount of sediment water exchange.

Six distinctive sediment types were identified by Sommerfield and Madsen (2003) and provided as GIS coverage's. Table taken from Sommerfield and Madsen.

Table 3. Characteristics of sedimentary environments.

Category	Backscatter Intensity and Continuity	Dominant Sediment Type	Bottom Morphology and Bedforms
1) Fine-grained deposition	Very weak to weak, continuous	Mud and fluid mud	Flat, no bedforms
2) Coarse-grained bedload	Moderate to strong, continuous	Moderately well-sorted sand and gravel	Wavy, well-developed fields of ripple and sand waves
3) Fine-grained reworking	Weak to moderate, discontinuous	Mud	Flat to wavy, sediment furrows
4) Mixed-grained reworking	Moderate to strong, discontinuous	Mixed gravel, sand, and mud	Flat to wavy, sediment ribbons and trails
5) Coarse-grained reworking	Strong, discontinuous	Poorly sorted sand and gravel	Flat to wavy, sediment ribbons
6) Non-deposition	Strong to very weak, discontinuous	Cobble and bedrock	wavy

Grain size analysis was available for 226 grab samples collected in the mapped areas from lower Zone 2 through upper zone 5. Percent, gravel, sand, silt and clay were reported. A Geographical Information System (GIS) approach was utilized to overlay the sediment grab sample onto the sediment types identifies by Sommerfield. Grab samples were then grouped into one of the six sedimentary environments classified by Sommerfield. Results were exported to Excel and box and whisker plots were constructed for each of the sedimentary environments. Results are provided in Fig 2.2.2.-1.

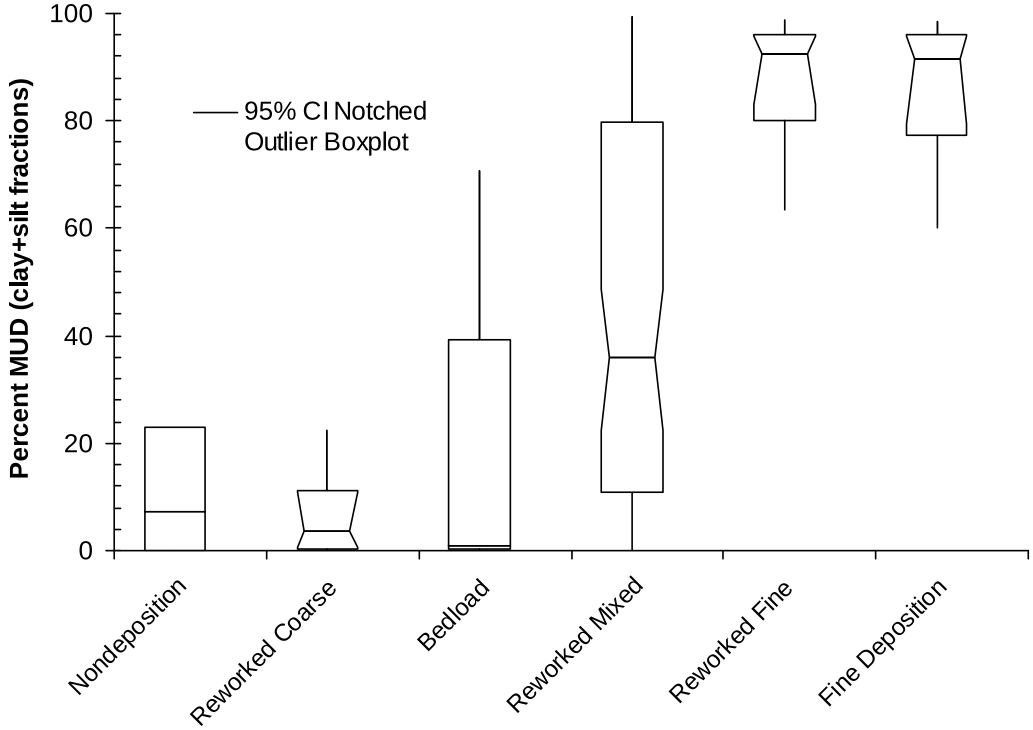


Figure 2.2.2.-1: Box and whisker plots of percentage of mud in sedimentary environments in the Delaware Estuary.

Sedimentary Environment	n=	Median % Mud
Nondeposition	14	7.2
Reworked Coarse	27	3.6
Bedload	9	1.0
Reworked Mixed	115	36.0
Reworked Fine	36	92.6
Fine Deposition	25	91.6

Utilizing the combined Sommerfield, DRBC and EPA sediment data sets it appeared that 3 distinct sedimentary groups on the basis of mud content where;

A = non deposition, reworked coarse and bedload
B = reworked mixed
C = reworked fine and fine deposition

The median mud content for each of these is provided below.

	Sediment Type defined by Dr. Sommerfield		
Sediment Type	A	B	C
Percentage of mud content (median) by sediment type	3.92	34.95	92.10

For those areas where sediment sampling and mapping did not occur during the Sommerfield Survey; near shore environments and in portions of zone 2, lower zone 5 and all of zone 6 additional sediment data from the DRBC and EPA were utilized in evaluating mud content.

Mud content was assigned by model segment for the entire Estuary. A Geographical Information System (GIS) approach was utilized to overlay the sediment types identified by Sommerfield onto the each of the model segments. The areal percent of each sediment type; “A”,”B” or “C” was determined in each model segment and a weighted mud content was calculated for the area in the model segment mapped by Sommerfield and extrapolated to the entire model segment.

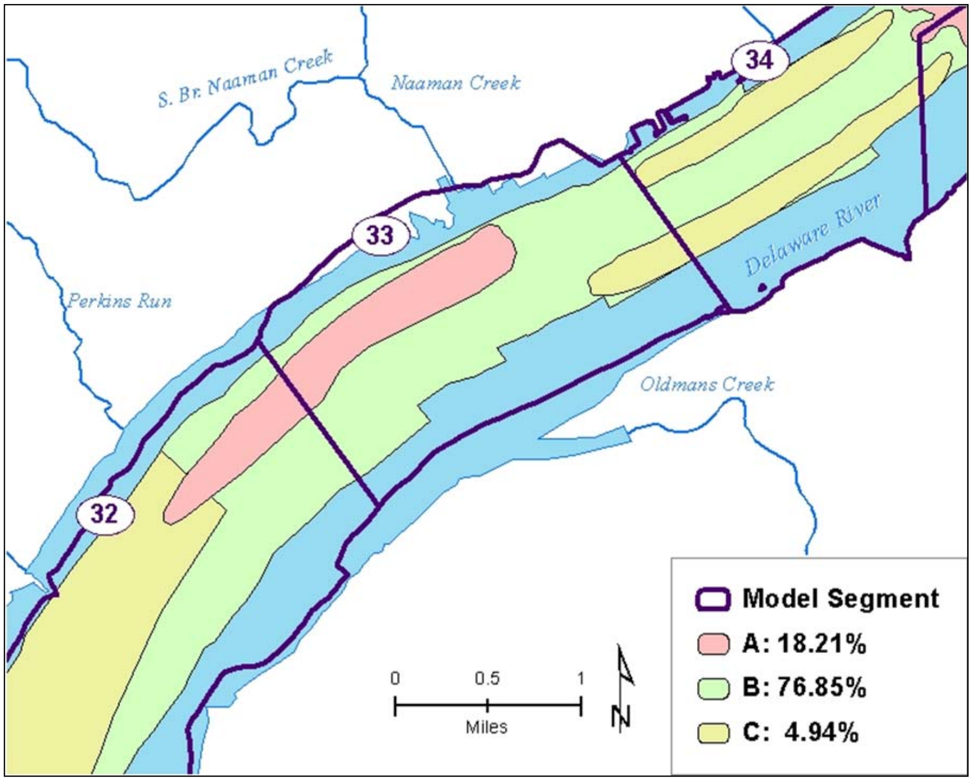


Figure 2.2.2.-2: Example masking of model segment 33 in Zone 5 of the Delaware Estuary.

Sediment Type	A	B	C
Percentage of mud content (median) by sediment type	3.92	34.95	92.10
Percentage of area covered for the segment 33	18.21	76.85	4.94

Weighted, average mud content for the segment 33 can be calculated as 0.039*0.182 + 0.350*0.769 + 0.921*0.049 = 0.321 or 32.1 %. Thus, in this masking process, sediment layers under the segment 33 will have 32.1% of the original surface area, or the volume (67.9% reduction or masking).

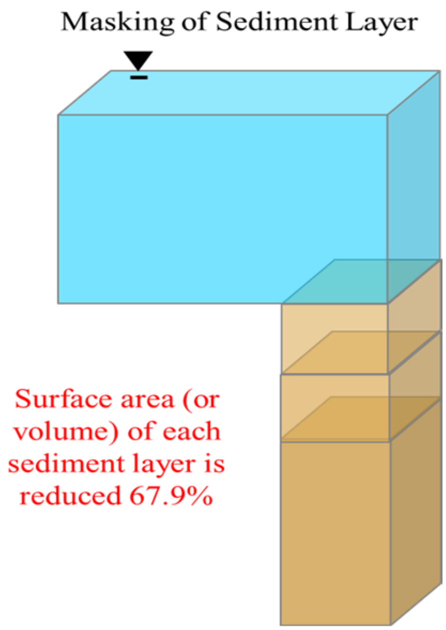


Figure 2.2.2-3: Illustration of masking procedure for model segment 33 in Zone 5 of the Delaware Estuary.

However, in Zones 2 and 3 where sediment type mapping was limited due to shallow water depths, additional sediment data collected by the DRBC and EPA was utilized to expand our interpretation of sediment types. The mud content in the mapped areas was combined on an area weighted basis with the additional information in the non-mapped areas to generate the total mud content by model segment (Figures 2.2.2-2 and 3).

Sommerfield and Madsen (2003) survey did not extend in lower Zone 5 and 6, therefore in these unmapped portions of the Estuary data collected by the DRBC and EPA were used to assign percent mud content on a model segment by segment basis. An analysis of mud content is provided by zone in the box and whisker plot in Figure 2.2.2-4. These data include all samples collected from zones 2-6, including those areas not mapped by Sommerfield.

Sediment surface areas were then reassigned proportional to the mud content in each model segment. A reduction in surface area will reduce the PCB exchanges between water column and sediment layer as a result of:

1. Reduced settling of BIC and PDC from water column to sediment layer;
2. Reduced resuspension of PDC from sediment layer to water column;
3. Reduced pore water diffusion from sediment layer to water column;

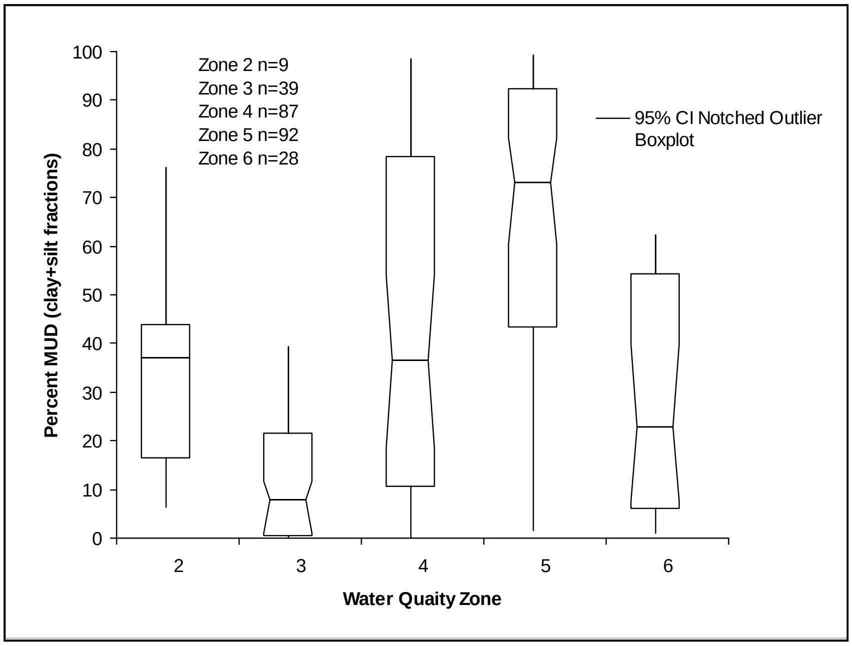


Figure 2.2.2-4: Box and whisker plots of percentage of mud by Zone in the Delaware Estuary.

2.2.3 Upstream Transport

Studies in recent years on sediment transport and turbidity maintenance in the estuarine turbidity maximum (ETM) zone in the Delaware Estuary using long-term field instrumentation have shed light on the entrapping mechanisms of suspended sediment (Cook et al., 2007; Wong and Sommerfield, 2009; Sommerfield, 2009; Sommerfield and Wong, 2011). Along with up-estuary tidal pumping, gravitational circulation is believed to be the main mechanism for trapping sediment within the ETM zone (Sommerfield and Wong, 2011). Two-layer gravitational circulation is most pronounced in the lower estuary during neap tides when turbulent mixing is reduced. Because of relatively higher suspended sediment concentrations near the bottom, the resulting circulation results in net up-estuary sediment flux and maintains higher suspended concentrations in the water column.

The 2002 and 2003 ambient monitoring cruises were split into two separate cruises near the river mile 60, an upper estuary cruise and a lower estuary cruise. These cruises were frequently not conducted on the same date although both biotic carbon (BIC) and particulate detrital carbon (PDC) data generally indicated elevated concentrations near the river mile 60 near the C&D Canal. The location of the ETM can migrate from the mouth of the Christina River (river mile 71) to just seaward of Artificial Island (river mile ~50) depending upon freshwater inflow to the estuary. However, data indicated that the higher PDC concentrations generally form around the river mile 60 as shown in Figure 2.2.3-1. Sommerfield (2009) also reported that the time-averaged location of the null point and the ETM was near the C&D Canal. Similar spatial profiles were also observed for the BIC.

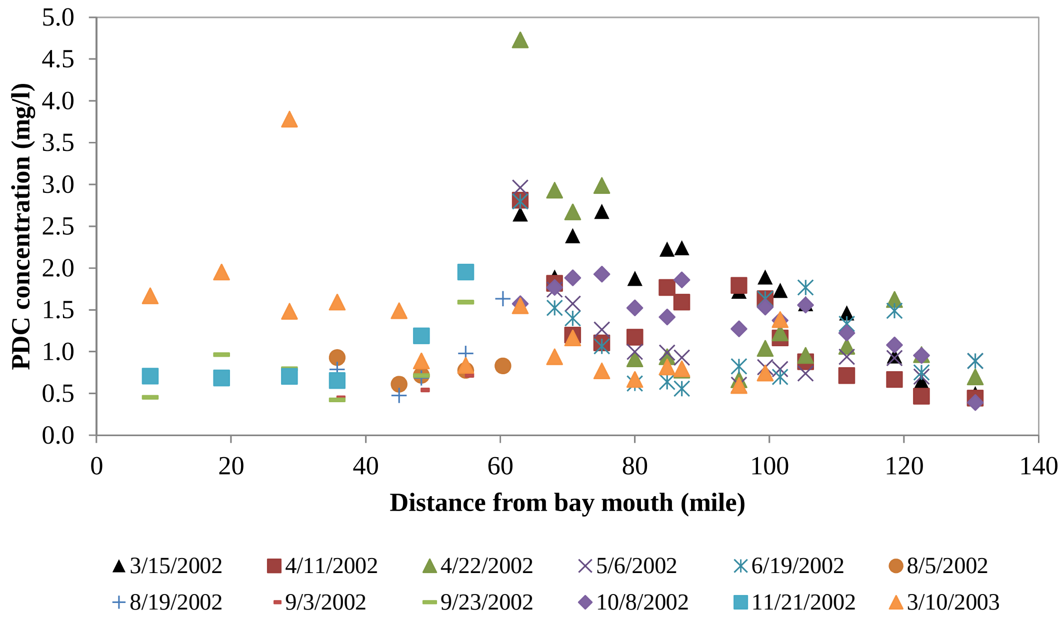


Figure 2.2.3-1: Particulate detrital carbon (PDC) concentrations during 2002 – 2003 ambient water column surveys in the Delaware Estuary and Bay.

The Stage 1 DELPCB model underestimated the biotic carbon (BIC) and PDC concentrations around the river mile 60 (DRBC, 2003c). The major reason cited was the inability of the Stage 1 DELPCB model to simulate two-layered flows in the ETM region because it is a one-dimensional model. In the Stage 2 DELPCB model, the upstream transport of BIC and PDC in the water column was incorporated in the model by assigning a constant upstream transport velocity of 0.1 m/sec for 20 percent of the cross sectional area of each water column segment in the lower portion of the Estuary and Bay (from River Mile 8 to River Mile 63) as shown in the Figure 2.2.3-2. The magnitudes of the upstream transport velocity at each segment interface were determined by numerical simulations of the model whose code had been modified to handle this transport of BIC and PDC in the water column.

Even though the degree of upstream transport should be affected by hydrologic, meteorological, and astronomical conditions, and other mechanisms such as tidal pumping as indicated in the studies cited above, the implementation of the constant upstream transport successfully served the purpose of entrapping BIC and PDC in the ETM zone. The Stage 2 DELPCB model was able to produce higher BIC and PDC concentrations near the ETM zone as indicated in Figures 4.3.1-1 and 4.3.2-1. PCBs sorbed to BIC and PDC (particulate bounded PCBs) were also transported upstream by this implementation. The mass added and subtracted by the upstream transport was also tracked and the results summarized in Tables 4.3.1-1 for BIC and 4.3.2-1 for PDC. The upstream transported PCB mass was also summarized in the PCB mass balance table for each homolog in the Section 4.

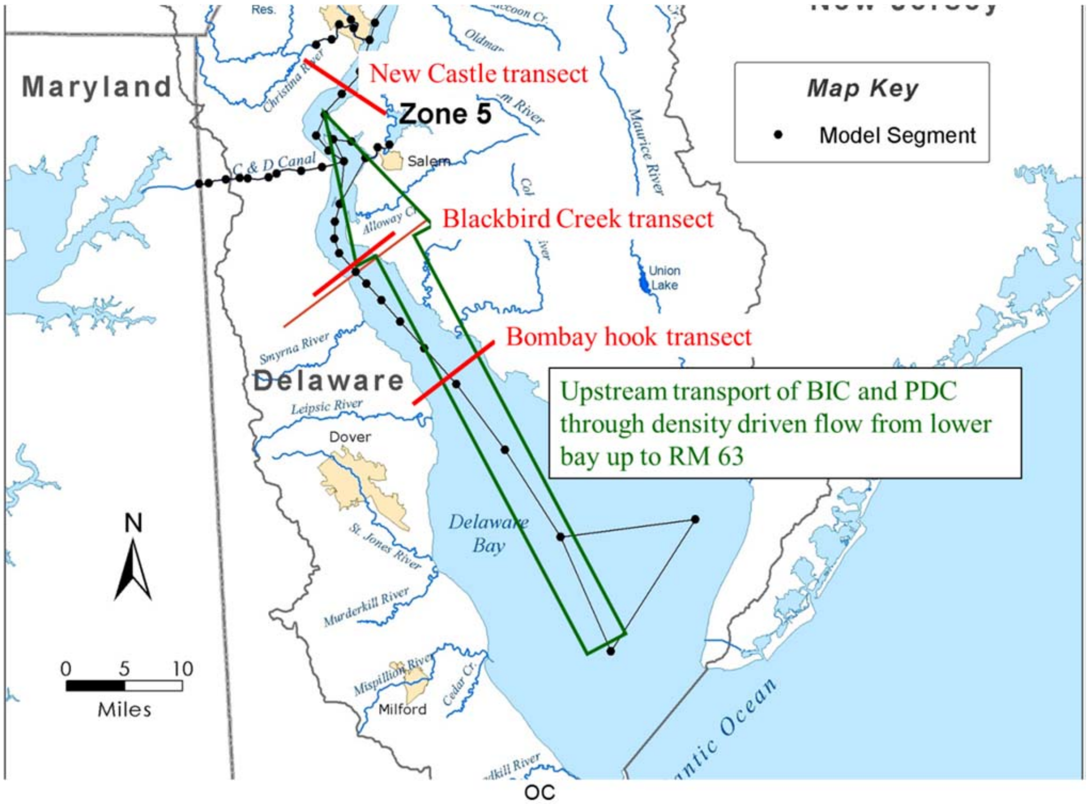


Figure 2.2.3-2: Model segments assigned an upstream transport velocity for BIC and PDC.

2.2.4 Incorporation of Dredging

Approximately 5 million cubic yards of sediments are annually dredged for the purpose of maintaining the navigational channel of the mainstem of the Delaware River between Philadelphia and the mouth of the Delaware Bay. This dredging activity can be a major sink of carbon and PCBs from the Delaware Estuarine system.

The previous two versions of the Delaware Estuary Model (DRBC, 2003a and Fikslin et al, 2006) implicitly handled the dredging impact. It was implemented by calibrating the resuspension rates for PDC to achieve the net burial rate of solid (particulate carbon and inorganic solid) around 1.0 centimeter per year for each model segment within the model domain given that gross settling velocities of PDC and BIC were assigned at 1 meters per day and 0.1 meters per day, respectively. The calibration target of the net burial rate of 1.0 cm per year was derived from two principles. The first was that any model segment would not have a net erosional condition to prevent from 'digging a hole' in a long-term simulation. The second principle was guided by examination of net burial rate analyses results in multiple sediment cores collected in tidal marshes of the Delaware Estuary.

Table 2.2.4-1: Annual dredging volume and frequency for the Philadelphia to the Sea project.

Ranges	RM from	RM to	Length, mile	Dredged volume, yd^3	dredging frequency, years
Brandywine Range	5.79	17.78	11.99	61,000	2
Miah Maull Range	17.78	26.33	8.55	13,000	4
Liston Range	31.2	51	19.8	179,000	1
Baker Range	51	52.97	1.97	29,000	3
Reedy Island Range	52.97	57.64	4.67	18,000	4
New Castle Range	57.64	62.68	5.04	1,126,000	1
Bulkhead Bar Range	62.68	63.16	0.48	10,000	5
Deepwater Point Range	63.16	67.77	4.61	858,000	1
Cherry Island Range	67.77	72.47	4.7	236,000	1
Bellevue Range	72.47	75.65	3.18	34,000	5
Marcus Hook Range	75.65	81.24	5.59	2,164,000	1
Chester Range	81.24	83.52	2.28	5,000	5
Eddystone Range	83.52	84.76	1.24	2,000	5
Tinicum Range	84.76	88.09	3.33	9,000	5
Billingsport Range	88.09	89.38	1.29	3,000	10
Mifflin Range	89.38	92.39	3.01	65,000	2
Eagle Point Range	92.39	94.9	2.51	3,000	10
Philadelphia Harbor	95.78	102.4	6.65	73,000	2

In this version of the DELPCB model, net burial rates of carbon (or solids) are recalculated for each model segment using the U.S. Army Corps of Engineers (USACE) dredging information. Long term, average annual maintenance dredging quantities for the Delaware River channel, based on about 15 or 20 years of data are obtained and summarized in Table 2.2.4-1 (personal communication, 2001). Where dredging record is not available, net sediment burial rate of 0.5 cm per year is assumed.

Porosity and density of sediment information were obtained from sediment grab samples and sediment cores. These values were used to calculate the dredged mass for each Range. Sedimentological and geographical survey results by Sommerfield and Madsen (2003) guided the decision process in determination of physical properties. Figure 2.2.4-1 illustrates the mass calculation processes using bottom sediment types, dredged volume, and other physical parameters in Marcus Hook Range.

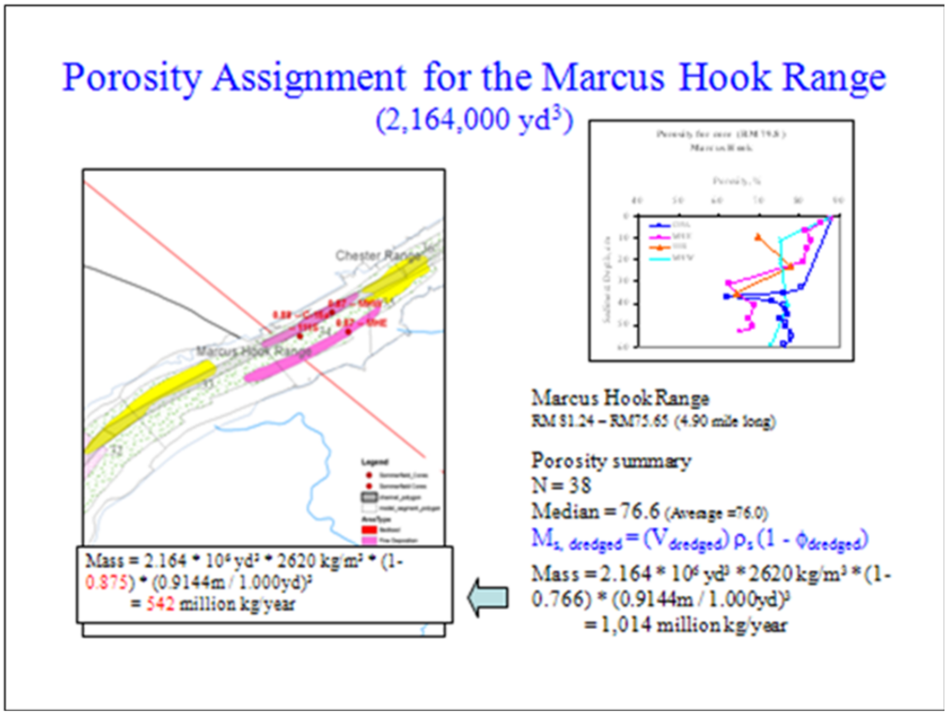


Figure 2.2.4-1: Dredged mass calculation process for Marcus Hook Range

The calculated mass is converted to a solid net burial rate for each model segment which becomes a calibration target for resuspension rate for the particulate detrital carbon (PDC) variable. Calibration targets and simulation results of net solid burial rates are depicted in Figure 2.2.4-2. Finally, dredging rates were assigned to achieve a final net burial rate of 0.25 centimeters per year for mainstem model segments. In the model, dredging rates were assigned as a daily average rate. Masses of PDC and PCBs were taken out from the buried sediment and became an ultimate sink. Calibrated model results show that approximately 68 million kilogram of PDC is buried annually and 48 million kilogram of PDC is dredged out from the Delaware Estuarine system. Approximately 67 percent of total dredging activity by volume is occurred in Marcus Hook and New Castle ranges. Flux exchanges between water column and sediment layer for each zone are summarized in the mass balance tables in Chapter 4.

We observed that the porosity of the dredged material and its organic carbon content were key parameters in linking dredged volumes and carbon burial rates. It should be noted that even though maintenance dredging occurs in navigational channels, the DELPCB model is one dimensional so that the dredged volumes (or net burial rates) are evenly distributed within a segment.

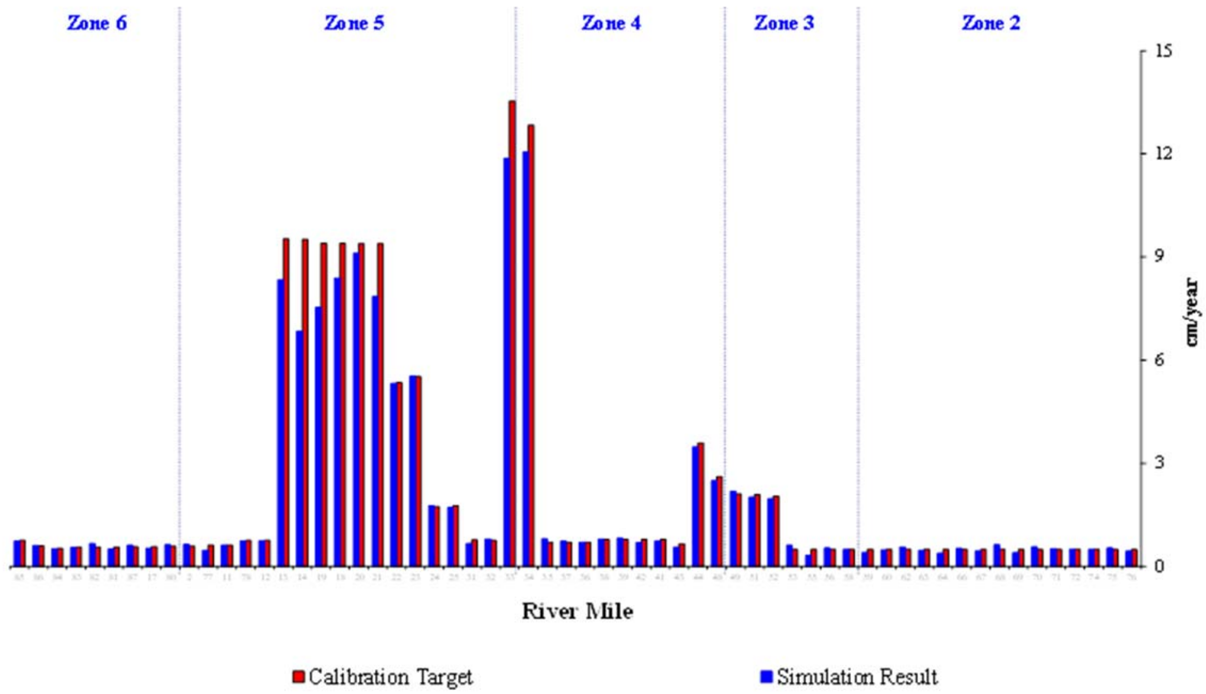


Figure 2.2.4-2: Model calibration targets and simulation results of net solid burial rates

3 PCB Homolog Model

3.1 Background

In 2003, the Delaware River Basin Commission and Limno-Tech, Inc. enhanced EPA's Water Quality Simulation Program (WASP) Version 5.12 to develop a general purpose sorbent dynamic penta-PCB model for the Delaware River Estuary (DELPCB) (DRBC, 2003a). 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, PCBs partition to particulate- PCB (by sorbing to BIC and PDC), truly dissolved-PCB, and dissolved organic carbon (DOC) bound-PCB phases. The model tracks all sources, losses and internal transformations of PCBs in the river and consists of four state variables: truly dissolved PCB, particulate PCB, DOC-bound PCB and total PCB.

The domain of the DELPCB model extended from the mouth of Delaware Bay (River Mile 0) to the head of the tide at Trenton NJ (River Mile 133). The model segmentation was extended to include two major tributaries, Schuylkill River and the Christina River. The C&D canal was also included in the model segmentation as an open boundary to properly simulate flux exchanges with the upper Chesapeake estuary. The model had 87 water column segments and three sediment layers with one to one mapping with the water column resulting in a total of 348 model segments.

The DELPCB model has two major components, the sorbent (carbon) submodel (or chasse) and a PCB homolog submodel. The sorbent submodel has two types of carbon state variables, biotic carbon (BIC) and particulate detrital carbon (PDC). The dissolved organic carbon was not a state variable, rather it was treated as a spatially and temporally varying parameter. The carbon submodel was calibrated based on net burial rates. Enhancement to the carbon chasse model was previously described in Section 2. Any enhancement or revision to the carbon chasse model would affect the simulation results of the PCBs.

Four PCB submodel to simulate four PCB homologs, tetra-PCB, penta-PCB, hexa-PCB and hepta-PCB. This process is described in Section 3. These four PCB homologs were selected as they comprise greater than 90% of the total PCBs found in fish tissue samples collected from the tidal Delaware River and Bay. The TOXIWASP5 model codes were strategically modified and tested to optimally simulate these hydrophobic contaminants.

The DELPCB model codes were modified to be able to assign spatially and temporally varying gaseous PCB concentrations as model input conditions in this version of the DELPCB model. Gaseous PCB concentrations were re-assessed based on intensive passive air monitoring data and wet/dry atmospheric deposition rates were revised and are discussed in the Section 3.3.1. The 'LOWESS' smoothing approach was used for the assignment of the initial sediment conditions and is discussed in the Section 3.3.2. Revisions to estimate six external PCB loading categories are described in the Section 3.3.3. Assignment of two upstream boundary and two downstream boundary conditions were re-evaluated in the Section 3.3.4. PCB homolog specific kinetic constants were derived and described in the Section 3.3.5.

3.2 Calibration Targets

To support development of the Delaware Estuary Polychlorinated Biphenyl (PCB) Homolog Modeling, accurate measurement of PCB concentrations and organic carbon in the Delaware Estuary was required. Ambient water samples were collected at twenty-four stations distributed throughout the entire main-stem of the Delaware Estuary (Figure 3.2-1 and Table 3.2-1). The objective of the monitoring was to measure particulate and dissolved PCBs, total suspended solids, dissolved organic carbon (DOC), chlorophyll a, and particulate organic carbon (POC) at low, high and intermediate flows. Ambient water samples were collected at different flows and tides during a seven year time period (Table 3.2-2). The data collected allowed quantitation of dissolved and particulate PCB levels as well as organic carbon. The data from monitoring date September 18, 2001 were used as initial conditions in the model. The data from monitoring dates March 15, 2002 through March 19, 2003 were used as calibration targets in the model. The data from monitoring dates April 2, 2003 through September 20, 2007 were used for hindcast model runs.

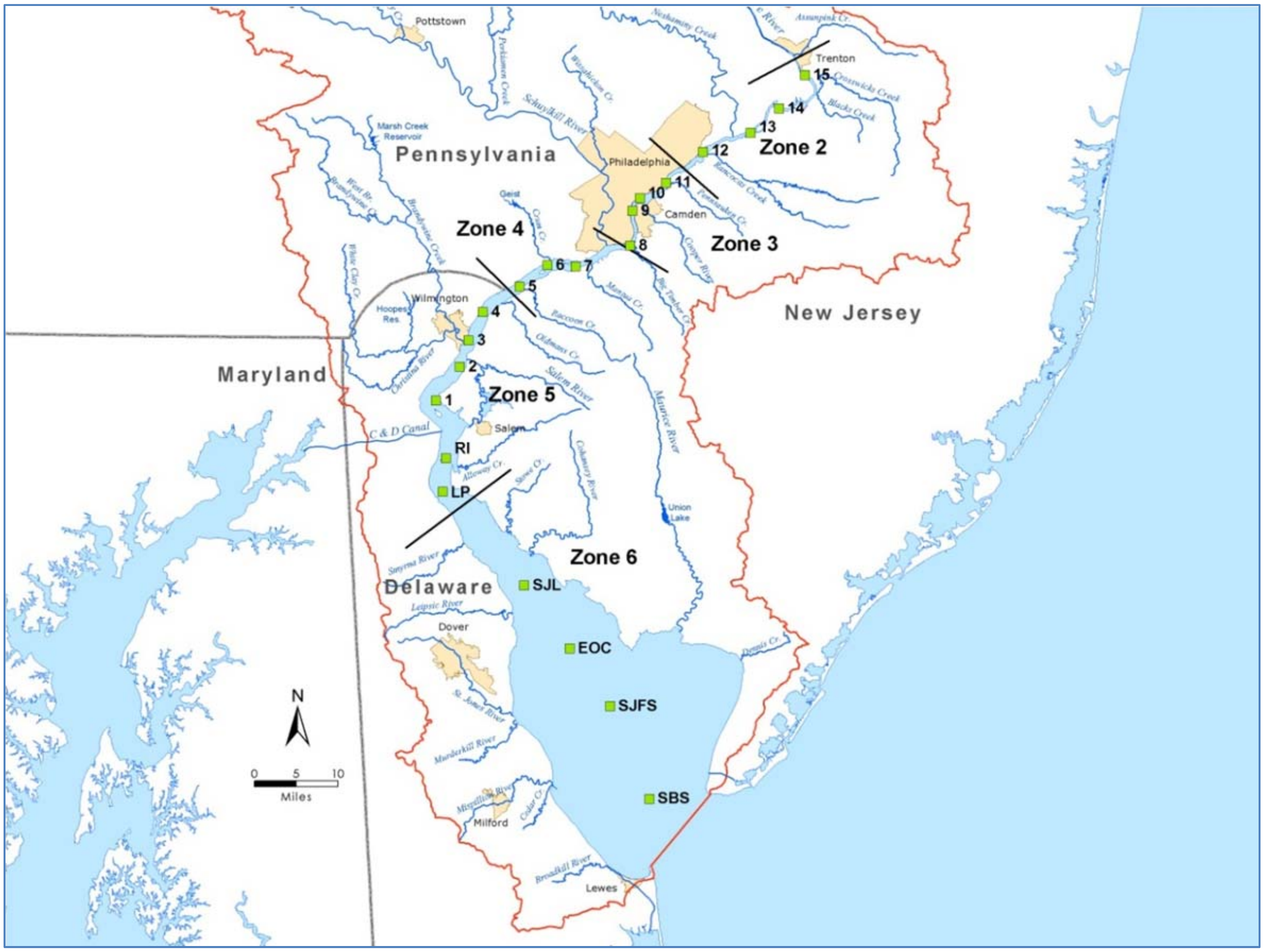


Figure 3.2-1: Map of Ambient Water Sampling Sites

TABLE 3.2-1: Ambient Water Sampling Sites

SITE	RIVER MILE	SITE DESCRIPTION	DELAWARE RIVER 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	Smyra 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 Marcus Hook Creek	Zone 4	39.81337 75.39057
6	84.0	Eddystone	Zone 4	39.85055 75.32709
7	87.9	Paulsboro	Zone 4	39.84871 75.26406
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

Table 3.2-2: Ambient Water Surveys

Date	Start Time a.m.	River flow at Trenton cfs	Flow Category	Mainstem RM	Tide	Starting Location	Model Run
9/18/01	7:49	3,020	L	63 - 118	low	Pea Patch Is.	Initial Conditions
3/15/02	8:40	5,810	L	63 - 131	low	Pea Patch Is.	Calibration
4/11/02	7:38	7,980	M	63 - 131	low	Pea Patch Is.	Calibration
4/22/02	8:17	8,860	M	63 - 131	high	Pea Patch Is.	Calibration
5/06/02	8:41	16,100	M	63 - 131	high	Pea Patch Is.	Calibration
6/19/02	NA	14,800	M	63 - 131	high*	Pea Patch Is.	Calibration
8/05/02	NA	3,360	L	36 - 55	high*	Ship John Light (Cohansey R.)	Calibration
8/19/02	9:32	3,510	L	36 - 55	low	Ship John Light (Cohansey R.)	Calibration
09/03/02	7:38	3,570	L	36 - 55	high	Ship John Light (Cohansey R.)	Calibration
9/23/02	11:54	3,430	L	6.5 - 55	low	S. Brown Shoal (Mispillion R.)	Calibration
10/08/02	8:18	3,560	L	63 - 131	low	Pea Patch Is.	Calibration
11/21/02	11:22	25,200	H	6.5 - 55	low	S. Brown Shoal (Mispillion R.)	Calibration
3/10/03	NA	15,398	M	6.5 - 55	high*	S. Brown Shoal (Mispillion R.)	Calibration
3/19/03	7:52	36,100	H	63 - 131	low	Pea Patch Is.	Calibration
4/02/03	6:53	32,700	H	63 - 131	mid -rising	Pea Patch Island	Hindcast
11/15/05	8:13	8,750	M	6.5 - 55	high	S. Brown Shoal (Mispillion R.)	Hindcast
6/20/06	6:00	8,380	M	6.5 - 55	high	S. Brown Shoal (Mispillion R.)	Hindcast
9/19/07	8:13	3,900	L	6.5 - 55	low	S. Brown Shoal (Mispillion R.)	Hindcast
9/20/07	6:00	3,700	L	63 - 131	high	Pea Patch Is.	Hindcast

* Tides are at the presumed sampling time for slack tide.
Flows are grouped into three categories low (L), medium (M), and high (H).

3.3 Model Setup

3.3.1 PCBs in the Atmosphere

Stage I:
In Stage I, wet and dry atmospheric deposition was estimated using data provided by Dr. Lisa Totten of Rutgers, the State University of New Jersey. Between November 2001 and January 2003, Dr. Totten collected over 30 sampling events at 6 stations and provided the atmospheric particulate and gas phase concentration of PCB congeners. Based on preliminary results, Dr. Totten estimated seasonal dry deposition rates and volume weighted rainfall concentrations for 7 sub-areas: WC, NE, CC, SW, 1/25W, LP and DB.

Stage II:
DELPCB codes were modified to be able to assign temporally, spatially varying gaseous PCB concentrations by the user in the model input file. This assignment was hard-wired in the Stage 1 model. The updated gas phase concentration of PCBs was estimated by homologue for each sub-area. The method and procedures derived to calculate the gaseous and Particulate PCBs concentrations, as well as the dry deposition, wet deposition and total deposition load, are summarized in the following steps:

1. **Define the Sub-areas used in Stage II for Gaseous PCB**
   There were 6 sub-areas used to cover the 87 segments in Stage 2, as shown below in Table 3.3.1-1:

Table 3.3.1-1: Sub-areas and assigned segments

Sub-area	Assigned segments
Background_1	63-76,
Background_2	1-16, 18-32,77-79
NE	55-62
CC	48-54
Zone_4	33-47
DB	17, 80-87

2. **Deriving coefficients in lnC-T equations for each sub-area**
   The methods used to derive the coefficients in lnC-T equations for each sub-area are summarized in the Table 3.3.1-2. The derived coefficients for each homologue and each sub-area are shown in Table 3.3.1-3.

Table 3.3.1-2: Method to derive coefficients in lnC-T equations for each sub-area

Sub-area	Active Value Used for Slope and Intercept	Passive Sites used for Calibration
Background_1	Background (LP+ AC + WC)	None
Background_2	Background (LP+ AC + WC)	None
NE	Urban (CC Site)	Average of Mill Creek, Cinnaminson
CC	Urban (CC Site)	None
Zone_4	Urban (CC Site)	Median Value of Billingsport School, Fort Mifflin, John Heinz NWR, Red Bank, Knollwood Park, Knollwood park and Widener Univ.
DB	Stage 1, DB	Median Value of Hancock Harbor (Cohansey River), Haskin Shellfish lab, and Cape May

Table 3.3.1-3: Derived coefficients by PCBs homolog for each zone.

Zones	homolog	slope	intercept
Background (LP+AC+WC) Zone 1 & 2	4	-3675	16.528
	5	-3329	15.04
	6	-3617	15.33
	7	-3912	15.02
NE	4	-5964	24.70193
	5	-6520	25.73273
	6	-7567	28.38989
	7	-8837	31.52777
Urban (CC)	4	-5964	27.76
	5	-6520	29.16
	6	-7567	32.24
	7	-8837	34.16
Zone_4	4	-5964	25.28559
	5	-6520	26.36478
	6	-7567	29.24908
	7	-8837	32.06157
B	4	-5429.35	21.88551
	5	-3777.47	15.63226
	6	-2834.19	11.83886
	7	-2075.14	9.12209

3.3.1.1 Gaseous PCB Concentration Calculation and Output to .txt files

The gaseous PCBs concentrations of different homolog in the modeling period were calculated based on the derived lnC-T equations and Temperatures for each segment. The temperatures used for each zone are listed below:

Table 3.3.1-4: Temperature for Each Zone.

Zones	Temperature used for Modeling
Background_1	NE AirPort
Background_2	Wilmington
NE	PA AirPort
CC	PA AirPort
Zone_4	PA AirPort
DB	Wilmington

The calculated concentrations for each segment were output to .txt files in the required format for PCB model input file replacement via VBA macro. The output txt file has name like “GaseousPCB575_5” representing the concentrations files for Penta (5)-PCBs with modeling period 575 days. Depends on the modeling period, it could also output PCBs concentrations with period of 365 days.

3. Results of the updated gaseous PCB concentrations (Penta-PCB as example)

The figures below are examples of output gaseous PCB concentration of Penta-PCB which selected from spring, summer and autumn seasons.

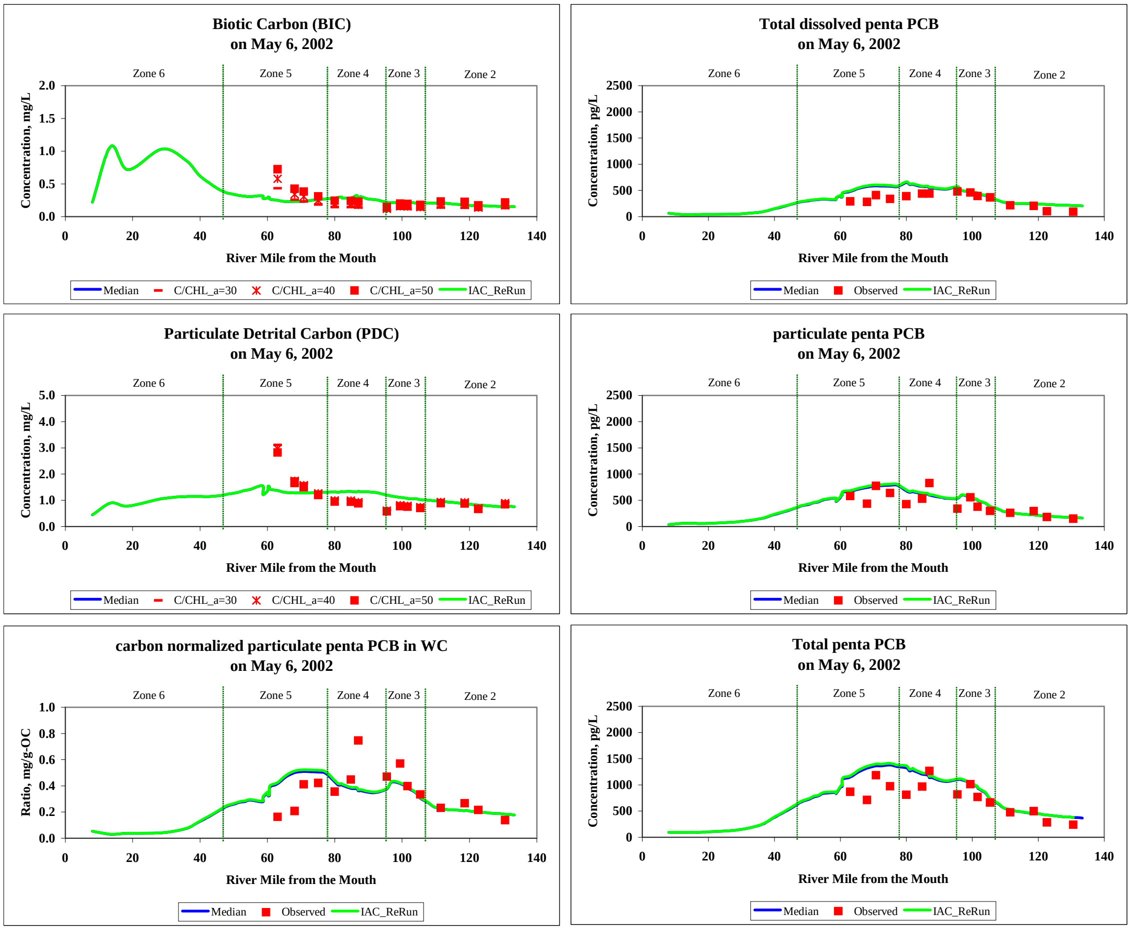


Figure 3.3.1-1: Gaseous PCB concentration output examples for spring.

.

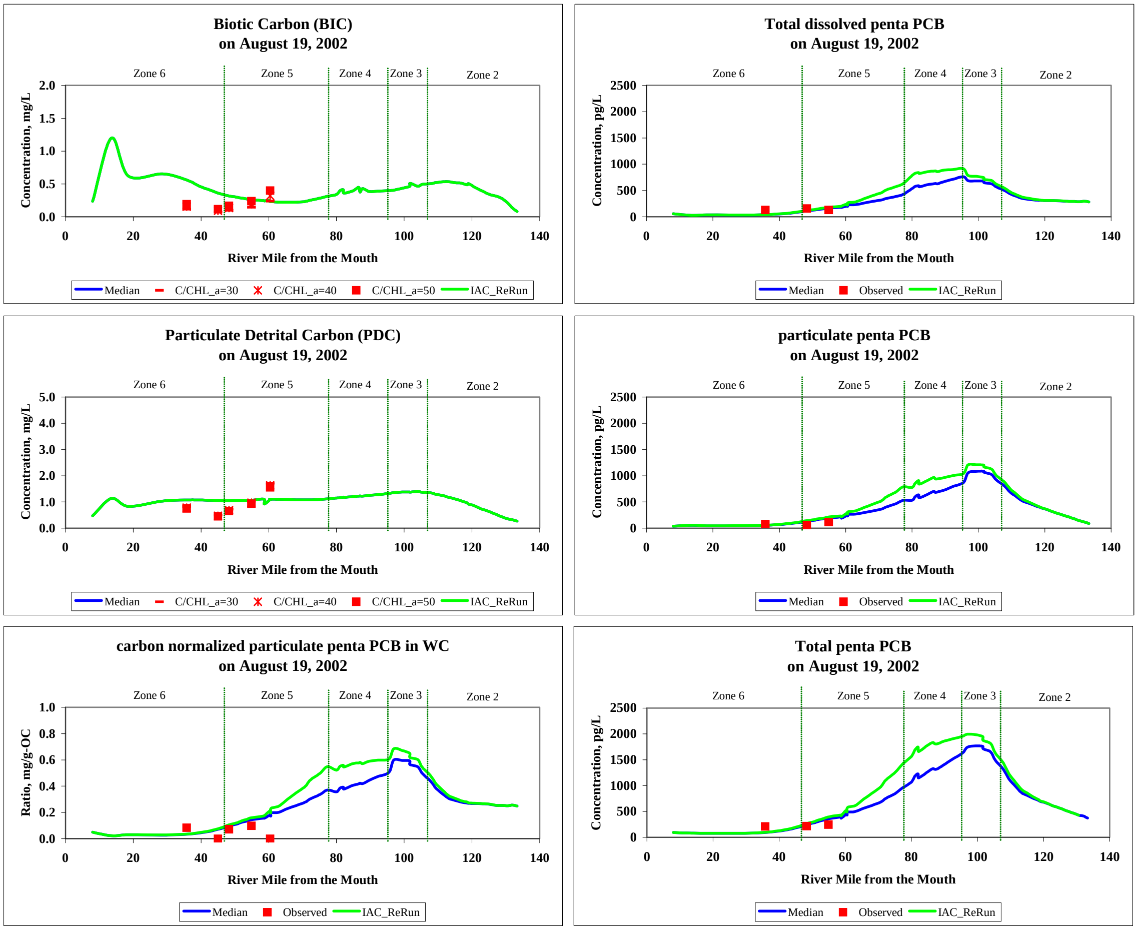


Figure 3.3.1-2: Gaseous PCB concentration output examples for summer.

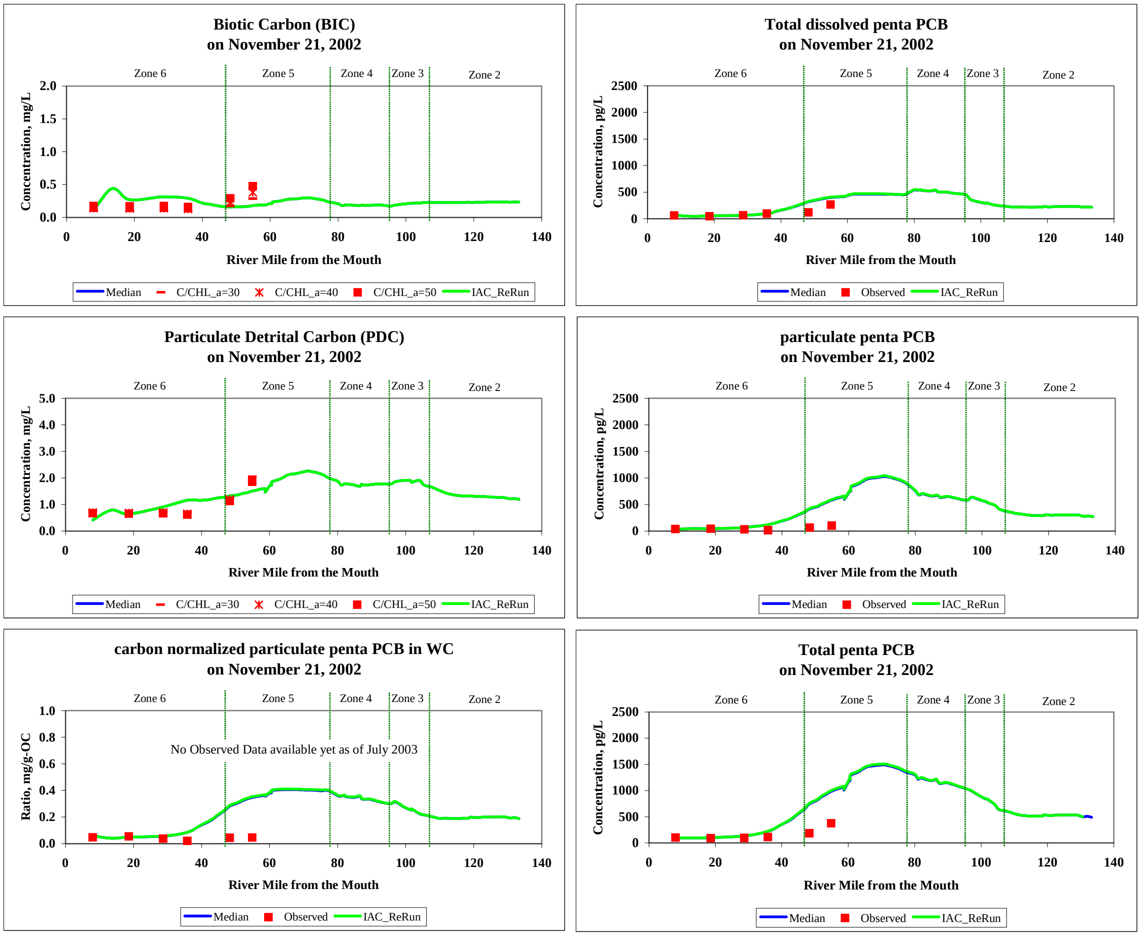


Figure 3.3.1-3: Gaseous PCB concentration output examples for fall.

4. Dry deposition load calculation

The dry PCB deposition flux for each day and each segments are calculated based on the previously calculated gaseous PCB concentrations using the equations listed below:

$$\text{Dry dep. flux } (ng/m^2/d) = pg/m^3 * cm/s * 24 * 3600s/d * 0.01m/cm * 0.001ng/pg$$
$$= 0.864 * \text{Particulate Conc. } (pg/m^3) * \text{ Vd}(cm/s)$$

$$\text{Particulate Conc. } (pg/m^3) = \text{Gaseous Conc. } (pg/m^3) * \text{ particulate/gaseous ratio}$$

While the ratio is directly obtained from Dr. Lisa Totten listed below:

Table 3.3.1-5: The ratio of particulate to gaseous PCB for each Homolog.

Homolog	Particulate/Gaseous PCB Ratio
4	0.025370949
5	0.038851407
6	0.114350071
7	0.205511504

And the Vd is selected as 0.5cm/s as suggested by Dr. Totten.

By multiplying the calculated dry deposition flux with the segment area (m^2), we got the dry deposition load for each segment:

Dry deposition load (kg/d) = Dry dep. flux ($ng/m^2/d$)*area (m^2)*10^{-12}kg/ng

The dry deposition load for each homolog at each segments during the modeling period (575days) could be calculated using the VBA macro and output to the relative tabs.

5. Wet deposition load calculation

The wet deposition load is calculated by using the volume weighted average concentrations of PCB in precipitation, which was calculated as follows:

VWM Conc in rain = Particle phase Conc * scavenging factor of 1.0e5

With the units of ng/L.

The wet deposition load was then calculated by following equations:

Wet deposition Load (kg/d)= VWM (ng/L)*area(m^2)* deposition rate (inch/d)* 10^{-12}kg/ng*0.0254m/inch*10^3L/m3

The dry deposition load for each homolog at each segments during the modeling period (575days) was calculated using the VBA macro and output to the relative tabs.

6. Total deposition load calculation

Based on the results of previous steps 5 and 6, by adding them up we got the total atmospheric deposition load of PCBs for each segment and each homolog. According to the format required, another VBA macro was created to generate the data to another Tab. In addition the Atmospheric PDC (kg/day) was added to the Tab by directly using Lisa's results.

3.3.2 Sediment Initial Conditions

The sediment initial conditions used in the model simulations for the four homologs were developed from a total of 73 samples were used to establish the initial sediment conditions for each of the PCB homologs (see Section 2.2.1.). These samples included the 51 DRBC samples analyzed by Axys Analytical Laboratories for 148 congeners, and 22 of the samples collected as part of the U.S. EPA's National Coastal Assessment Program in 2001 and reanalyzed by Axys Analytical Laboratories for 209 congeners. The parameters included in this data set include PCBs, Total Organic Carbon (TOC) and Inorganic Solids (ISS). This data set was believed to better represent the sediment quality of the Delaware Estuary and Bay for the calibration period.

This data set was analyzed using a statistical procedure called locally weighted scatterplot smoothing or LOWESS that fits regression surfaces to data through multivariate smoothing. This procedure is more useful that traditional parametric models because it can be used when the underlying parametric surface is not known and when the data contains outliers (Cohen, 1999). The procedure fits quadratic functions of the predictors at the centers of neighborhoods. The neighborhoods of data points are selected so that they include a specified percentage of the data points in each neighborhood (called the smoothing parameter). The data points are also weighted as a function of their distance from the center of the neighborhood.

In this application of LOWESS, fitting is done to selected reaches in the tidal river or bay to obtain predicted concentrations of the parameter of interest for each reach. This value is then assigned to the model segments within that reach.

Section 2.2.2 presents the results of applying the LOWESS procedure to data sets for penta-PCBs, Total Organic Carbon (TOC) and Inorganic Solids (ISS). Figures 3.3.2-1 to 3 present the results of the LOWESS analysis to data sets for tetra-PCB, hexa-PCB and hepta-PCB, respectively.

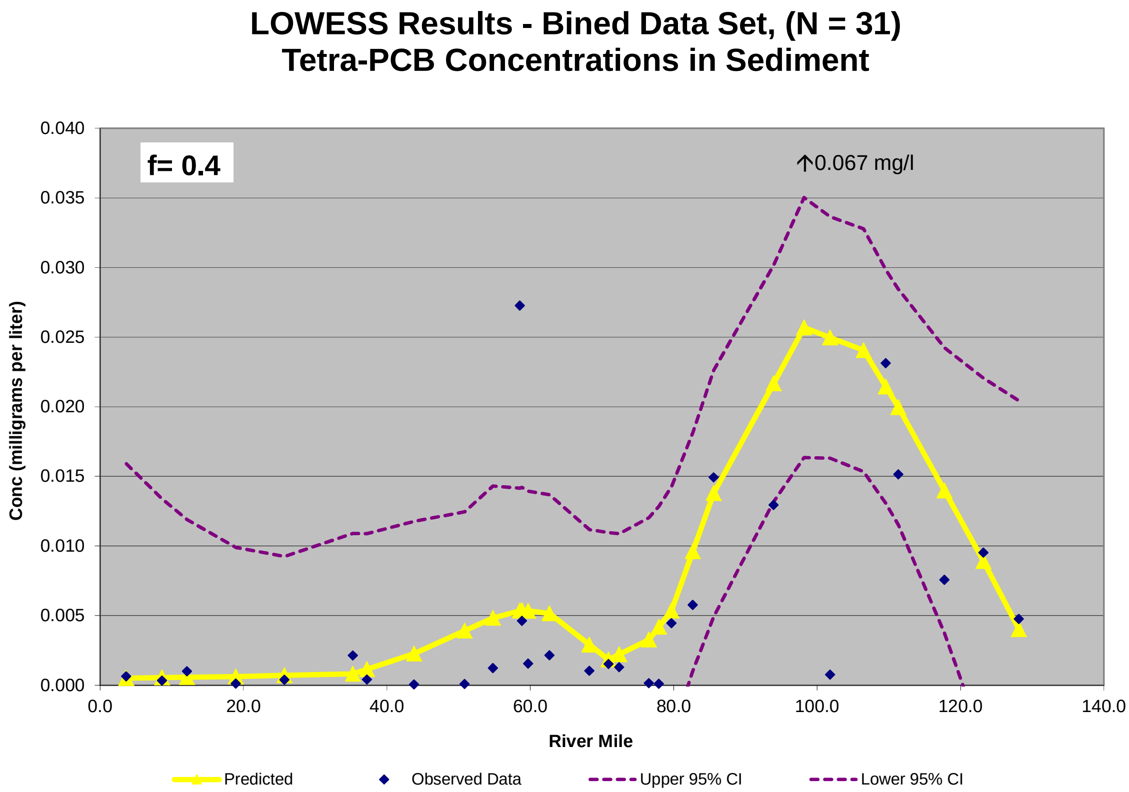


Figure 3.3.2-1: Plot of bined tetra-PCB sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay. The yellow line indicates the smoothed regression line that was fit to the data and used in the initial conditions in the PCB water quality model.

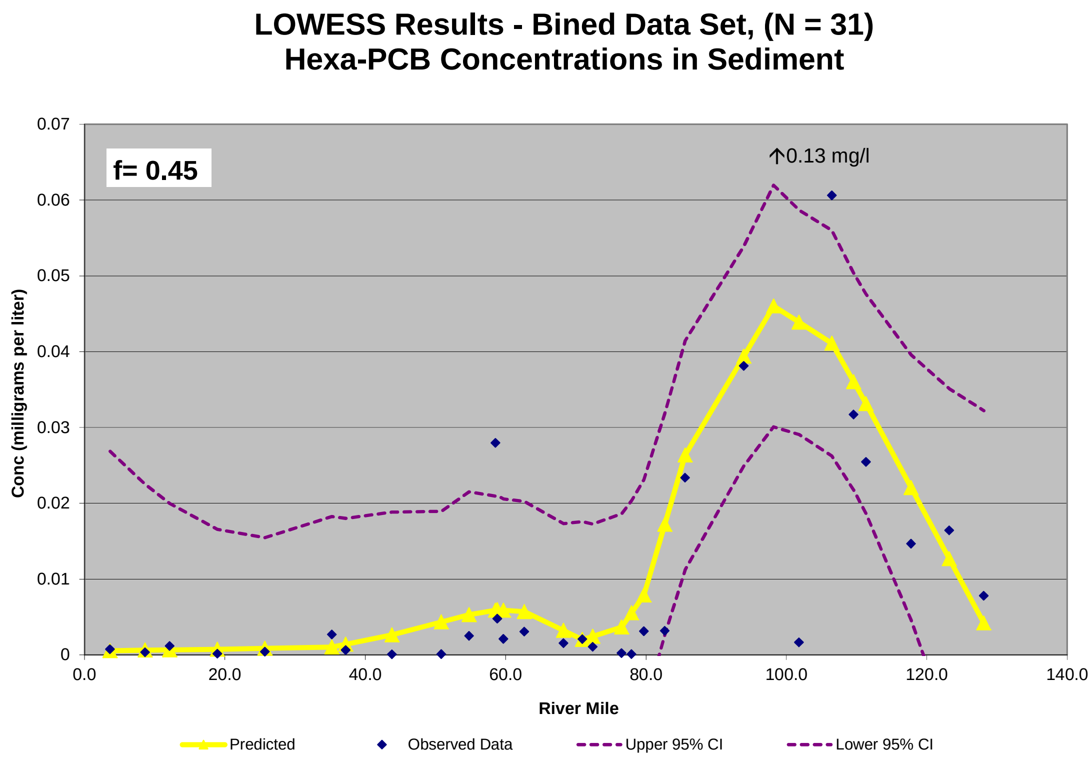


Figure 3.3.2-2: Plot of bined hexa-PCB sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay. The yellow line indicates the smoothed regression line that was fit to the data and used in the initial conditions in the PCB water quality model.

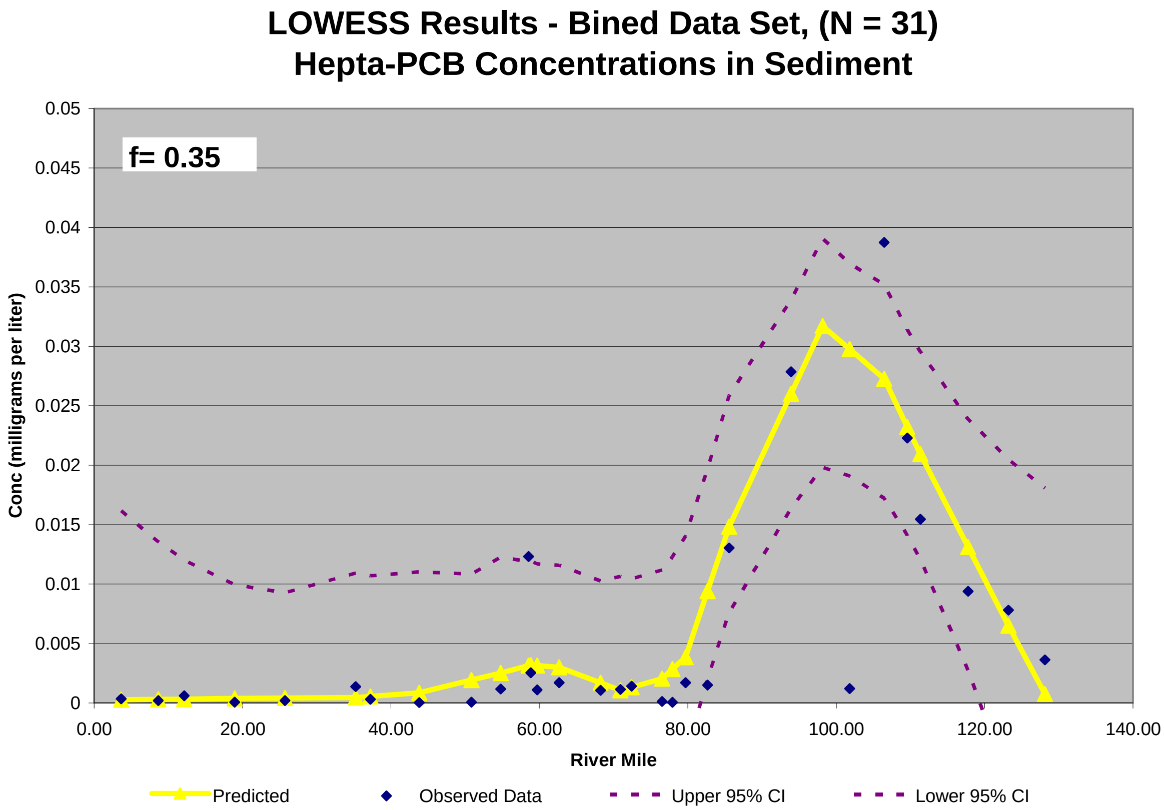


Figure 3.3.2-3: Plot of bined hepta-PCB sediment concentrations in the Delaware Estuary between Trenton, NJ and the mouth of Delaware Bay. The yellow line indicates the smoothed regression line that was fit to the data and used in the initial conditions in the PCB water quality model.

3.3.3 Forced Loadings

3.3.3.1 Generic Description - CSOs and Non-Point Sources

We computed loadings from Combined Sewer Overflows (CSOs) and Non-point source runoff (NPS) for Tetra, Penta, Hexa, and Hepta homologs using the methods comparable to those employed in the Stage 1 PCB TMDLs and reported in DRBC 2006. All estimates of flow remained the same as in the Stage 1 PCB TMDL.

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 homolog specific concentration of the other five treatment plants with CSO systems (Philadelphia Northeast and Southwest, DELCORA, 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 PCB concentrations from the non-impacted influent line was used to estimate the Philadelphia Southwest CSO load.

NPS loads were estimated using the framework developed by Camp Dresser McKee (CDM) (Smullen 2003) for the Stage 1 PCB TMDLs, updated with Delaware estuary specific runoff concentrations measured by DRBC in 2005 and 2007.

For the Stage 1 TMDLs, 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. 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. In the Stage 1 PCB TMDLs, 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. The literature review yielded a 50th percentile EMC value of 61.99 ng/L. In the Stage 1 TMDLs, 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 revised loads, DRBC computed EMCs from stormwater data collected in 2005 and 2007.

We compared these new EMCs to the literature derived EMCs from the Stage 1 PCB TMDL. Figure 3.3.3-1 below shows the new sample specific EMCs and quantiles of the literature EMCs. The new EMCs agree well with the literature derived values. The new EMCs are mostly within the range between the 5^{th} and 75^{th} percentile. The median EMC value from the stormwater measurements is 37,285 pg/L total PCBs, compared to the literature derived median of 61,990 pg/L. The lower values of the current EMCs seem intuitively reasonable considering the length of time that has passed since PCB manufacturing was banned and the age of the literature values.

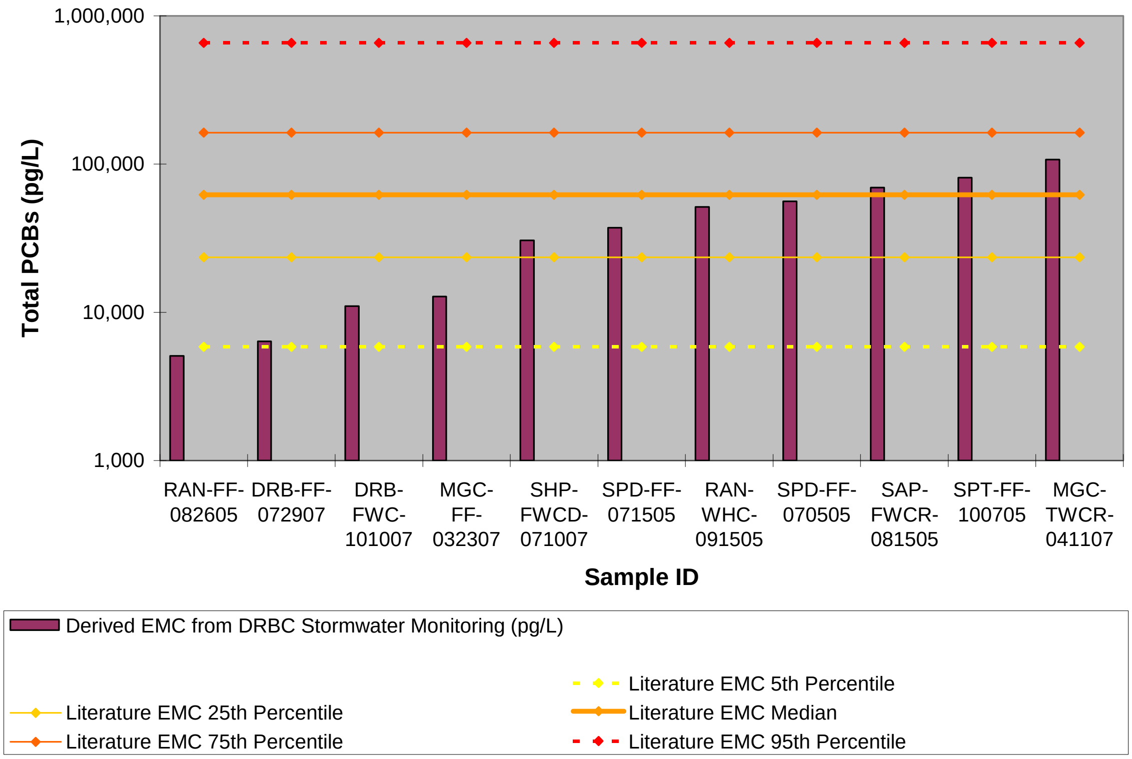


Figure 3.3.3-1. Comparison of Computed EMCs from DRBC Stormwater Monitoring to Literature Derived EMCs from Stage 1 PCB TMDL

DRBC used the runoff data collected in 2005 and 2007 to compute EMCs for Tetra, Penta, Hexa, and Hepta-PCBs. The new EMCs were used to compute loads for the urban-suburban land use category. Since PCB congeners were measured directly, we totaled congeners within the homolog groups to compute homolog EMCs, rather than extrapolating from an estimate of total PCBs.

For the agricultural, rural/open/ forested, and open water/wet-wetlands land use categories, the framework utilized revised atmospheric deposition estimates (described in Section 3.3.1) and an assumed pass-through rate to estimate PCB homolog 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.

3.3.3.2 Contaminated Sites

Contaminated site loads for PCBs were estimated from computed soil loss and estimated surface soil PCB concentrations. The current load estimates included three important refinements from the Stage 1 PCB TMDL estimates:

1. DRBC reconciled the previous contaminated site list with the 2007 Delaware River Toxics Reduction Program (DelTRiP) Annual Report. DelTRiP represented a much more coordinated and intensive effort to identify all toxics sites within the Delaware Basin and to obtain additional site data.
2. DRBC converted all solids load estimates to the U.S. Department of Agriculture, Natural Resources Conservation Service's (NRCS) Revised Universal Soil Loss Equation 2 (RUSLE2) soil loss model. In the Stage 1 PCB TMDLs, EPA estimated solids load for federal lead sites using the USLE, a predecessor to RUSLE2, and the states used a simplified regional solids yield estimate for state lead sites.
3. PCB estimates were developed for Tetra-, Penta-, Hexa-, and Hepta-PCBs.

The Delaware River Toxics Reduction Program (DelTRiP) was created in 2004 as a joint effort between the Delaware River Basin Commission, United States Environmental Protection Agency (USEPA), Pennsylvania Department of Environmental Protection (PADEP), New Jersey Department of Environmental Protection (NJDEP), and Delaware Department of Natural Resources and Environmental Control (DNREC). The New York State Department of Environmental Conservation joined in 2007. The goal of DelTRiP, which was funded by a grant from the USEPA, was to identify, prioritize, track, and report the status of sites within the basin that significantly contribute or have the potential to significantly contribute toxic loadings to the Delaware River Basin. Since its inception, DelTRiP has been focused on identifying sites contaminated with PCBs.

In 2006, the USEPA, NJDEP, PADEP, and DNREC submitted about 1,000 sites to DelTRiP as potential PCB sources; of those, 263 were identified as containing PCBs. DRBC compiled and published the first DelTRiP annual report in 2006, which included a listing of these 263 identified sites. In researching the sites for the 2007 report, DRBC staff found that many of the 263 sites had been previously remediated to their respective state standards. The 2007 DelTRiP report details the remediation history of these sites, as well as the ongoing PCB remediation (which includes ongoing site investigation and active remediation) at 56 sites. From this effort, we estimated that 45 sites within the model domain are contributing PCB loads to the estuary.

The 2007 Annual Report is available at:
http://www.state.nj.us/drbc/deltrip/2007/index.htm

Table 3.3.3-1 Contaminated Sites and Site Information

Facility	Acres	Total PCB Soil Concentration (ug/kg)	Lat	Long	Site Slope	Soil Code	Majority Soil type Description	Surrounding Soil Type	County	Area (ft2)	Slope Length (ft)	Base Soil Loss (t/ac/yr)	Total PCB kg/day	Tetra Load kg/day	Penta Load kg/day	Hexa Load kg/day	Hepta Load kg/day
CONRAIL, Morrisville Lagoons - PA-441*	1	4911	40.195278	-74.792222	1.3		Urban Land	gravelly loam, silt loam	Bucks	43560	209	1.3	1.58679E-05	4.06219E-06	2.49444E-06	1.65661E-06	8.04505E-07
Pennwalt Corp. - Cornwells Heights - PA-0031*	1.4	824	40.070313	-74.942052	4.4		Urban Land	sandy silt loam	Bucks	60984	247	3.5	1.00353E-05	2.56904E-06	1.57755E-06	1.04769E-06	5.0879E-07
Roebling Steel Co.	12	8081	40.120831	-74.770839	1.7		Urban Land, Sandy		Burlington	522720	723	0.36	8.67673E-05	2.22124E-05	1.36398E-05	9.05851E-06	4.3991E-06
Conrail-Wayne Junction - PA-215	4	32090	40.023359	-75.159324	4.5		Urban Land	silt loam	Philadelphia	174240	417	5.7	0.001818494	0.000465534	0.000285867	0.000189851	9.21976E-05
Metal Bank - PA-2119	2.5	43708	40.024169	-75.027781	2.8		Urban Land	silt loam	Philadelphia	108900	330	3.2	0.000869077	0.000222484	0.000136619	9.07316E-05	4.40622E-05
Harrison Avenue Landfill	75	28030	39.947844	-75.105422	2.6		Urban Land	sandy loam	Camden	3267000	1,807	2.7	0.014107675	0.003611565	0.002217727	0.001472841	0.000715259
ABM-Wade, 58th Street Dump - PA-0179	3	367.2	39.925732	-75.214101	5.6		Urban Land	silt loam	Philadelphia	130680	361	7	1.91659E-05	4.90647E-06	3.01288E-06	2.00092E-06	9.71711E-07
O'Donnell Steel Drum - PA-0305	0.17	1725	39.929367	-75.233868	3.8		Urban Land	silt loam	Philadelphia	7405.2	86	4.5	3.27988E-06	8.39649E-07	5.15597E-07	3.42419E-07	1.6629E-07
Front Street Tanker - PA-2298	0.01	89000	39.830871	-75.385434	2.1		Made Land, Gravelly materials	silt loam	Delaware	435.6	21	1.5	3.31809E-06	8.49432E-07	5.21604E-07	3.46409E-07	1.68227E-07
8th Street Drum - PA-3272	0.8	60	39.842299	-75.382277	6.8		Made Land, Gravelly materials	silt loam	Delaware	34848	187	7.1	8.47046E-07	2.16844E-07	1.33156E-07	8.84316E-08	4.29452E-08
East 10th Street Site - PA-2869	16	15524	39.820759	-75.414734	4.5		Made Land, Gravelly materials	silt loam	Delaware	696960	835	6.8	0.004197975	0.001074682	0.000659922	0.000438269	0.000212837
Lower Darby Creek Area Site - PA-3424	26	487	39.9025	-75.254167	12.6		Made Land, Sanitary Landfill (Gravelly Loam)		Delaware	1132560	1,064	24	0.000755302	0.000193357	0.000118734	7.88536E-05	3.82938E-05
Bridgeport Rental & Oil Services (BROS)	2	129000	39.801669	-75.321661	0.9		Udorthents, dredged materials (Loam)		Gloucester (NJ)	87120	295	0.83	0.000532237	0.000136253	8.36677E-05	5.55656E-05	2.69844E-05
Dana Transport Inc.	0.92	36	40.354167	-75.938333	12.9		Urban Land	silt loam	Berks	40075.2	200	16	1.3171E-06	3.37177E-07	2.07048E-07	1.37505E-07	6.67768E-08
Castle Ford - DE-192	0.05	510	39.669892	-75.560799	2.1	Am	Fine Silty, Fine, Fine Silty		New Castle	2178	47	2	1.26759E-07	3.24502E-08	1.99265E-08	1.32336E-08	6.42666E-09
Forbes Steel & Wire Corp. - DE-165	0.18	4100	39.724717	-75.5441	5.7	Am	Fine Silty, Fine, Fine Silty		New Castle	7840.8	89	5.9	1.08222E-05	2.77048E-06	1.70125E-06	1.12984E-06	5.48686E-07
Old Airport Road Site - DE-283	58	600	39.70104	-75.612235	6.6	MsB	Fine Silty, Fine Loamy,		New Castle	2526480	1,589	12	0.001037929	0.00026571	0.000163163	0.00010836	5.2623E-05
Rogers Corner Dump - DE-246	16.3	270	39.720000	-75.557773	5.6	Tm	Fine Loamy		New Castle	710028	843	7.3	7.98512E-05	2.04419E-05	1.25526E-05	8.33647E-06	4.04846E-06
Industrial Products - DE-030	5	180	39.647484	-75.596207	1.7	MsB	Fine Silty, Fine Loamy,		New Castle	217800	467	1.9	4.25014E-06	1.08804E-06	6.68122E-07	4.43715E-07	2.15482E-07
Chicago Bridge and Iron - DE-038	12	12155	39.664932	-75.563214	1.6	Tm	Fine Loamy		New Castle	522720	723	1.6	0.000580047	0.000148492	9.11835E-05	6.0557E-05	2.94084E-05
Ludlow Industrial Park Drum Site - DE-121*	20.6	750	39.74375	-75.503472	1.1	Am	Fine Silty, Fine, Fine Silty		New Castle	897336	947	2	7.68008E-05	1.9661E-05	1.20731E-05	8.018E-06	3.8938E-06
AMTRAK Former Refueling Facility	20	43.3	39.741667	-75.524722	0.4	Ou	Fine Silty, Fine Loamy		New Castle	871200	933	0.43	9.25537E-07	2.36937E-07	1.45494E-07	9.6626E-08	4.69247E-08
Gates Engineering	0.5	0.01	39.738611	-75.555555	3.6	Ma	Made Land and Urban Land		New Castle	21780	148	3.4	4.22529E-11	1.08167E-11	6.64215E-12	4.4112E-12	2.14222E-12
AMTRAK Wilmington Railyard	70	170	39.746944	-75.522222	1.8	Ou	Fine Silty, Fine Loamy		New Castle	3049200	1,746	2.2	6.50694E-05	1.66578E-05	1.02289E-05	6.79325E-06	3.29902E-06
NeCastro Auto Salvage	115	0.82	39.704444	-75.612222	0.4	Ou	Fine Silty, Fine Loamy		New Castle	5009400	2,238	0.44	1.03127E-07	2.64005E-08	1.62115E-08	1.07664E-08	5.22853E-09
Hercules Research Center	10	3.38	39.758333	-75.633611	0.0	Ha	Silt Loam		New Castle	435600	660	0.092	7.7288E-09	1.97857E-09	1.21497E-09	8.06886E-10	3.9185E-10
Dravo Ship Yard	10	39	39.730278	-75.561944	4.0	Ma	Made Land and Urban Land		New Castle	435600	660	5.4	5.23439E-06	1.34E-06	8.22845E-07	5.4647E-07	2.65383E-07
DP&L/Congo Marsh	10	0.2	39.727778	-75.539167	3.3	Ou	Fine Silty, Fine Loamy		New Castle	435600	660	4.3	2.1375E-08	5.472E-09	3.36015E-09	2.23155E-09	1.08371E-09
American Scrap & Waste	68	80	39.735833	-75.538889	2.2	Ou	Fine Silty, Fine Loamy		New Castle	2962080	1,721	2.9	3.92107E-05	1.00379E-05	6.16392E-06	4.09359E-06	1.98798E-06
Pusey & Jones Shipyard	25	0.47	39.734722	-75.545833	2.6	Ma	Made Land and Urban Land		New Castle	1089000	1,044	3.5	1.02215E-07	2.6167E-08	1.60681E-08	1.06712E-08	5.18228E-09
Bafundo Roofing	0.5	2300	39.714167	-75.549996	5.3	Am	Fine Silty, Fine, Fine Silty		New Castle	21780	148	7	2.0008E-05	5.12204E-06	3.14525E-06	2.08883E-06	1.0144E-06
Kreiger Finger Property	5	232	39.733056	-75.551389	1.7	Ma	Made Land and Urban Land		New Castle	217800	467	1.9	5.47796E-06	1.40236E-06	8.61135E-07	5.71899E-07	2.77733E-07
Electric Hose & Rubber	0.5	1300	39.741944	-75.530278	2.6	Ou	Fine Silty, Fine Loamy		New Castle	21780	148	2.5	4.03888E-06	1.03395E-06	6.34912E-07	4.21659E-07	2.04771E-07
Penn Del Metal Recycling	3.8	220	39.765556	-75.555000	33.3	TaB2	Silt Loam		New Castle	165528	407	70	0.000145449	3.7235E-05	2.28646E-05	1.51849E-05	7.37428E-06
E. 7th Street North & South	0.5	850	39.556667	-75.533333	0.0	Ou	Fine Silty, Fine Loamy		New Castle	21780	148	0.092	9.71816E-08	2.48785E-08	1.52769E-08	1.01458E-08	4.92711E-09
Delaware Compressed Steel	2.56	18	39.733398	-75.556015	0.4	Ou	Fine Silty, Fine Loamy		New Castle	111513.6	334	0.42	4.81027E-08	1.23143E-08	7.56174E-09	5.02192E-09	2.4388E-09
Newport City Landfill	8	0.43	39.712222	-75.598611	0.0	Ou	Fine Silty, Fine Loamy		New Castle	348480	590	0.092	7.86599E-10	2.01369E-10	1.23653E-10	8.2121E-11	3.98806E-11
DuPont Louviers - MBNA	0.5	1.4	39.716111	-75.746667	7.8	GnB2	Silt Loam		New Castle	21780	148	7.5	1.30487E-08	3.34046E-09	2.05125E-09	1.36228E-09	6.61568E-10
North American Smelting Co.	6	15.66	39.715329	-75.527894	5.1	Am	Fine Silty, Fine, Fine Silty		New Castle	261360	511	12	2.80241E-06	7.17417E-07	4.40539E-07	2.92572E-07	1.42082E-07
RSC Realty	10	25			5.3				New Castle	435600	660	7.6	4.72238E-06	1.20893E-06	7.42358E-07	4.93016E-07	2.39425E-07
Wilmington Coal Gas - N	0.5	32.8	39.735833	-75.562222	3.1	Ma	Made Land and Urban Land		New Castle	21780	148	2.9	1.18209E-07	3.02614E-08	1.85824E-08	1.2341E-08	5.99318E-09
Del Chapel Place	5	3.3	39.681389	-75.744722	2.4	Am	Fine Silty, Fine, Fine Silty		New Castle	217800	467	4.6	1.88647E-07	4.82935E-08	2.96553E-08	1.96947E-08	9.56439E-09
Kruse Playground	0.6	13	39.747222	-75.541944	12.6	Ma	Made Land and Urban Land		New Castle	26136	162	16	3.10186E-07	7.94076E-08	4.87612E-08	3.23834E-08	1.57264E-08
Budd Metal	5	9.3	39.720278	-75.548889	0.9	Am	Fine Silty, Fine, Fine Silty		New Castle	217800	467	1.4	1.61804E-07	4.14217E-08	2.54355E-08	1.68923E-08	8.20345E-09
Fox Point Park Phase II	60	14.3	39.76	-75.488052	7.5	Ou	Fine Silty, Fine Loamy		New Castle	2613600	1,617	14	2.98554E-05	7.64298E-06	4.69327E-06	3.1169E-06	1.51367E-06

RUSLE2 combines empirical field data and process based equations to provide estimates of soil loss from an interactive computer interface. RUSLE2 embodies the latest formulation (2001) of soil erosion predictive tools and research begun in 1940, and it is the current NRCS supported application for estimating soil loss. The predecessor application, USLE, is no longer supported by NRCS. RUSLE2 is informed by a more comprehensive and current body of knowledge and research data than previous approaches and allows for more accurate representation of site specific conditions (such as slope and soil type) leads to better comparison between sites. In addition, RUSLE2 allows for descriptive site management practices (such as specific soil management tilling, crop covers, silt fences, and vegetated swales) as opposed to non-descriptive numeric coefficients. More information about RUSLE2 is available at: http://fargo.nserl.purdue.edu/rusle2_dataweb/RUSLE2_Index.htm

RUSLE2 factors include:

- Erosivity (a characteristic of rainfall)
- Erodibility (a characteristic of soil)
- Slope length
- Slope steepness
- Cover-management
- Supporting practices

For this application, we estimated soil types from the NRCS soils data at: http://websoilsurvey.nrcs.usda.gov/app/ and from county soils maps. Average site slope was determined for each site from GIS Digital Elevation Models (DEMs). Dimensions of erodible soil were determined from the DelTRiP site data.

We used representative total PCB surface soil concentrations from DelTRiP (where available) or the Stage 1 PCB TMDL estimates. Because most data sets were not reported in terms of homologs or congeners, we multiplied total PCB estimates by the estimated proportion of Tetra, Penta, Hexa, and Hepta-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 homolog proportions of domestic production.

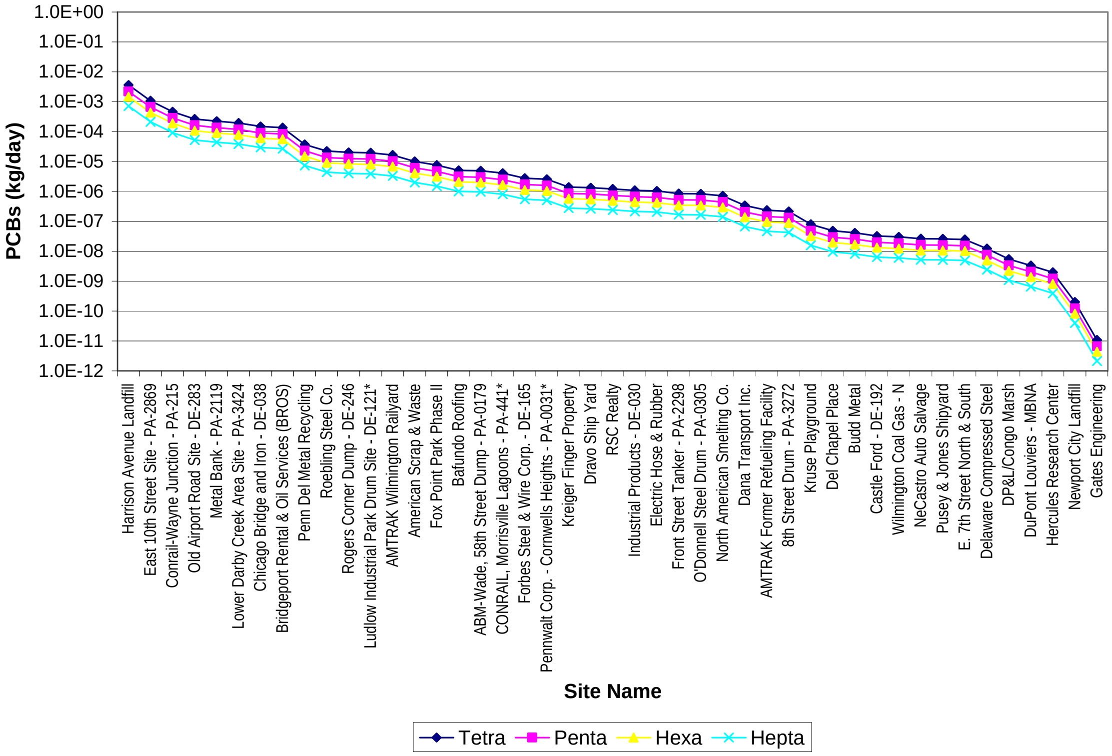


Figure 3.3.3-2 PCB Homolog Loads by Site

As shown in Figure 3.3.3-2 above, PCB loads ranged from 3.6 x 10^{-3} kg/day (3.6 grams per day) of Tetra PCB at the highest loading site to 2.1 x 10^{-12} kg/day (2.1 nanograms per day) of Hepta PCB for the lowest loading site. Overall, we estimate that contaminated sites contribute 6.3 grams of Tetra-PCB, 3.9 grams of Penta-PCB, 2.6 grams of Hexa PCB, and 1.2 grams of Hepta-PCB to the estuary each day.

3.3.3.3 Tributaries

In sum, 30 tributaries (as listed in Table 3.3.3-2, not including the Delaware River at Trenton and the Schuylkill River, which should be discussed in another section in the same chapter) drained into the Estuary portion of the Delaware River and were included in the model domain. The USGS maintains many gages in the Delaware River Basin and provides flow information via its web site, NWIS Web Data for the Nation (http://waterdata.usgs.gov/nwis/discharge). Tributary flows were taken from existing USGS gages when available and extrapolated from nearby streams when stream gages were not available. However, not all these tributaries were gaged and had continuous monitoring data for the calibration period. For those tributaries without monitoring data, the tributary flows were estimated by a unit area based method –computing the product of the drainage area and precipitation-runoff coefficient of the adjacent tributary. Selection of gaged streams used for extrapolation was based primarily on underlying geology. Drainage areas for streams without gages and for drainage areas downstream of gaging station were calculated using Geographic Information System (GIS) methods.

Table 3.3.3-2 Tributary Flow Gages and Extrapolation Index

	Tributary	Gage	Extrapolated from (if not gaged)
1	Alloways	Not gaged	Raccoon
2	Big Timber	Not gaged	Cooper
3	Brandywine	USGS1481500	
4	Broadkill	Not gaged	St. Jones
5	Cedar	Not gaged	St. Jones
6	Chester	USGS1477000	
7	Christina	USGS1478000	
8	Cohansey	Not gaged	Maurice
9	Cooper	USGS1467150	
10	Crosswicks	USGS1464500	
11	Darby	Not gaged	Chester
12	Frankford	USGS1467087	
13	Leipsic	Not gaged	St. Jones
14	Mantua	Not gaged	Raccoon
15	Maurice	USGS1411500	
16	Mispillion	Not gaged	St. Jones
17	Muderkill	Not gaged	St. Jones
18	Neshaminy	USGS1465500	
19	Newton	Not gaged	Cooper
20	Pennypack	USGS1467048	
21	Pennsauken	Not gaged	Cooper
22	Poquessing	USGS1465798	
23	Raccoon	USGS1477120	
24	Rancocas	USGS1467000	
25	Red Clay	USGS1480015	
26	Salem	USGS1482500	
27	Smyrna	Not gaged	St. Jones
28	St. Jones	USGS1483700	
29	Stowe	Not gaged	Maurice
30	White Clay	USGS1479000	

The loads of four major PCB homologs from all the tributaries were explicitly evaluated by computing the product of gaged or extrapolated daily flows at the monitoring locations and median value of sampled instream concentrations for wet and dry weather, toggled by precipitation data at the closest weather station. For any days in the simulation period with a 24-hour rainfall being less that 0.1-inch the tributary specific mean dry weather concentration was used, otherwise the tributary specific mean wet weather concentration was used. The dry and wet weather concentrations used in this computation were also listed in Table 3.3.3-2.

Table 3.3.3-3 Summary of Tributary PCB concentrations for four homologs (pg/L)

		Tetra		Penta		Hexa		Hepta	
	Tributary	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1	Neshaminy	60	350	81	617	55	598	19	322
2	Poquessing	175	860	157	1722	96	1843	39	1222
3	Pennypack	380	886	314	1283	156	1481	61	1117
4	Frankford	341	4059	466	8258	824	18494	666	17480
5	Darby	1006	1662	1526	5736	1418	7813	683	5668
6	Chester	427	2347	375	6101	244	6894	103	3847
7	Brandywine	71	1009	103	1990	81	2445	41	1396
8	White Clay	67	1194	84	3135	46	2822	17	1607
9	Red Clay	307	10989	224	13395	68	9272	22	5105
10	Christina	247	925	487	4283	334	4538	100	1502
11	Crosswicks	364	127	534	209	382	241	218	141
12	Rancocas	295	687	465	1097	477	1242	261	684
13	Pennsauken	657	2554	912	5652	793	5773	404	2915
14	Cooper	1238	218	1346	327	1244	402	768	318
15	Big Timber	1134	1071	1419	1269	1203	1139	552	594
16	Mantua	1767	2905	3557	6936	2582	6015	976	2100
17	Salem	191	773	178	926	134	947	63	578
18	Raccoon	600	1390	544	1836	351	1606	171	792
19	Alloways	241	971	352	1831	313	2221	160	1471
20	Maurice	44	177	71	371	67	476	18	164
21	Cohansey	380	1534	941	4902	795	5638	242	2226
22	Stowe*	276	255	337	413	270	476	133	179
23	Smyrna*	276	255	337	413	270	476	133	179
24	Leipsic*	276	255	337	413	270	476	133	179
25	Murderkill	138	556	166	862	150	1066	70	645
26	Mispillion	283	146	337	139	270	107	133	68
27	Cedar*	276	255	337	413	270	476	133	179
28	Broadkill*	276	255	337	413	270	476	133	179
29	St. Jones	276	255	391	413	349	369	162	179
30	Newton	881	3554	982	5114	762	5399	324	2983

Please note that five of the tributaries in above list (marked by *), were not sampled for PCB concentration measurements. Considering the fact that all these five tributaries were located in Zone 6, we calculated the median value of concentrations for each homolog and weather conditions for the rest tributaries with sampling data in Zone 6. The dry and wet weather concentrations for these five "no-data" tributaries were estimated as the median concentration of other tributaries in the same zone (Zone 6). As such, the tributary PCB loadings for the four homologs were commutated. A summary of estimated annual load was listed in Table 3.3.3-4 and the zonal loads were show in Figure 3.3.3-3.

Table 3.3.3-4: Estimated Annual Tributary PCB Loads for Four Homologs (kg)

	Zone	Tetra	Penta	Hexa	Hepta
Neshaminy	2	0.034	0.057	0.052	0.027
Poquessing	2	0.012	0.023	0.024	0.016
Pennypack	2	0.033	0.042	0.042	0.030
Crosswicks	2	0.031	0.046	0.036	0.020
Rancocas	2	0.076	0.120	0.128	0.070
Frankford	3	0.056	0.111	0.245	0.230
Pennsauken	3	0.054	0.104	0.102	0.051
Cooper	3	0.031	0.035	0.034	0.022
Newton	3	0.024	0.032	0.031	0.016
Darby	4	0.068	0.158	0.189	0.124
Chester	4	0.050	0.104	0.111	0.061
Big Timber	4	0.078	0.095	0.082	0.039
Mantua	4	0.089	0.191	0.149	0.054
Raccoon	4	0.027	0.029	0.023	0.011
Brandywine	5	0.069	0.129	0.150	0.085
White Clay	5	0.030	0.074	0.066	0.037
Red Clay	5	0.124	0.147	0.100	0.055
Christina	5	0.017	0.069	0.071	0.023
Salem	5	0.035	0.038	0.036	0.020
Alloways	5	0.026	0.044	0.049	0.030
Maurice	6	0.012	0.022	0.026	0.008
Cohansey	6	0.030	0.086	0.087	0.032
Stowe	6	0.010	0.014	0.012	0.005
Smyrna	6	0.015	0.020	0.018	0.008
Leipsic	6	0.012	0.016	0.014	0.006
Murderkill	6	0.016	0.023	0.026	0.015
Mispillion	6	0.006	0.007	0.006	0.003
Cedar	6	0.008	0.011	0.010	0.004
Broadkill	6	0.012	0.016	0.015	0.007
St. Jones	6	0.018	0.026	0.023	0.011
Sum		1.105	1.890	1.954	1.121

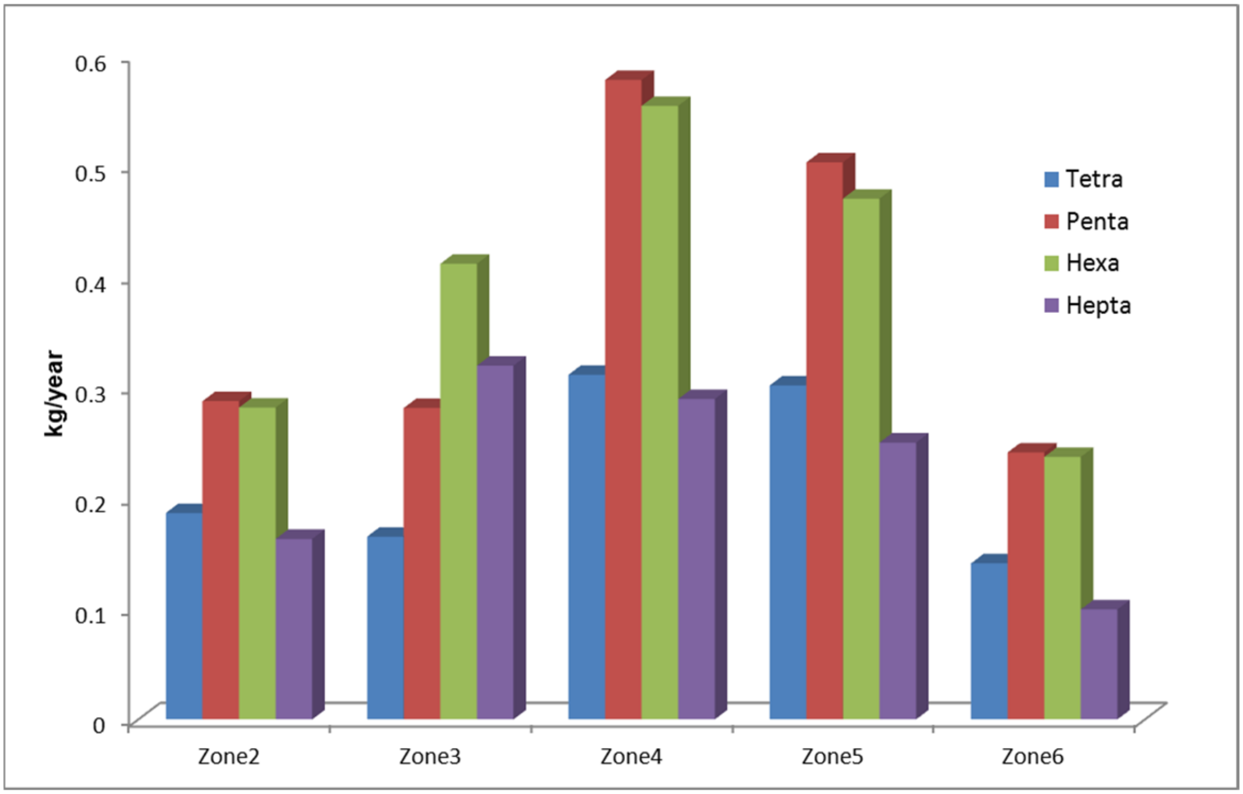


Figure 3.3.3-3: PCB Homolog Loads from Tributaries by Zone.

3.3.3.4 Point Source Loadings for Tetra-PCBs, Penta-PCBs, Hexa-PCBs and Hepta-PCBs

Point source PCB concentrations for the Stage 1 PCB TMDL were revised to better characterize PCB loads. Effluent data from dischargers which were not original included in the Stage 1 efforts were captured, and more accurate Stage 1 PCB concentrations for existing dischargers were extrapolated using PCB data from the Stage 2 efforts.

Analytical results submitted in support of the Stage 1 PCB TMDL effort required the analysis of 82 PCB congeners (a subset of all 209 congeners see Table 3.3.3-5), furthermore the analytical methodology was not specified, nor were reporting conventions.

Two analytical methods were utilized in the analysis of PCBs during the Stage 1 PCB TMDL; Method 1668, Revision A and Method 8082A modified for analysis of 82 congeners. Detection limits (DL) varied by method with Method 1668, Revision A typically achieving a DL of between 50-75 pg/L, whereas Method 8082A achieved detection limits of between 500-1,200 pg/L. Analytical results from both methods were blended and used to calculate PCB loads. This approach of analyzing for selected PCB congeners and the elevated detection limits associated with method 8082A increased analytical uncertainty and may have reduced accuracy of PCB loads.

As part of the Stage 2 PCB TMDL the Commission specified analytical methodology, and sampling and reporting requirements were specifically defined to meet the data quality objectives of reducing analytical uncertainly and improving data comparability. Utilizing these protocols detections limits of between 1-3 pg/L were achieved. These guidelines can be found at http://www.state.nj.us/drbc/PCB_info.htm.

Table 3.3.3-5: Percent of 209 PCB congeners represented in wastewater samples measured for the Stage 1 TMDLs.

Homolog	Stage 2 congeners	Stage 1 congeners	Percent of congeners
Mono	3	0	0%
Di	12	1	8%
Tri	24	6	25%
Tetra	42	13	31%
Penta	46	22	48%
Hexa	42	18	43%
Hepta	24	13	54%
Octa	12	8	67%
Nona	3	3	100%
Deca	1	1	100%

To provide better estimates of the Stage 1 loads two approaches were employed based on the initial analytical method utilized. For those dischargers who had originally utilized Method 1668, Revision A, a comparison of both datasets was utilized in developing a ratio between the original 82 congeners and the total 209 on a homolog basis. This ratio was then used to calculate estimated Stage 1 PCB concentrations on a homolog basis for all congeners. These results were used in calculating PCB loads. The flow diagram in Figure 3.3.3-4 depicts the steps used in the estimating a revised Stage 1 PCB concentration for those dischargers which had used Method 1668, Revision A for both the Stage 1 and 2 sampling events.

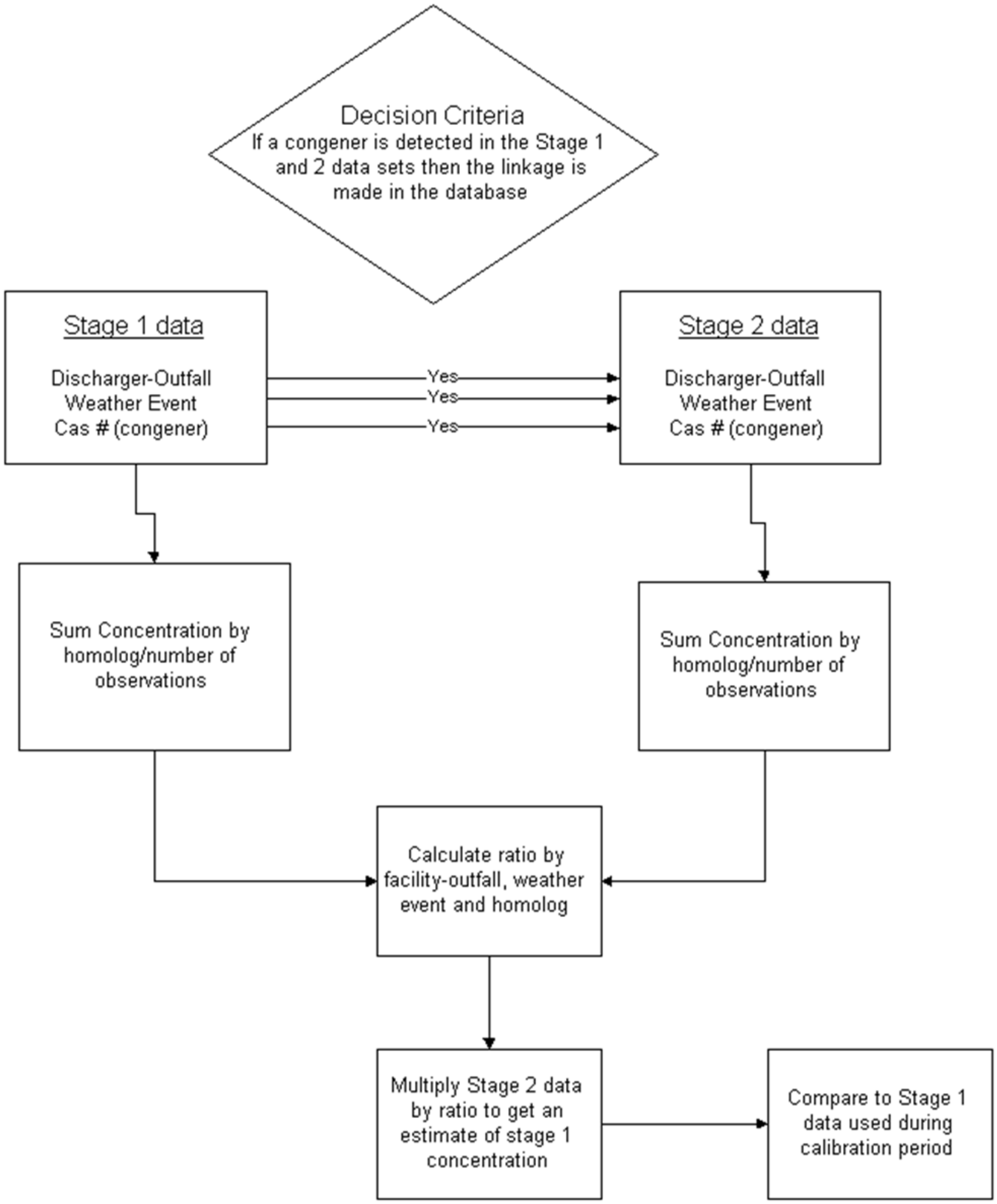
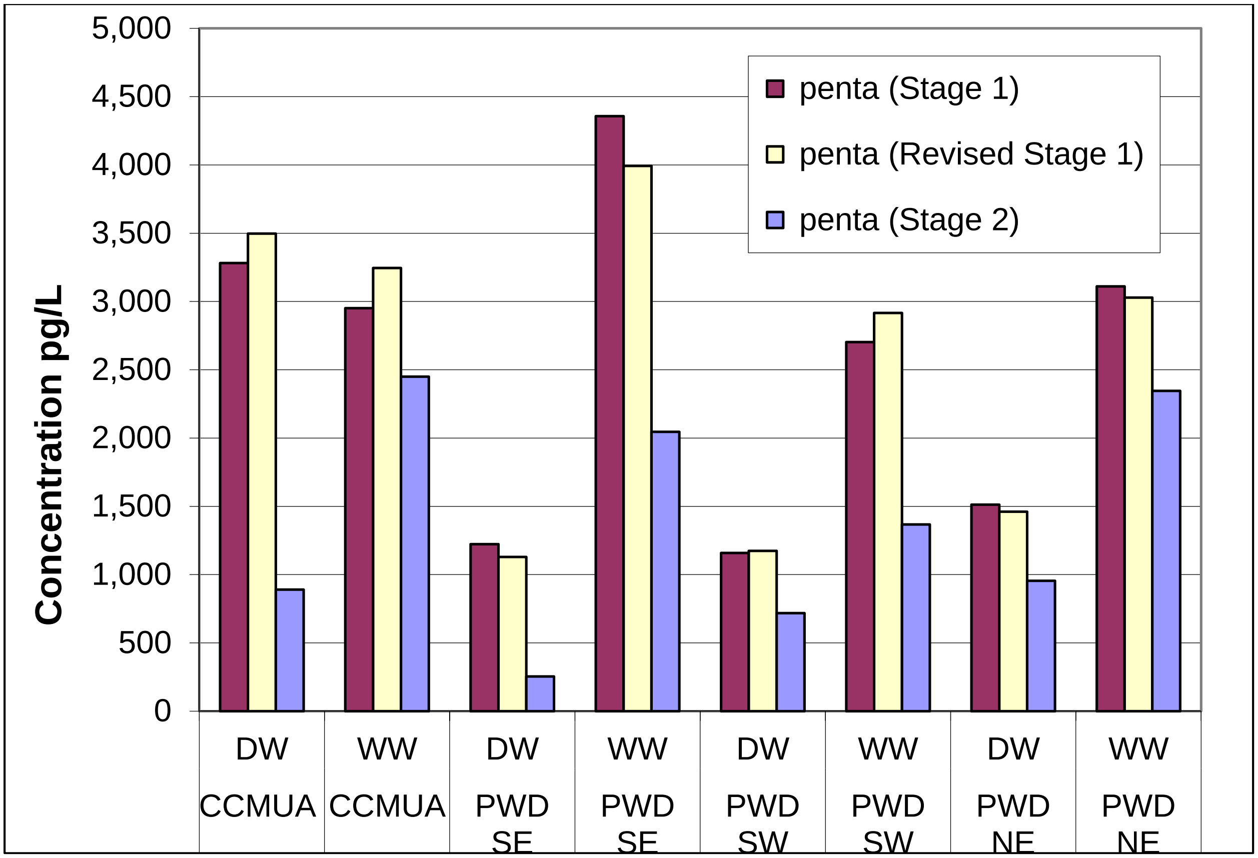


Figure 3.3.3-4: Flow diagram depicting the steps used in the estimating a revised Stage 1 PCB concentration for those dischargers which had used Method 1668, Revision A for both the Stage 1 and 2 sampling events.

Results for the penta-PCB homolog for selected dischargers utilizing the ratio approach are provided in Figure 3.3.3-5.



Note: CCMUA = Camden County Municipal Utility Authority
PWD = Philadelphia Water Department
DW = Dry weather sample, WW = wet weather sample

Figure 3.3.3-5: Results of applying the ratio approach for the penta-PCB homolog for selected dischargers.

A review of the data for dischargers who had initially utilized Method 8082A indicated that many were municipal dischargers. Therefore, in order to calculate an estimated Stage 1 PCB load for these dischargers, an evaluation of municipal dischargers that had used Method 1668A in both Stage 1 and 2 was undertaken. Seven municipal dischargers had utilized method 1668A, and ratios were developed for the tetra, penta, hexa and hepta homologs for both wet weather and dry weather events (Table 3.3.3-6). The median value of these ratios for wet and dry weather was then utilized to calculate revised Stage 1 PCB homolog concentrations for municipal dischargers that originally utilized Method 8082A.

Table 3.3.3-6: Median ratios from municipal facilities that utilized Method 1668A in both Stage 1 and 2 PCB discharge monitoring .

Median ratios of 209 congeners to 82 congeners for four PCB Homologs for wet and dry weather samples	
Homolog/weather	Median ratio
tetra DW	1.6
tetra WW	1.7
penta DW	1.6
penta WW	1.8
hexa DW	1.4
hexa WW	2.0
hepta DW	2.5
hepta WW	1.9

Using the revised PCB homolog concentrations, loads were calculated as in the Stage 1 PCB TMDL. Daily point discharge homolog-PCB loads were estimated by computing the product of daily effluent flows and outfall specific mean wet and mean or dry weather concentrations, as the sum of homolog 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.

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 method or rinsate blanks. Non-contact cooling water dischargers were not included in this analysis.

Table 3.3.3-7 presents the estimated 577 day penta-PCB load for each point discharge in the model ranked by loading in descending order. Discharge ID is a combination of the facility NPDES number and the outfall number or name.

Table 3.3.3-7: Estimated penta-PCB loading for each point source discharge for the 577 day calibration period.

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	NJ0023701-001	9.0487E-03	PA0011622-002	3.7782E-04
DE0020320-001	7.4880E-01	PA0028380-001	8.9147E-03	PA0045021-001	3.7258E-04
PA0026689-001	7.1471E-01	NJ0004235-001A	8.6842E-03	PA0012637-007	2.9499E-04
PA0026671-001	5.8881E-01	NJ0029467-001A	7.9817E-03	PA0011096-020	2.9379E-04
NJ0026182-001	4.7225E-01	NJ0005045-001	7.0556E-03	PA0013714-005	2.9365E-04
PA0026662-001	3.7951E-01	NJ0027545-001	6.9896E-03	DE0021539-001	2.8078E-04
PA0027103-001	1.7854E-01	NJ0030333-001	6.9876E-03	DE0020036-001	2.7789E-04
NJ0020923-001	1.4056E-01	NJ0021601-001	5.9230E-03	PA0013323-003	2.3286E-04
NJ0026301-001	1.2740E-01	NJ0033022-001	5.9191E-03	NJ0005584-002A	2.0318E-04
PA0013323-002	9.1370E-02	NJ0024856-001	5.8058E-03	NJ0004375-001A	1.9012E-04
NJ0005100-001	7.9901E-02	PA0013463-103	5.8024E-03	NJ0005363-017	1.6382E-04
NJ0022519-001	7.1610E-02	NJ0004278-001A	5.7937E-03	PA0013021-004A	1.5785E-04
NJ0024686-001	6.5488E-02	PA0013021-001A	5.5074E-03	PA0013323-007	1.3565E-04
NJ0023361-001	5.9494E-02	PA0051713-001	5.2291E-03	DE0050911-002	9.7221E-05
NJ0005100-662	5.9347E-02	NJ0005240-001A	4.2929E-03	NJ0064696-001A	9.0635E-05
NJ0005029-001A	5.7396E-02	NJ0005584-003A	4.0422E-03	DE0000051-004	8.8493E-05
PA0011533-015	5.7219E-02	NJ0025178-001A	3.7151E-03	PA0013323-016	8.5916E-05
DE0020001-001	4.6842E-02	NJ0020532-001	3.5158E-03	DE0050601-016	7.0783E-05
NJ0004219-001A	4.6606E-02	PA0013021-005A	3.5148E-03	PA0012637-008	6.3916E-05
PA0026701-001	4.6247E-02	PA0012769-009	3.2945E-03	PA0057690-019	5.7861E-05
PA0012629-002	4.3794E-02	NJ0004995-441C	2.8908E-03	PA0057690-021	5.7861E-05
PA0050202-001	3.9670E-02	DE0000612-001	2.8184E-03	NJ0033022-002	5.2926E-05
NJ0021598-001	3.6554E-02	NJ0024651-001A	2.5746E-03	NJ0033952-001A	5.0389E-05
PA0013463-002	3.5422E-02	NJ0005134-001A	2.3775E-03	PA0013081-029	4.9497E-05
NJ0005401-001A	3.1947E-02	DE0021555-001	2.3568E-03	NJ0005185-002A	4.4247E-05
NJ0024015-001	3.1680E-02	NJ0021610-001	2.2231E-03	NJ0004332-001B	4.0366E-05
PA0057479-DD2	2.8296E-02	PA0013463-203	2.1851E-03	PA0013714-001	3.7003E-05
PA0012637-201	2.8031E-02	NJ0005240-002A	2.0267E-03	PA0011622-001	2.5376E-05
PA0050202-101	2.3802E-02	NJ0022021-001	1.9017E-03	NJ0005363-005	2.0281E-05
PA0026468-001	2.2163E-02	PA0013021-007A	1.7158E-03	NJ0004171-005A	1.7600E-05
NJ0023507-001	2.1591E-02	DE0000647-001	1.3074E-03	PA0012637-006	1.6974E-05
DE0050962-004	2.0670E-02	DE0020001-003	1.2556E-03	PA0013323-008	1.0378E-05
NJ0021709-001	2.0138E-02	PA0012777-003	1.2548E-03	DE0050601-034	8.5629E-06
PA0026450-001	2.0040E-02	DE0050962-003	1.1549E-03	NJ0131342-001A	7.0549E-06
DE0000051-001	1.8588E-02	DE0050911-001	1.0375E-03	PA0011622-004	6.4714E-06
DE0020338-001	1.7399E-02	DE0020001-002	9.8862E-04	NJ0004286-003	6.4344E-06
PA0027294-001	1.6954E-02	NJ0004286-001A	9.7524E-04	NJ0025411-462A	6.1644E-06
PA0013323-001	1.6772E-02	NJ0035394-003A	9.3212E-04	NJ0004391-002A	4.8856E-06
NJ0024660-002	1.6630E-02	NJ0004669-001A	8.8145E-04	DE0000558-041	4.3311E-06
NJ0024007-001	1.6145E-02	NJ0004219-007	8.2656E-04	NJ0005401-003A	3.7411E-06
NJ0024678-001	1.5170E-02	PA0043818-001	6.8206E-04	NJ0005363-006	3.5698E-06
NJ0024023-001	1.3390E-02	NJ0005622-489	5.6779E-04	PA0057690-047	2.7909E-06
PA0057690-012	1.3045E-02	NJ0005002-WTPA	5.3604E-04	DE0050601-033	2.6184E-06
NJ0024449-001	1.1099E-02	NJ0025411-461C	5.2767E-04	NJ0005100-011	2.1883E-06
NJ0027481-001	1.0899E-02	NJ0005185-001A	4.8469E-04	PA0012777-007	1.6461E-06
PA0057479-DD3	1.0296E-02	NJ0005266-002A	4.6582E-04	DE0050466-001	3.6509E-07
PA0012777-001	9.2169E-03	NJ0004391-003A	4.2689E-04	NJ0004332-002A	9.0978E-09

3.3.3.5 Municipal Separate Stormwater Sewer Systems (MS4s)

Municipal Separate Storm Sewer Systems (MS4s) are a conveyance or system of conveyances that is owned by a state, city, town, village, or other public entity that discharges to waters of the U.S.; designed or used to collect or convey stormwater (including storm drains, pipes, ditches, etc.); not a combined sewer; and not part of a Publicly Owned Treatment Works (sewage treatment plant). Polluted stormwater runoff is commonly transported through MS4s, from which it is often discharged untreated into local water bodies. To prevent harmful pollutants from being washed or dumped into an MS4, operators are required to obtain a NPDES permit coverage for their stormwater discharges and develop a stormwater management program.

A November 22, 2002 EPA Memorandum entitled, "Establishing Total Maximum Daily Load (TMDL) Wasteload Allocations (WLAs) for Stormwater Source and NPDES Permit Requirements Based on Those WLAs" clarified existing regulatory requirements for municipal separate storm sewer systems (MS4s) connected with TMDLs, i.e. that where a TMDL has been developed, the MS4 community must receive a WLA rather than a LA. EPA's regulations require NPDES-regulated stormwater discharges to be addressed by the WLA component of a TMDL.

MS4s are located on the land use of urban. In order to estimate the portion of the PCB load that corresponds to separate storm sewer systems (MS4), we considered the area within each zone, downstream of the tributary monitoring locations. In order to be consistent with the WLAs, we only considered MS4's likely to discharge to the mainstem Delaware or tidal portions of tributaries. Since delineated MS4 service areas have not been identified for many communities, we assumed that approximately 90% of areas categorized as High Intensity Residential area, and 70% of areas categorized as either Low Intensity Residential or Commercial / Industrial / Transportation are served by MS4 systems. We assumed that the entire PCB load associated with MS4s would correspond to the Non-Point Source Runoff category previously defined.

In order to determine what portion of runoff volume corresponds to MS4 service areas, we used SCS curve number method to calculate the MS4 stormwater load. We computed both MS4 and non-MS4 runoff volumes for the 19 month continuous simulation period using the methodologies contained in Urban Hydrology for Small Watersheds, Technical Release 55, Soil Conservation Service (currently, Natural Resources Conservation Service), June 1986. Table 3.3.3-7 below shows the computation of the composite Curve Number (CN) for both the MS4 and non-MS4 areas by zone. Land use categories corresponding to wetlands and open water were not included in the calculation of composite CNs. Using the composite CNs for MS4 and daily 24-hour precipitation totals, we computed daily runoff volumes. The daily 24-hour precipitation totals are daily means of the recorded totals from the Wilmington, Philadelphia, and Neshaminy precipitation gages. We summed the total runoff depth for the 19-month continuous simulation period and multiplied by the area to compute a total runoff volume from MS4 service areas.

The current PCB loads from MS4s for each homolog by Zone were calculated using the runoff volume as shown in Table 3.3.3-7 and Event Mean Concentration (EMC) defined for each homolog (Figure 3.3.3-6). These EMC values were generated based on available sampling data. The MS4 EMC values for tetra-, penta-, hexa- and hepta- PCBs were respectively 4306, 6790, 10457, 5634 pg/L.

Table 3.3.3-7: MS4 Areas, Calculated Composite Curve Numbers and PCB loads for by each Zone.

	Zone 2	Zone 3	Zone 4	Zone 5	Zone6
Curve Number	84.7	88.1	85.9	85.6	84.9
MS4 Area (acre)	42,658	25,493	38,756	26,111	32,830
Flow (million gallon)	3,805	3,698	4,073	2,552	2,687
Tetra (kg/year)	0.062	0.060	0.066	0.042	0.044
Penta (kg/year)	0.098	0.095	0.105	0.066	0.069
Hexa (kg/year)	0.151	0.146	0.161	0.101	0.106
Hepta (kg/year)	0.081	0.079	0.087	0.054	0.057

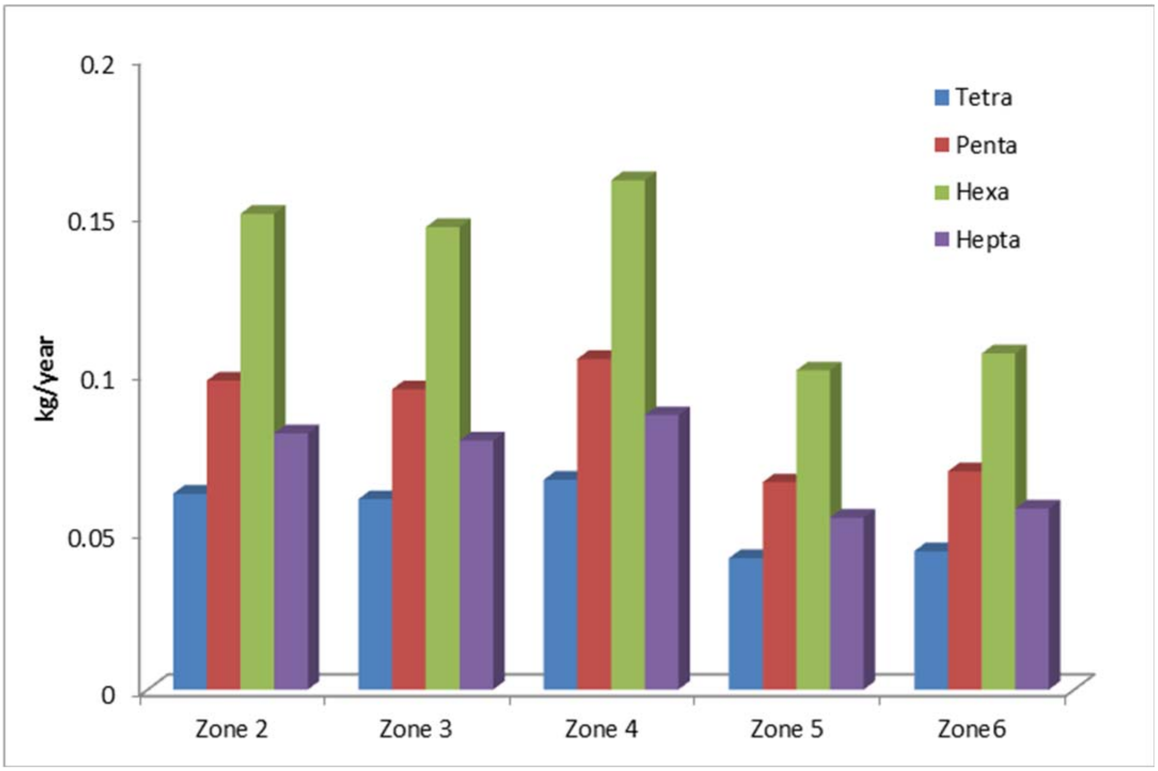


Figure 3.3.3-6: Annual MS4 PCB Loads for Four PCB Homologs (Zone 2-6)

3.3.4 Boundaries

3.3.4.1 Upstream Boundaries (Trenton and Schuylkill)

Upstream model boundaries representing the Delaware River at Trenton and the Schuylkill River at Philadelphia require a PCB concentration time series. In the Stage 1 PCB TMDLs model, we employed a simplified method that toggled between wet weather and dry weather PCB concentrations, based on samples collected during high and low flows respectively. For the current model we compared the method used in Stage 1 to 5 more refined time series development methods. The methods investigated included:

- LOADEST Model using whole water concentration;
- LOADEST Model using separate particulate and dissolved PCB concentrations;
- LOADEST Model using particulate concentration and the geometric mean of dissolved concentration;
- HQI Method (described in more detail below);
- Turbidity based method (described briefly below); and
- Stage 1 method (described in detail at http://www.state.nj.us/drbc/TMDL/RevisedModelCalibrationReport090506.pdf)

Upon careful review, we found that the HQI Method most accurately reproduced observations during the calibration period over the full range of flows, as shown below in Figure 3.3.4-1. Therefore, the HQI Method was utilized to develop PCB and POC concentrations at the upstream model boundaries at the Delaware River at Trenton and the Schuylkill River at Philadelphia.

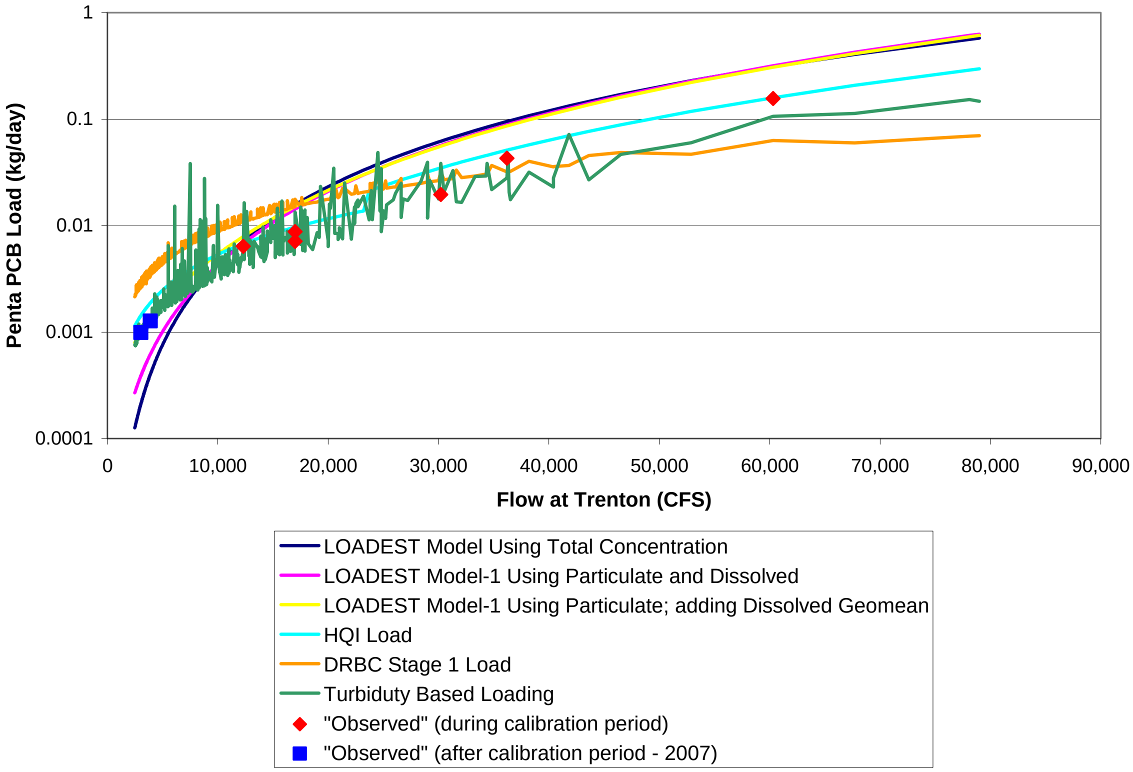


Figure 3.3.4-1 Comparison of Boundary Estimation Methods to Observations

<u>HQI Method</u>

The HQI method was developed by Hydroqual, Inc. (HQI) and presented to DRBC staff during the Loadings Subcommittee meetings in 2004. Andrew Thuman of HQI developed a specific application for the Delaware and Schuylkill Rivers. In this method, HQI developed two tiered relationships between normalized POC and normalized flow for flood and non-flood conditions, as shown in Figure 3.3.4-2 below.

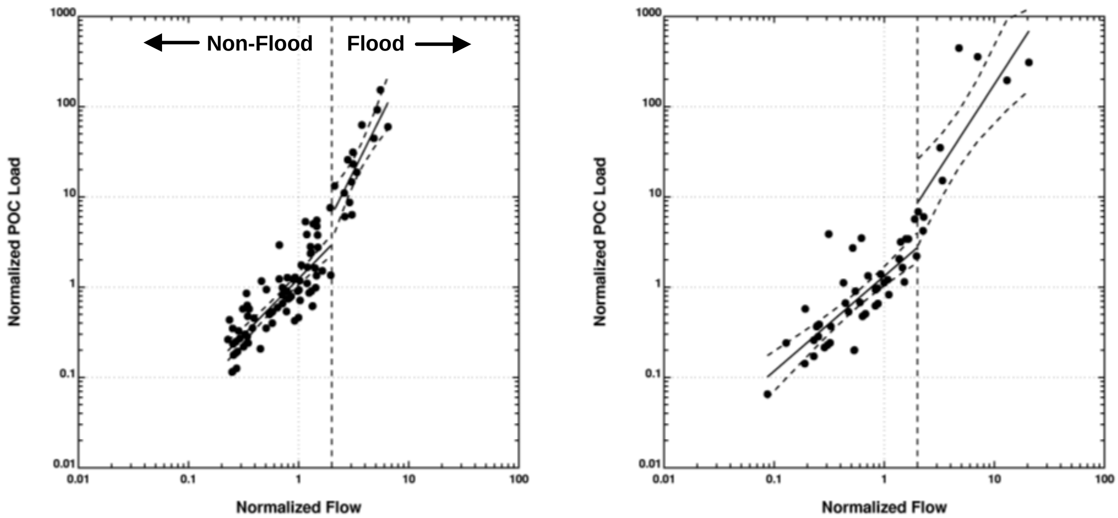
In this application a normalized daily flow rate QN is calculated from:

$$Q_N = \frac{Q_d}{Q_m}$$

where:

Qd	=	Daily flow rate
Qm	=	Long term average flow rate

Similarly, a normalized daily POC load (LN) is calculated from:



Delaware River at Trenton

Schuylkill River at Philadelphia

Figure 3.3.4-2 Normalized POC versus Normalized Flow

$$L_N = \frac{L_d}{L_m}$$

where:

L_d = Daily POC load
L_m = Long term average POC load

Paired values of Q_N and L_N are then plotted as in Figure 3.3.4-2 to define the relationship between the two for non-flood and flood tiers. This allows calculation of daily POC load from the flow time series. DRBC recomputed the median carbon normalized particulate PCBs for Tetra, Penta, Hexa, and Hepta PCBs using all the data and recomputed median dissolved PCBs using all the data. For each day in the time series, the homolog specific concentration is computed as the sum of the median dissolved PCB concentration and the

$$POC_{daily} = POC_{avg} \times 10^{\log\left(\frac{Q_{daily}}{Q_{avg}}\right)m+b}$$

where:

POC_{daily} = POC load for each day (tons/day)
POC_{avg} = Average POC load (non-flood) (tons/day)
Q_{daily} = Daily flow (CFS)
Q_{avg} = Average flow (CFS)
m = Slope of the regression line between normalized POC load and normalized flow shown in Figure 3.3.4-2. Different values of m were specified for flood versus

non-flood conditions.

b = Intercept of the regression line between normalized POC load and normalized flow shown in Figure 3.3.4-2. Different values of b were specified for flood versus non-flood conditions.

From the daily POC, we computed a daily PCB concentration for each homolog using:

$$PCB_{daily} = POC_{daily} \times \left({}^{PCB}\!/_{POC} \right) + PCB_{diss}$$

where:

PCB_{daily} = Whole water PCB load for each holomog
POC_{daily} = POC load for each day (tons/day)

$({}^{PCB}/_{POC})$ = Median of the carbon normalized particulate PCB concentration for each homolog

PCB_{diss} = Median of the dissolved PCB concentration for each homolog

Daily PCB loads were converted to daily PCB concentrations for specification of model upstream boundary conditions.

Figures 3.3.4-3 and 3.3.4-4 below show the computed time series for the four homologs at the Delaware River at Trenton and the Schuylkill River at Philadelphia.

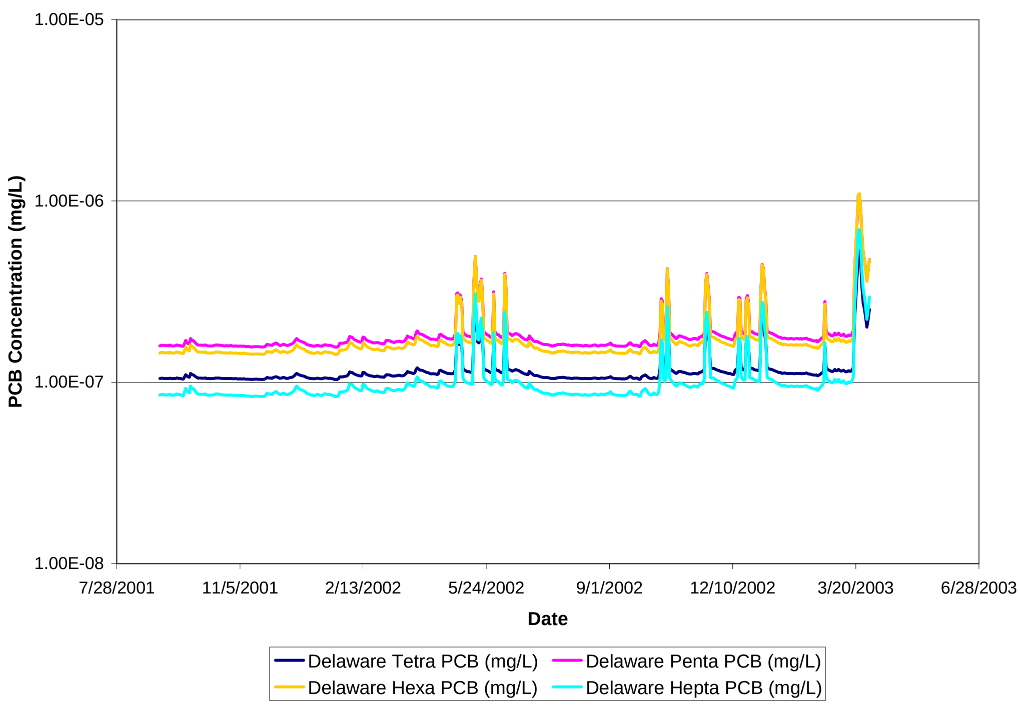


Figure 3.3.4-3 PCB Time Series, Delaware River at Trenton

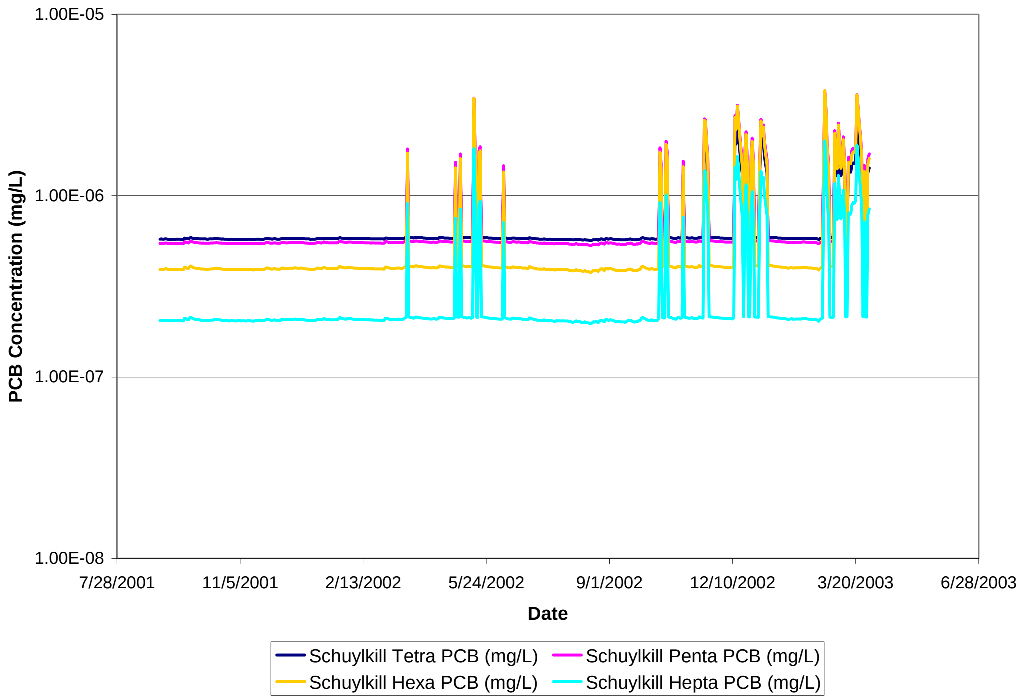


Figure 3.3.4-4 PCB Time Series, Schuylkill River at Philadelphia

Turbidity Based Method

We developed and tested, but ultimately did not select, another method for estimating PCB time series using continuous real time turbidity measurements at Trenton and Philadelphia. In employing this method, we established relationships between turbidity and total suspended solids (TSS) at each location. From the continuous turbidity measurements, turbidity-TSS relationships, and real time flow measurements, we constructed a solids loading time series. We used the solids time series and a median fraction of organic carbon (f_{oc}) to construct a particulate carbon loading time series. We multiplied the particulate carbon values by a median carbon normalized particulate PCB homolog concentrations to obtain a particulate PCB homolog loading time series. We consolidated time step loadings values (15 minutes at Trenton and 20 minutes at Philadelphia) into daily loadings and divided by daily flow to obtain particulate PCB concentrations. Upon review of the dissolved PCB data, and similar to the HQI method described above, we assigned a median dissolved PCB homolog concentration and added this to the daily particulate PCB concentration to estimate daily whole water PCB homolog concentrations.

The turbidity based method surpassed the Stage 1 TMDL method and the LOADEST methods in terms of agreement with the data. The logic of this method is also appealing, in that it uses a separate measurement, independent of flow, to estimate the solids and ultimately the PCB time series. Flow based load estimates attribute the same solids concentrations to equal flow values on the rising and falling limbs of the hydrograph. Field observation, as indicated in Figure 3.3.4-5, shows this assumption can be incorrect.

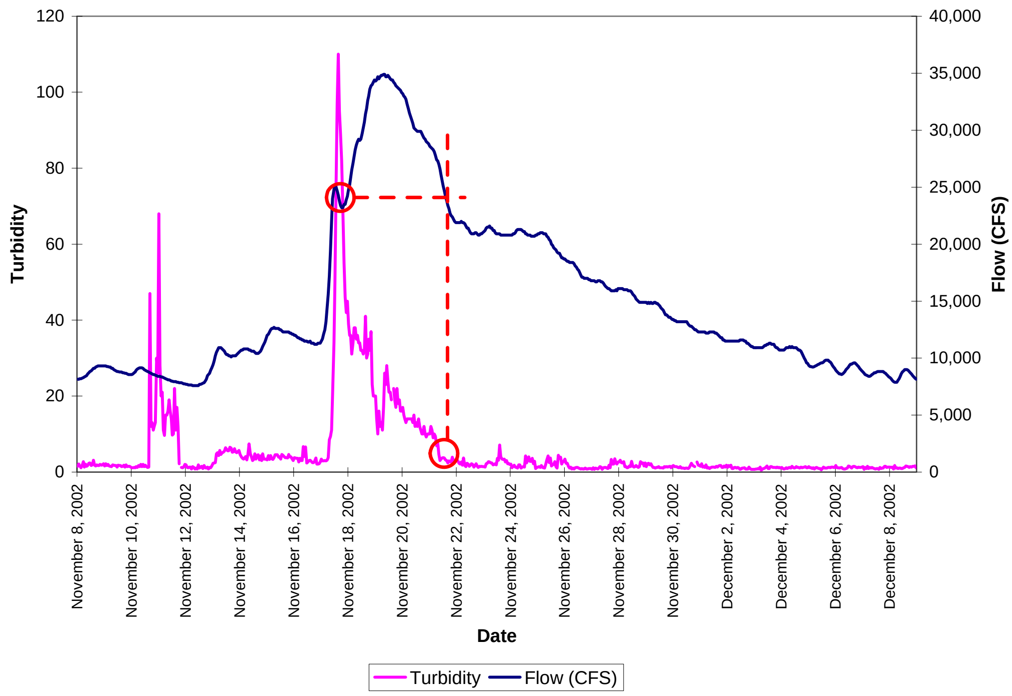


Figure 3.3.4-5 Comparison of Flow and Turbidity Time Series, Delaware River at Trenton

Ultimately, however, the HQI Method provided better agreement over the full range of flows, and was selected as the best method for estimating the PCB time series.

Carbon Time Series

Since the HQI method computes boundary carbon conditions as an intermediate step, the HQI method was used to specify the upstream model boundary carbon concentration as well.

3.3.4.2 Downstream Open Boundaries (C&D Canal and Ocean)

Data collected since the Stage 1 TMDLs in the C&D Canal and near the mouth of Delaware Bay were evaluated to:

1) update the penta-PCB concentrations to be used in the Stage 2 model simulations, and
2) establish concentrations for both of the boundaries for tetra-, hepta- and hexa-PCBs for model simulations for these homologs.

Available data for this evaluation included four samples collected in the C&D Canal, and 11 samples collected near the ocean boundary at the mouth of Delaware Bay.

C&D Canal

In the Stage 1 modeling runs, a constant penta-PCB Concentration of 902 pg/L was assigned as the boundary concentration. This concentration was based upon a single measurement in March 2003, and was consistent with PCB concentrations estimated from fish tissue data. In the revised calibration modeling runs, a constant penta-PCB Concentration of 651 pg/L was assigned as the boundary concentration based upon one additional data point (Fikslin et al, 2006). Additional water column data are currently available to update this concentration.

Samples were collected using a 10 liter Niskin bottle from the north side of the canal at Chesapeake City, MD. Samples were collected on April 1, 2003, August 20, 2003, November 13, 2003 and June 21, 2004. The results for four PCB homologs are presented in Figure 3.3.4-6 along with the results for the four homologs from the March 2003 sample. The relative proportion of each of the homologs in the samples is similar with penta- and hexa-PCBs having the highest concentrations and hepta-PCBs the lowest concentration.

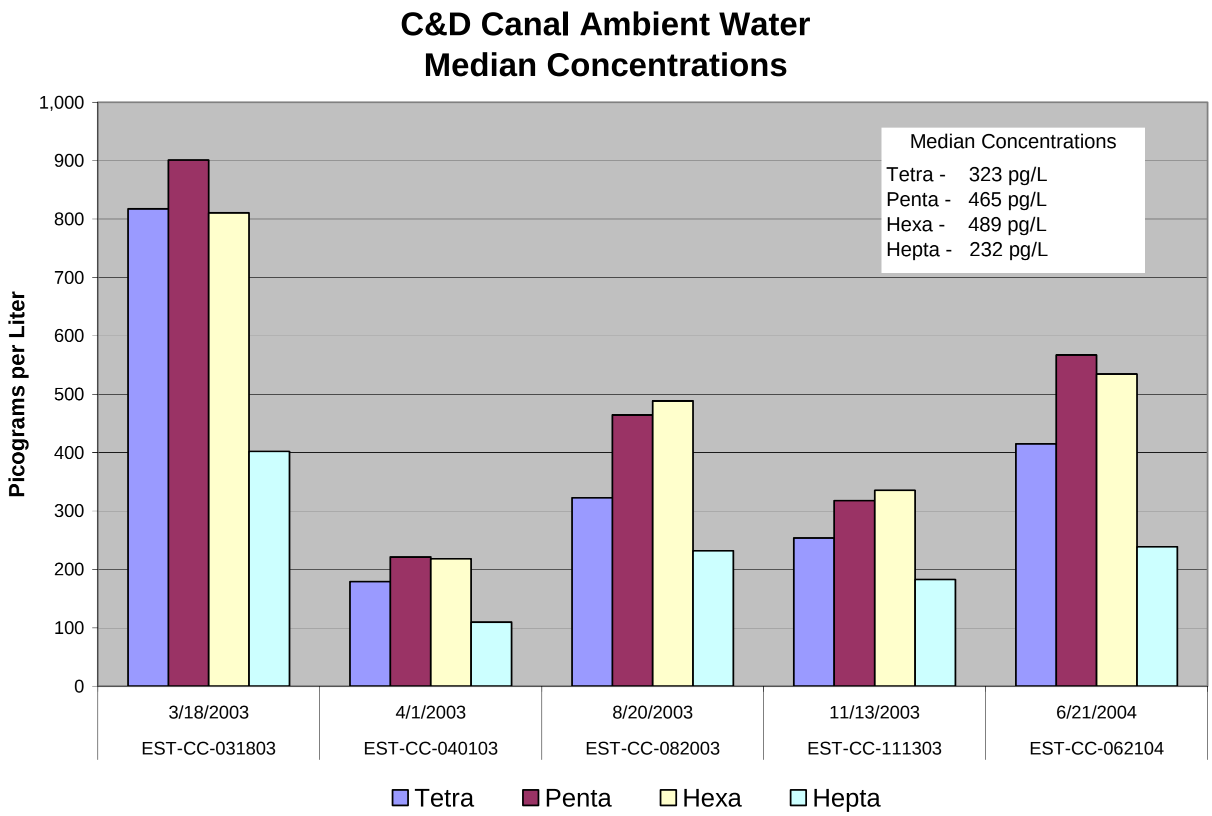


Figure 3.3.4-6: Results of ambient water samples collected in the C&D Canal at Chesapeake City, MD between March 2003 and June 2004.

Median values for each of the four homologs are presented in Table 3.3.4-1. For comparison purposes, a value of 651 pg/L was utilized in the original Stage 1 penta-PCB model. These concentrations were assigned as constant boundary concentrations in the model for the C&D Canal.

Table 3.3.4-1: Median concentrations of four different homologs in ambient water samples collected in the C&D Canal at Chesapeake City, MD between March 2003 and June 2004.

	Tetra	Penta	Hexa	Hepta
Median (pg/L)	323	465	489	232
Mean (pg/L)	398	494	477	233

<u>Ocean Boundary</u>
In the Stage 1 modeling runs, a constant penta-PCB ocean boundary concentration of 200 pg/L was specified. This value 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 in the revised model calibration (Fikslin et al, 2006). This change was consistent with observations that the model was over-predicting PCB concentrations in the lower portion of the estuary.

Eleven (11) ambient water samples were collected during four surveys at four sites in lower Delaware Bay and in coastal waters just outside of the mouth of the bay in November 2003, November 2005, June 2006 and September 2007. In the June 2006 survey, samples were collected at 0.6 of the water depth and at the surface. Little difference in both dissolved and particulate phases were observed at stations where both depths were sampled. Data from samples collected at 0.6 times the water depth were analyzed to establish a boundary conctration for each of the four homologs. This analysis is presented in Table 3.3.4-2. The median concentration for each of the four homologs were assigned as constant boundary concentrations in the respective homolog model.

The recalculated median penta-PCB value was 164 pg/L. This compares to a value of 200 pg/L used in the 2003 calibration report, and a value of 100 pg/L used in the revised calibration report.

Table 3.3.4-2: Summary of the statistical analyses of the concentrations of four PCB homologs in ambient water samples collected in the lower Delaware Bay and coastal waters near the mouth of Delaware Bay between November 2003 and September 2007.

	PCB Homologs			
	Tetra-PCB	Penta-PCB	Hexa-PCB	Hepta-PCB
Median	117	164	230	107
Mean	148	283	334	154
N	11	11	11	11
Min	56	82	74	27
25%	90	115	134	74
75%	182	296	380	185
90%	260	334	761	268
Max	318	1292	1023	499

3.3.5 Constants and Parameters

3.3.5.1 Henry's Law Constants

A required step in developing TMDLs for penta-PCBs for Zones 2 through 6 of the Delaware Estuary is to include the exchange of tetra, penta, hexa and hepta-PCBs between the gas phase in the atmosphere and these PCB homologs in the water. In the current model framework, the gas phase air concentrations are assigned, and are not dynamically simulated by the model. The Henry's Law Constant (KH) plays an important role in modeling the diffusive exchange of PCBs between gaseous and aqueous phases. Gaseous exchange in the Stage 1 PCB TMDL was limited to the penta homolog and utilized the Henry's Law Constant from six congeners. This list of congeners has been expanded to include an additional nine penta congeners and to also include congeners from the tetra, hexa and hepta homologs (Table 3.3.5-1).

In the Stage 2 PCB TMDL gaseous exchange was calculated for the most prevalent congeners in the tetra, penta, hexa and hepta homologs. Ambient data collected from 2005-2007 was used in this analysis (n=37). This data set was chosen due to the inclusion of all 209 congeners assuming that the congener patterns had not changed since 2003. Congeners were characterized by homologs for both the dissolved and particulate fractions. The relative proportion of congeners in each faction was similar and it was decided to utilize the dissolved fraction for the calculation of the gas water exchange.

Henry's Law constants were taken from Bamford et. 2000, 2002, and cross referenced to those identified in the ambient data set. In the case of coeluting congeners, for those reported in the ambient data did not have a direct match in the Bamford dataset they were linked with a coeluting congener in the Bamford data set when available.

Relative contribution from this subset of congeners was normalized to 100% and use in the calculation of gaseous exchange for the tetra, penta, hexa and hepta homologs.

Table 3.3.5-1: Percent of mass of each PCB homolog represented by Bamford congeners

Homolog	Number of Bamford Congeners	Percent of mass represented by Bamford congeners
tetra	16	95.3%
penta	15	92.8%
hexa	14	94.6%
hepta	9	81.2%

In Figures 3.3.5-1 to 3.3.5-4, there is a graphical depiction of the congeners by homolog, their percent contribution and whether they are represented in the Bamford data set.

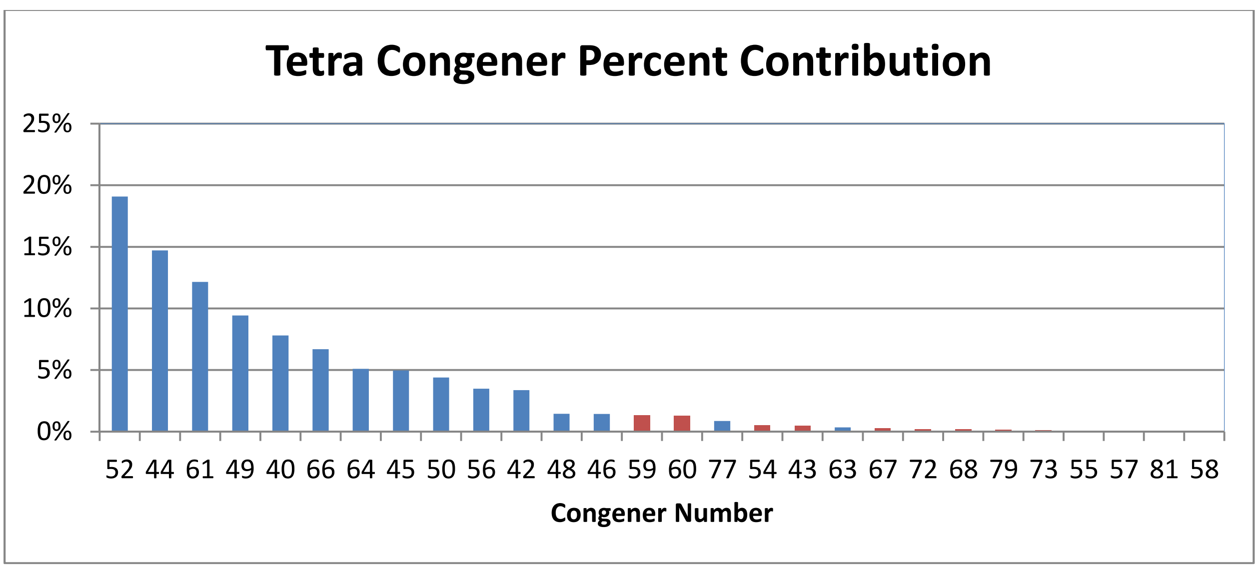


Figure 3.3.5-1: Percent contribution of congeners in the tetra-PCB homolog group. Where: indicates a Bamford congener or coelutes with a Bamford congener.

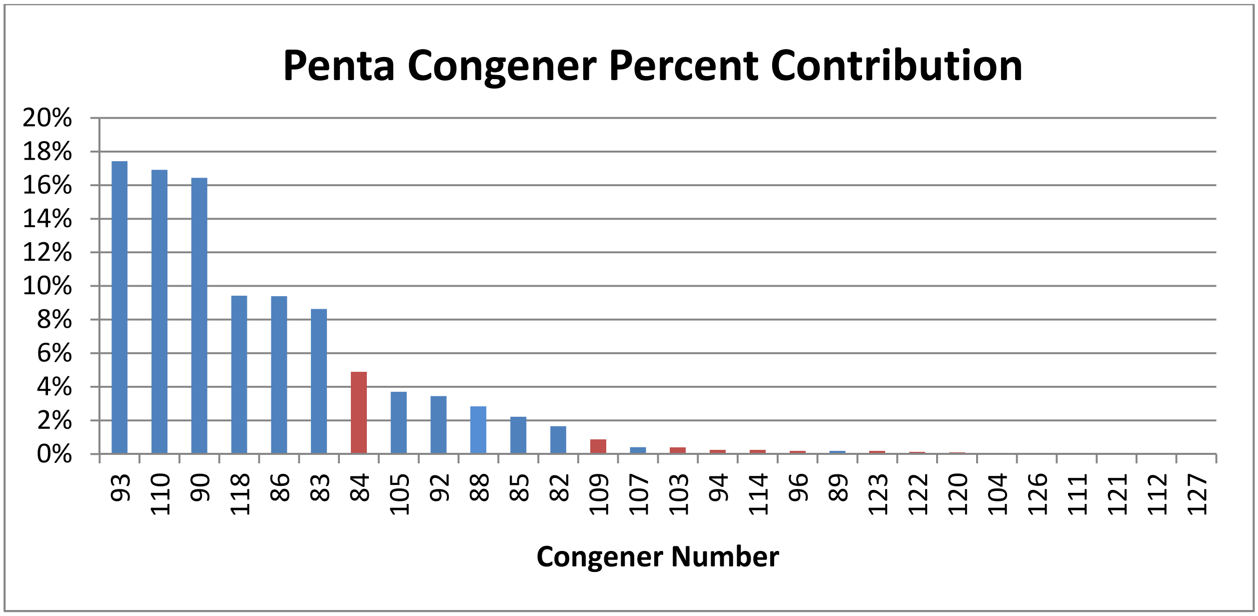


Figure 3.3.5-2: Percent contribution of congeners in the penta-PCB homolog group. Where: indicates a Bamford congener or coelutes with a Bamford congener

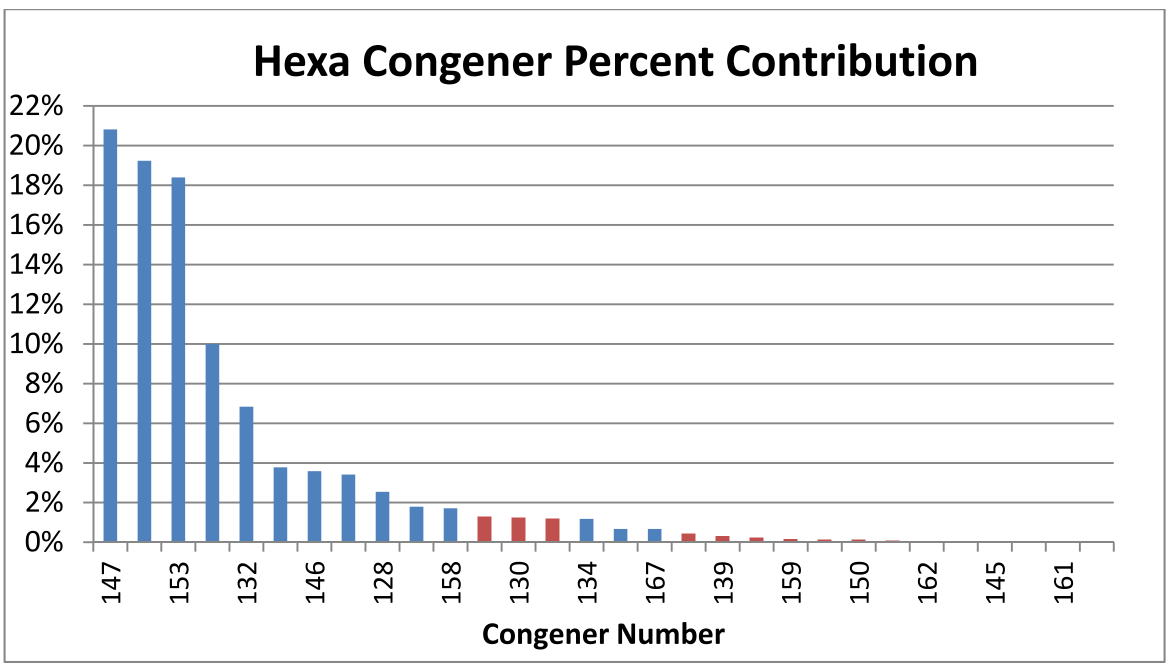


Figure 3.3.5-3: Percent contribution of congeners in the hexa-PCB homolog group. Where: indicates a Bamford congener or coelutes with a Bamford congener.

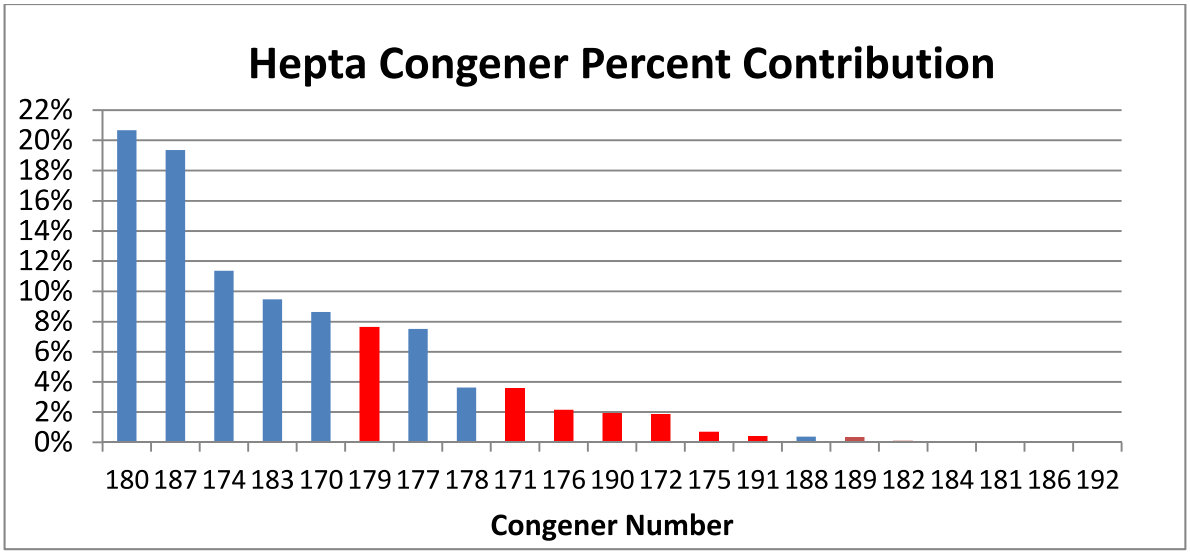


Figure 3.3.5-4: Percent contribution of congeners in the hepta-PCB homolog group. Where: indicates a Bamford congener or coelutes with a Bamford congener.

3.3.5.2 Organic Carbon-Water Partition Coefficient (K_{oc})

Organic Carbon-Water Partition Coefficient (K_{oc}) is one of the critical coefficients in modeling the hydrophobic contaminants like PCBs. In the Stage 1 modeling work (DRBC, 2003c), Octanol-Water partition coefficients (K_{ow}) for penta PCBs were obtained from the literature (Hawker and Connell, 1988) and then converted to K_{oc} using the relationship developed by Karickhoff (1981).

Hansen et al. (1999) estimated log K_{oc} for all 209 PCB congeners based on 48 experimental data points. These published log K_{oc} values were used for each homolog group. Individual congener specific log K_{oc} are weighted based on congener distribution within each of tetra, penta, hexa, and hepta homologs. There were no spatial variations based on data evaluations performed during Stage 1. Therefore, weighted log K_{oc} for each homolog were calculated and used in each homolog model. Log K_{oc} is used in the model to partition PCBs to particulate organic carbon. For partitioning to dissolved organic carbon (DOC), the model requires input for log K_{doc}. Based upon suggestions provided by the Model Expert Panel during Stage 1 model development, we used a value of 10 percent of log Koc for log K_{doc}.

Assigned organic carbon-water partition coefficients for POC and DOC are summarized in Table 3.3.5-2 and individual congener specific organic carbon-water partition coefficients and corresponding weighting factors for four homologs are summarized in Table 3.3.5-3.

Table 3.3.5-2: Stage 2 model input values for logK_{oc} and logK_{doc}

PCB Homolog group	weighted logKoc	logKdoc
tetra PCB	5.29	4.29
penta PCB	5.68	4.68
hexa PCB	6.04	5.04
hepta PCB	6.41	5.41

An assigned value for the particulate organic carbon-water partition coefficient (logK_{oc}) used in Stage 1 modeling work was 6.26 whereas, the newly derived input value using more recent information is 5.68 for penta homolog. This lower logK_{oc} in Stage 2 will yield more truly dissolved phase PCBs in water column and potentially increase the volatilization flux.

Table 3.3.5-3 : Congener specific weighting factors and $\log K_{oc}$ for the tetra- through hepta-PCB homologs.

PCB #	homolog group	weighting factor	logKoc from literature (Hansen, 1999)	weighed logKoc
40	Tetra	0.082	5.39	0.44
42	Tetra	0.035	5.31	0.19
44	Tetra	0.154	5.30	0.82
45	Tetra	0.052	5.12	0.27
46	Tetra	0.015	5.16	0.08
48	Tetra	0.015	5.23	0.08
49	Tetra	0.099	5.22	0.52
50	Tetra	0.046	5.01	0.23
52	Tetra	0.200	5.20	1.04
56	Tetra	0.037	5.47	0.20
63	Tetra	0.004	5.37	0.02
64	Tetra	0.053	5.36	0.29
66	Tetra	0.070	5.41	0.38
70	Tetra	0.127	5.40	0.69
77	Tetra	0.009	5.63	0.05
81	Tetra	0.000	5.59	0.00
82	Penta	0.018	5.86	0.10
83	Penta	0.093	5.71	0.53
85	Penta	0.024	5.78	0.14
86	Penta	0.101	5.74	0.58
89	Penta	0.002	5.63	0.01
90	Penta	0.177	5.64	1.00
91	Penta	0.031	5.55	0.17
92	Penta	0.037	5.61	0.21
93	Penta	0.188	5.51	1.03
104	Penta	0.001	5.27	0.00
105	Penta	0.040	5.83	0.23
107	Penta	0.004	5.72	0.02
110	Penta	0.182	5.81	1.06
118	Penta	0.102	5.73	0.58
126	Penta	0.000	5.95	0.00
128	Hexa	0.027	6.32	0.17
132	Hexa	0.072	6.06	0.44
134	Hexa	0.012	5.98	0.07
135	Hexa	0.106	5.90	0.62
136	Hexa	0.040	5.79	0.23
137	Hexa	0.007	6.17	0.04
138	Hexa	0.203	6.19	1.26
141	Hexa	0.036	6.12	0.22
146	Hexa	0.038	6.04	0.23
149	Hexa	0.220	5.94	1.31
153	Hexa	0.194	6.06	1.18
156	Hexa	0.019	6.10	0.12
158	Hexa	0.018	6.20	0.11
167	Hexa	0.007	6.02	0.04
170	Hepta	0.106	6.66	0.71
174	Hepta	0.140	6.39	0.90
177	Hepta	0.093	6.41	0.59
178	Hepta	0.045	6.24	0.28
180	Hepta	0.255	6.53	1.66
182	Hepta	0.002	6.28	0.01
183	Hepta	0.117	6.30	0.73
187	Hepta	0.239	6.28	1.50
188	Hepta	0.005	6.02	0.03

4 Results

4.1 Model Calibration

The general approach used to calibrate the updated DELPCB model for the four homologs involved the specification of 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 component of the calibration 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 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. Additional data collected since March 2003 was also used to refine model inputs and for comparison to model simulations particularly where little or no data were available for previous calibration exercises.

Model performance assessments and calibration/validation usually include both graphical comparisons and statistical tests. Comparisons of simulated and observed state variables in spatial plots, bivariate plots and cumulative frequency distribution plots were 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. Mass balance component analyses were performed for all of the carbon and PCB homolog state variables to check that the models correctly tracked and conserved mass.

4.2 Summary of Short-Term Model 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. In this report, we used the calibrated DYNHYD5 model that was used in December 2003 TMDL development. Second, with an assigned PDC gross settling velocity of 1.5 meters/day in most model segments, 3.0 meters/day in two model segments near Marcus Hook, BIC gross settling velocity of 0.15 meters/day and assigned decay rates for BIC in the water column and for PDC in both water column and sediment, we then adjust the resuspension rates iteratively for each model segment from Zone 2 through 6 to match the dredging volumes reported by the U.S. Army Corps of Engineers (COE). Figure 2.2.4-2 compares the PDC mass buried per year in each model segment to the PDC mass burial rate from the COE data.

For the PCB calibration, we specify partition coefficients of PCB to the organic carbons BIC and PDC, Henry's Law constant for air water exchange, and assume no PCB decay. Table 4.2-1 lists the input parameters and coefficients for all of the PCB water quality model including the homolog-specific parameters K_{oc}, K_{doc} and molecular weight.

No further adjustment of the coefficients in any of the PCB water quality models was performed.

Table 4.2-1: Input Parameters and Values for the PCB Water Quality Model

Parameter	Description	Homolog	Value	Unit	Source
Vsbic	BIC Settling Velocity		0.15	m/day	Calibration
Vspdc	PDC Settling Velocity		1.5	m/day	Calibration
Vrpdc	PDC Resuspension Velocity		0-9.46	cm/yr	Calibration
m2	Sediment Solids		70,000-120,000	mg/L	Site specific data
PDCs	PCD Concentration - Sediment		8,000-22,000	mg/L	Site specific data
Kdbicw	BIC Decay rate		0.2	1/day	Calibration
Kdpdcw	PDC Decay rate		0.05	1/day	Calibration
Kdpdcs	PCD Decay rate - Sediment		0.00026	1/day	Estimated from site specific SOD measurements
DOCw	Dissoved organic carbon - water column		4-9	mg/L	Site specific data
DOCs	Dissoved organic carbon - sediment		10	mg/L	Literature
Koc	Partition Coefficient - organic carbon	tetra	5.29	logL/kg	Literature
		penta	5.68	logL/kg	Literature
		hexa	6.04	logL/kg	Literature
		hepta	6.41	logL/kg	Literature
Kdoc	Partition Coefficient - DOC	tetra	4.29	logL/kg	Estimated as 10% Koc
		penta	4.68	logL/kg	Estimated as 10% Koc
		hexa	5.04	logL/kg	Estimated as 10% Koc
		hepta	5.41	logL/kg	Estimated as 10% Koc
MOLWT	molecular weight	tetra	291.99	g/mole	Literature
		penta	326.44	g/mole	Literature
		hexa	360.88	g/mole	Literature
		hepta	395.32	g/mole	Literature
EI	Longitudinal dispersion coefficient		0-250	m^2/sec	Calibration
Ev	Vertical diffusivity between sediment and water column		1.00E-08	m^2/sec	Literature
	Vertical diffusivity between surface and deep sediments		1.00E-10	m^2/sec	Assumed to be molecular diffusion rate

4.3 Short-Term Model Calibration and Validation Results

Model calibration results are presented for each state variable in the organic carbon model, BIC and PDC, and the PCB homolog water quality models. Results include spatial plots of model simulations versus observed data, bivariate plots of predicted versus observed values, cumulative frequency distribution plots comparing observed and predicted values, and mass balance tables for the 12 month cycling period.

4.3.1 Biotic Carbon or BIC

Spatial plots of observed and simulated BIC concentrations for 12 ambient surveys conducted in 2002 and 2003 are presented in Figure 4.3.1-1. Each plot includes both the simulated concentrations using the Stage 1 and Stage 2 models. The observed data is calculated from measurements of particulate organic carbon and an estimate of the percentage of the POC that is biotic carbon. Carbon to chlorophyll-a ratios of 30, 40 and 50 to 1 were used to generate the observed values.

Bivariate plots of observed and simulated BIC concentrations for 12 ambient surveys conducted in 2002 and 2003 are presented in Figure 4.3.1-2. Observed BIC values are plotted on the X-axis while simulated BIC values are plotted on the Y-axis. If the model simulation results match the observed value, then the point should fall on the line bisecting the graph. This line is represented by a slope of 1.0 and an intercept of 0.0.

The results of a mass balance analysis for BIC are presented in Table 4.3.1-1. This table presents the mass flux in kilograms (kg) for various components in both the water column and surface sediment layer for the 12 month period used in long-term model simulations. Note that positive values indicate loading or fluxes to the water column or sediment layer, while negative values indicate a loss from the water column or sediment layer.

4.3.2 Particulate Detrital Carbon or PDC

Spatial plots of observed and simulated PDC concentrations for 12 ambient surveys conducted in 2002 and 2003 are presented in Figure 4.3.2-1. Each plot includes both the simulated concentrations using the Stage 1 and Stage 2 models. The observed data is based upon measurements of particulate organic carbon from water samples following filtration through a 0.7 micron glass fiber filter.

Bivariate plots of observed and simulated PDC concentrations for 12 ambient surveys conducted in 2002 and 2003 are presented in Figure 4.3.2-2. Observed PDC values are plotted on the X-axis while simulated PDC values are plotted on the Y-axis. If the model simulation results match the observed value, then the point should fall on the line bisecting the graph. This line is represented by a slope of 1.0 and an intercept of 0.0.

The results of a mass balance analysis for PDC in the water column and sediment layers are presented in Tables 4.3.2-1 and -2. These tables present the mass flux in kilograms (kg) for various components in both the water column and the three sediment layers for the 12 month period used in long-term model simulations. Note that positive values indicate loading or fluxes to the water column or sediment layer, while negative values indicate a loss from the water column or sediment layer.

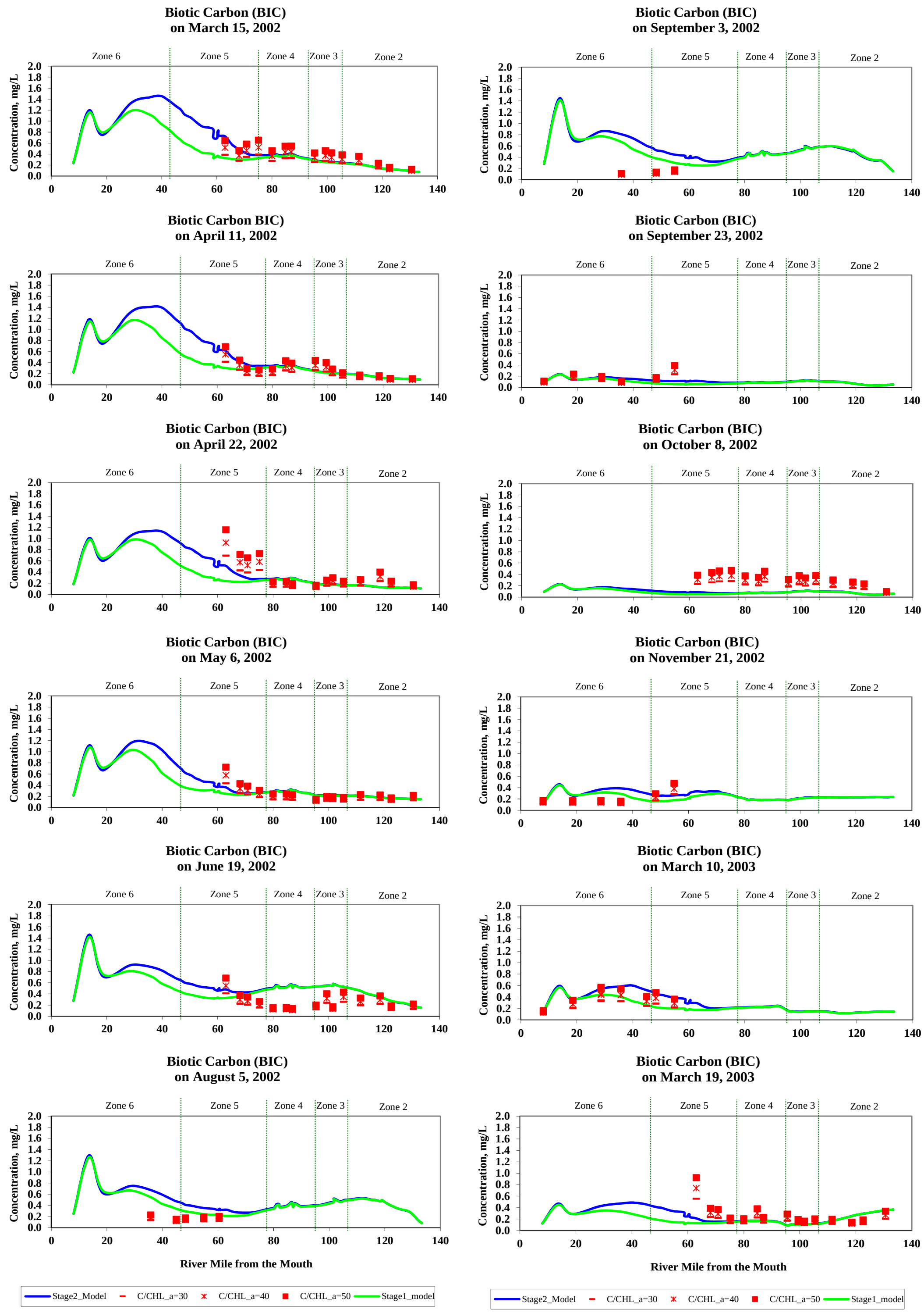


Figure 4.3.1-1: Spatial plots of biotic carbon (BIC) during 12 ambient surveys in 2002 - 2003.

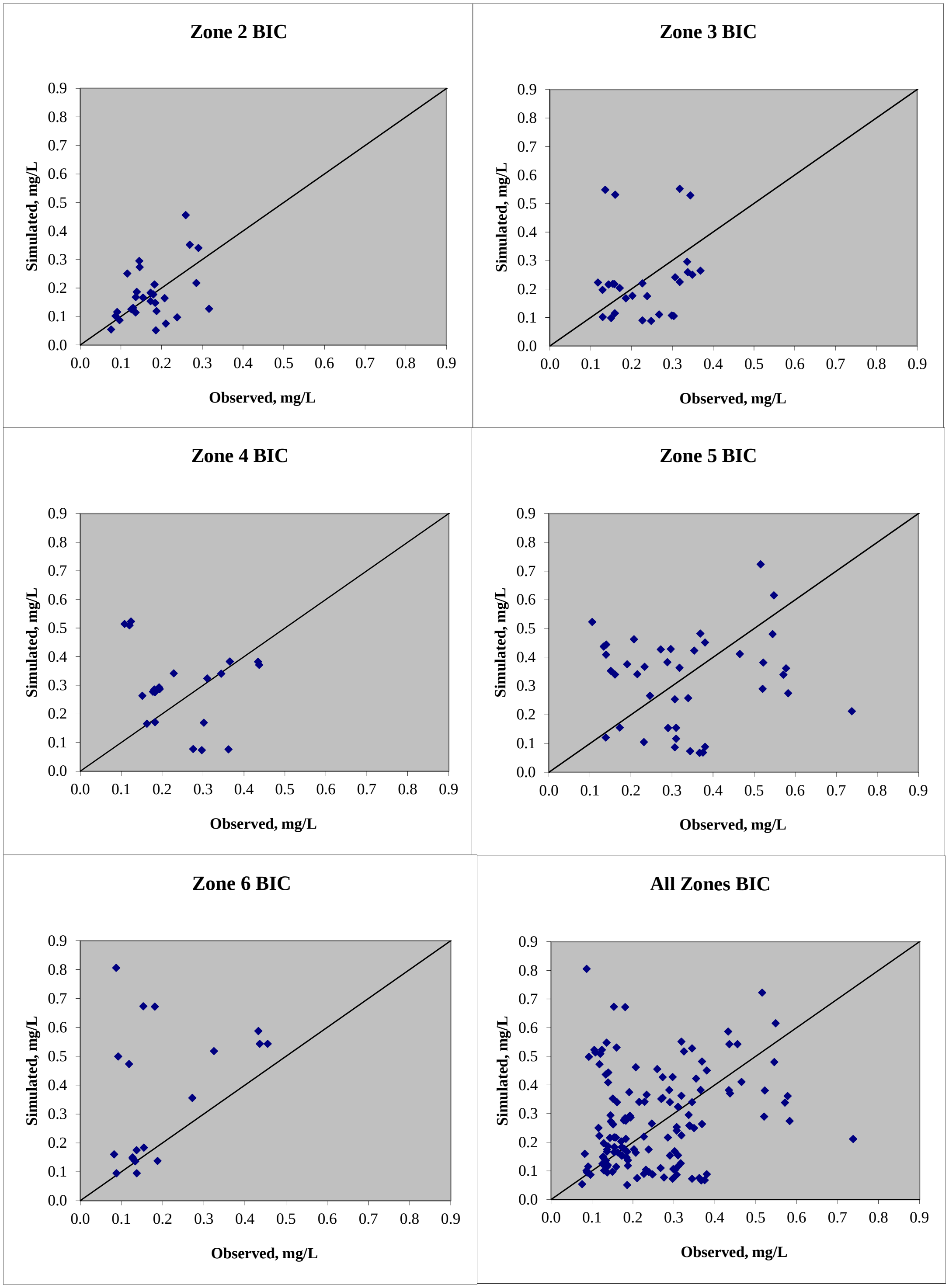


Figure 4.3.1-2: Bivariate plots for biotic carbon (BIC) during 12 ambient surveys in 2002 - 2003.

Table 4.3.1-1: BIC mass balance for water column and surface sediment layer for 12-month model cycling period.

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Water Column Mass Balance Component Analysis by Zone for Biotic Carbon, BIC (kg)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	4.093E+06	3.116E+06	5.556E+06	1.204E+07	5.148E+08	5.396E+08	2.481E+07
Dredging	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Schuykill River	----	----	1.132E+06	----	----	1.132E+06	1.132E+06
C&D Canal	----	----	----	1.103E+06	----	1.103E+06	1.103E+06
Exchange at Smaller Tributary Boundaries	0.000E+00	0.000E+00	0.000E+00	0.000E+00	----	0.000E+00	0.000E+00
Water Withdrawls (Segs 60, 66, 69)	-4.423E+04	----	----	----	----	-4.423E+04	-4.423E+04
Upstream Interface Advection	1.518E+06	2.672E+06	2.776E+06	4.141E+06	5.884E+06	1.518E+06	1.518E+06
Upstream Interface Dispersion	----	1.133E+03	2.062E+01	3.889E+04	-2.519E+06	----	----
Downstream Interface Advection	-2.672E+06	-2.776E+06	-4.141E+06	-5.884E+06	-2.102E+08	-2.102E+08	-5.884E+06
Downstream Interface Dispersion	-1.133E+03	-2.062E+01	-3.889E+04	2.519E+06	----	----	2.519E+06
Net Sediment-Water Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Net of Settling and Resuspension	-9.978E+04	-6.223E+04	-2.389E+05	-1.946E+06	-1.078E+07	-1.312E+07	-2.347E+06
Kinetics (BIC Decay)	-2.790E+06	-2.947E+06	-5.042E+06	-1.973E+07	-2.886E+08	-3.192E+08	-3.051E+07
Upstream Transport (Loss to Upstream)	----	0.000E+00	0.000E+00	0.000E+00	-7.942E+06	-7.942E+06	0.000E+00
Upstream Transport (Gain from Downstream)	0.000E+00	0.000E+00	0.000E+00	7.942E+06	----	7.942E+06	7.942E+06
Model Reported Excess Mass	**-1.012E+01**	**-4.884E+00**	**-2.867E+03**	**-6.752E+02**	**1.733E+03**	**-1.824E+03**	**-3.557E+03**
Change in Mass (ΣFluxes - Excess)	**3.649E+03**	**3.425E+03**	**6.385E+03**	**2.254E+05**	**5.634E+05**	**8.023E+05**	**2.389E+05**
Initial Mass	9.189E+03	6.095E+03	1.376E+04	1.267E+05	2.303E+06	2.459E+06	1.557E+05
Final Mass	1.284E+04	9.520E+03	2.015E+04	3.521E+05	2.866E+06	3.261E+06	3.946E+05
Change in Mass (Initial - Final)	**3.648E+03**	**3.425E+03**	**6.385E+03**	**2.254E+05**	**5.634E+05**	**8.023E+05**	**2.389E+05**
Water Column Mass Balance Closure (kg)	**-2.036E-01**	**-2.566E-01**	**6.627E-01**	**-7.135E-01**	**-8.161E-01**	**-1.327E+00**	**-5.110E-01**
Percent Tracking Error	**-0.001586%**	**-0.002696%**	**0.003289%**	**-0.000203%**	**-0.000028%**	**-0.000041%**	**-0.000129%**
Model Reported Excess Mass (kilograms)	**-10**	**-5**	**-2,867**	**-675**	**1,733**	**-1,824**	**-3,557**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-9.978E+04	-6.223E+04	-2.389E+05	-1.946E+06	-1.078E+07	-1.312E+07	-2.347E+06
Gross Resuspension (kg)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Surface Sediment Layer Mass Balance Component Analysis by Zone for Biotic Carbon, BIC (kg)

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	9.978E+04	6.223E+04	2.389E+05	1.946E+06	1.078E+07	1.312E+07	2.347E+06
Net Sediment-Water Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Net Particle Mixing	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Net Porewater Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Dredging	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Burial	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Kinetics (BIC Decay)	-9.978E+04	-6.223E+04	-2.389E+05	-1.946E+06	-1.078E+07	-1.312E+07	-2.347E+06
Model Reported Excess Mass	**1.864E-02**	**3.115E-04**	**5.246E-03**	**1.523E-01**	**-1.987E+00**	**-1.811E+00**	**1.765E-01**
Change in Mass (ΣFluxes - Excess)	**4.020E-04**	**5.653E-05**	**4.024E-04**	**-1.749E-03**	**4.498E-03**	**3.610E-03**	**-8.881E-04**
Initial Mass	3.697E-22	1.816E-22	7.377E-22	4.776E-21	1.415E-20	2.022E-20	6.065E-21
Final Mass	3.697E-22	1.816E-22	7.377E-22	4.776E-21	1.415E-20	2.022E-20	6.065E-21
Change in Mass (Initial - Final)	**-3.277E-27**	**-1.573E-27**	**-1.539E-27**	**-1.459E-26**	**3.646E-26**	**1.548E-26**	**-2.098E-26**
Surface Sediment Mass Balance Closure (kg)	**-4.020E-04**	**-5.653E-05**	**-4.024E-04**	**1.749E-03**	**-4.498E-03**	**-3.610E-03**	**8.881E-04**
Percent Tracking Error	**n/a**	**n/a**	**n/a**	**n/a**	**n/a**	**n/a**	**n/a**
Model Reported Excess Mass (kilograms)	**0**	**0**	**0**	**0**	**-2**	**-2**	**0**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-9.978E+04	-6.223E+04	-2.389E+05	-1.946E+06	-1.078E+07	-1.312E+07	-2.347E+06
Gross Resuspension (kg)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00

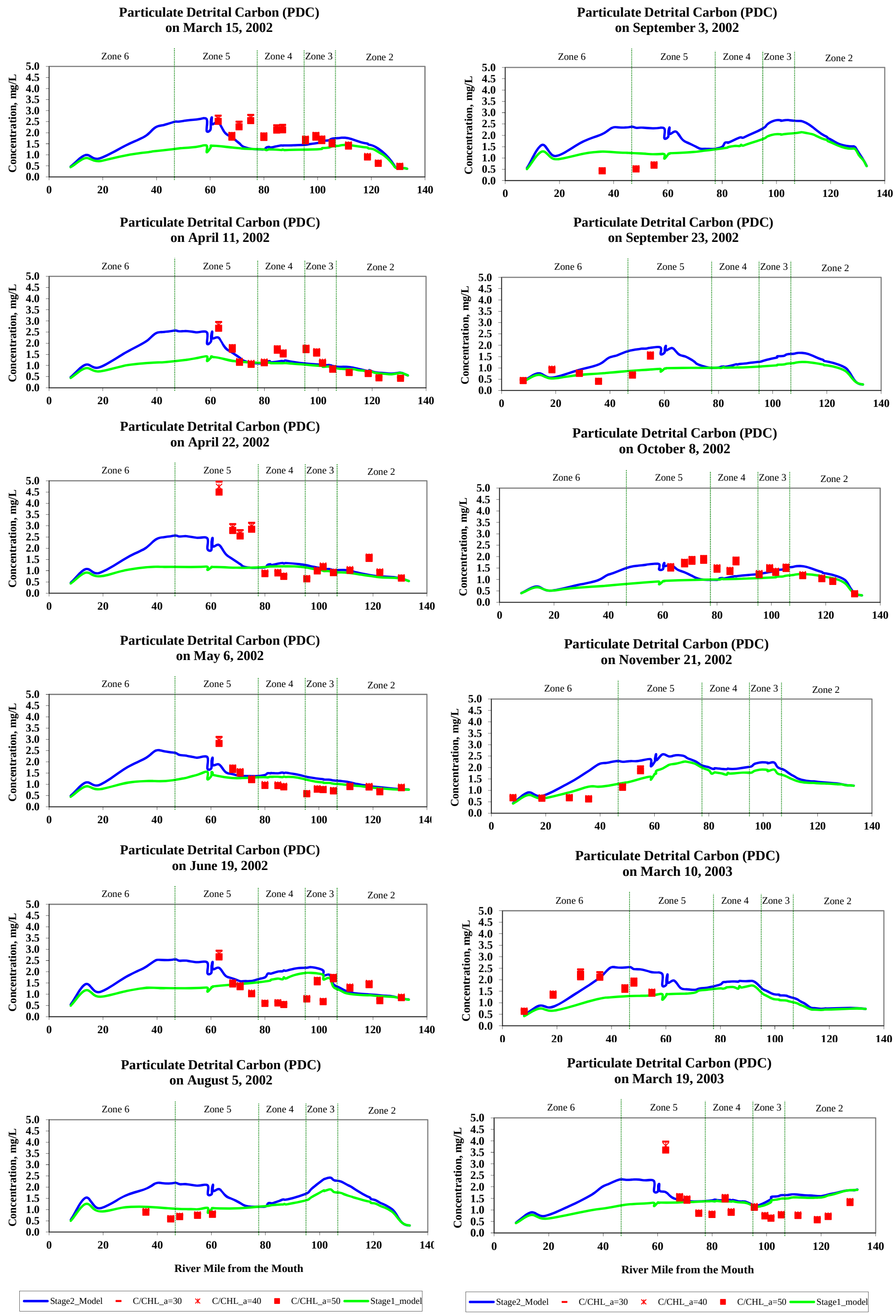


Figure 4.3.2-1: Spatial plots of particulate detrital carbon (PDC) during 12 ambient surveys in 2002 - 2003.

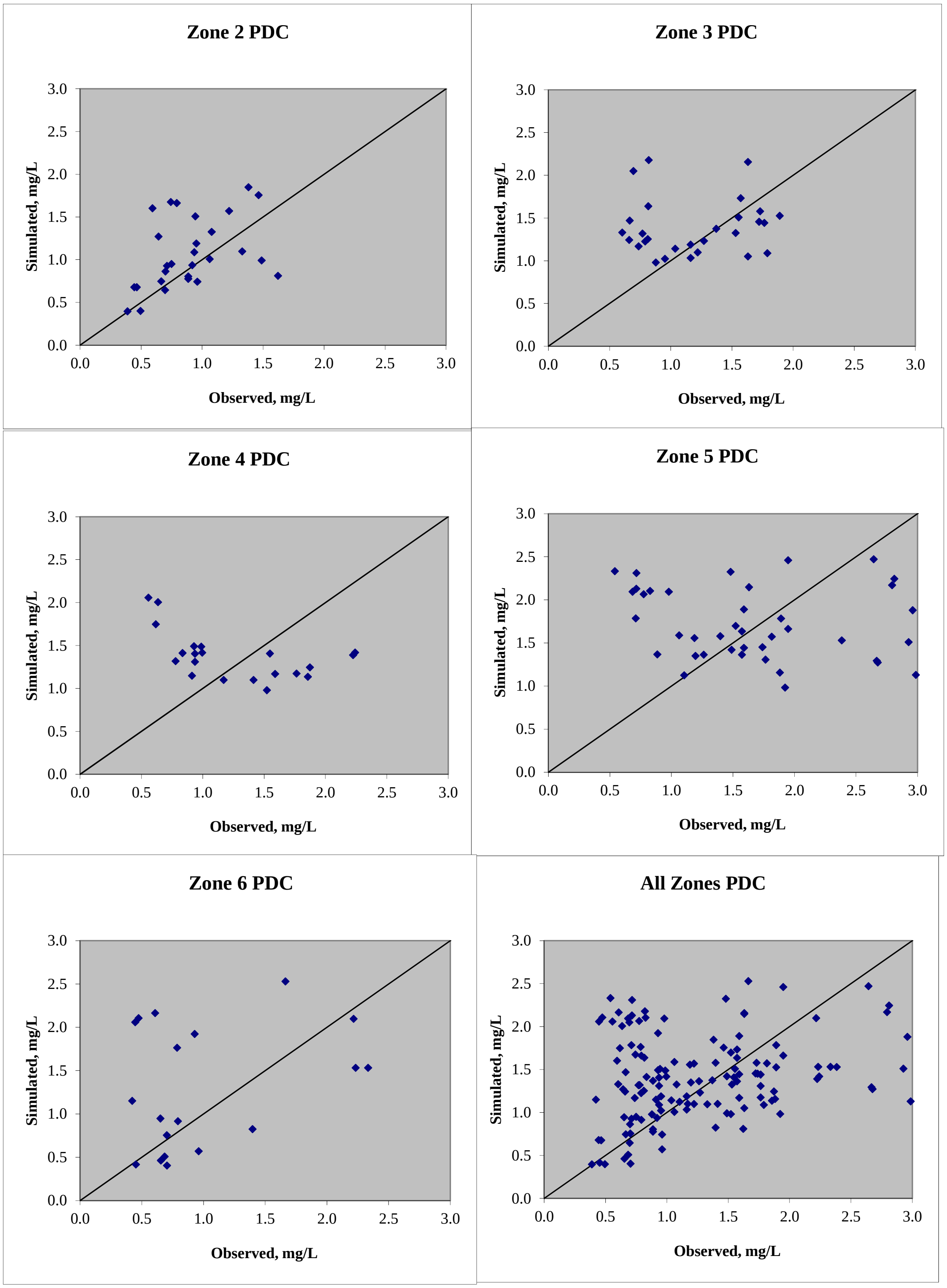


Figure 4.3.2-2: Bivariate plots for particulate detrital carbon (PDC) during 12 ambient surveys in 2002 - 2003.

Table 4.3.2-1: PDC mass balance for water column and surface sediment layer for 12-month model cycling period.

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Water Column Mass Balance Component Analysis by Zone for Particulate Detrital Carbon, PDC (kg)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	9.733E+06	5.373E+06	5.001E+06	1.216E+07	5.848E+07	9.075E+07	3.227E+07
Dredging	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Schuykill River	----	----	5.800E+06	----	----	5.800E+06	5.800E+06
C&D Canal	----	----	----	2.393E+06	----	2.393E+06	2.393E+06
Exchange at Smaller Tributary Boundaries	0.000E+00	0.000E+00	0.000E+00	0.000E+00	----	0.000E+00	0.000E+00
Water Withdrawls (Segs 60, 66, 69)	-2.312E+05	----	----	----	----	-2.312E+05	-2.312E+05
Upstream Interface Advection	7.777E+06	1.586E+07	1.926E+07	2.184E+07	3.116E+07	7.777E+06	7.777E+06
Upstream Interface Dispersion	----	-9.220E+04	8.466E+04	1.948E+05	-1.565E+06	----	----
Downstream Interface Advection	-1.586E+07	-1.926E+07	-2.184E+07	-3.116E+07	-1.760E+08	-1.760E+08	-3.116E+07
Downstream Interface Dispersion	9.220E+04	-8.466E+04	-1.948E+05	1.565E+06	----	----	1.565E+06
Net Sediment-Water Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Net of Settling and Resuspension	-1.292E+06	-9.941E+05	-7.189E+06	-3.380E+07	-2.483E+07	-6.810E+07	-4.327E+07
Kinetic (Gain from BIC Decay)	2.806E+06	2.966E+06	5.092E+06	2.050E+07	2.933E+08	3.247E+08	3.136E+07
Kinetic (Loss from PDC Decay)	-3.082E+06	-3.825E+06	-6.051E+06	-2.607E+07	-1.468E+08	-1.858E+08	-3.903E+07
Upstream Transport (Loss to Upstream)	----	0.000E+00	0.000E+00	0.000E+00	-3.304E+07	-3.304E+07	0.000E+00
Upstream Transport (Gain from Downstream)	0.000E+00	0.000E+00	0.000E+00	3.304E+07	----	3.304E+07	3.304E+07
Model Reported Excess Mass	**-7.287E+02**	**-1.247E+02**	**-5.016E+02**	**-5.519E+03**	**3.206E+03**	**-3.668E+03**	**-6.874E+03**
Change in Mass (ΣFluxes - Excess)	**-5.975E+04**	**-5.145E+04**	**-3.570E+04**	**6.605E+05**	**8.152E+05**	**1.329E+06**	**5.136E+05**
Initial Mass	1.734E+05	2.052E+05	3.262E+05	1.101E+06	5.841E+06	7.647E+06	1.806E+06
Final Mass	1.136E+05	1.537E+05	2.905E+05	1.761E+06	6.656E+06	8.976E+06	2.319E+06
Change in Mass (Initial - Final)	**-5.975E+04**	**-5.145E+04**	**-3.571E+04**	**6.605E+05**	**8.152E+05**	**1.329E+06**	**5.136E+05**
Water Column Mass Balance Closure (kg)	**-2.991E-01**	**1.222E+00**	**-6.672E+00**	**1.501E+01**	**-9.214E+00**	**4.337E-02**	**9.258E+00**
Percent Tracking Error	**-0.000263%**	**0.000795%**	**-0.002297%**	**0.000852%**	**-0.000138%**	**0.000000%**	**0.000399%**
Model Reported Excess Mass (kilograms)	**-729**	**-125**	**-502**	**-5,519**	**3,206**	**-3,668**	**-6,874**

Additional Sediment - Water Flux Information

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Gross Settling (kg)	-4.868E+06	-3.274E+06	-1.445E+07	-9.923E+07	-2.001E+08	-3.219E+08	-1.218E+08
Gross Resuspension (kg)	3.576E+06	2.280E+06	7.260E+06	6.543E+07	1.753E+08	2.538E+08	7.855E+07

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Surface Sediment Layer Mass Balance Component Analysis by Zone for Particulate Detrital Carbon, PDC (kg)

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	1.292E+06	9.941E+05	7.189E+06	3.380E+07	2.483E+07	6.810E+07	4.327E+07
Net Sediment-Water Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Net Particle Mixing	9.971E+00	-2.115E+01	6.286E+01	-3.040E+02	-5.026E+02	-7.549E+02	-2.524E+02
Net Porewater Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Dredging	-3.401E+05	-5.563E+05	-5.802E+06	-2.684E+07	-1.417E+07	-4.771E+07	-3.354E+07
Burial	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Kinetic (Gain from BIC Decay)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Kinetic (Loss from PDC Decay)	-5.084E+05	-2.180E+05	-6.734E+05	-3.588E+06	-3.267E+06	-8.255E+06	-4.988E+06
Model Reported Excess Mass	**9.120E+00**	**-1.294E+01**	**1.585E+01**	**-2.153E+01**	**-9.522E+01**	**-1.047E+02**	**-9.503E+00**
Change in Mass (ΣFluxes - Excess)	**4.438E+05**	**2.198E+05**	**7.134E+05**	**3.374E+06**	**7.390E+06**	**1.214E+07**	**4.751E+06**
Initial Mass	7.304E+06	3.354E+06	1.108E+07	6.509E+07	1.618E+08	2.487E+08	8.683E+07
Final Mass	7.748E+06	3.574E+06	1.179E+07	6.847E+07	1.692E+08	2.608E+08	9.158E+07
Change in Mass (Initial - Final)	**4.438E+05**	**2.198E+05**	**7.134E+05**	**3.374E+06**	**7.390E+06**	**1.214E+07**	**4.751E+06**
Surface Sediment Mass Balance Closure (kg)	**1.278E-02**	**2.165E-02**	**4.716E-02**	**-2.863E-01**	**-1.634E+00**	**-1.839E+00**	**-2.047E-01**
Percent Tracking Error	**0.0000002%**	**0.0000006%**	**0.0000004%**	**-0.0000004%**	**-0.0000010%**	**-0.0000007%**	**-0.0000002%**
Model Reported Excess Mass (kilograms)	**9**	**-13**	**16**	**-22**	**-95**	**-105**	**-10**

Additional Sediment - Water Flux Information

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Gross Settling (kg)	-4.868E+06	-3.274E+06	-1.445E+07	-9.923E+07	-2.001E+08	-3.219E+08	-1.218E+08
Gross Resuspension (kg)	3.576E+06	2.280E+06	7.260E+06	6.543E+07	1.753E+08	2.538E+08	7.855E+07

Table 4.3.2-2: PDC mass balance for middle and deep sediment layers for the 12-month model cycling period

.

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Middle Sediment Layer Mass Balance Component Analysis by Zone for Particulate Detrital Carbon, PDC (kg)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Middle Sediment Layer							
Net Particle Mixing	-9.971E+00	2.115E+01	-6.286E+01	3.040E+02	5.026E+02	7.549E+02	2.524E+02
Net Porewater Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Burial	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Kinetic (Loss from PDC Decay)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Model Reported Excess Mass	**-9.971E+00**	**2.115E+01**	**-6.286E+01**	**3.040E+02**	**5.026E+02**	**7.549E+02**	**2.524E+02**
Change in Mass (ΣFluxes - Excess)	**-1.400E-09**	**6.380E-10**	**-7.265E-10**	**1.597E-07**	**-9.006E-08**	**6.812E-08**	**1.582E-07**
Initial Mass	7.304E+06	3.354E+06	1.108E+07	6.509E+07	1.618E+08	2.487E+08	8.683E+07
Final Mass	7.304E+06	3.354E+06	1.108E+07	6.509E+07	1.618E+08	2.487E+08	8.683E+07
Change in Mass (Initial - Final)	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**
Surface Sediment Mass Balance Closure (kg)	**1.400E-09**	**-6.380E-10**	**7.265E-10**	**-1.597E-07**	**9.006E-08**	**-6.812E-08**	**-1.582E-07**
Percent Tracking Error	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**
Model Reported Excess Mass (kilograms)	**-10**	**21**	**-63**	**304**	**503**	**755**	**252**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-4.868E+06	-3.274E+06	-1.445E+07	-9.923E+07	-2.001E+08	-3.219E+08	-1.218E+08
Gross Resuspension (kg)	3.576E+06	2.280E+06	7.260E+06	6.543E+07	1.753E+08	2.538E+08	7.855E+07

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Deep Sediment Layer Mass Balance Component Analysis by Zone for Particulate Detrital Carbon, PDC (kg)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Deep Sediment Layer							
Net Particle Mixing	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Net Porewater Diffusion	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Burial	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Kinetic (Loss from PDC Decay)	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Model Reported Excess Mass	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**
Change in Mass (ΣFluxes - Excess)	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**
Initial Mass	4.382E+07	2.012E+07	6.647E+07	3.905E+08	9.711E+08	1.492E+09	5.209E+08
Final Mass	4.382E+07	2.012E+07	6.647E+07	3.905E+08	9.711E+08	1.492E+09	5.209E+08
Change in Mass (Initial - Final)	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**
Surface Sediment Mass Balance Closure (kg)	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**	**0.000E+00**
Percent Tracking Error	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**	**0.0000000%**
Model Reported Excess Mass (kilograms)	**0**	**0**	**0**	**0**	**0**	**0**	**0**

Additional Sediment - Water Flux Information

Gross Settling (kg)	-4.868E+06	-3.274E+06	-1.445E+07	-9.923E+07	-2.001E+08	-3.219E+08	-1.218E+08
Gross Resuspension (kg)	3.576E+06	2.280E+06	7.260E+06	6.543E+07	1.753E+08	2.538E+08	7.855E+07

4.3.3 Penta-PCBs

Spatial plots of observed and simulated penta-PCB concentrations for 12 ambient surveys conducted in 2002 and 2003 are presented in Figure 4.3.3-1 to 13. Each figure depicts the results for one of the ambient survey dates, and includes the BIC and PDC plot for that date. Each plot within the figure includes both the simulated concentrations using the Stage 1 and Stage 2 models. For PCBs, individual plots are presented for total dissolved penta-PCBs, particulate penta-PCBs, total penta-PCBs and carbon-normalized penta-PCBs (also known as R1).

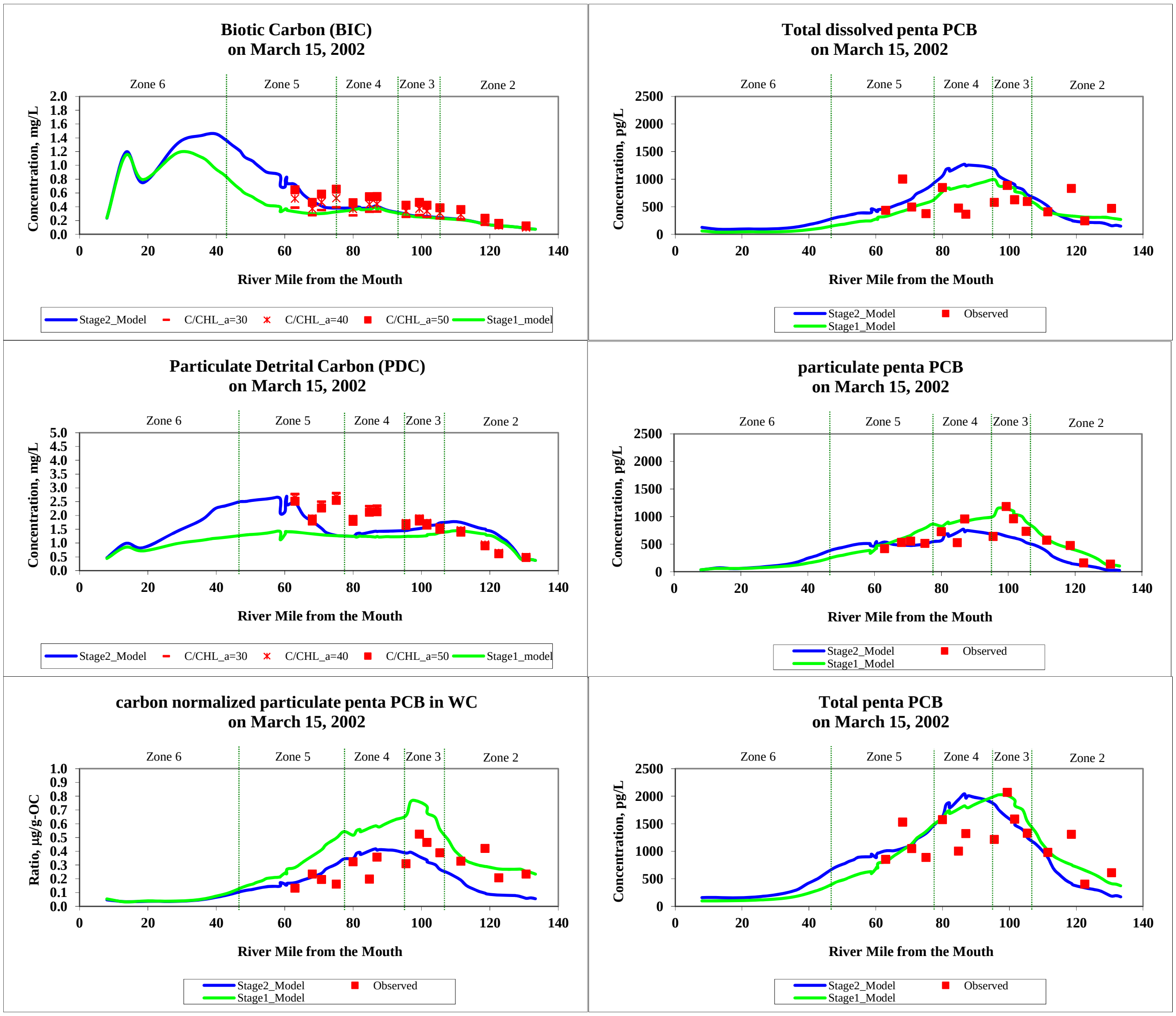


Figure 4.3.3-1: Spatial plots of BIC, PDC and various phases of penta-PCB during March 15, 2002 ambient survey.

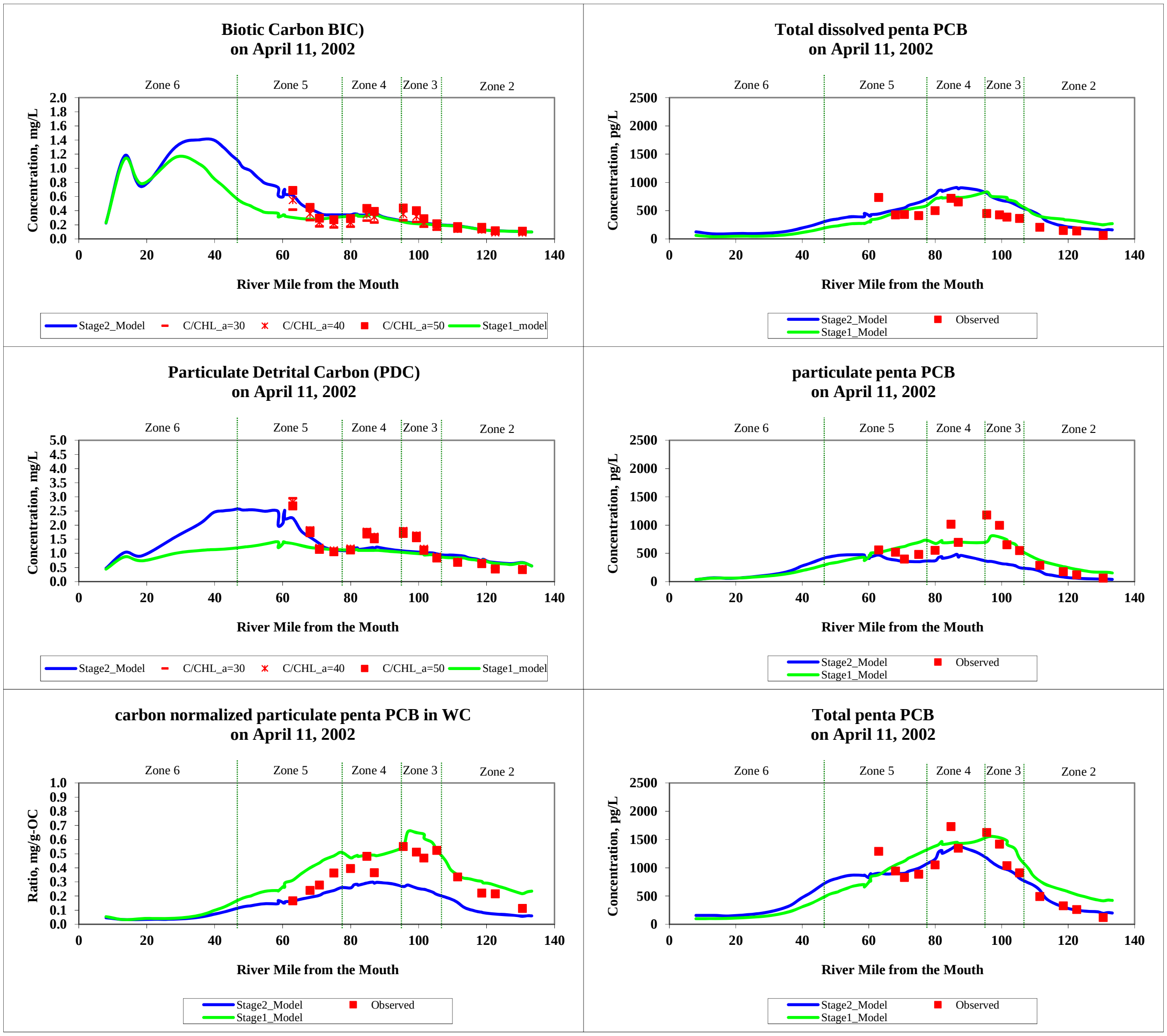


Figure 4.3.3-2: Spatial plots of BIC, PDC and various phases of penta-PCB during April 11, 2002 ambient survey.

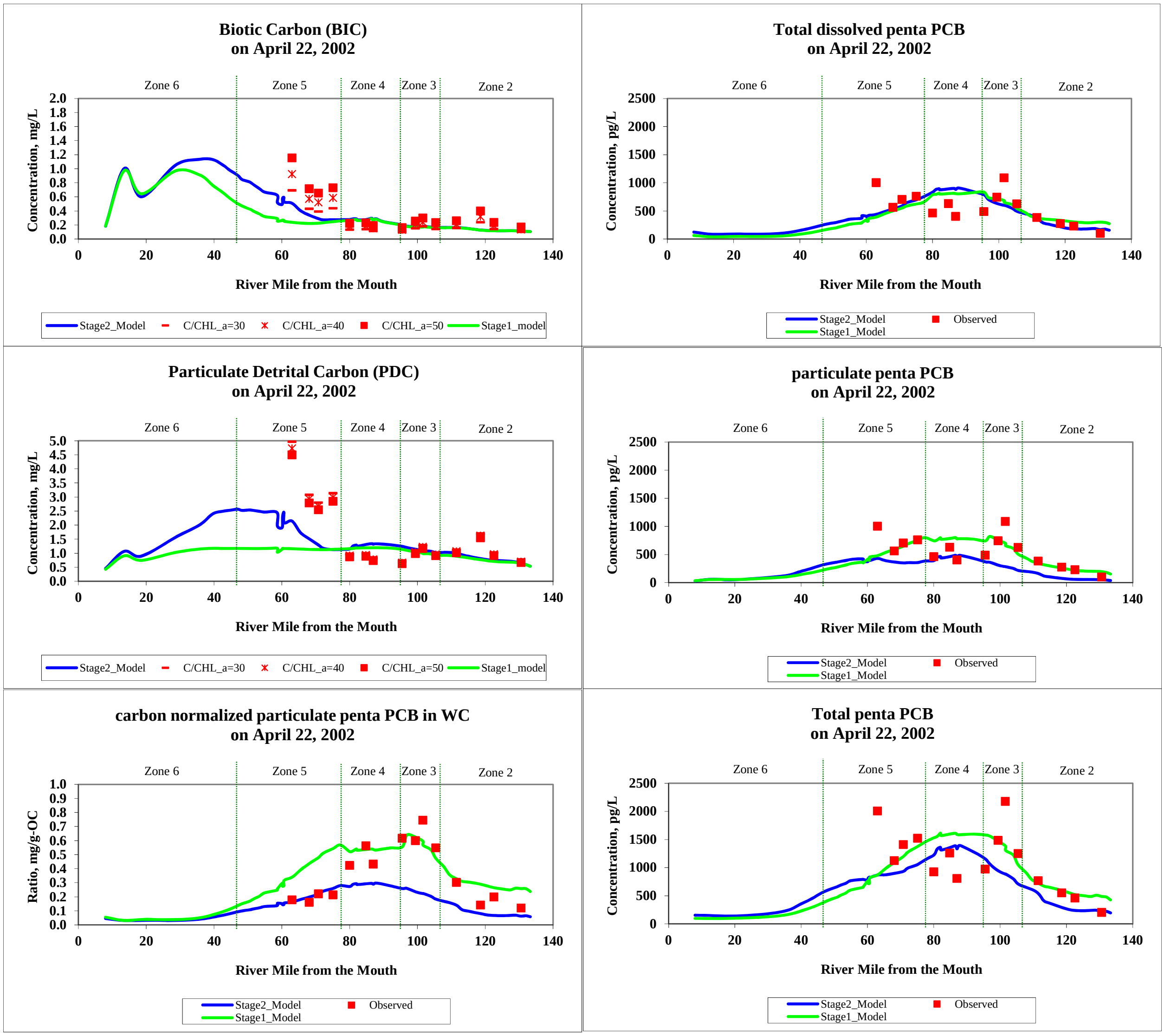


Figure 4.3.3-3: Spatial plots of BIC, PDC and various phases of penta-PCB during April 22, 2002 ambient survey.

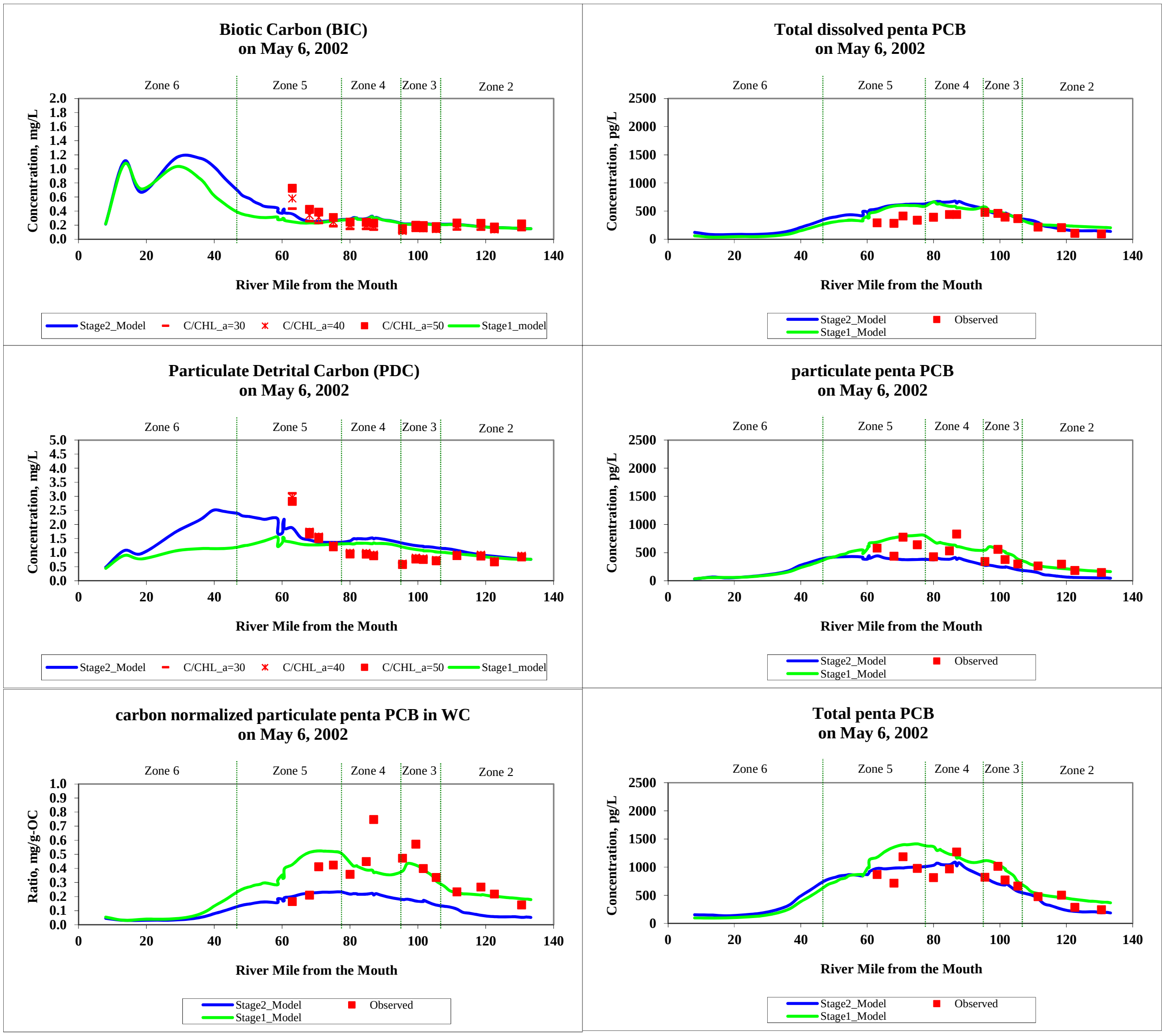


Figure 4.3.3-4: Spatial plots of BIC, PDC and various phases of penta-PCB during May 6, 2002 ambient survey.

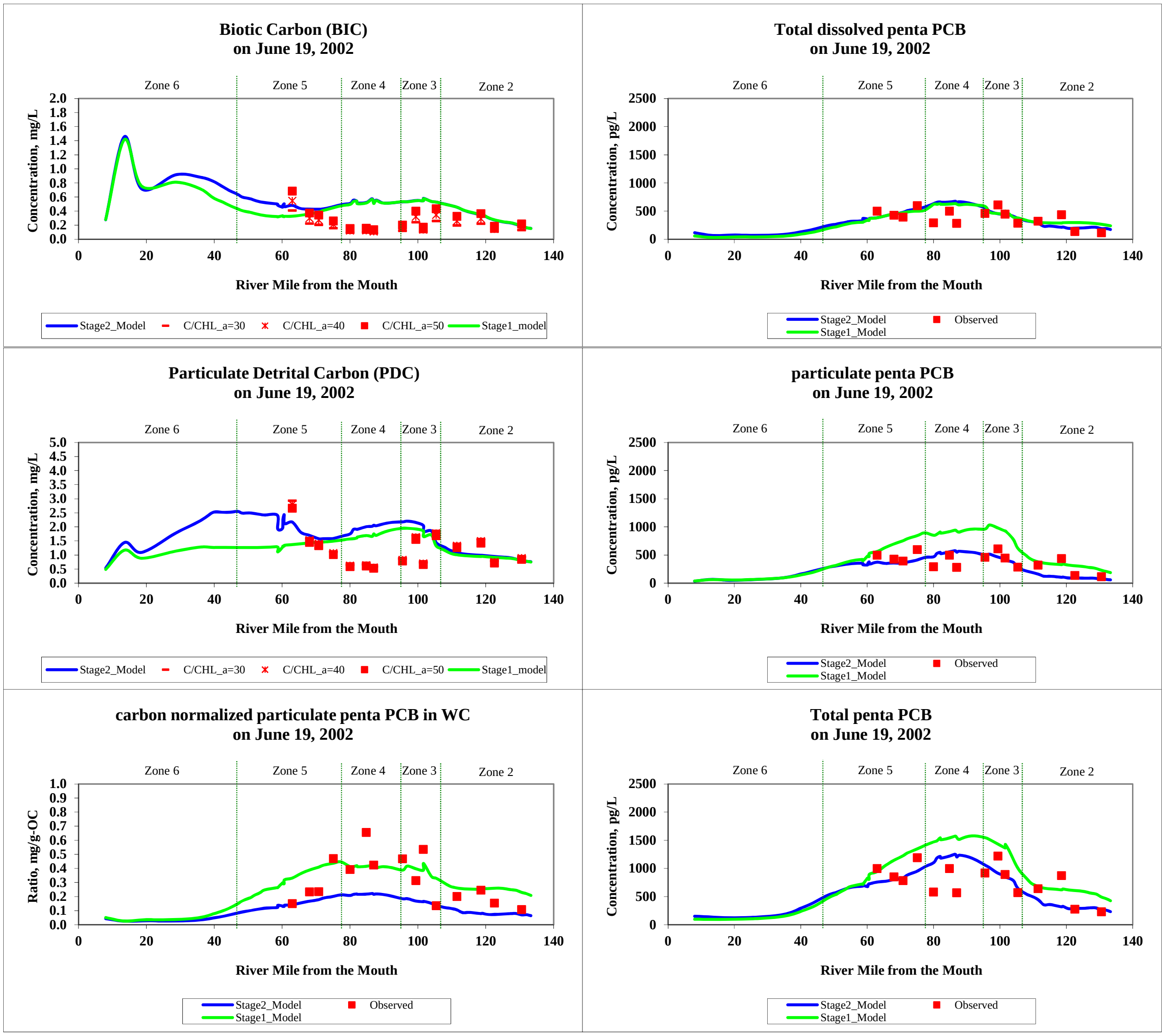


Figure 4.3.3-5: Spatial plots of BIC, PDC and various phases of penta-PCB during June 19, 2002 ambient survey.

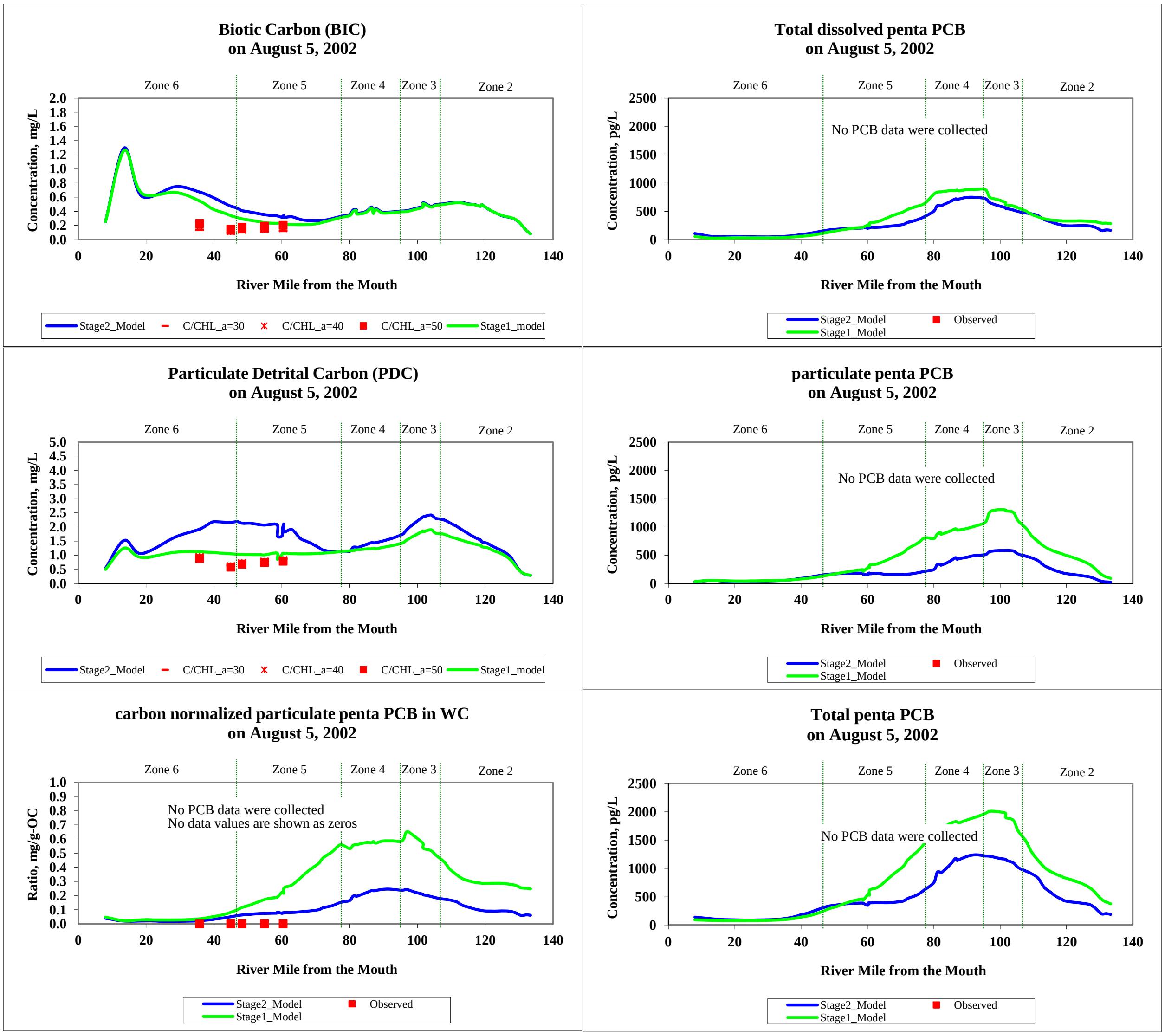


Figure 4.3.3-6: Spatial plots of BIC, PDC and various phases of penta-PCB during August 5, 2002 ambient survey.

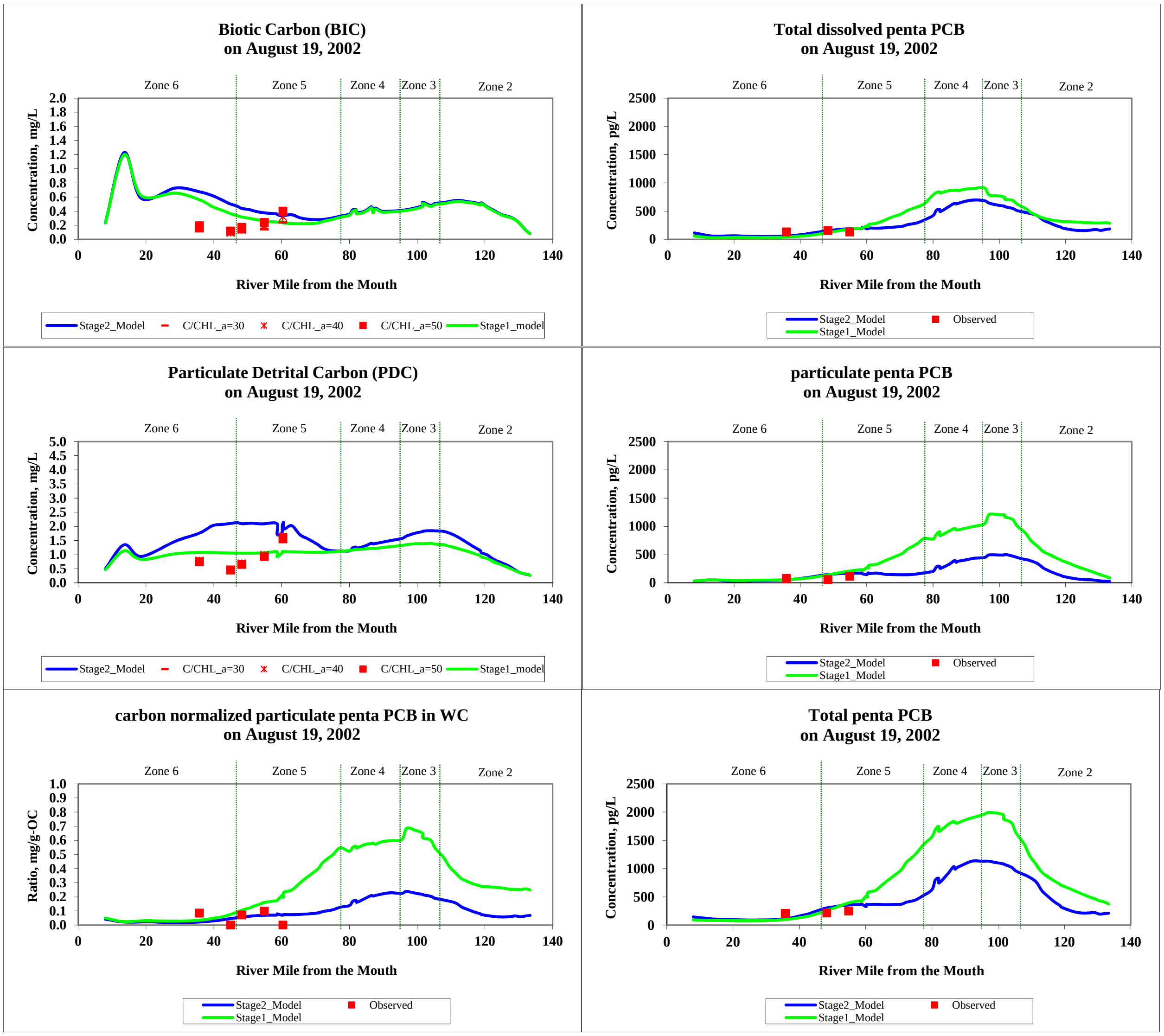


Figure 4.3.3-7: Spatial plots of BIC, PDC and various phases of penta-PCB during August 19, 2002 ambient survey.

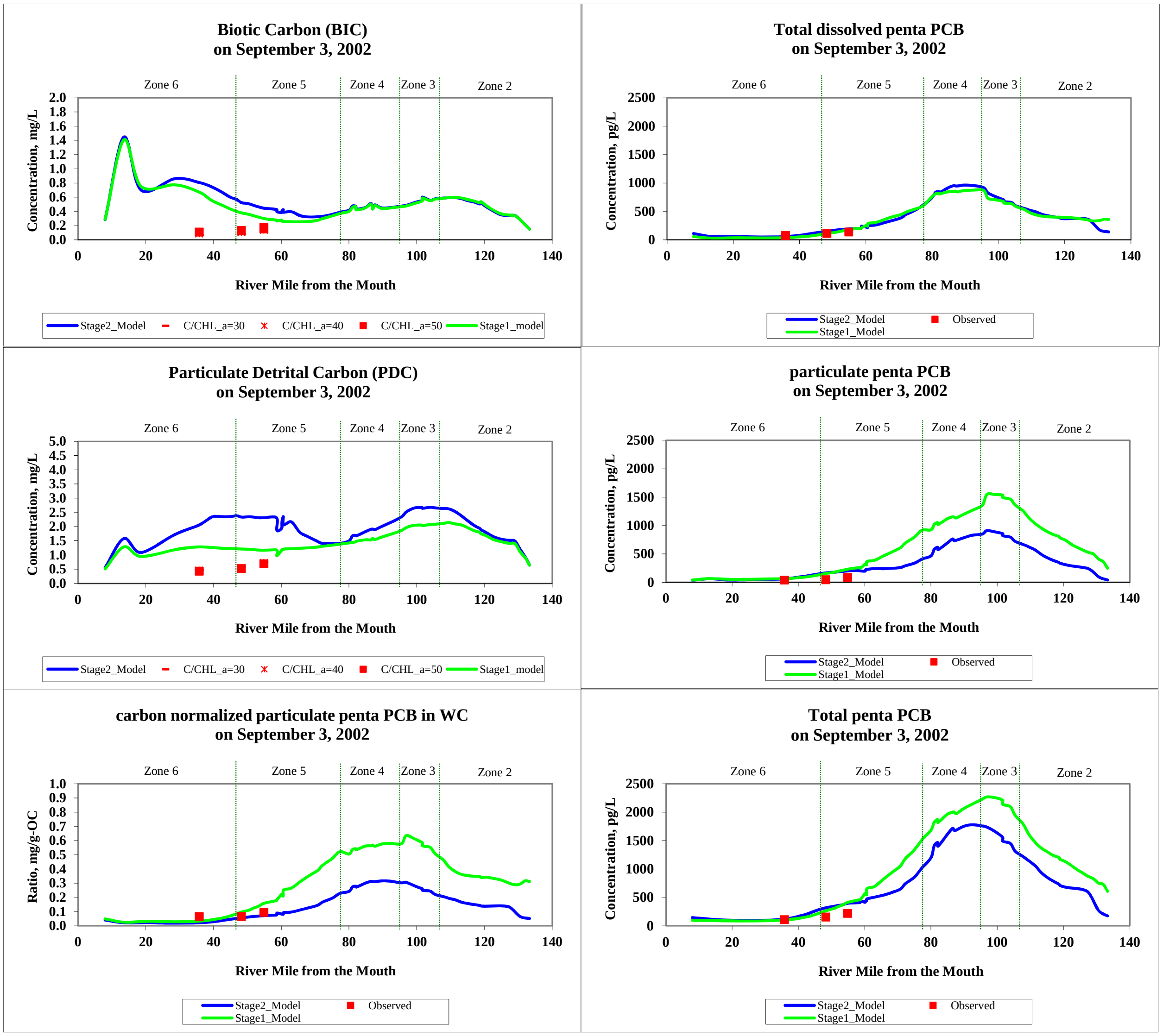


Figure 4.3.3-8: Spatial plots of BIC, PDC and various phases of penta-PCB during September 3, 2002 ambient survey.

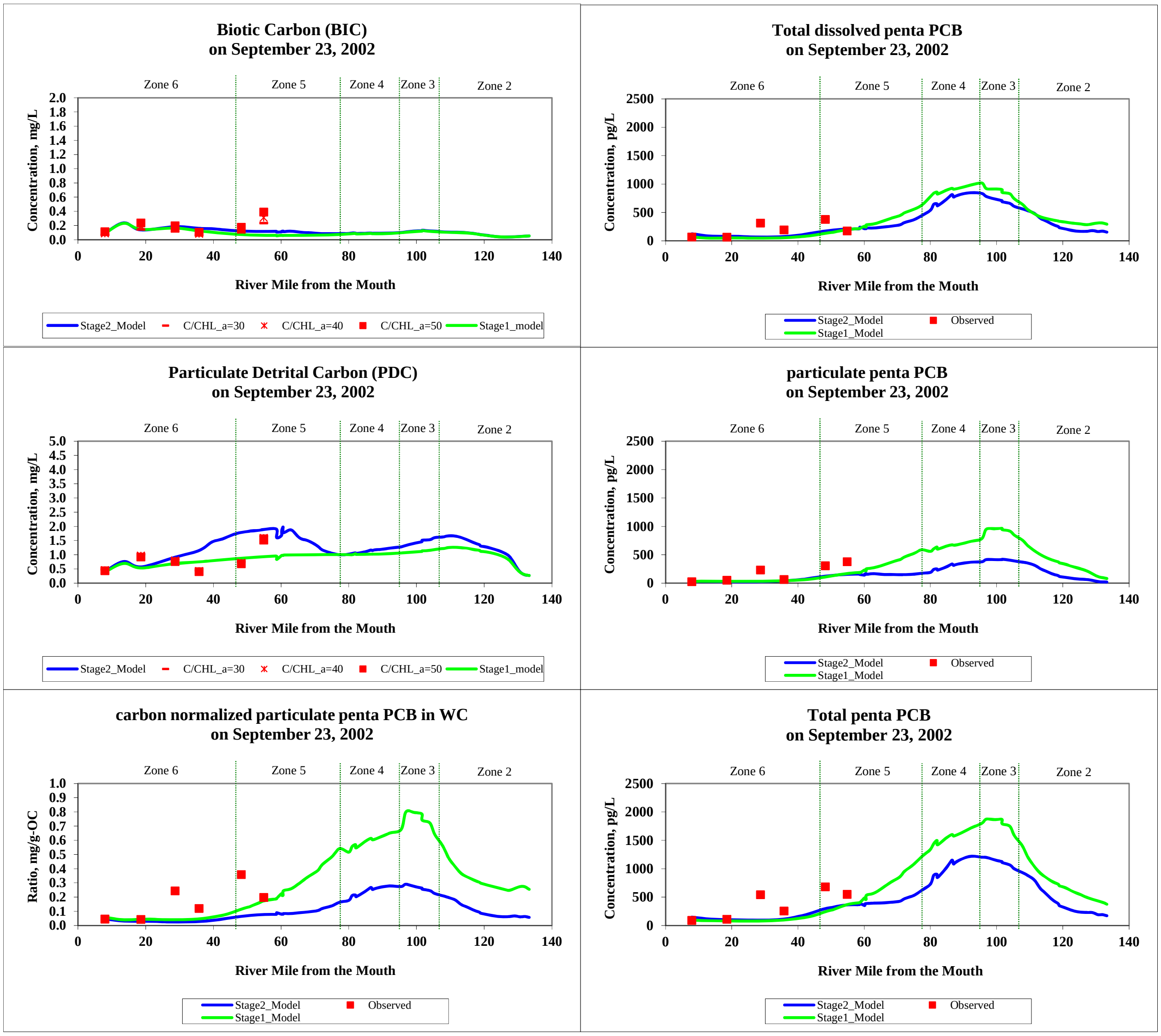


Figure 4.3.3-9: Spatial plots of BIC, PDC and various phases of penta-PCB during September 23, 2002 ambient survey.

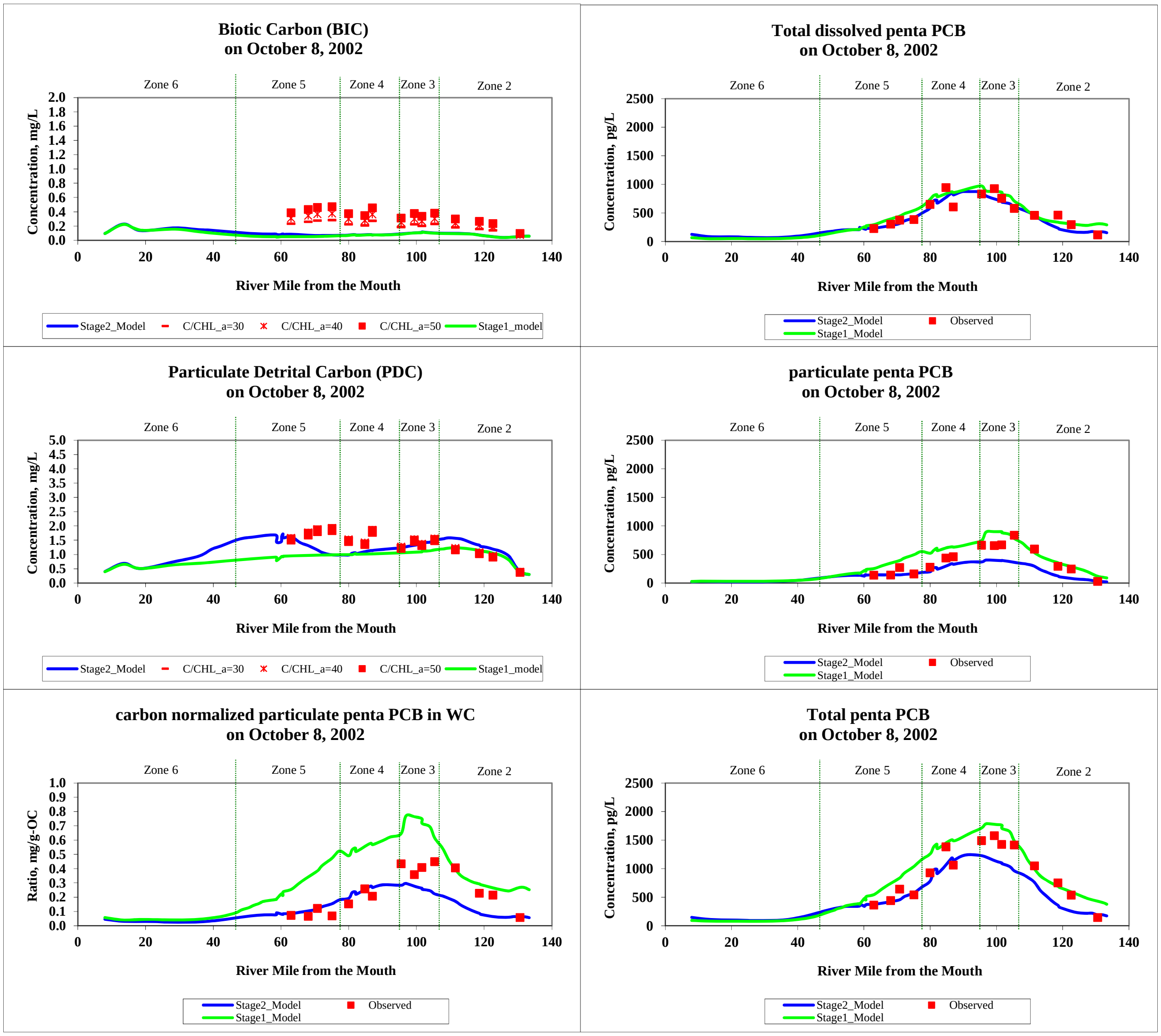


Figure 4.3.3-10: Spatial plots of BIC, PDC and various phases of penta-PCB during October 8, 2002 ambient survey.

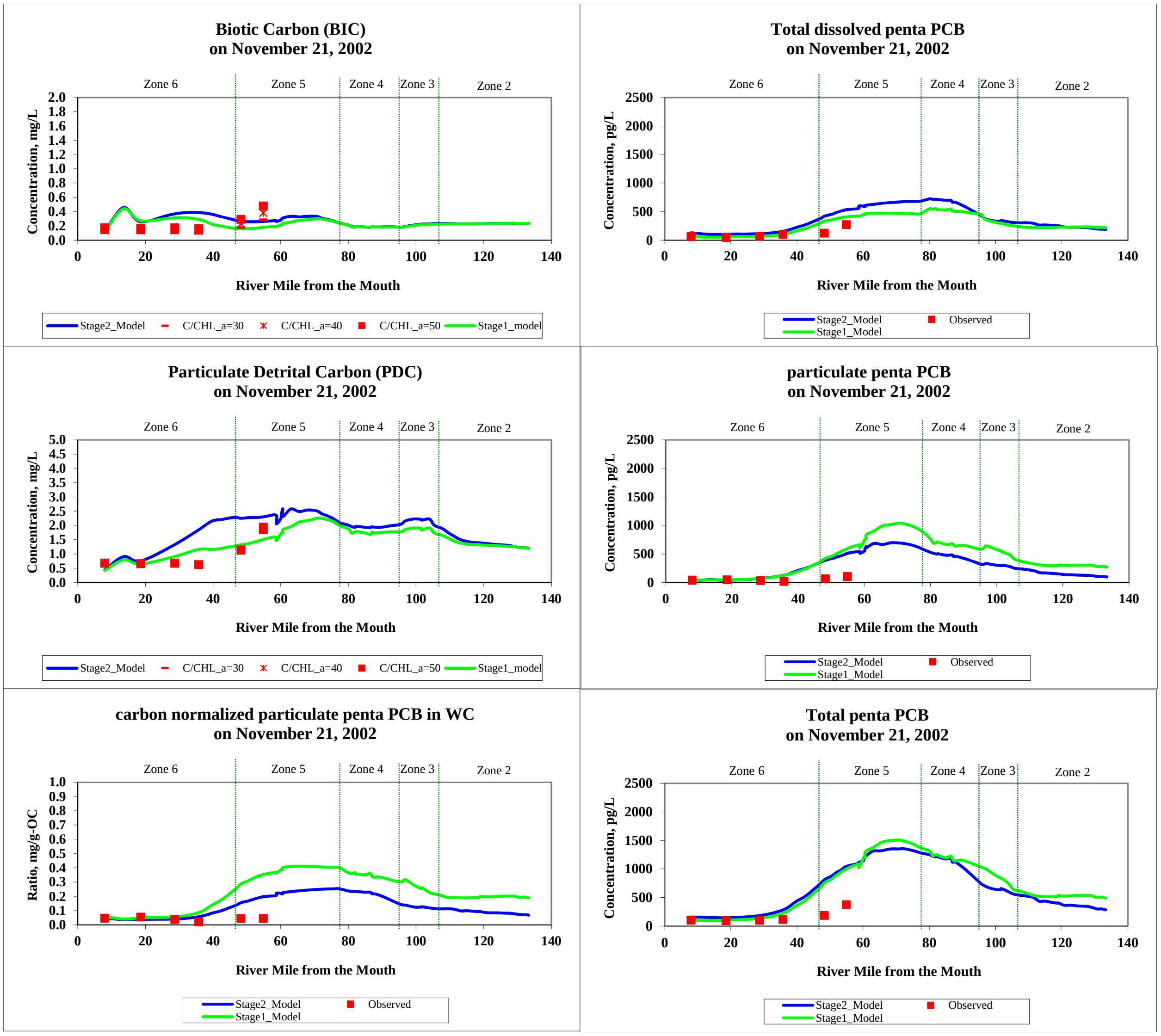


Figure 4.3.3-11: Spatial plots of BIC, PDC and various phases of penta-PCB during November 21, 2002 ambient survey.

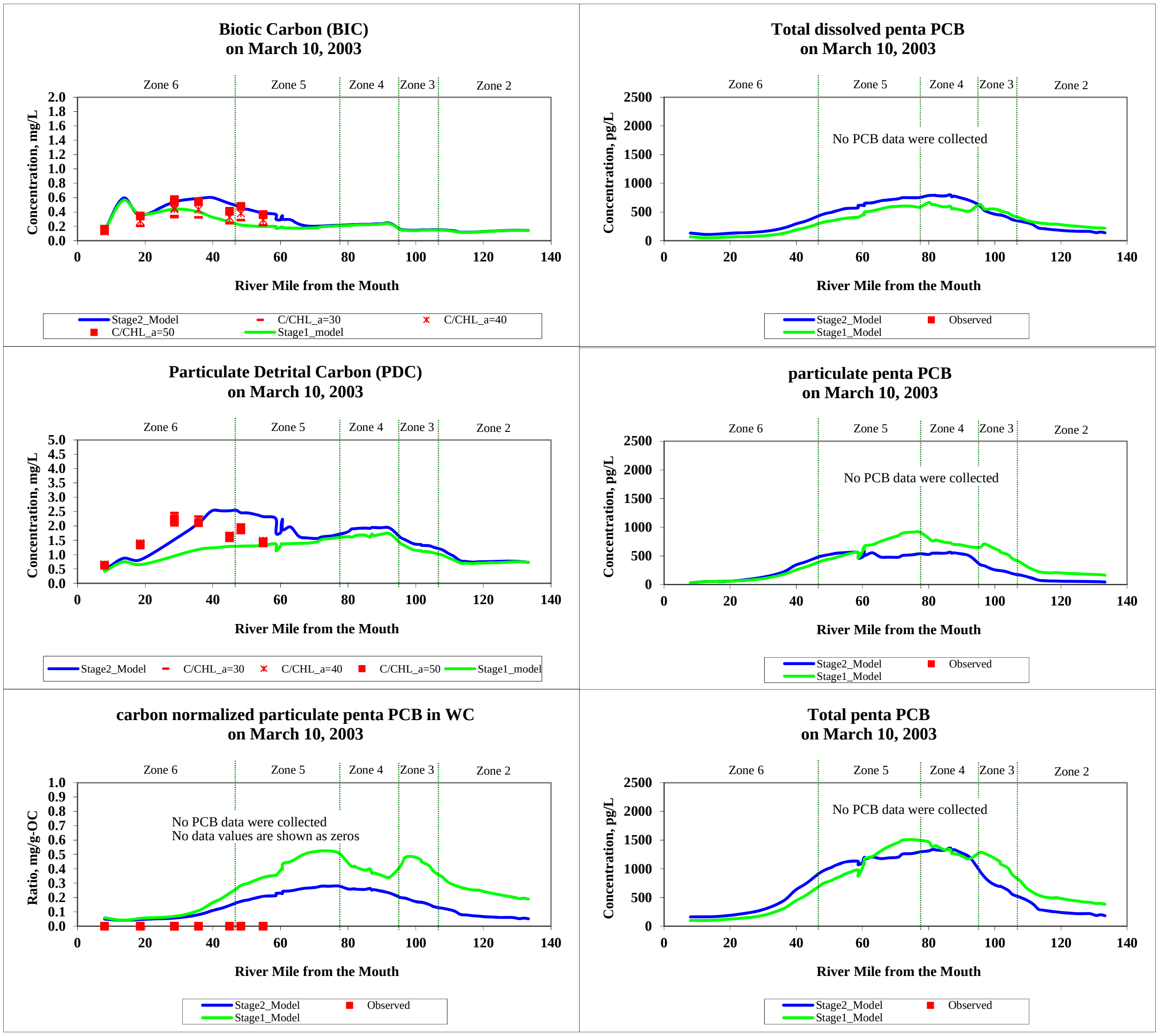


Figure 4.3.3.3-12: Spatial plots of BIC, PDC and various phases of penta-PCB during March 10, 2003 ambient survey.

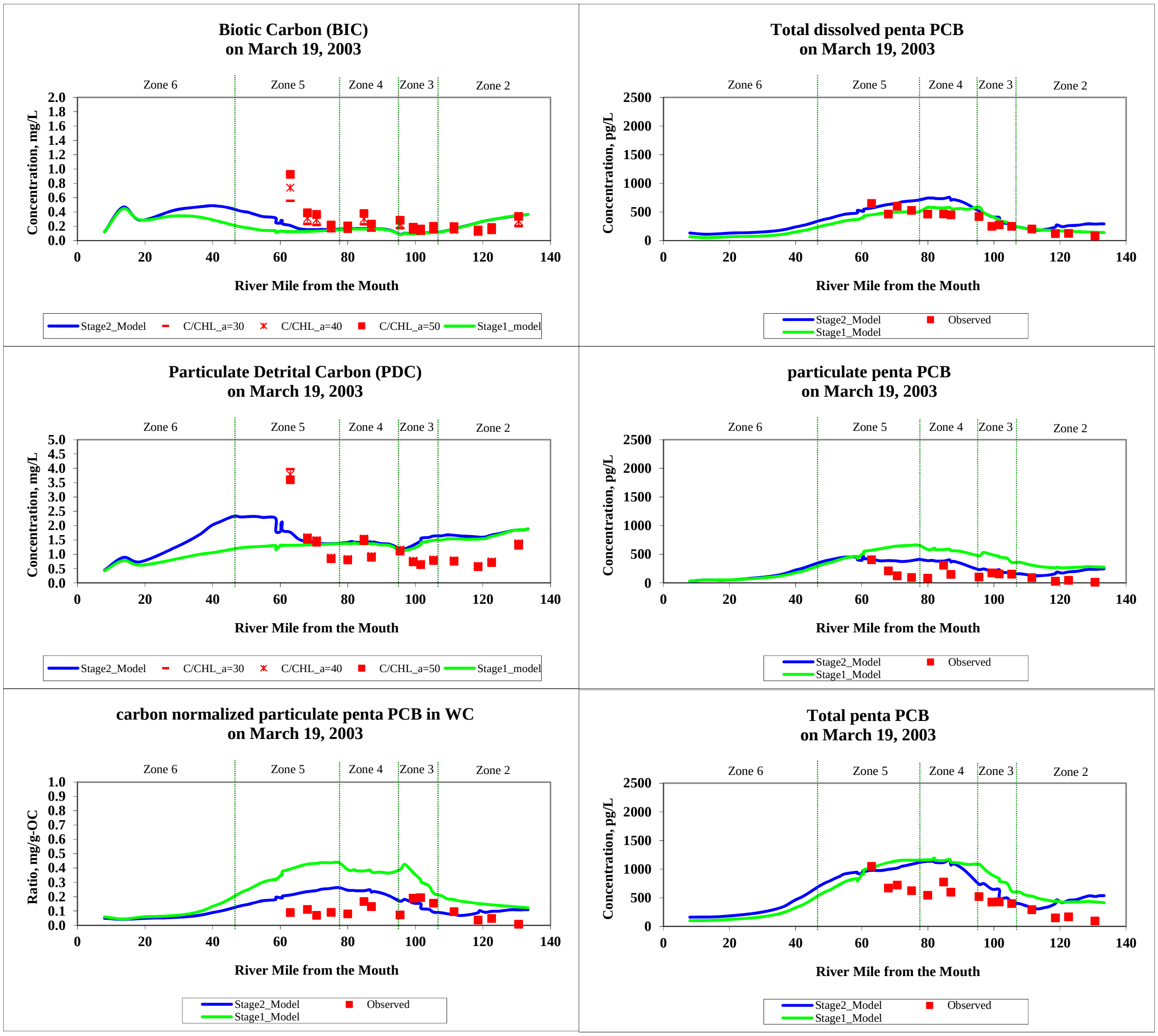


Figure 4.3.3-13: Spatial plots of BIC, PDC and various phases of penta-PCB during March 19, 2003 ambient survey.

Bivariate plots of observed and simulated penta-PCB concentrations are presented for each of the phases of PCBs tracked by the model and for carbon-normalized penta-PCBs (R1) by Zone during the ambient surveys conducted in 2002 and 2003. Truly dissolved penta-PCBs (DDPCB) are presented in Figure 4.3.3-14. Particulate penta-PCBs (PPCB) are presented in Figure 4.3.3-15. Total penta-PCBs (TPCB) are presented in Figure 4.3.3-16. Carbon-normalized penta-PCBs (R1) are presented in Figure 4.3.3-17. Observed penta-PCB values for each phase are plotted on the X-axis while simulated penta-PCB values for that phase are plotted on the Y-axis. If the model simulation results match the observed value, then the point should fall on the line bisecting the graph. This line is represented by a slope of 1.0 and an intercept of 0.0.

Cumulative frequency distribution plots of observed and predicted total, dissolved and particulate penta-PCBs during the one year cycling period are presented in Figure 4.3.3-18. These plots indicate the comparability of observed and predicted values over the range of values for that parameter. Notable observations include the comparability at the median of the distributions (50%), and at the tails of the distributions. The latter indicate the performance of the model for extreme observations.

The results of a mass balance analysis for total penta-PCBs in the water column and sediment layers are presented in Table 4.3.3-1. This table presents the mass flux in milligrams per day (mg/day) for various components in the water column and the surface sediment layer for the 12 month period used in long-term model simulations. Note that positive values indicate loading or fluxes to the water column or sediment layer, while negative values indicate a loss from the water column or sediment layer. Figure 4.3.3-19 graphically presents the mass flux for each Zone and model component.

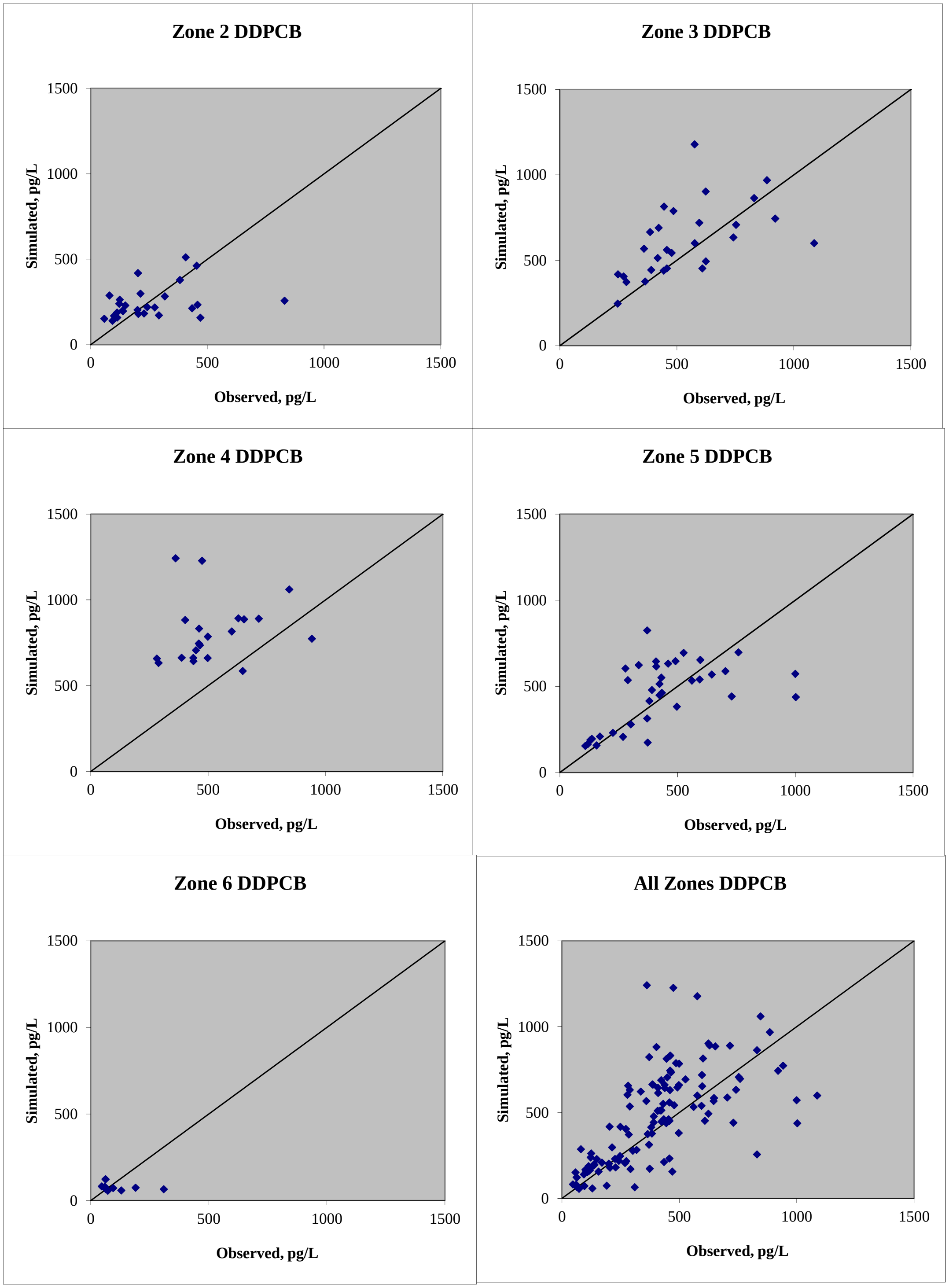


Figure 4.3.3-14: Bivariate plots of truly dissolved penta-PCBs (DDPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

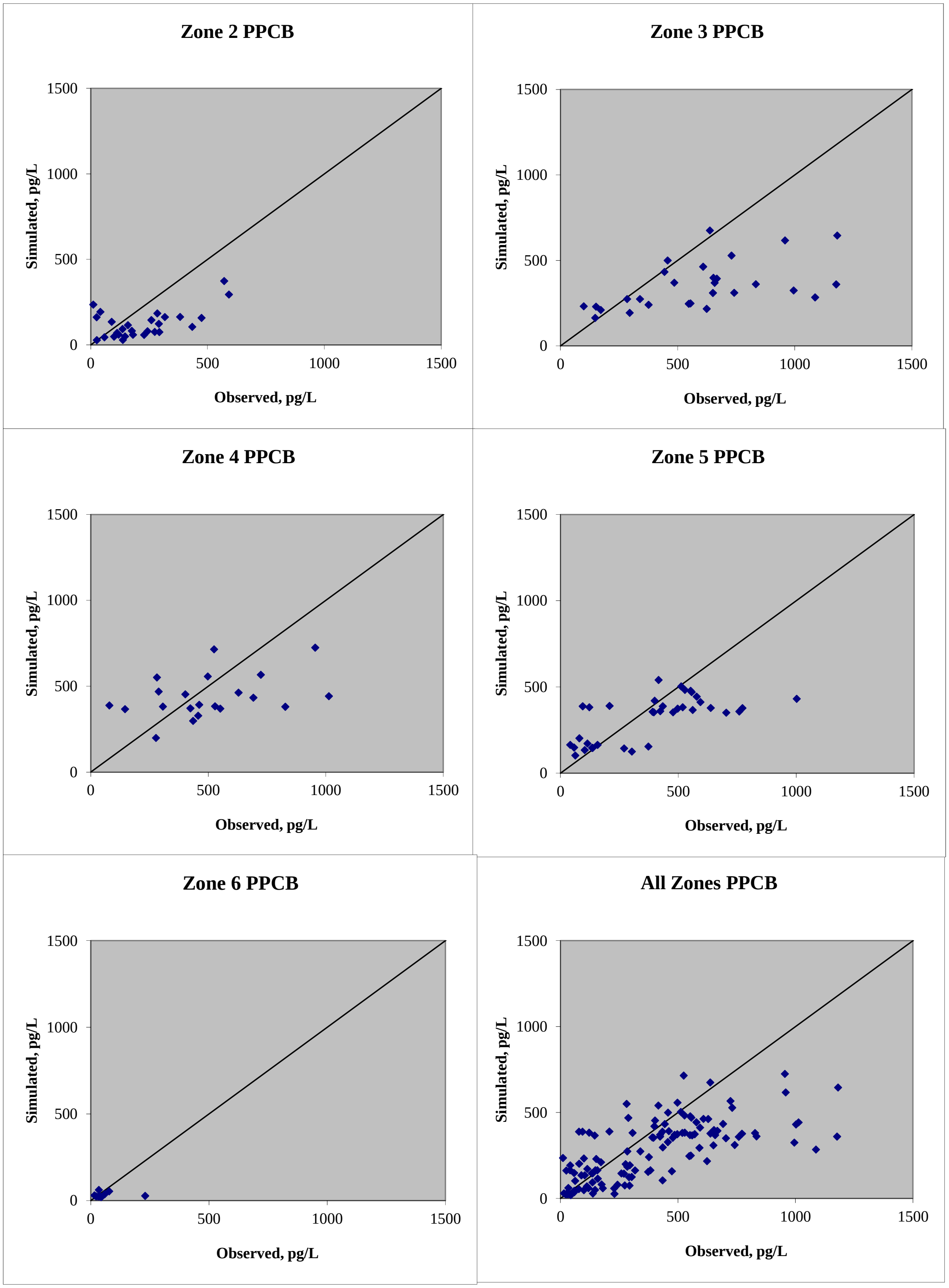


Figure 4.3.3-15: Bivariate plots of particulate penta-PCBs (PPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

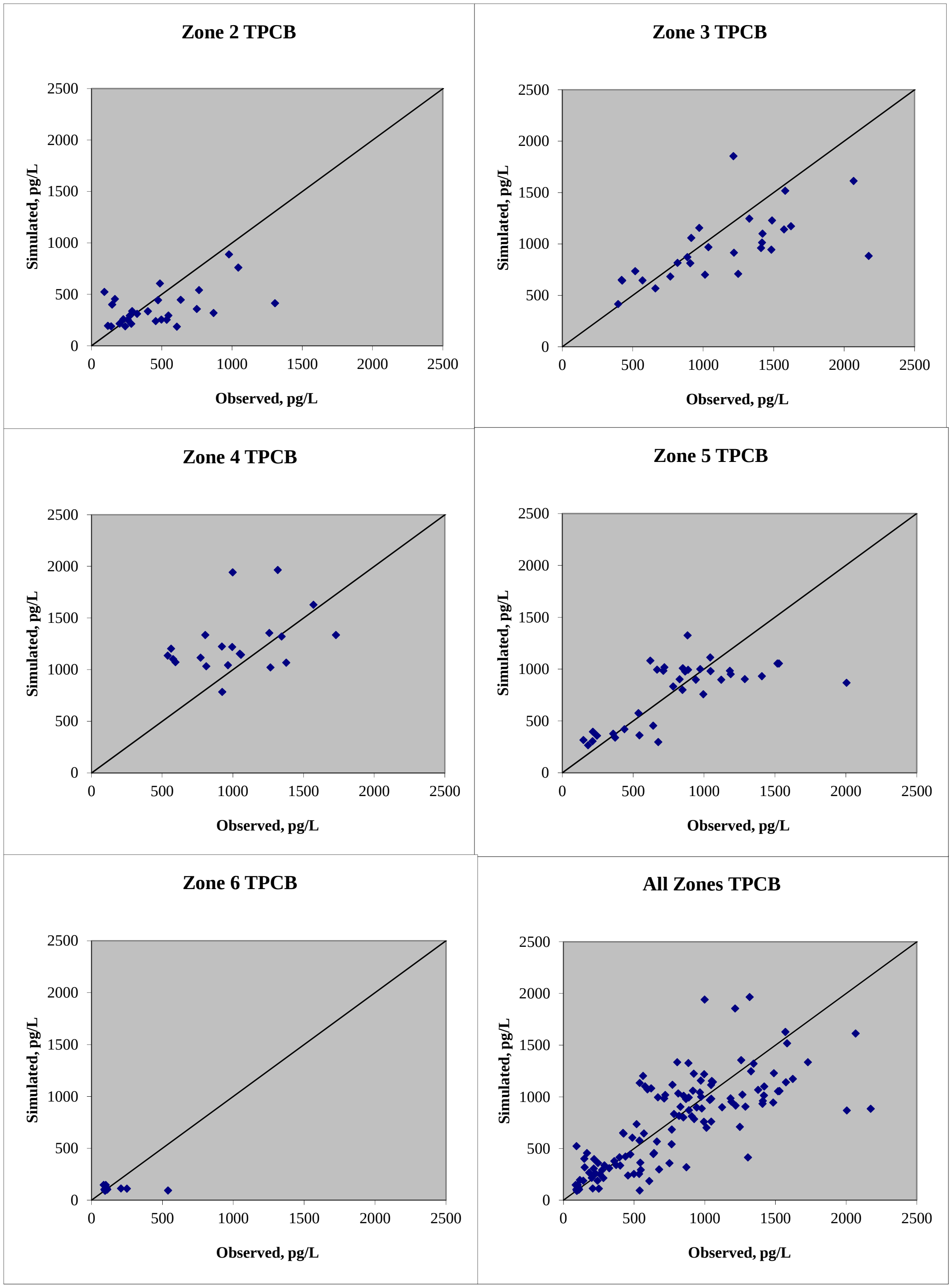


Figure 4.3.3-16: Bivariate plots of total penta-PCBs (TPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

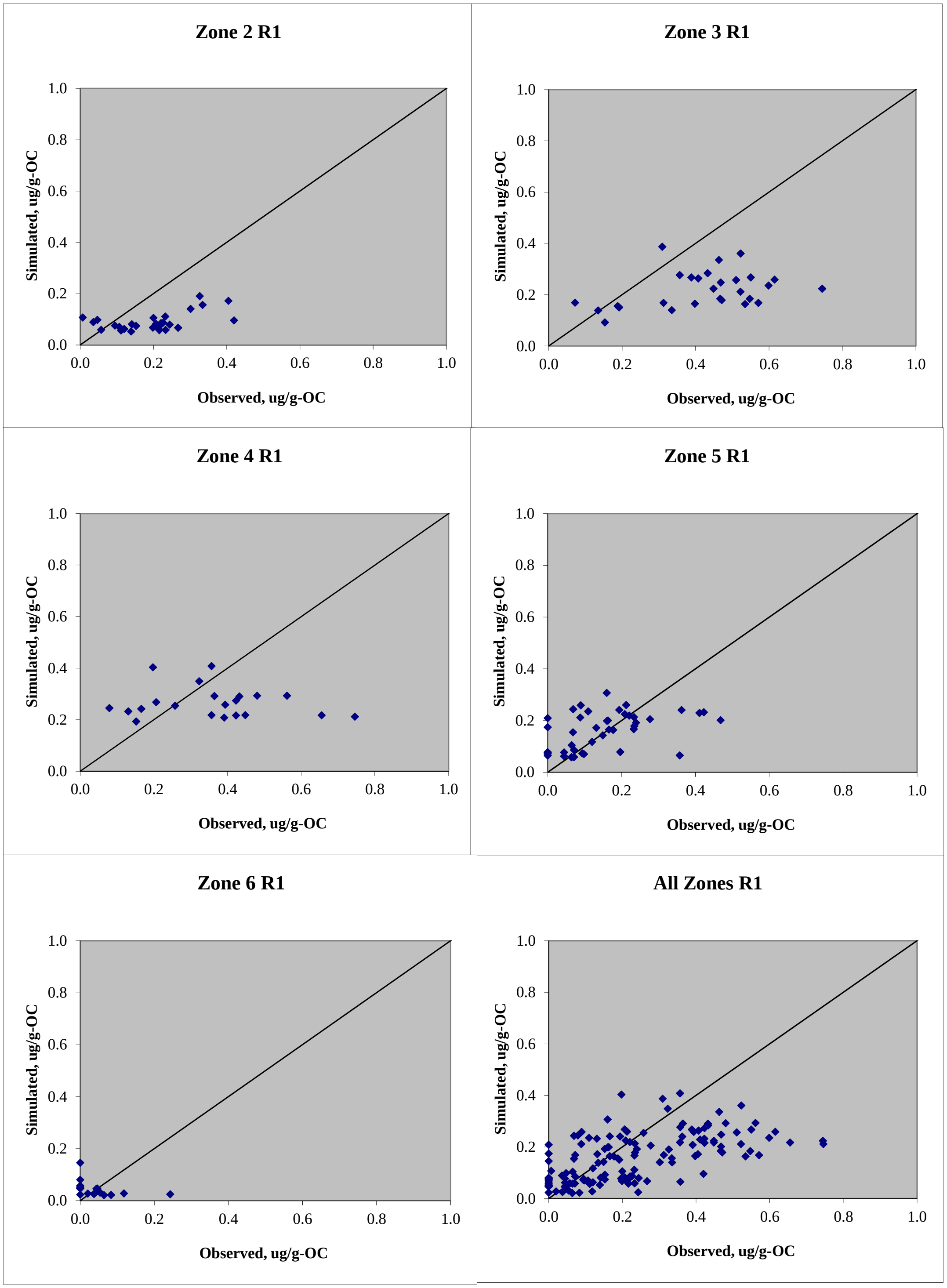
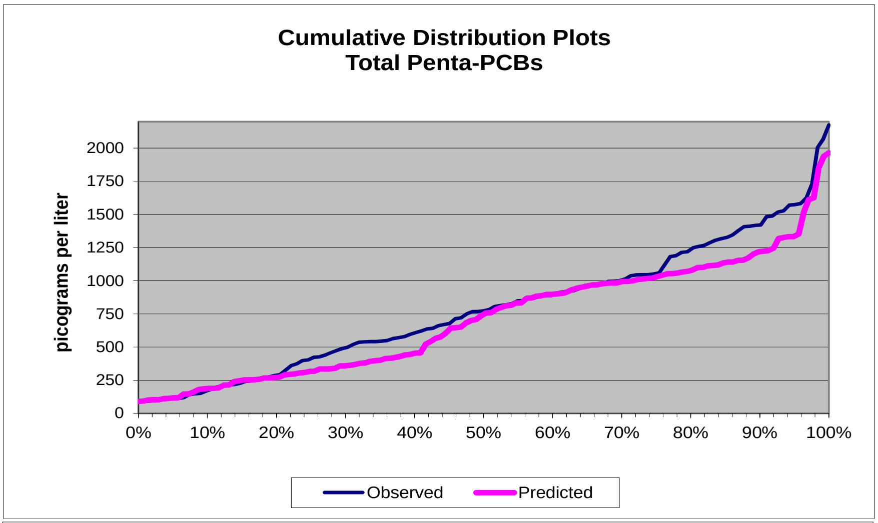
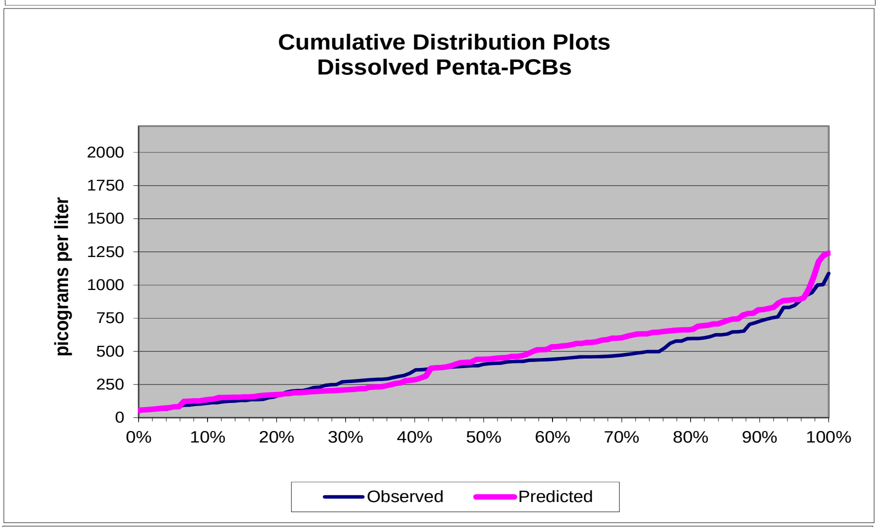


Figure 4.3.3-17: Bivariate plots of carbon-normalized penta-PCBs (R1) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.





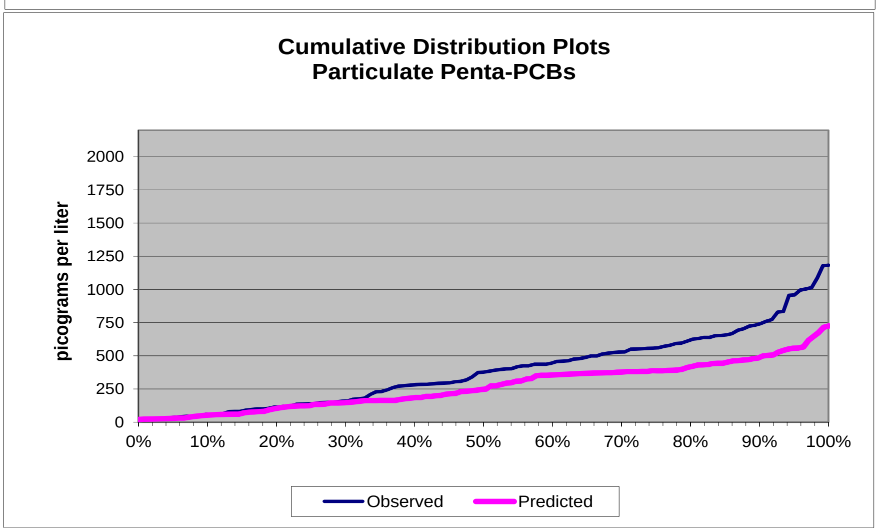


Figure 4.3.3-18: CFD plots of total (TPCB), dissolved (DPCB) and particulate (PPCB) penta-PCBs during the 12-month model cycling period.

Table 4.3.3-1: Daily averaged Penta PCB mass balance in milligrams/day (mg/day) for water column and surface sediment layer for the 12-month model cycling period.

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Water Column Mass Balance Component Analysis by Zone for penta PCB (mg/day)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	6,096	8,863	10,012	10,246	4,973	40,190	35,217
Dredging	0	0	0	0	0	0	0
Schuykill River	----	----	6,811	----	----	6,811	6,811
C&D Canal	----	----	----	-3,799	----	-3,799	-3,799
Exchange at Smaller Tributary Boundaries	0	0	0	0	----	0	0
Water Withdrawls (Segs 60, 66, 69)	-295	----	----	----	----	-295	-295
Upstream Interface Advection	5,785	19,484	35,001	55,599	36,063	5,785	5,785
Upstream Interface Dispersion	----	-429	-274	1,231	8,357	----	----
Downstream Interface Advection	-19,484	-35,001	-55,599	-36,063	47,744	47,744	-36,063
Downstream Interface Dispersion	429	274	-1,231	-8,357	----	----	-8,357
Air-Water Exchange	-4,168	-7,104	-18,487	-49,150	-97,539	-176,447	-78,908
Net Sediment-Water Diffusion	1,489	1,690	3,771	4,735	2,771	14,456	11,685
Net of Settling and Resuspension	9,966	11,902	19,500	13,385	12,089	66,842	54,753
Upstream Transport (Loss to Upstream)	----	0	0	0	-12,282	-12,282	0
Upstream Transport (Gain from Downstream)	0	0	0	12,282	----	12,282	12,282
Model Reported Excess Mass	**0**	**0**	**-2**	**-9**	**1**	**-11**	**-12**
Change in Mass (ΣFluxes - Excess)	**-180.824**	**-320.398**	**-493.689**	**117.315**	**2,175.952**	**1,298.357**	**-877.596**
Initial Mass (mg)	133,892	272,655	544,127	717,554	1,196,188	2,864,416	1,668,228
Final Mass (mg)	67,891	155,710	363,920	760,364	1,990,430	3,338,316	1,347,886
Change in Mass [Initial - Final] (mg/d)	**-180.825**	**-320.395**	**-493.717**	**117.287**	**2,176.004**	**1,298.354**	**-877.650**
Water Column Mass Balance Closure (mg/d)	**-0.001**	**0.003**	**-0.028**	**-0.028**	**0.051**	**-0.002**	**-0.054**
Percent Tracking Error	**-0.0003098%**	**0.0005978%**	**-0.0028286%**	**-0.0013280%**	**0.0009441%**	**-0.0000264%**	**-0.0014594%**
Model Reported Excess Mass (mg/day)	**-0.476**	**-0.450**	**-2.267**	**-8.928**	**1.395**	**-10.728**	**-12.122**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-1,958	-2,902	-11,991	-46,761	-30,978	-94,590	-63,612
Gross Resuspension (mg/day)	11,925	14,804	31,492	60,145	43,067	161,433	118,366

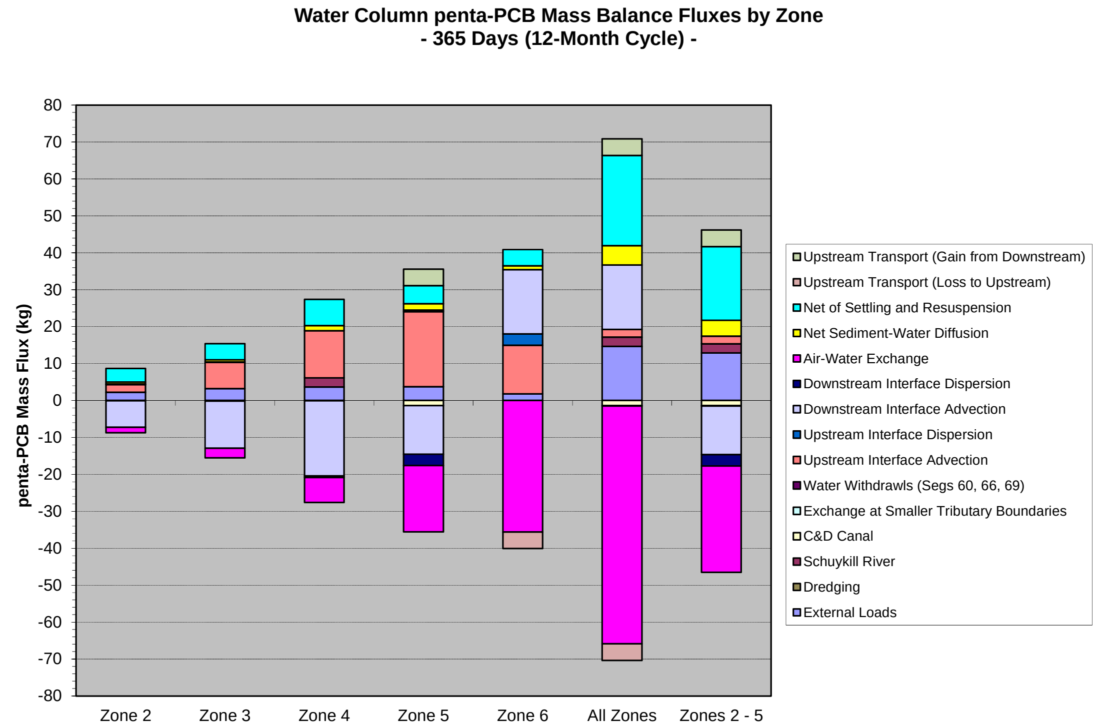
version May 20, 2010 - MB365

DELPCB 12-Month Cycle Surface Sediment Layer Mass Balance Component Analysis by Zone for penta PCB (mg/day)

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	-9,966	-11,902	-19,500	-13,385	-12,089	-66,842	-54,753
Net Sediment-Water Diffusion	-1,489	-1,690	-3,771	-4,735	-2,771	-14,456	-11,685
Net Particle Mixing	6,349	8,823	19,739	25,865	9,672	70,447	60,775
Net Porewater Diffusion	0	1	3	5	1	11	10
Dredging	-827	-3,747	-15,997	-32,875	-3,219	-56,665	-53,446
Burial	0	0	0	0	0	0	0
Model Reported Excess Mass	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Change in Mass (ΣFluxes - Excess)	**-5,933.4**	**-8,515.2**	**-19,526.3**	**-25,124.5**	**-8,405.9**	**-67,505.3**	**-59,099.4**
Initial Mass (mg)	8,679,494	10,059,270	21,632,313	29,523,452	16,427,165	86,321,694	69,894,529
Final Mass (mg)	6,514,153	6,951,218	14,505,205	20,353,014	13,359,014	61,682,605	48,323,590
Change in Mass [Initial - Final] (mg/d)	**-5,932.4**	**-8,515.2**	**-19,526.3**	**-25,124.5**	**-8,405.9**	**-67,504.4**	**-59,098.5**
Surface Sediment Mass Balance Closure (mg/d)	**0.960**	**0.000**	**0.000**	**0.000**	**0.000**	**0.959**	**0.960**
Percent Tracking Error	**0.0053776%**	**0.0000020%**	**-0.0000008%**	**-0.0000002%**	**-0.0000008%**	**0.0005677%**	**0.0007249%**
Model Reported Excess Mass (mg/day)	**0.012**	**-0.010**	**0.035**	**-0.095**	**0.002**	**-0.056**	**-0.058**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-1,958	-2,902	-11,991	-46,761	-30,978	-94,590	-63,612
Gross Resuspension (mg/day)	11,925	14,804	31,492	60,145	43,067	161,433	118,366



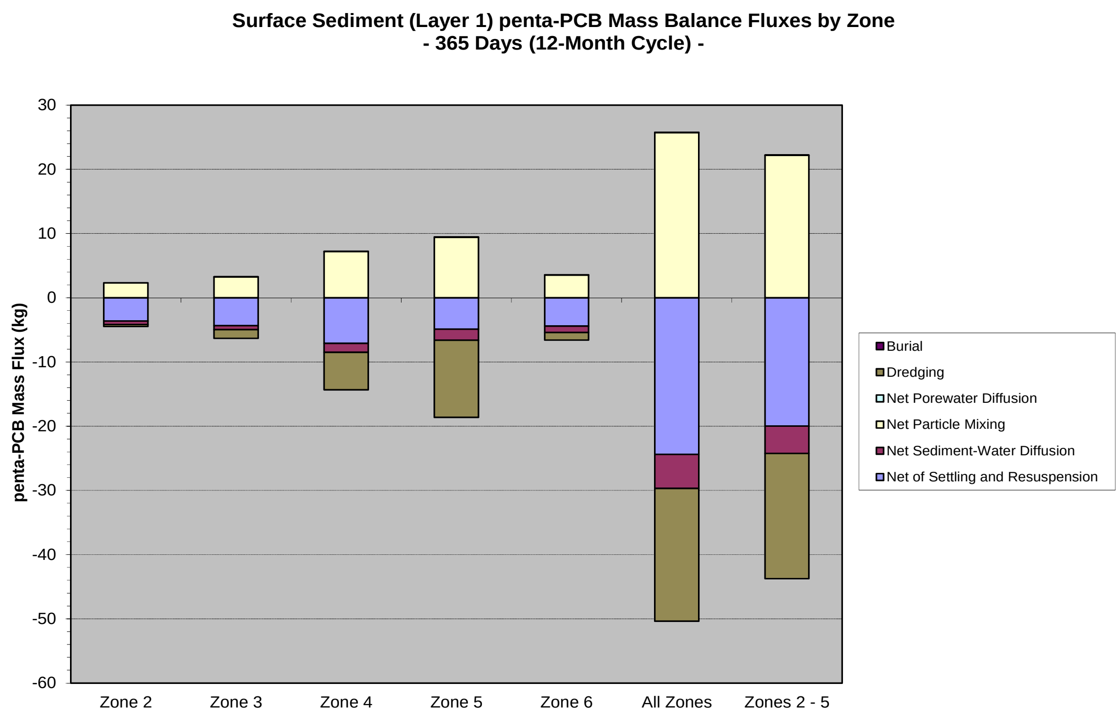


Figure 4.3.3-19: Penta-PCB mass fluxes in the water column and surface sediment layer in kilograms for the 12 month model cycling period by Zone.

4.3.4 Tetra-PCBs

A spatial plot of observed and simulated Tetra-PCB concentrations for 11 ambient surveys conducted between March 1, 2002 and March 31, 2003 is presented in Figure 4.3.4-1. The figure depicts the results for all 11 ambient surveys along with the minimum, median and maximum predicted concentrations from model simulations during that period.

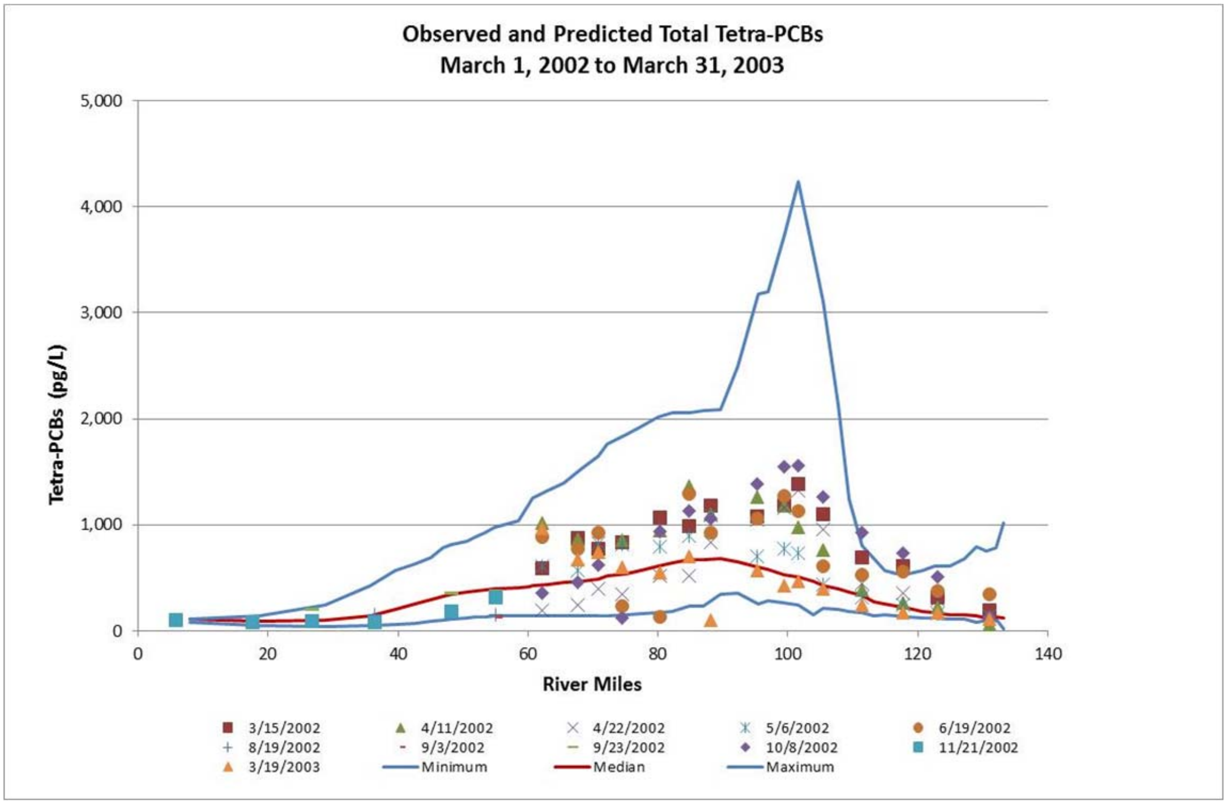


Figure 4.3.4-1: Spatial plots of tetra-PCBs in the water column during 11 surveys conducted during the period March 1, 2002 and March 31, 2003 in the tidal Delaware River and Bay.

Bivariate plots of observed and simulated tetra-PCB concentrations are presented for each of the phases of PCBs tracked by the model and for carbon-normalized tetra-PCBs (R1) by Zone during the ambient surveys conducted in 2002 and 2003. Truly dissolved tetra-PCBs (DDPCB) are presented in Figure 4.3.4-2. Particulate tetra-PCBs (PPCB) are presented in Figure 4.3.4-3. Total tetra-PCBs (TPCB) are presented in Figure 4.3.4-4. Carbon-normalized tetra-PCBs (R1) are presented in Figure 4.3.4-5. Observed tetra-PCB values for each phase are plotted on the X-axis while simulated tetra-PCB values for that phase are plotted on the Y-axis. If the model simulation results match the observed value, then the point should fall on the line bisecting the graph. This line is represented by a slope of 1.0 and an intercept of 0.0.

Cumulative frequency distribution plots of observed and predicted total, dissolved and particulate tetra-PCBs during the one year cycling period are presented in Figure 4.3.4-6.

The results of a mass balance analysis for total tetra-PCBs in the water column and sediment layers are presented in Tables 4.3.4-1. This table presents the mass flux in milligrams per day (mg/day) for various components in the water column and the surface sediment layer for the 12 month period used in long-term model simulations. Note that positive values indicate loading or fluxes to the water column or sediment layer, while negative values indicate a loss from the water column or sediment layer. Figure 4.3.4-7 graphically presents the mass flux for each Zone and model component.

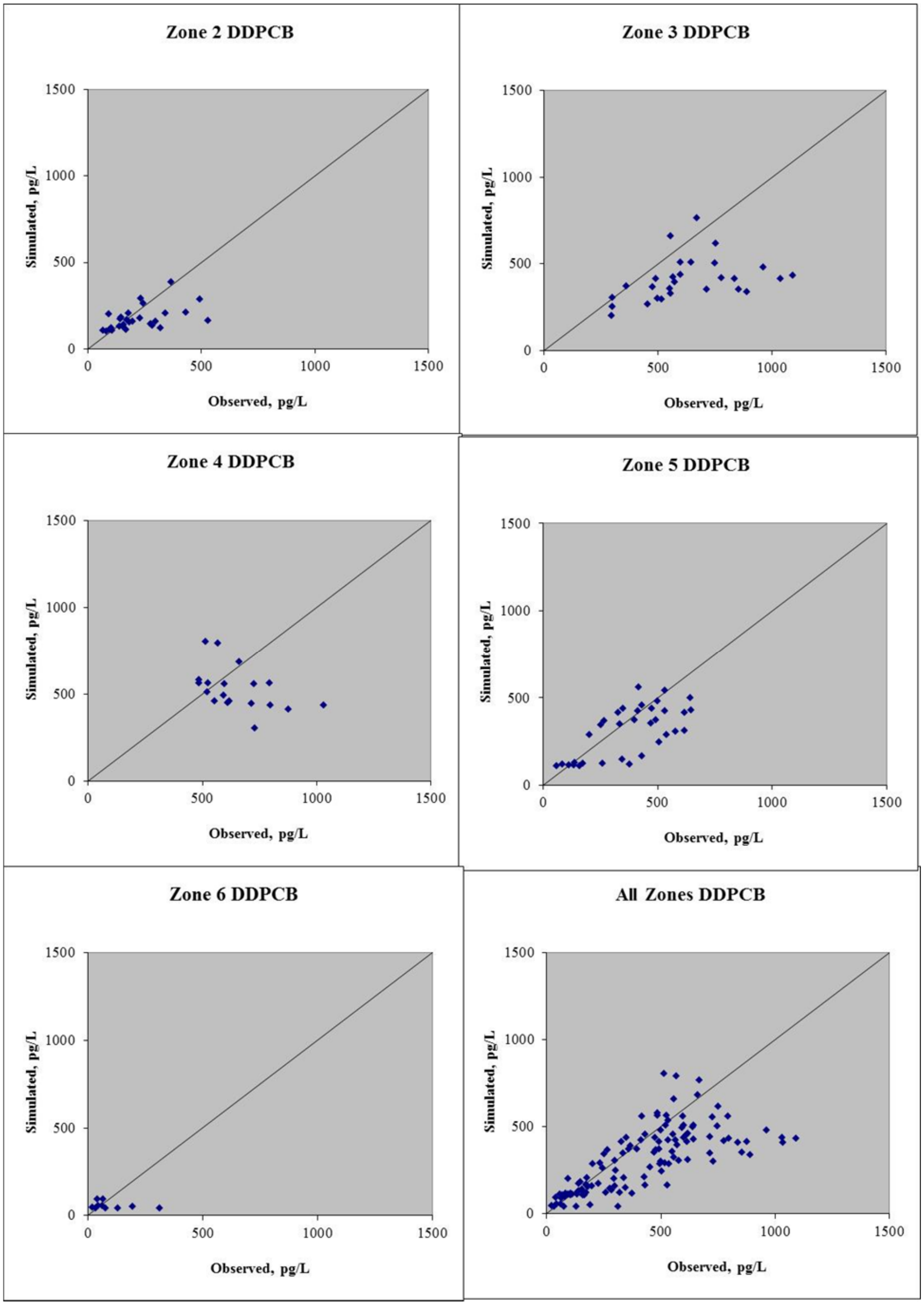


Figure 4.3.4-2: Bivariate plots of truly dissolved Tetra-PCBs (DDPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

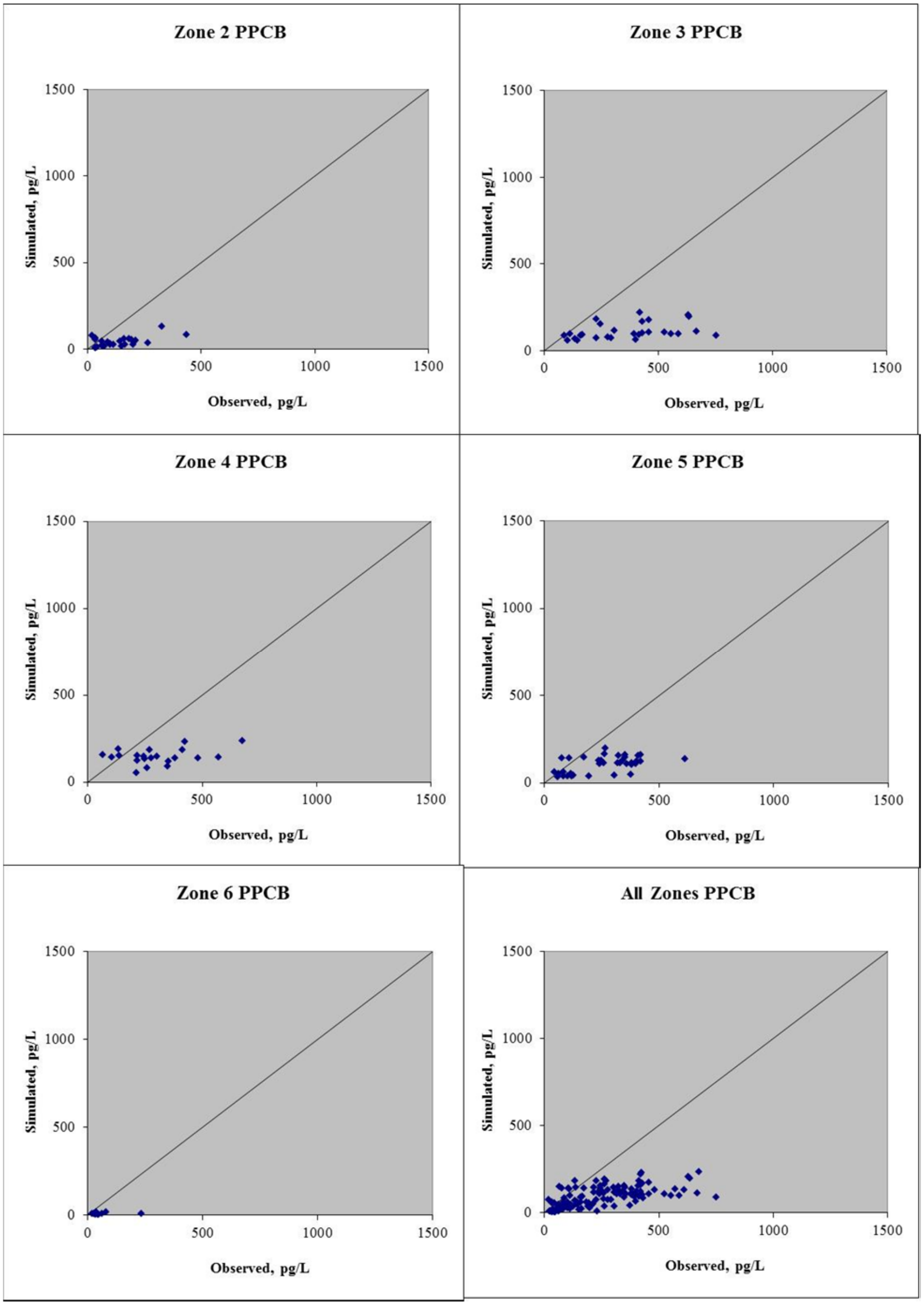


Figure 4.3.4-3: Bivariate plots of particulate Tetra-PCBs (PPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

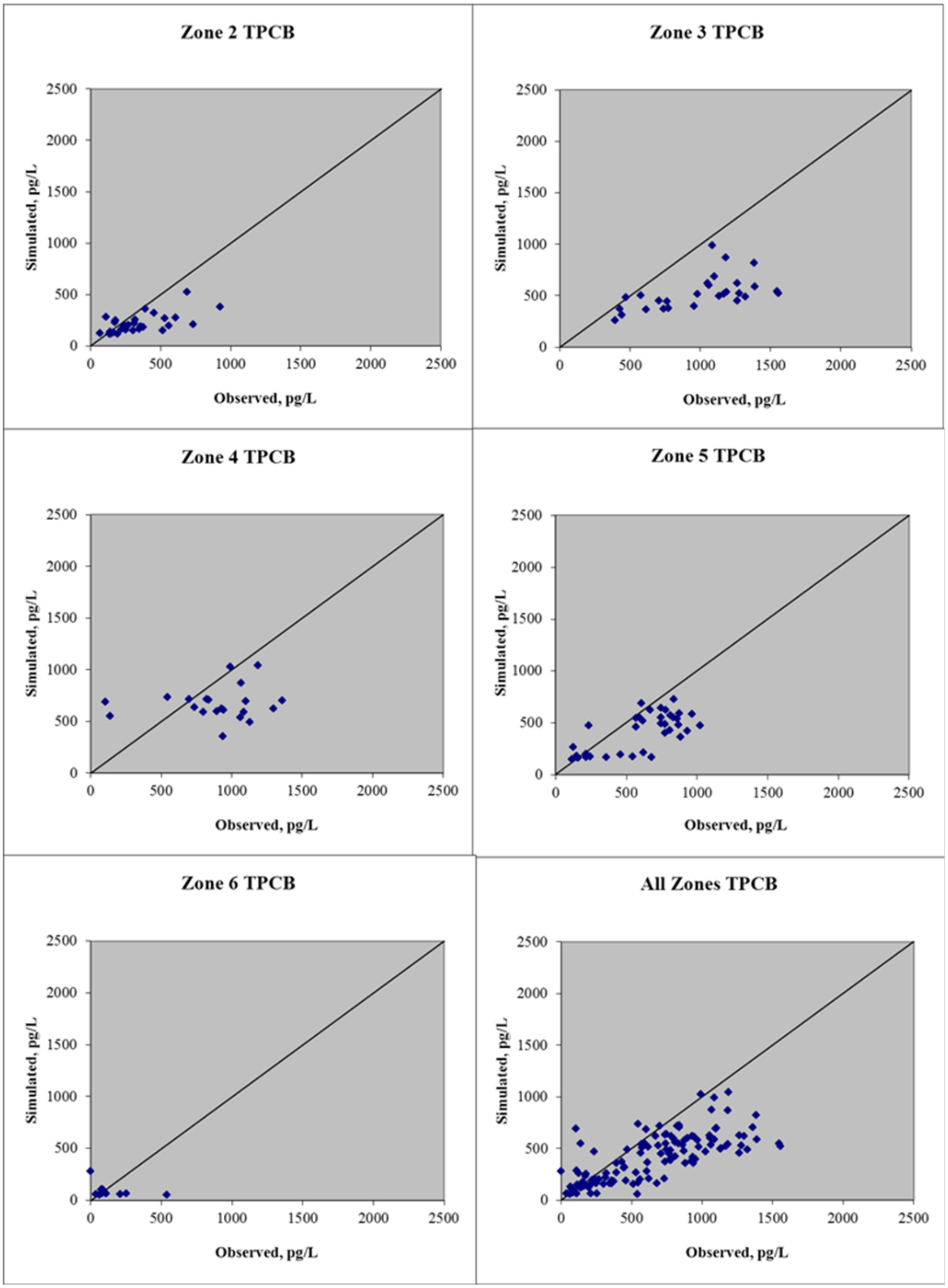


Figure 4.3.4-4: Bivariate plots of total Tetra-PCBs (TPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

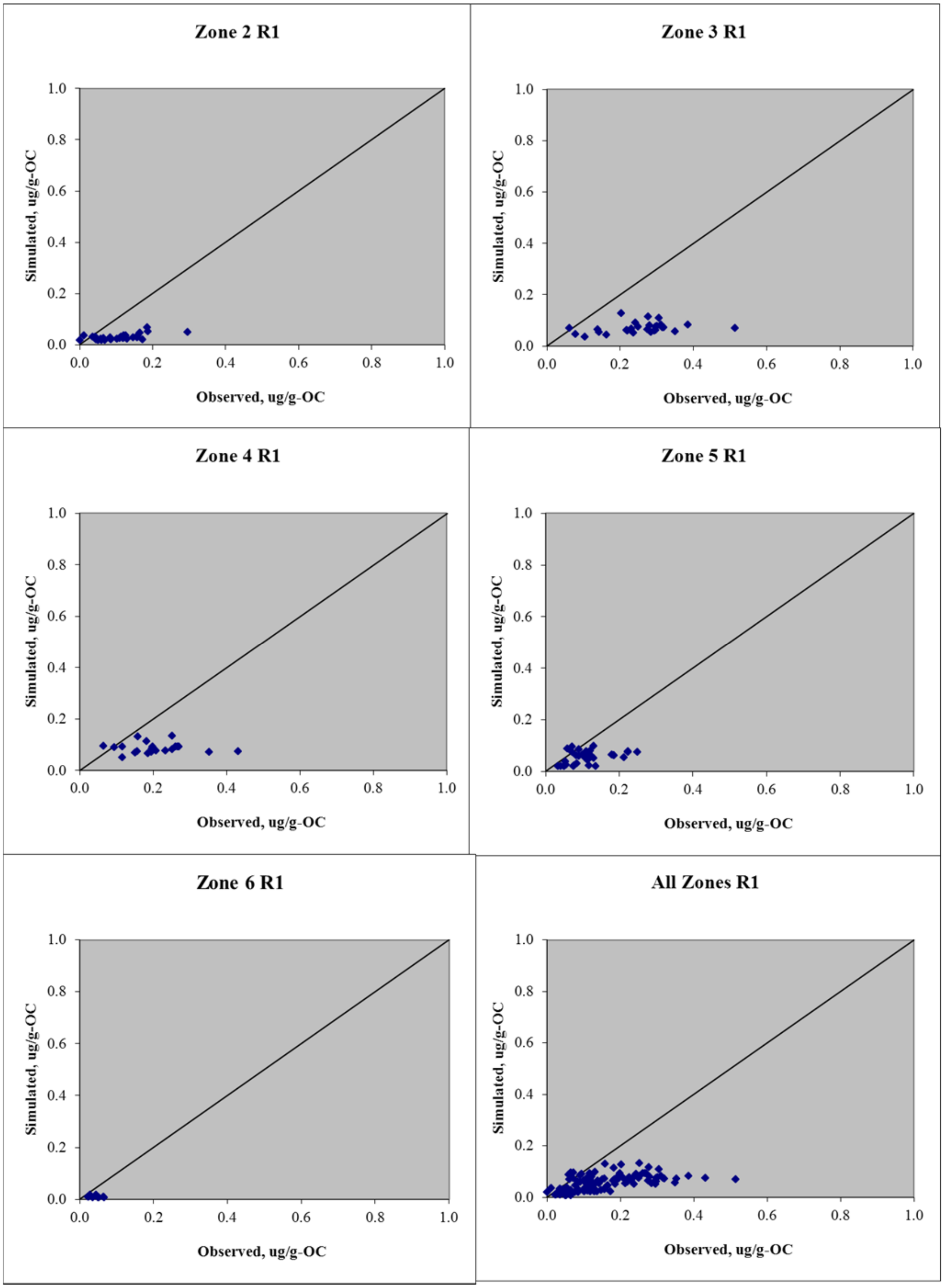


Figure 4.3.4-5: Bivariate plots of carbon-normalized Tetra-PCBs (R1) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

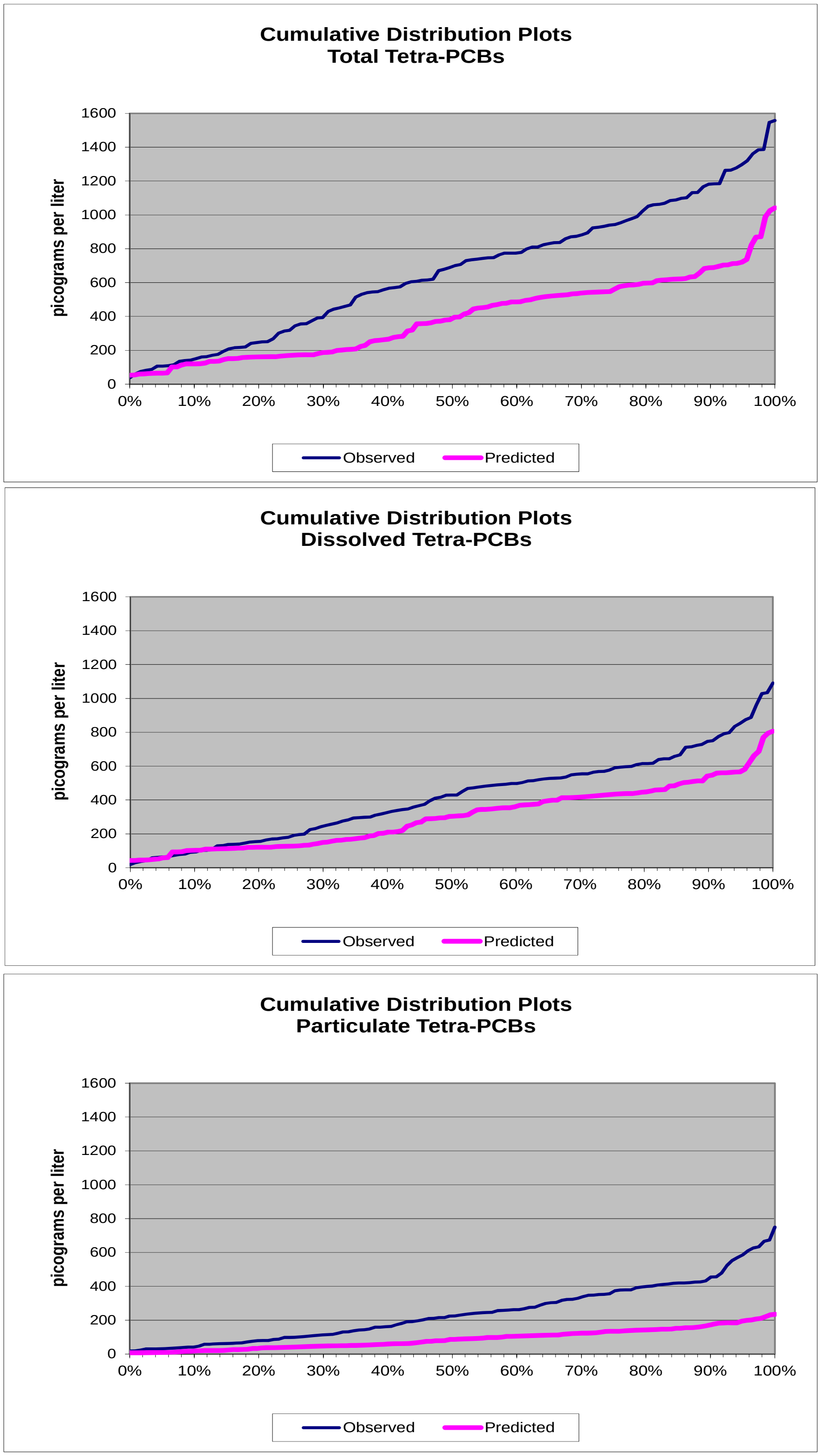


Figure 4.3.4-6: CFD plots of total (TPCB), dissolved (DPCB) and particulate (PPCB) tetra-PCBs during the 12-month model cycling period.

Table 4.3.4-1: Daily averaged Tetra-PCB mass balance for water column and surface sediment layer for 12-month period

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Water Column Mass Balance Component Analysis by Zone for tetra PCB (mg/day)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	3,749	8,619	5,841	4,933	3,627	26,768	23,141
Dredging	0	0	0	0	0	0	0
Schuykill River	----	----	5,755	----	----	5,755	5,755
C&D Canal	----	----	----	-952	----	-952	-952
Exchange at Smaller Tributary Boundaries	0	0	0	0	----	0	0
Water Withdrawls (Segs 60, 66, 69)	-159	----	----	----	----	-159	-159
Upstream Interface Advection	3,477	10,554	20,306	30,456	20,083	3,477	3,477
Upstream Interface Dispersion	----	-212	-90	565	3,420	----	----
Downstream Interface Advection	-10,554	-20,306	-30,456	-20,083	43,183	43,183	-20,083
Downstream Interface Dispersion	212	90	-565	-3,420	----	----	-3,420
Air-Water Exchange	-3,373	-5,050	-14,049	-39,008	-89,648	-151,128	-61,480
Net Sediment-Water Diffusion	1,435	1,228	3,146	5,432	4,161	15,401	11,240
Net of Settling and Resuspension	5,162	4,874	9,686	16,924	19,335	55,980	36,646
Upstream Transport (Loss to Upstream)	----	0	0	0	-4,569	-4,569	0
Upstream Transport (Gain from Downstream)	0	0	0	4,569	----	4,569	4,569
Model Reported Excess Mass	**0**	**-21**	**-1**	**-11**	**2**	**-32**	**-34**
Change in Mass (ΣFluxes - Excess)	**-51.311**	**-182.778**	**-424.531**	**-572.336**	**-410.344**	**-1,641.300**	**-1,230.956**
Initial Mass (mg)	58,382	147,015	343,794	630,267	1,511,107	2,690,566	1,179,459
Final Mass (mg)	39,653	80,300	188,841	421,367	1,361,333	2,091,494	730,161
Change in Mass [Initial - Final] (mg/d)	**-51.312**	**-182.781**	**-424.529**	**-572.330**	**-410.339**	**-1,641.291**	**-1,230.952**
Water Column Mass Balance Closure (mg/d)	**-0.001**	**-0.003**	**0.001**	**0.006**	**0.004**	**0.009**	**0.004**
Percent Tracking Error	**-0.0007892%**	**-0.0013005%**	**0.0002666%**	**0.0005532%**	**0.0001199%**	**0.0001487%**	**0.0002023%**
Model Reported Excess Mass (mg/day)	**-0.251**	**-21.068**	**-1.470**	**-10.772**	**1.550**	**-32.011**	**-33.561**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-642	-912	-3,986	-15,592	-11,977	-33,109	-21,131
Gross Resuspension (mg/day)	5,804	5,785	13,672	32,516	31,312	89,089	57,777

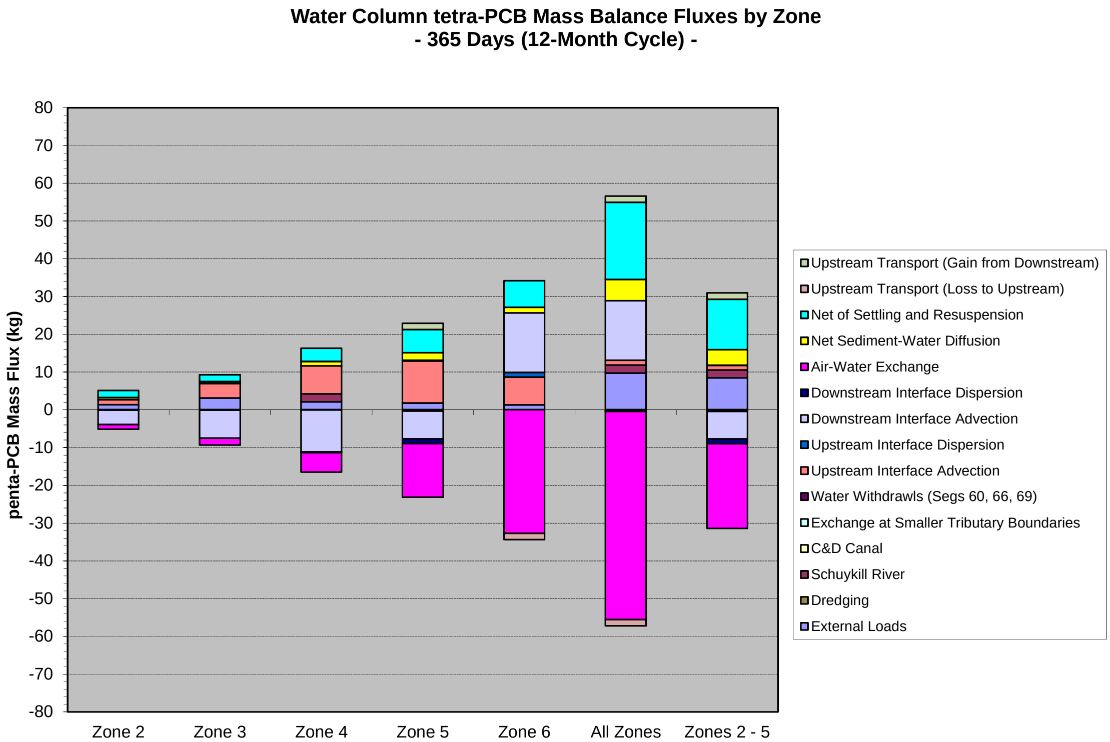
version May 20, 2010 - MB365

DELPCB 12-Month Cycle Surface Sediment Layer Mass Balance Component Analysis by Zone for tetra PCB (mg/day)

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	-5,162	-4,874	-9,686	-16,924	-19,335	-55,980	-36,646
Net Sediment-Water Diffusion	-1,435	-1,228	-3,146	-5,432	-4,161	-15,401	-11,240
Net Particle Mixing	3,826	4,031	10,394	19,957	13,055	51,263	38,208
Net Porewater Diffusion	0	1	3	7	3	15	12
Dredging	-434	-1,421	-7,157	-16,428	-2,341	-27,783	-25,442
Burial	0	0	0	0	0	0	0
Model Reported Excess Mass	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Change in Mass (ΣFluxes - Excess)	**-3,204.9**	**-3,490.4**	**-9,591.7**	**-18,820.5**	**-12,779.4**	**-47,886.8**	**-35,107.4**
Initial Mass (mg)	4,426,756	3,921,112	9,507,332	16,871,160	13,326,174	48,052,533	34,726,359
Final Mass (mg)	3,257,361	2,647,126	6,006,374	10,001,668	8,661,700	30,574,229	21,912,529
Change in Mass [Initial - Final] (mg/d)	**-3,203.8**	**-3,490.4**	**-9,591.7**	**-18,820.5**	**-12,779.4**	**-47,885.8**	**-35,106.4**
Surface Sediment Mass Balance Closure (mg/d)	**1.066**	**0.000**	**0.000**	**0.000**	**0.000**	**1.066**	**1.066**
Percent Tracking Error	**0.0119427%**	**0.0000002%**	**-0.0000004%**	**-0.0000006%**	**0.0000004%**	**0.0012723%**	**0.0017750%**
Model Reported Excess Mass (mg/day)	**0.024**	**0.003**	**-0.004**	**0.019**	**-0.008**	**0.034**	**0.042**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-642	-912	-3,986	-15,592	-11,977	-33,109	-21,131
Gross Resuspension (mg/day)	5,804	5,785	13,672	32,516	31,312	89,089	57,777



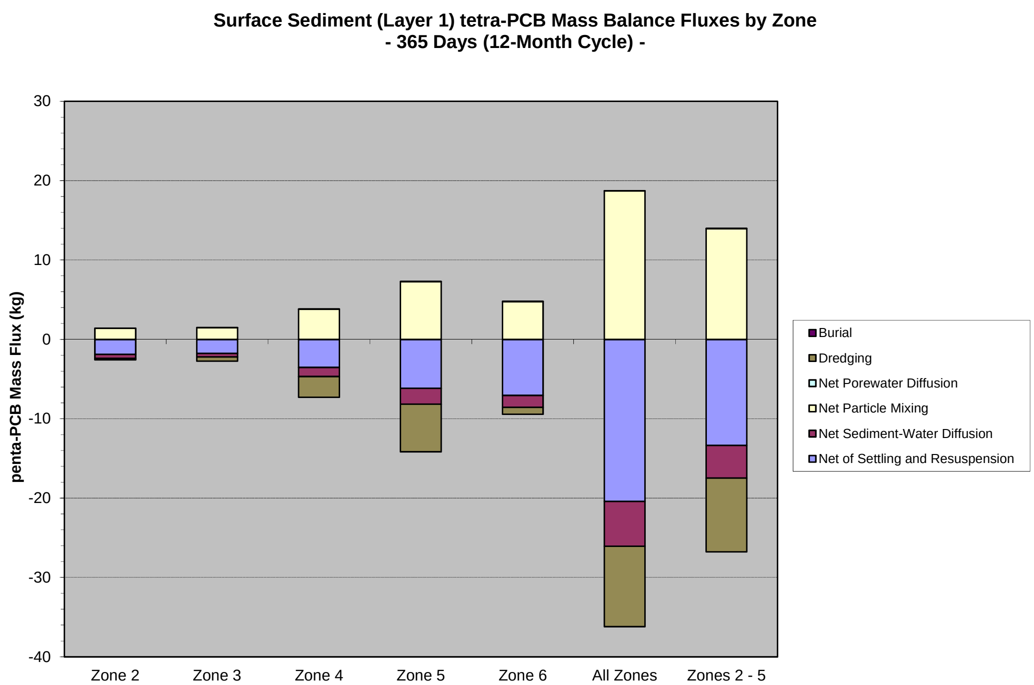


Figure 4.3.4-7: Tetra-PCB mass fluxes in the water column and surface sediment layer in kilograms for the 12 month model cycling period by Zone.

4.3.5 Hexa-PCBs

A spatial plot of observed and simulated hexa-PCB concentrations for 11 ambient surveys conducted between March 1, 2002 and March 31, 2003 are presented in Figure 4.1.3.4-1. The figure depicts the results for all 11 ambient surveys along with the minimum, median and maximum predicted concentrations from model simulations during that period.

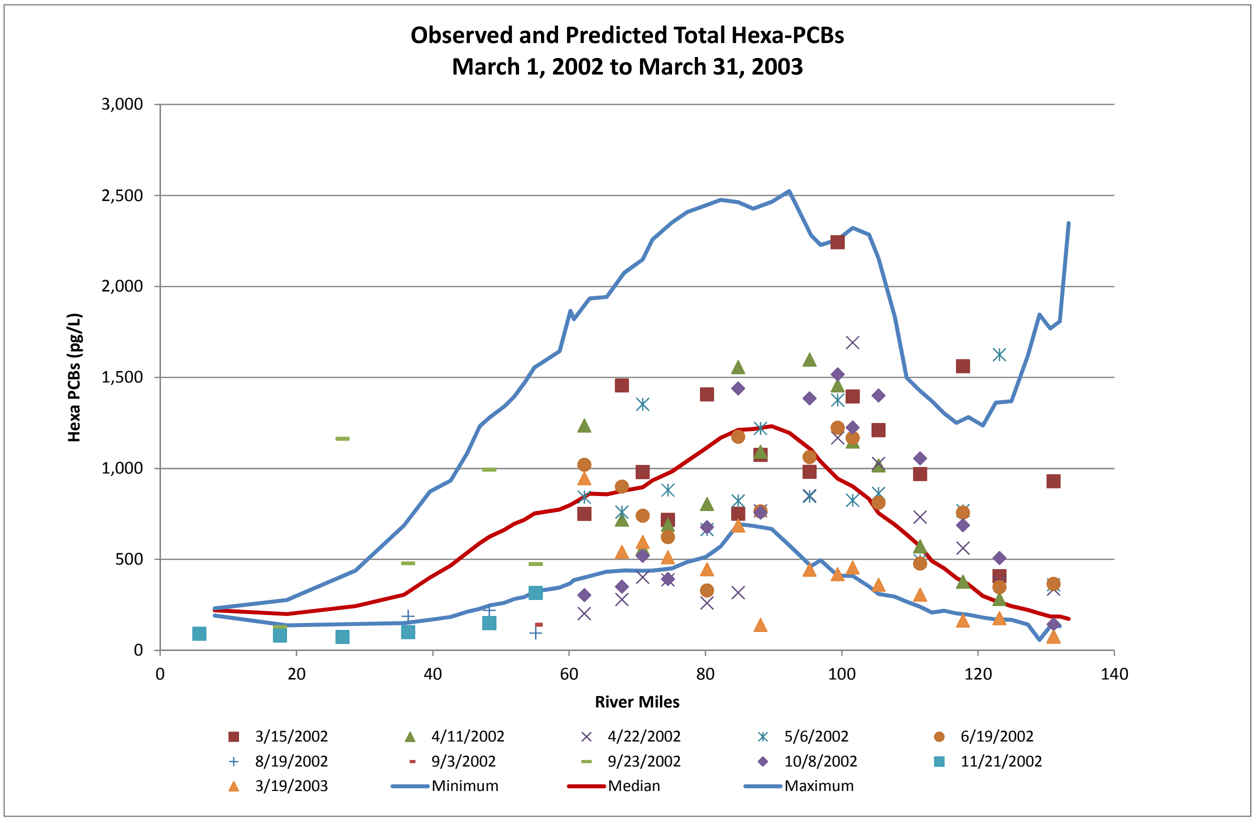


Figure 4.3.5-1: Spatial plots of Hexa-PCBs in the water column during 11 surveys conducted during the period March 1, 2002 and March 31, 2003 in the tidal Delaware River and Bay.

Bivariate plots of observed and simulated hexa-PCB concentrations are presented for each of the phases of PCBs tracked by the model and for carbon-normalized hexa-PCBs (R1) by Zone during the ambient surveys conducted in 2002 and 2003. Truly dissolved hexa-PCBs (DDPCB) are presented in Figure 4.3.5-2. Particulate hexa-PCBs (PPCB) are presented in Figure 4.3.5-3. Total tetra-PCBs (TPCB) are presented in Figure 4.3.5-4. Carbon-normalized hexa-PCBs (R1) are presented in Figure 4.3.5-5. Observed hexa-PCB values for each phase are plotted on the X-axis while simulated tetra-PCB values for that phase are plotted on the Y-axis. If the model simulation results match the observed value, then the point should fall on the line bisecting the graph. This line is represented by a slope of 1.0 and an intercept of 0.0.

Cumulative frequency distribution plots of observed and predicted total, dissolved and particulate hexa-PCBs during the one year cycling period are presented in Figure 4.3.5-6.

The results of a mass balance analysis for total hexa-PCBs in the water column and sediment layers are presented in Table 4.3.5-1. This table presents the mass flux in milligrams per day (mg/day) for various components in the water column and the surface sediment layer for the 12 month period used in long-term model simulations. Note that positive values indicate loading or fluxes to the water column or sediment layer, while negative values indicate a loss from the water column or sediment layer. Figure 4.3.5-7 graphically presents the mass flux for each Zone and model component.

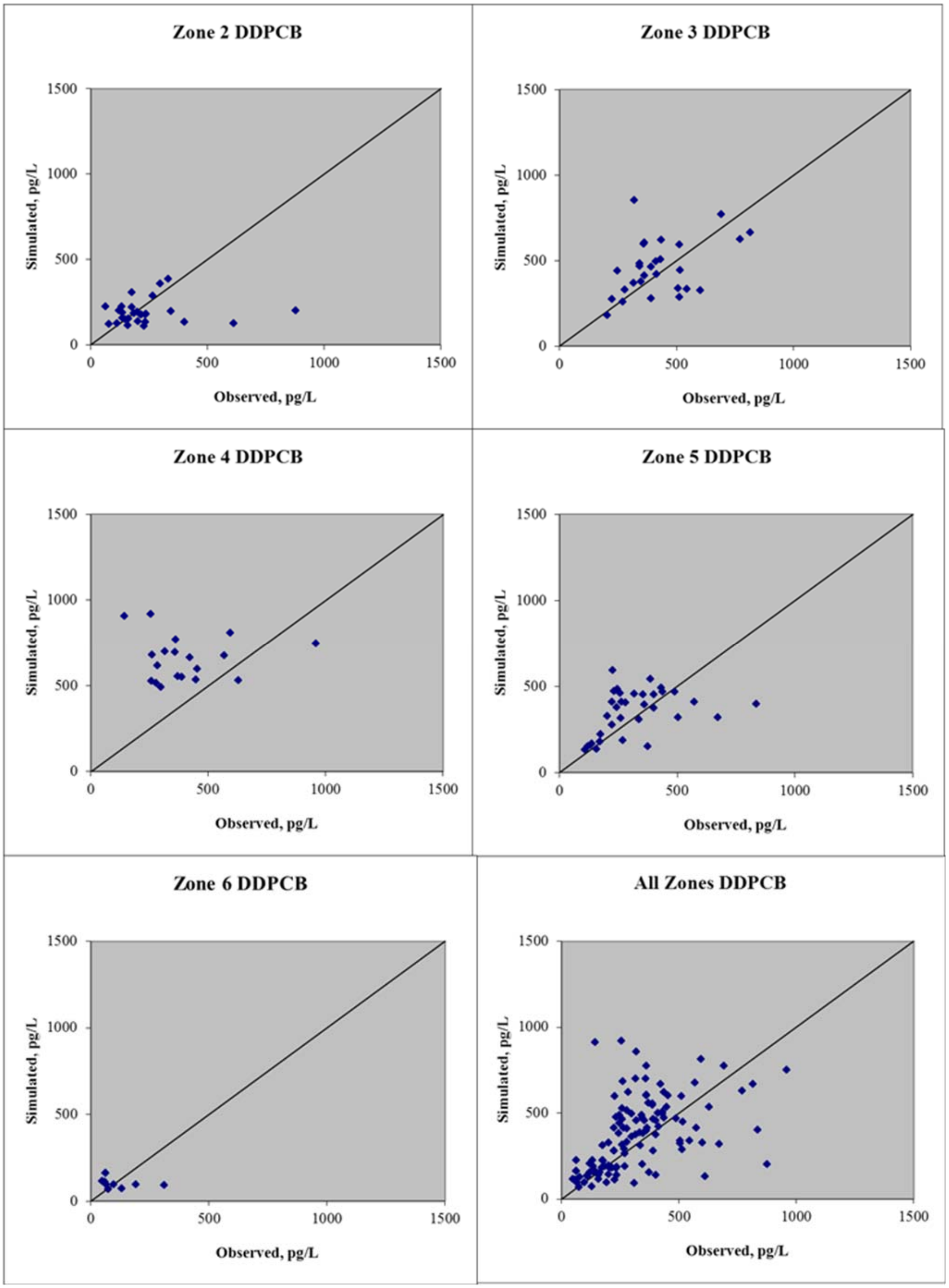


Figure 4.3.5-2: Bivariate plots of truly dissolved Hexa-PCBs (DDPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

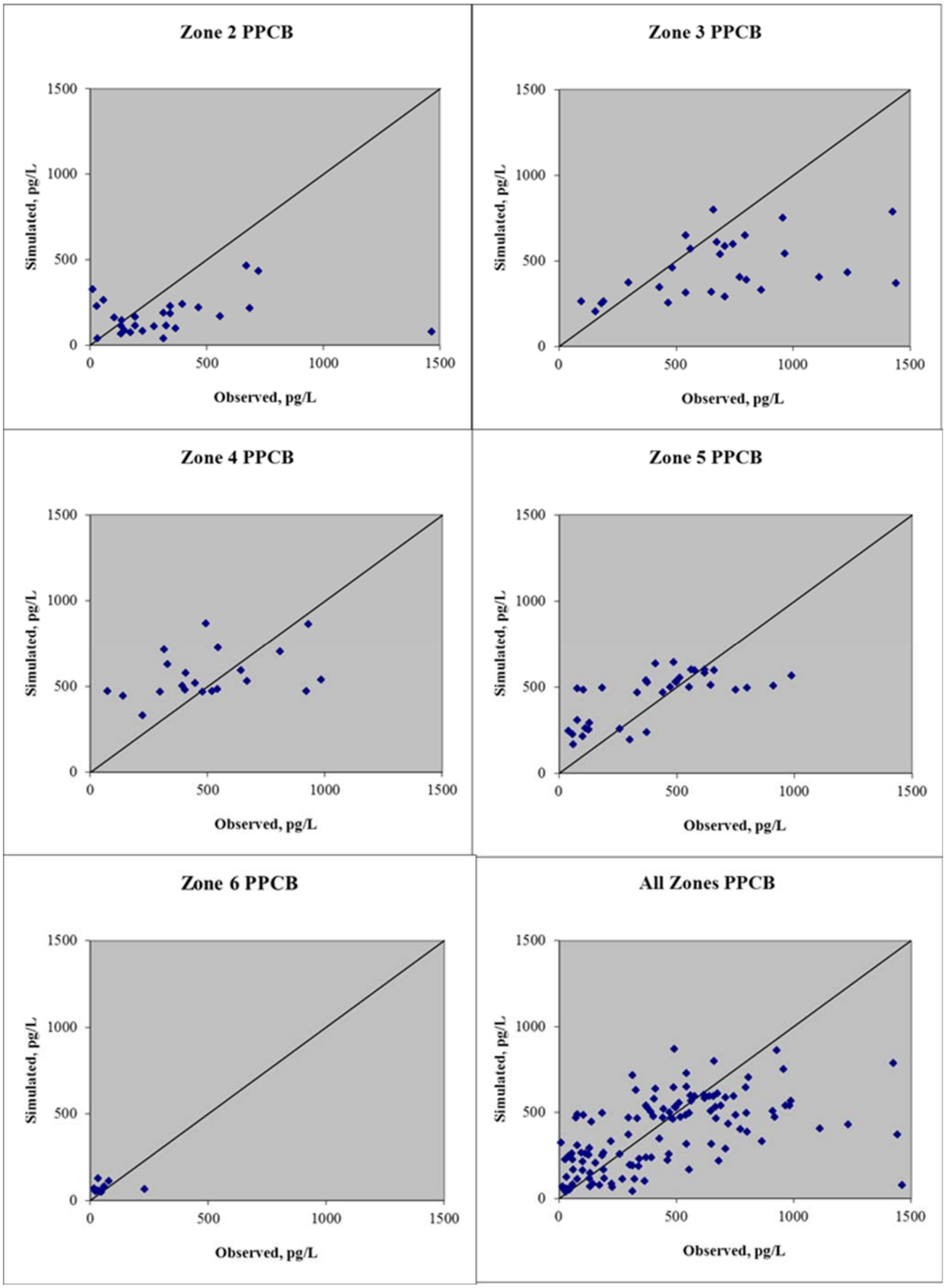


Figure 4.3.5-3: Bivariate plots of particulate Hexa-PCBs (PPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

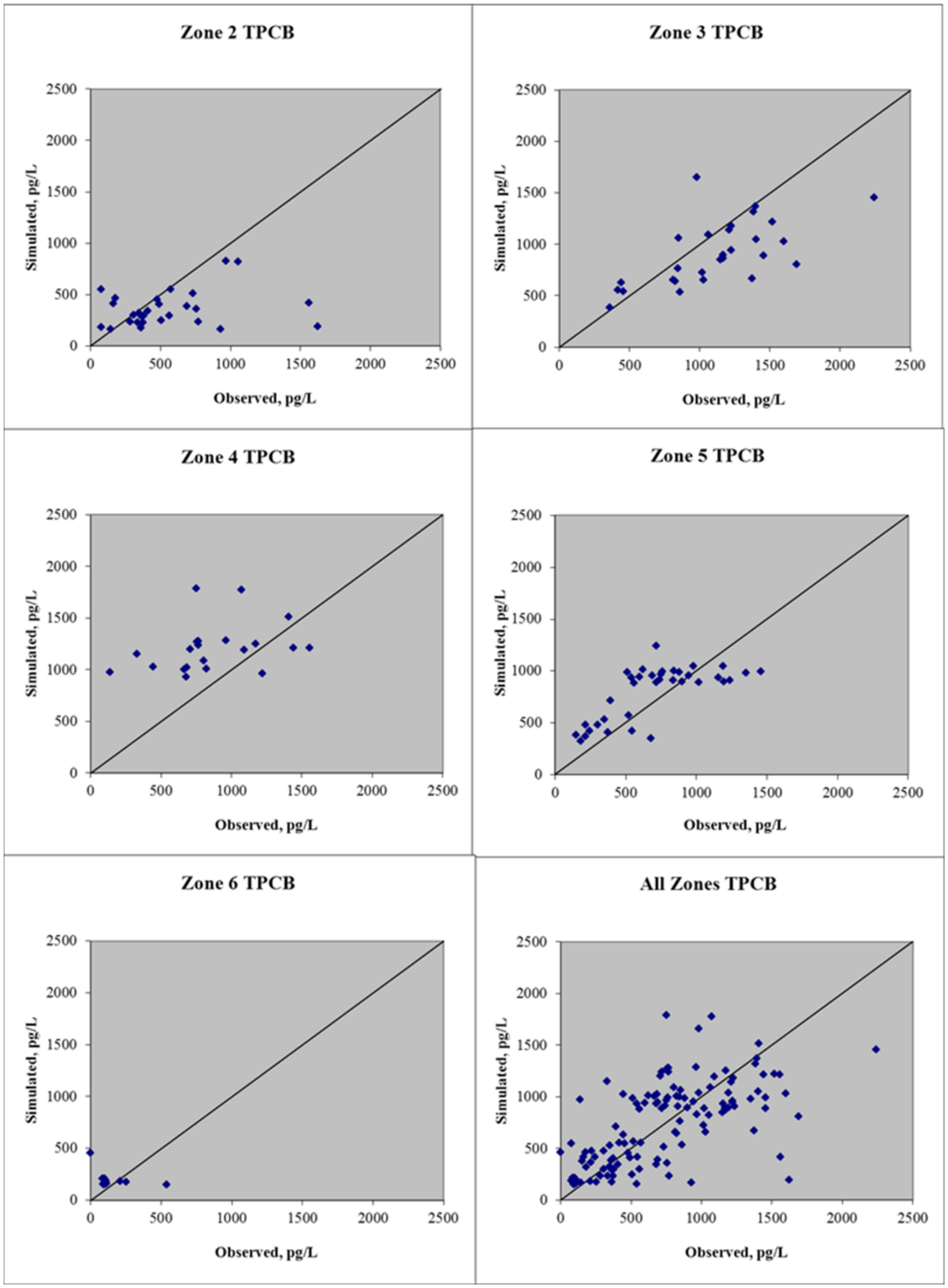


Figure 4.3.5-4: Bivariate plots of total Hexa-PCBs (TPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

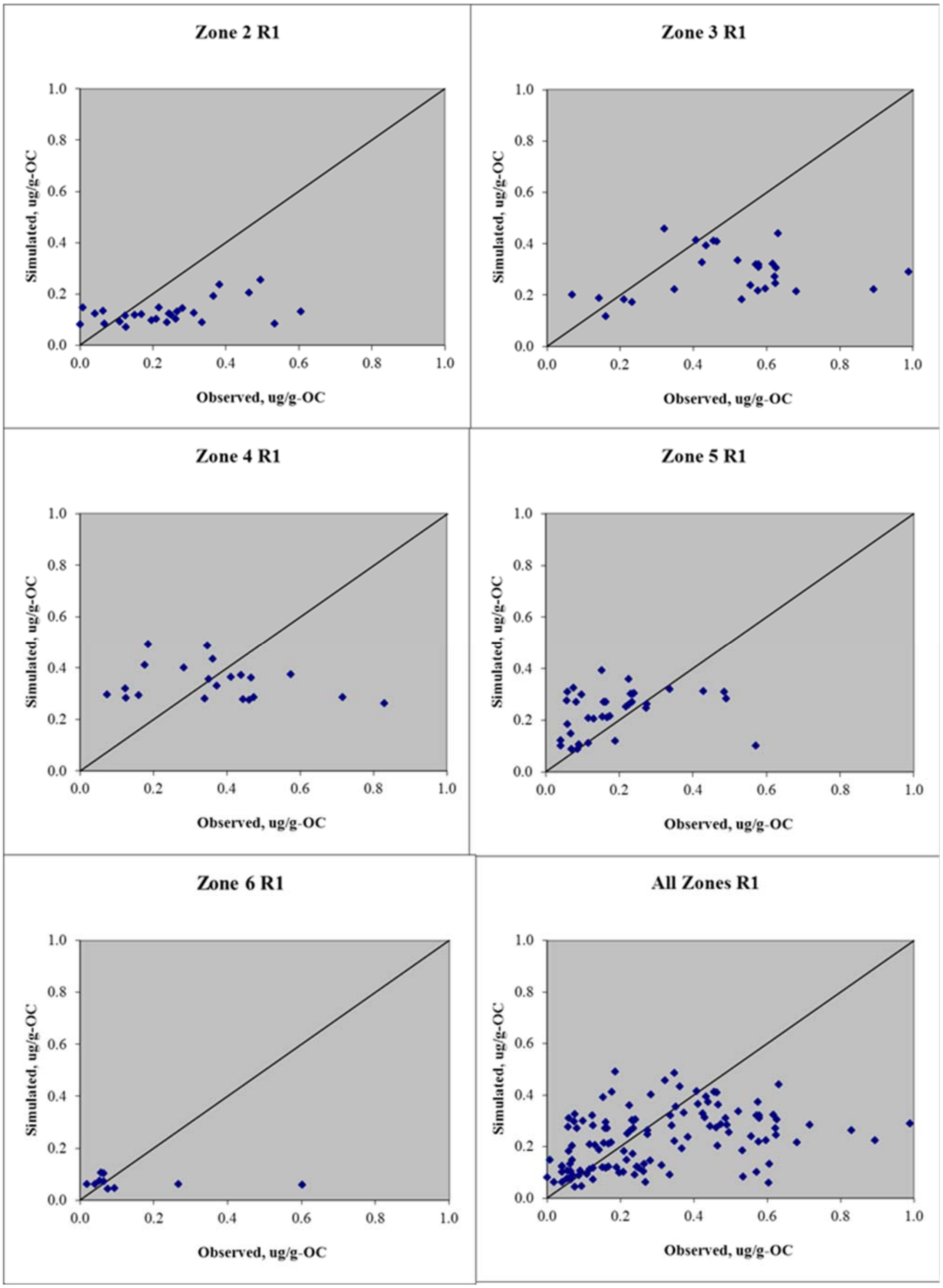
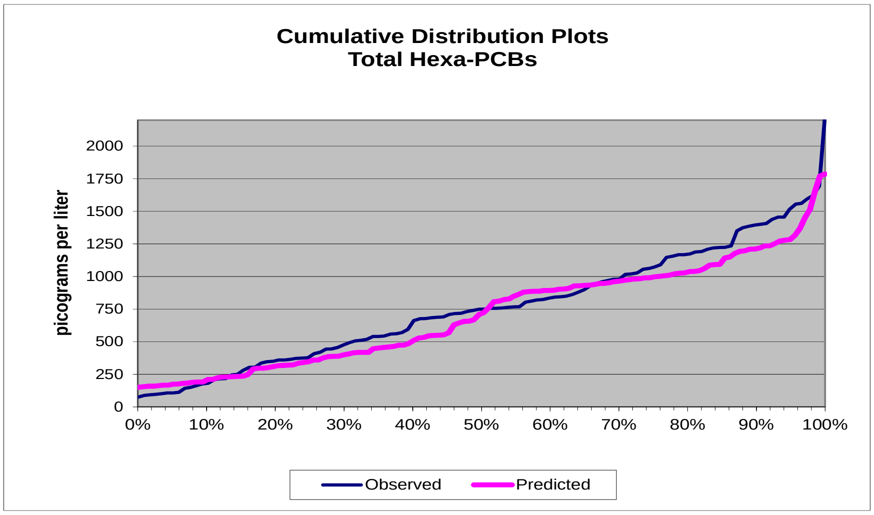
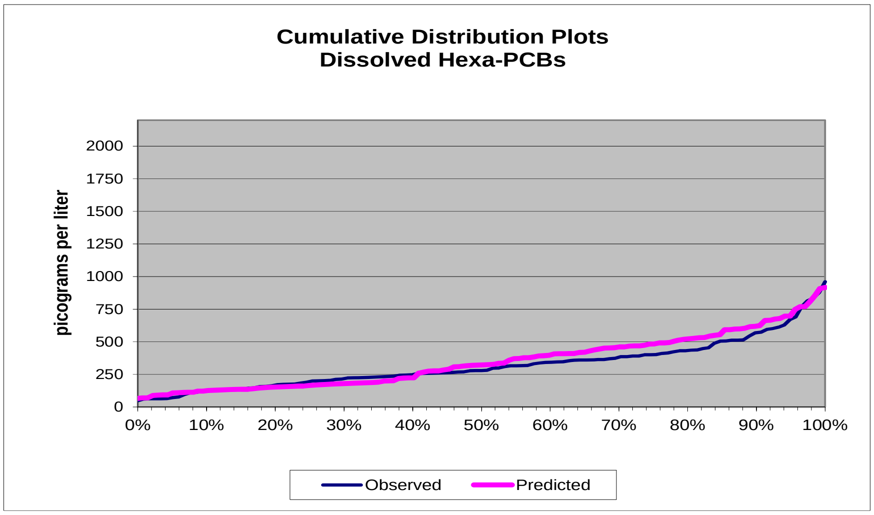


Figure 4.3.5-5: Bivariate plots of carbon-normalized Hexa-PCBs (R1) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.





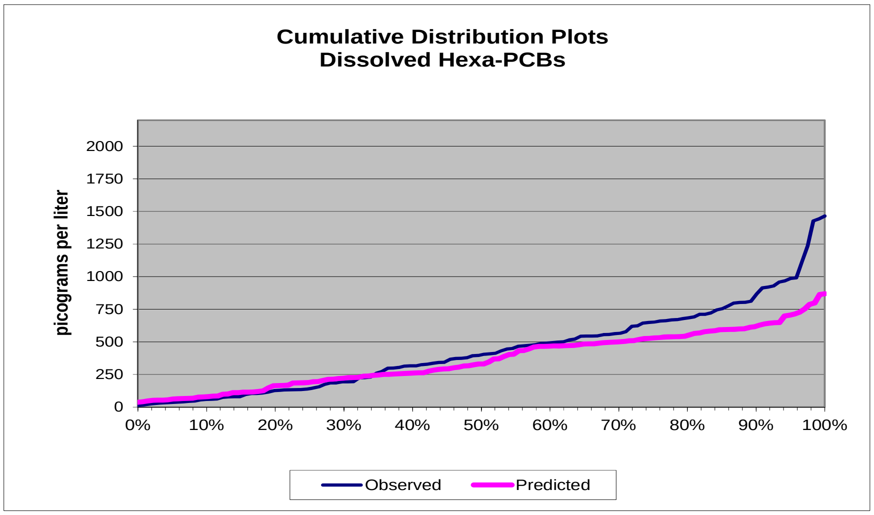


Figure 4.3.5-6: CFD plots of total (TPCB), dissolved (DPCB) and particulate (PPCB) hexa-PCBs during the 12-month model cycling period.

Table 4.3.5-1: Daily averaged Hexa-PCB mass balance for water column and surface sediment layer for 12-month period.

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Water Column Mass Balance Component Analysis by Zone for hexa PCB (mg/day)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	6,938	6,950	10,091	8,843	7,389	40,211	32,822
Dredging	0	0	0	0	0	0	0
Schuykill River	----	----	5,585	----	----	5,585	5,585
C&D Canal	----	----	----	-1,863	----	-1,863	-1,863
Exchange at Smaller Tributary Boundaries	0	0	0	0	----	0	0
Water Withdrawls (Segs 60, 66, 69)	-280	----	----	----	----	-280	-280
Upstream Interface Advection	5,398	18,145	29,975	50,074	31,190	5,398	5,398
Upstream Interface Dispersion	----	-327	-282	1,008	6,365	----	----
Downstream Interface Advection	-18,145	-29,975	-50,074	-31,190	50,495	50,495	-31,190
Downstream Interface Dispersion	327	282	-1,008	-6,365	----	----	-6,365
Air-Water Exchange	-2,411	-3,535	-9,591	-26,952	-82,325	-124,814	-42,488
Net Sediment-Water Diffusion	802	780	2,009	1,955	1,994	7,541	5,546
Net of Settling and Resuspension	7,268	7,363	12,543	-11,150	-219	15,803	16,023
Upstream Transport (Loss to Upstream)	----	0	0	0	-14,994	-14,994	0
Upstream Transport (Gain from Downstream)	0	0	0	14,994	----	14,994	14,994
Model Reported Excess Mass	**-1**	**0**	**-2**	**-15**	**3**	**-15**	**-19**
Change in Mass (ΣFluxes - Excess)	**-101.028**	**-317.667**	**-749.751**	**-631.705**	**-108.799**	**-1,908.949**	**-1,800.151**
Initial Mass (mg)	94,027	237,656	565,314	899,362	2,669,081	4,465,440	1,796,359
Final Mass (mg)	57,152	121,710	291,659	668,788	2,629,363	3,768,672	1,139,309
Change in Mass [Initial - Final] (mg/d)	**-101.028**	**-317.660**	**-749.740**	**-631.710**	**-108.815**	**-1,908.952**	**-1,800.137**
Water Column Mass Balance Closure (mg/d)	**0.000**	**0.007**	**0.011**	**-0.005**	**-0.017**	**-0.003**	**0.013**
Percent Tracking Error	**0.0002785%**	**0.0020034%**	**0.0013944%**	**-0.0002675%**	**-0.0002302%**	**-0.0000312%**	**0.0004280%**
Model Reported Excess Mass (mg/day)	**-1.249**	**-0.408**	**-2.395**	**-14.530**	**3.371**	**-15.211**	**-18.582**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-2,501	-3,223	-14,073	-56,624	-46,879	-123,299	-76,420
Gross Resuspension (mg/day)	9,769	10,585	26,615	45,473	46,660	139,102	92,443

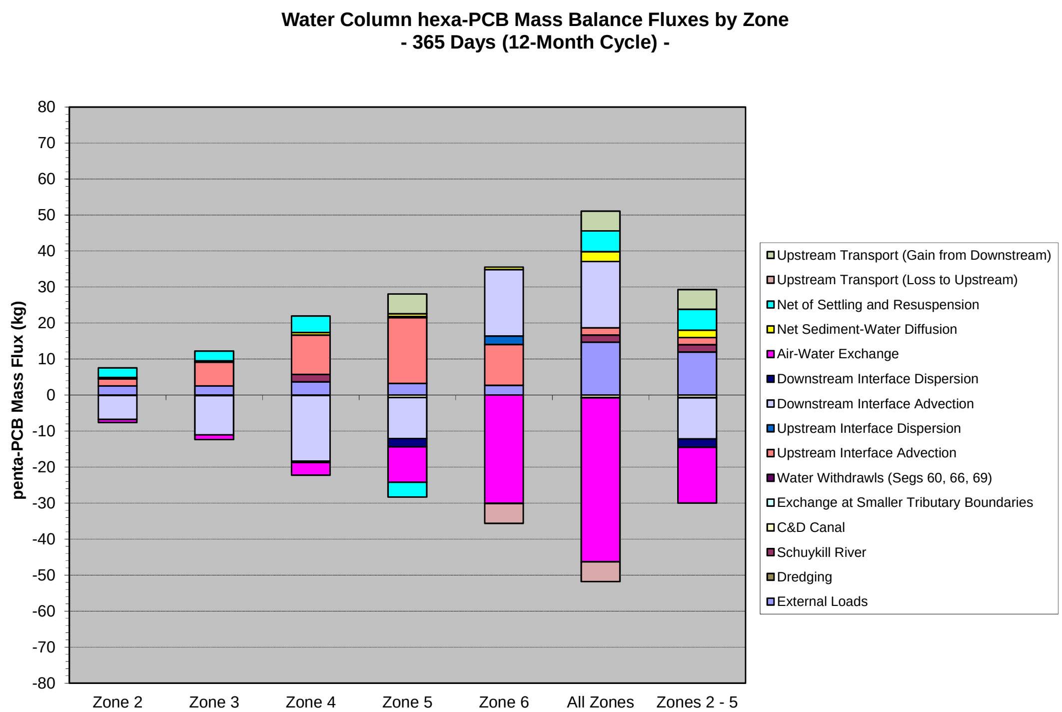
version May 20, 2010 - MB365

DELPCB 12-Month Cycle Surface Sediment Layer Mass Balance Component Analysis by Zone for hexa PCB (mg/day)

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	-7,268	-7,363	-12,543	11,150	219	-15,803	-16,023
Net Sediment-Water Diffusion	-802	-780	-2,009	-1,955	-1,994	-7,541	-5,546
Net Particle Mixing	4,973	5,962	15,184	8,748	3,569	38,436	34,868
Net Porewater Diffusion	0	1	2	1	0	4	3
Dredging	-703	-2,629	-13,791	-24,095	-3,519	-44,737	-41,218
Burial	0	0	0	0	0	0	0
Model Reported Excess Mass	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Change in Mass (ΣFluxes - Excess)	**-3,799.5**	**-4,808.9**	**-13,156.6**	**-6,151.0**	**-1,724.5**	**-29,640.5**	**-27,915.9**
Initial Mass (mg)	6,963,562	6,851,024	17,208,111	19,513,326	16,350,087	66,886,111	50,536,024
Final Mass (mg)	5,577,010	5,095,793	12,405,955	17,268,229	15,720,641	56,067,628	40,346,987
Change in Mass [Initial - Final] (mg/d)	**-3,798.8**	**-4,808.9**	**-13,156.6**	**-6,151.0**	**-1,724.5**	**-29,639.7**	**-27,915.2**
Surface Sediment Mass Balance Closure (mg/d)	**0.776**	**0.000**	**0.000**	**0.000**	**0.000**	**0.776**	**0.776**
Percent Tracking Error	**0.0050815%**	**-0.0000007%**	**0.0000005%**	**-0.0000007%**	**0.0000001%**	**0.0005053%**	**0.0007022%**
Model Reported Excess Mass (mg/day)	**0.014**	**-0.006**	**-0.060**	**0.075**	**0.006**	**0.029**	**0.023**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-2,501	-3,223	-14,073	-56,624	-46,879	-123,299	-76,420
Gross Resuspension (mg/day)	9,769	10,585	26,615	45,473	46,660	139,102	92,443



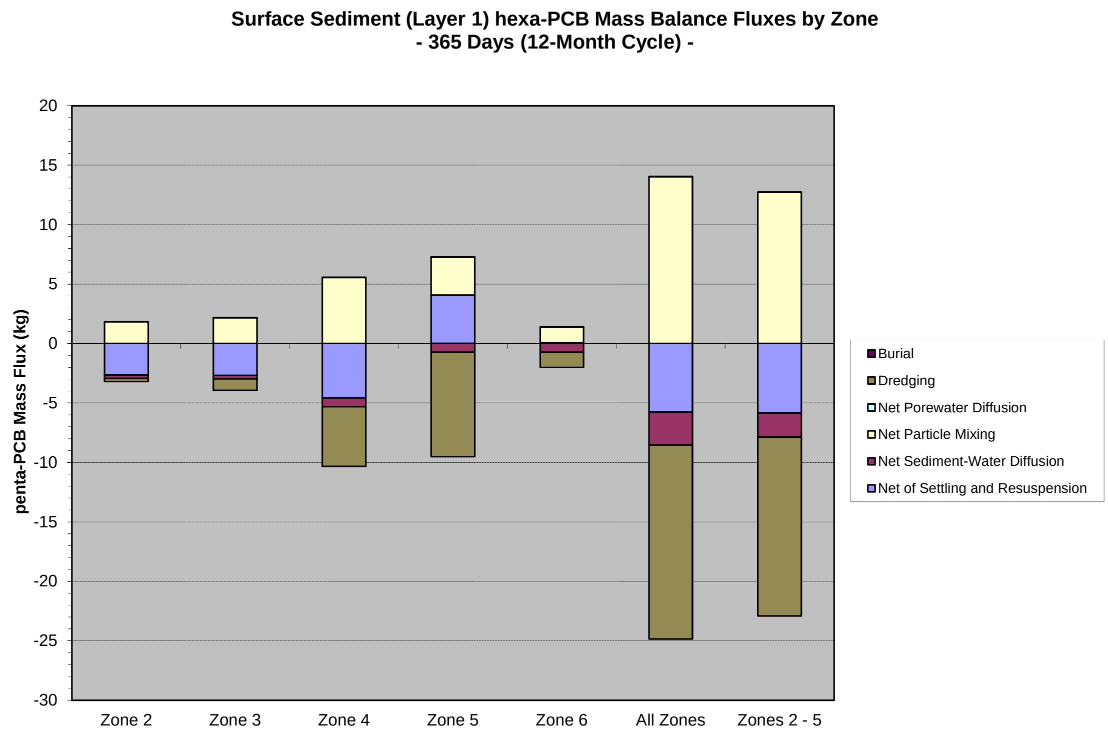


Figure 4.3.5-7: Hexa-PCB mass fluxes in the water column and surface sediment layer in kilograms for the 12 month model cycling period by Zone.

4.3.6 Hepta-PCBs

A spatial plot of observed and simulated hepta-PCB concentrations for 11 ambient surveys conducted between March 1, 2002 and March 31, 2003 are presented in Figure 4.3.6-1. The figure depicts the results for all 11 ambient surveys along with the minimum, median and maximum predicted concentrations from model simulations during that period.

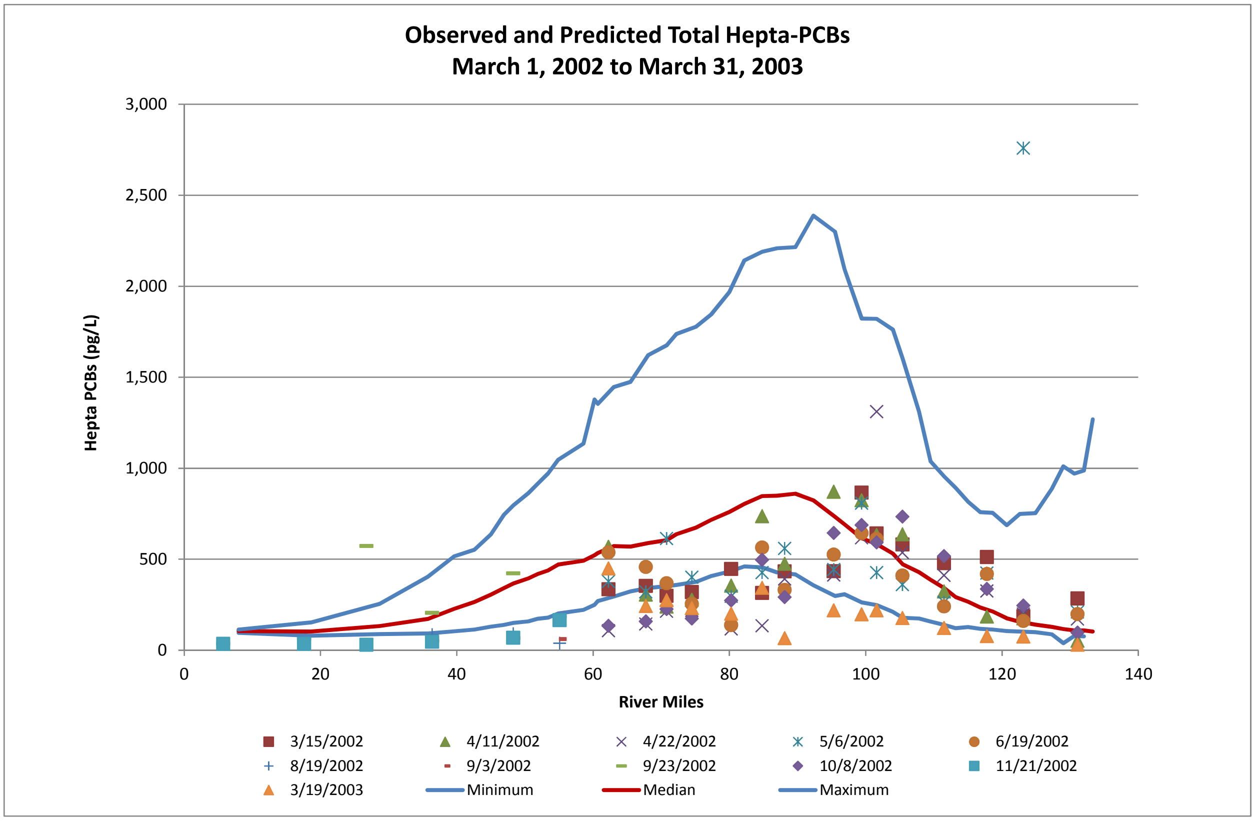


Figure 4.3.6-1: Spatial plots of Hepta-PCBs in the water column during 11 surveys conducted during the period March 1, 2002 and March 31, 2003 in the tidal Delaware River and Bay.

Bivariate plots of observed and simulated hepta-PCB concentrations are presented for each of the phases of PCBs tracked by the model and for carbon-normalized hepta-PCBs (R1) by Zone during the ambient surveys conducted in 2002 and 2003. Truly dissolved hepta-PCBs (DDPCB) are presented in Figure 4.3.6-2. Particulate hepta-PCBs (PPCB) are presented in Figure 4.3.6-3. Total tetra-PCBs (TPCB) are presented in Figure 4.3.6-4. Carbon-normalized hepta-PCBs (R1) are presented in Figure 4.3.6-5. Observed hepta-PCB values for each phase are plotted on the X-axis while simulated tetra-PCB values for that phase are plotted on the Y-axis. If the model simulation results match the observed value, then the point should fall on the line bisecting the graph. This line is represented by a slope of 1.0 and an intercept of 0.0.

Cumulative frequency distribution plots of observed and predicted total, dissolved and particulate hepta-PCBs during the one year cycling period are presented in Figure 4.3.6-6.

The results of a mass balance analysis for total hepta-PCBs in the water column and sediment layers are presented in Table 4.3.6-1. This table presents the mass flux in milligrams per day (mg/day) for various components in the water column and the surface sediment layer for the 12 month period used in long-term model simulations. Note that positive values indicate loading or fluxes to the water column or sediment layer, while negative values indicate a loss from the water column or sediment layer. Figure 4.3.6-7 graphically presents the mass flux for each Zone and model component.

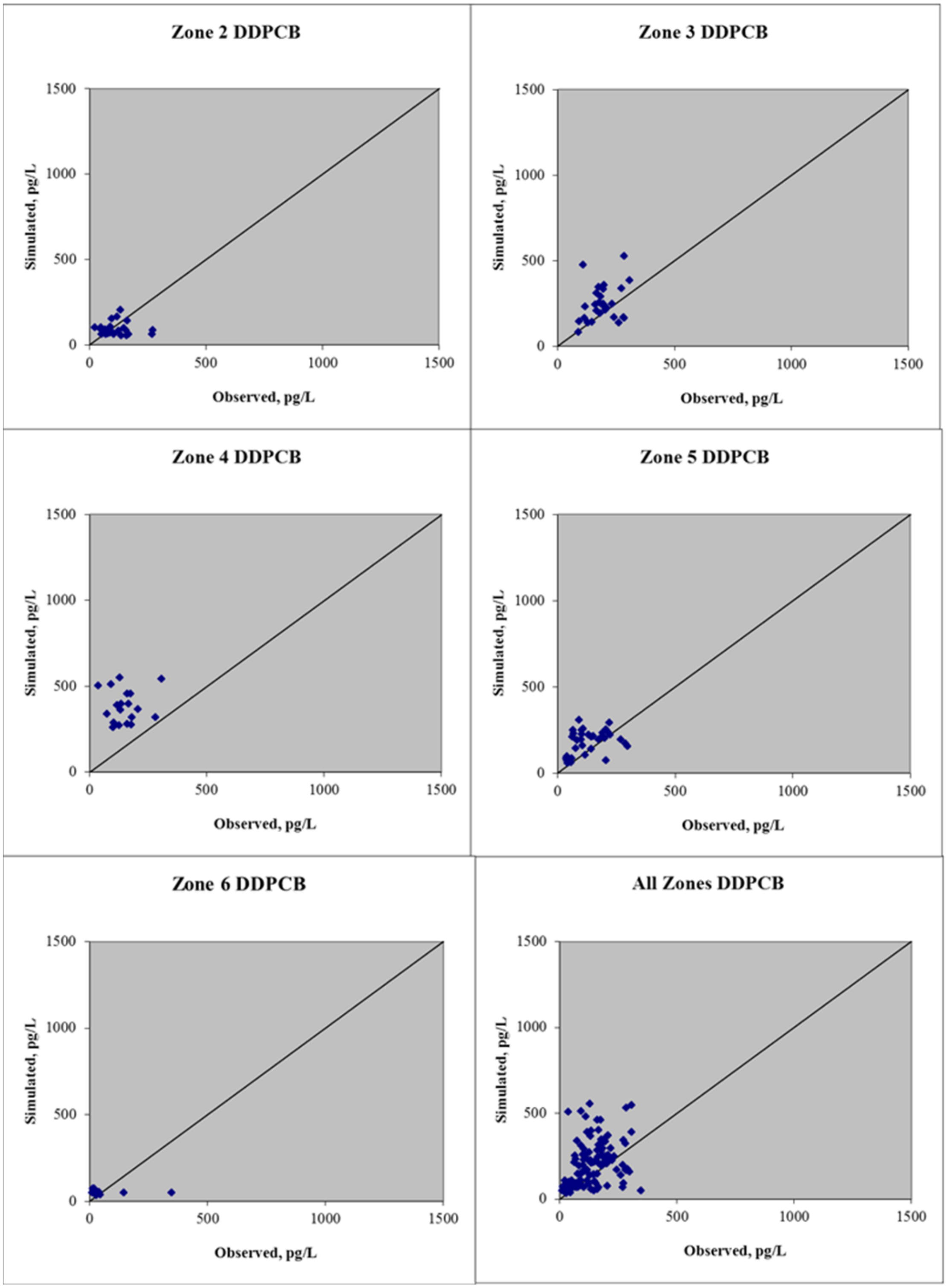


Figure 4.3.6-2: Bivariate plots of truly dissolved Hepta-PCBs (DDPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

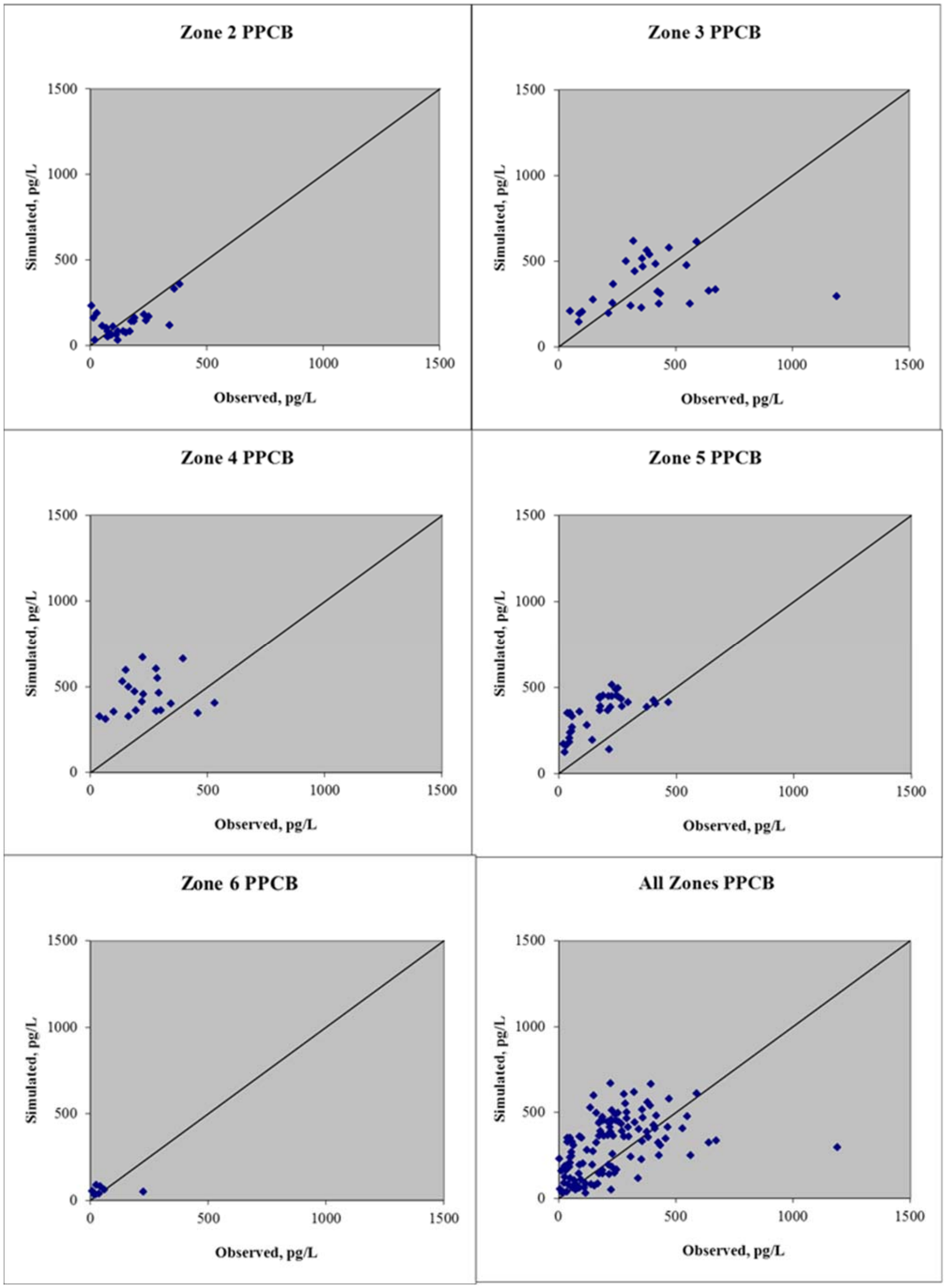


Figure 4.3.6-3: Bivariate plots of particulate Hepta-PCBs (PPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

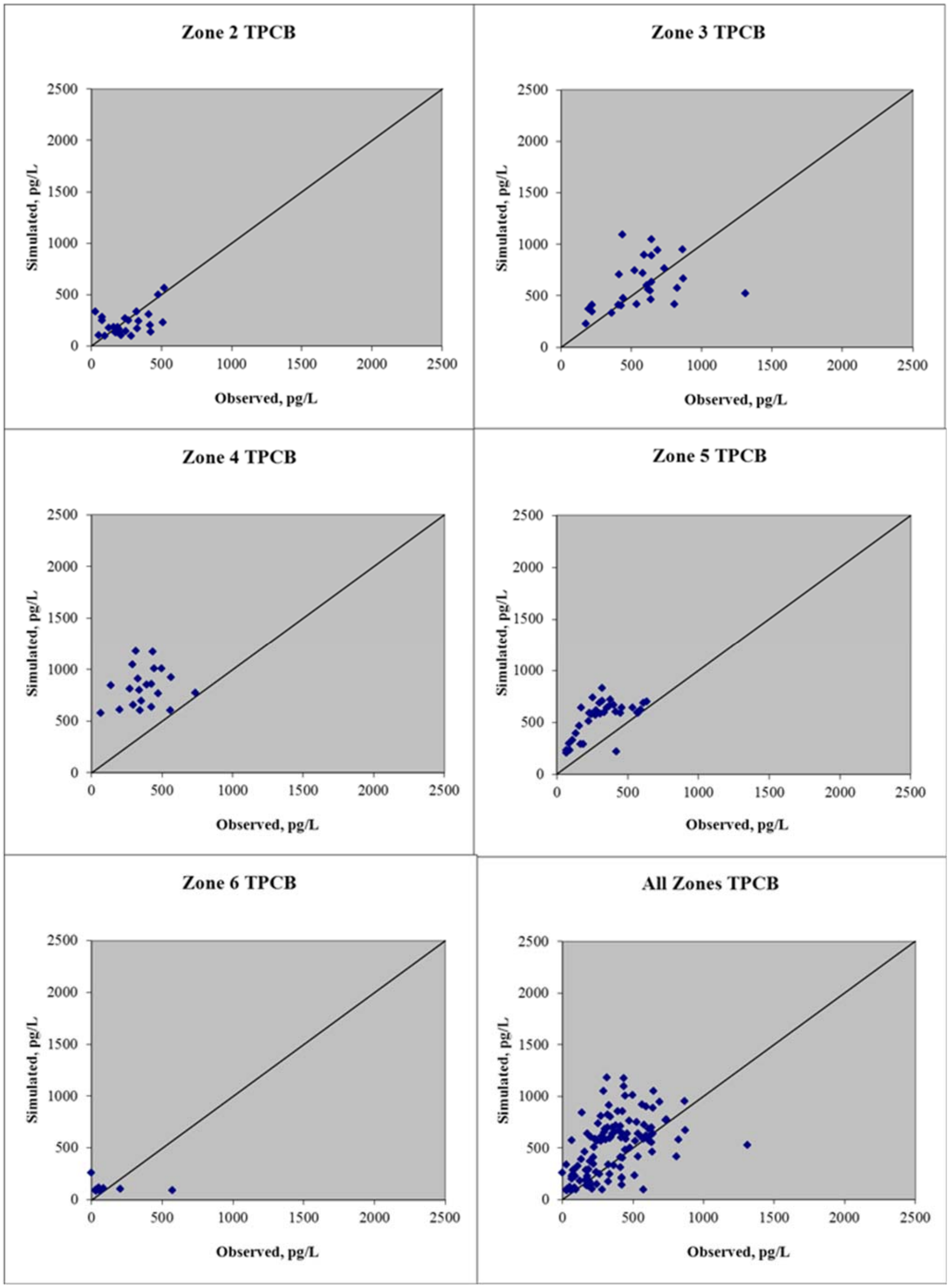


Figure 4.3.6-4: Bivariate plots of total Hepta-PCBs (TPCB) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

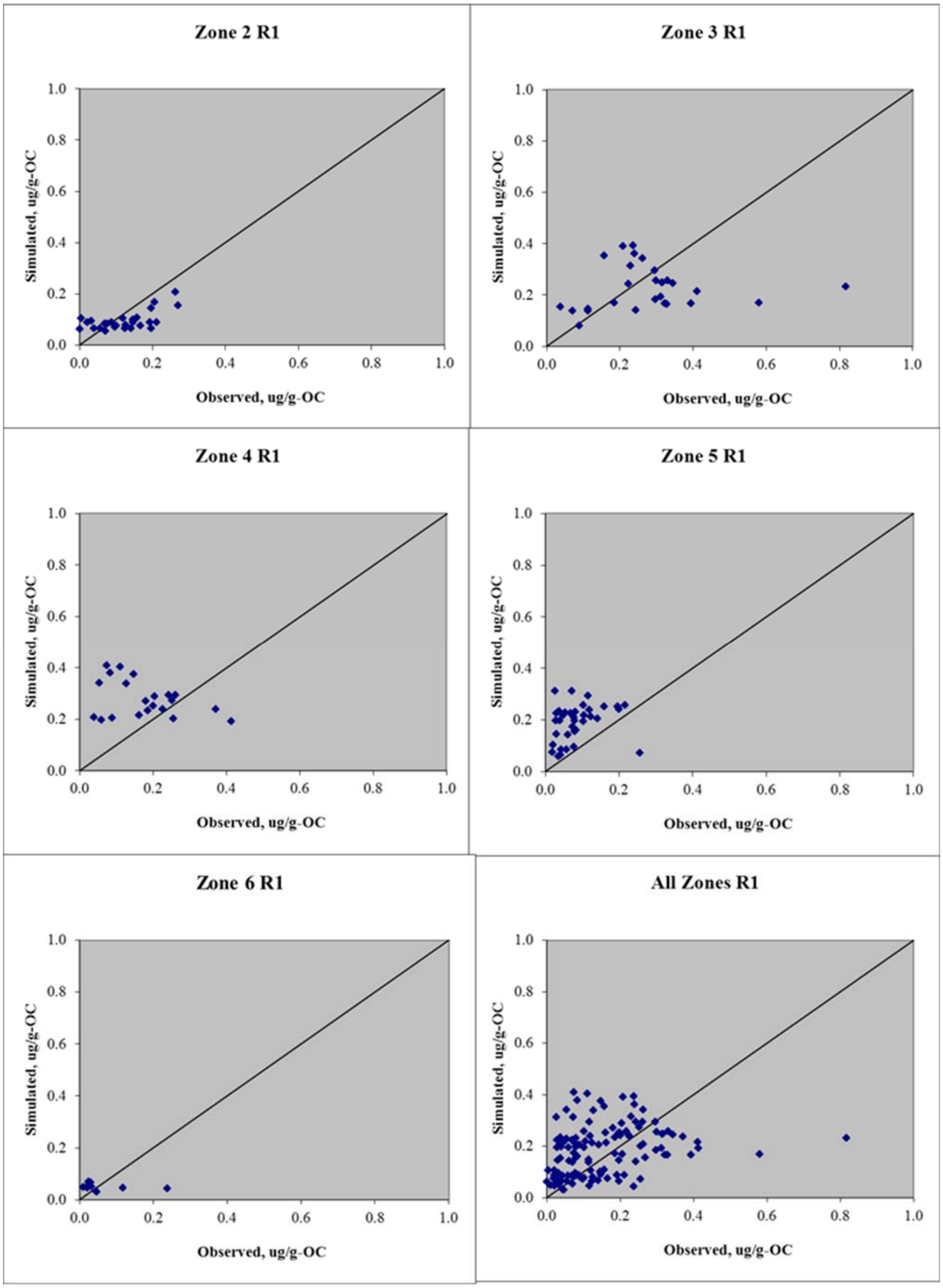


Figure 4.3.6-5: Bivariate plots of carbon-normalized Hepta-PCBs (R1) in each Zone and for All Zones Combined for the ambient surveys conducted in 2002 and 2003.

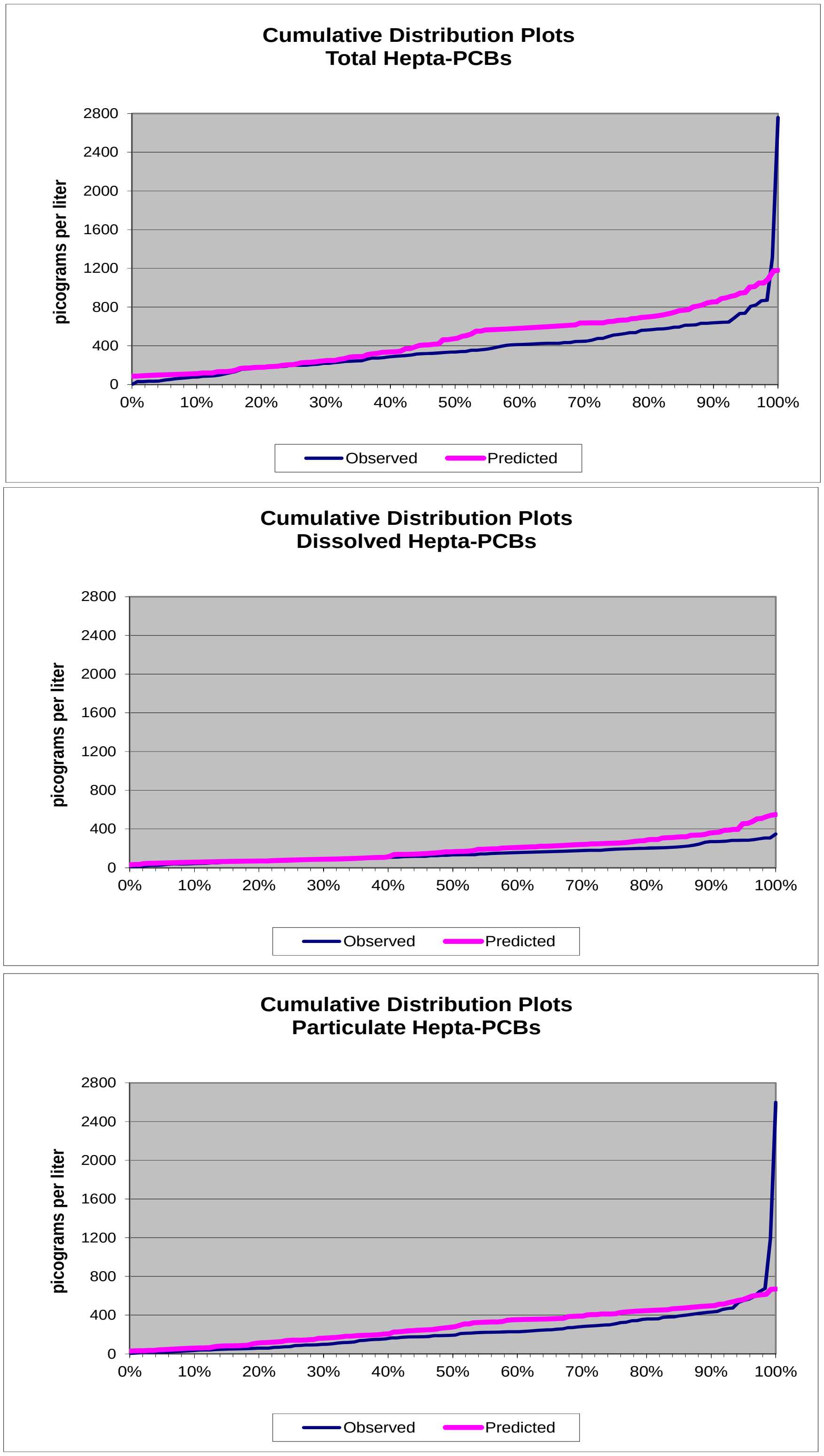


Figure 4.3.6-6: CFD plots of total (TPCB), dissolved (DPCB) and particulate (PPCB) hepta-PCBs during the 12-month model cycling period.

Table 4.3.6-1: Daily averaged Hepta-PCB mass balance for water column and surface sediment layer for 12-month period.

version May 20, 2010 - MB365

DELPCB 12-Month Cycle Water Column Mass Balance Component Analysis by Zone for hepta PCB (mg/day)

Mass Flux Type	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	All Zones	Zones 2 - 5
Water Column							
External Loads	3,804	4,602	9,992	5,175	5,255	28,828	23,573
Dredging	0	0	0	0	0	0	0
Schuykill River	----	----	2,934	----	----	2,934	2,934
C&D Canal	----	----	----	-1,806	----	-1,806	-1,806
Exchange at Smaller Tributary Boundaries	0	0	0	0	----	0	0
Water Withdrawls (Segs 60, 66, 69)	-175	----	----	----	----	-175	-175
Upstream Interface Advection	3,244	11,026	19,669	34,772	18,440	3,244	3,244
Upstream Interface Dispersion	----	-265	-242	740	4,889	----	----
Downstream Interface Advection	-11,026	-19,669	-34,772	-18,440	9,554	9,554	-18,440
Downstream Interface Dispersion	265	242	-740	-4,889	----	----	-4,889
Air-Water Exchange	-731	-1,231	-3,408	-8,890	-21,394	-35,654	-14,260
Net Sediment-Water Diffusion	373	418	934	793	819	3,338	2,519
Net of Settling and Resuspension	4,189	4,674	5,124	-17,590	-7,574	-11,176	-3,602
Upstream Transport (Loss to Upstream)	----	0	0	0	-9,829	-9,829	0
Upstream Transport (Gain from Downstream)	0	0	0	9,829	----	9,829	9,829
Model Reported Excess Mass	**-1**	**0**	**-2**	**-8**	**2**	**-9**	**-11**
Change in Mass (ΣFluxes - Excess)	**-54.776**	**-200.720**	**-508.403**	**-297.123**	**157.931**	**-903.091**	**-1,061.022**
Initial Mass (mg)	53,421	149,619	366,174	500,431	1,241,491	2,311,136	1,069,645
Final Mass (mg)	33,428	76,357	180,610	391,985	1,299,127	1,981,507	682,380
Change in Mass [Initial - Final] (mg/d)	**-54.776**	**-200.717**	**-508.395**	**-297.112**	**157.907**	**-903.092**	**-1,061.000**
Water Column Mass Balance Closure (mg/d)	**0.000**	**0.003**	**0.008**	**0.011**	**-0.023**	**-0.001**	**0.022**
Percent Tracking Error	**0.0004871%**	**0.0014043%**	**0.0016133%**	**0.0010275%**	**-0.0006592%**	**-0.0000195%**	**0.0011982%**
Model Reported Excess Mass (mg/day)	**-0.754**	**-0.256**	**-1.840**	**-7.884**	**1.584**	**-9.149**	**-10.733**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-1,811	-2,532	-11,392	-42,775	-29,960	-88,468	-58,509
Gross Resuspension (mg/day)	5,999	7,206	16,516	25,185	22,386	77,292	54,906

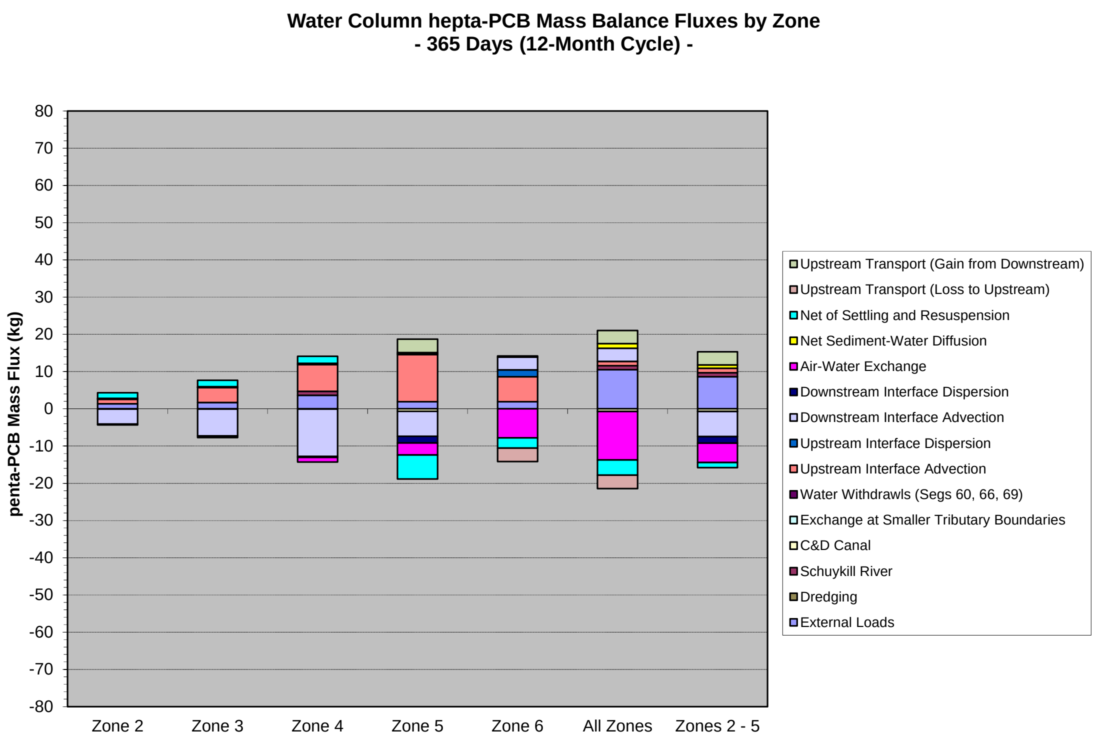
version May 20, 2010 - MB365

DELPCB 12-Month Cycle Surface Sediment Layer Mass Balance Component Analysis by Zone for hepta PCB (mg/day)

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	-4,189	-4,674	-5,124	17,590	7,574	11,176	3,602
Net Sediment-Water Diffusion	-373	-418	-934	-793	-819	-3,338	-2,519
Net Particle Mixing	2,853	3,857	8,075	-252	-1,843	12,690	14,533
Net Porewater Diffusion	-1	0	1	0	0	0	0
Dredging	-410	-1,810	-8,855	-14,526	-1,727	-27,327	-25,601
Burial	0	0	0	0	0	0	0
Model Reported Excess Mass	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Change in Mass (ΣFluxes - Excess)	**-2,120.7**	**-3,045.1**	**-6,837.3**	**2,018.1**	**3,185.0**	**-6,800.0**	**-9,985.0**
Initial Mass (mg)	4,113,126	4,625,283	10,524,095	9,985,081	7,160,435	36,408,020	29,247,584
Final Mass (mg)	3,339,472	3,513,825	8,028,468	10,721,670	8,322,974	33,926,408	25,603,435
Change in Mass [Initial - Final] (mg/d)	**-2,119.6**	**-3,045.1**	**-6,837.3**	**2,018.1**	**3,185.0**	**-6,798.9**	**-9,984.0**
Surface Sediment Mass Balance Closure (mg/d)	**1.065**	**0.000**	**0.000**	**0.000**	**0.000**	**1.065**	**1.065**
Percent Tracking Error	**0.0116420%**	**-0.0000002%**	**-0.0000011%**	**-0.0000001%**	**0.0000000%**	**0.0011456%**	**0.0015180%**
Model Reported Excess Mass (mg/day)	**0.012**	**0.016**	**0.088**	**-0.032**	**0.017**	**0.101**	**0.084**

Additional Sediment - Water Flux Information

Gross Settling (mg/day)	-1,811	-2,532	-11,392	-42,775	-29,960	-88,468	-58,509
Gross Resuspension (mg/day)	5,999	7,206	16,516	25,185	22,386	77,292	54,906



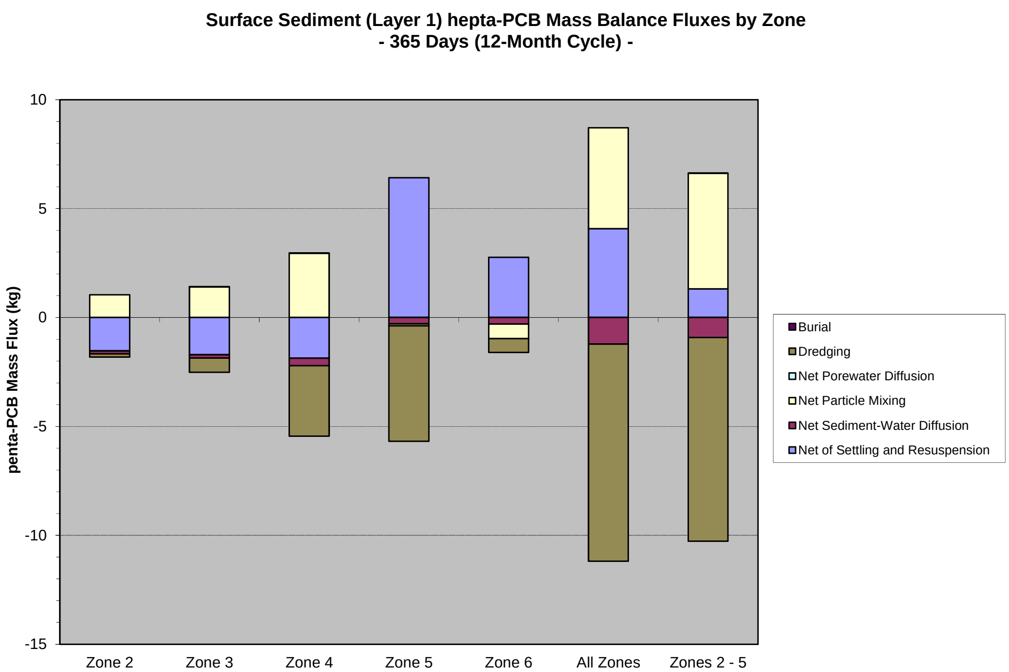


Figure 4.3.6-7: Hepta-PCB mass fluxes in the water column and surface sediment layer in kilograms for the 12 month model cycling period by Zone.

4.4 Hindcast Simulations

4.4.1 Introduction

The four homolog models were simulated for the 61-year period from 1950 to 2010 to evaluate the long-term behavior of the model. For practical purposes, a representative one year hydrodynamic condition was cycled from year to year (DRBC, 2003c) to complete the 61-year simulation. Information from three, spatially distributed, relatively undisturbed sediment cores from tidal marshes of the Delaware Estuary were used to reconstruct historical PCB loading conditions for each of four homologs to represent urban, suburban and background loading conditions.

Detailed description of development of historical loadings is discussed in Section 4.4.2. Historical and contemporary data used in model evaluations are discussed in Section 4.4.3. Simulated results are compared with available PCBs data collected in the water column, the surficial sediment layer and fish tissue. Comparisons between the simulated and historical data are graphically compared and discussed in Section 4.4.4.

Hydrophobic contaminants, like PCBs tend to attach to organic carbon in the water column and the particulate-associated organic carbons either settled to the sediment layer or are washed out of the Delaware Estuarine system. Approximately 0.03 to 8 percent of the surficial sediment mass in the Delaware estuary are composed of organic carbon based on analytical results from 158 surficial sediment grab samples collected from year 2000 to 2010. Even though a similar range of the fraction of organic carbon can be found in suspended solid particles in the water column, a greater (or denser) concentration of solids exists in the sediment layer. At least 200 times or more organic carbon mass are available in the sediment layer than in the water column on a volumetric basis. As a consequence, a greater amount of PCBs are stored in the sediment layer. Sediment layers play a role as a large buffer (like a reservoir) for external PCB loads. Changes of PCB concentrations in the sediment layer are much slower than concentration changes in the water column, and may not be detectable during the short-term, 19 month calibration period. Thus, decadal scale simulations are an important evaluation process in a modeling of hydrophobic contaminants since large portions of PCBs are partitioned to the particulate organic carbon and settle to the sediment layer. Exchanges of PCBs between the water column and the surface sediment layer occur through diffusion of PCBs, settling and resuspension of PCBs-contained particulate organic carbon. While PCB concentrations in the water column quickly respond to changes in external PCB loads into the system from multiple sources, PCB concentration changes in the sediment layer are relatively slower because the large mass of sediment has limited exchange with the water column requiring a longer time period to reach an equilibrium condition.

All model kinetics, coefficients, and constants were kept same as assigned in the short term calibration except the external loadings, gaseous PCB concentrations, boundary and initial conditions. All initial PCB concentrations for the water column and the sediment layers were set to zero based on three reasons. The first reason was that there were no such data available to define the condition in 1950. The second was that the most of core data detected very low levels of PCBs pre-1950. The last reason was that the earliest observed data points to compare with the simulated results were from 1969 and 20 years seemed to be sufficient time for the model to ramp-up.

The goal of this task is to demonstrate that the coefficients selected for model parameters during the short term calibration of the four homolog models can reasonably reproduce temporal and spatial trends of PCB concentrations in the water column, the sediment layer and the fish tissue when historical external loadings, boundary conditions and gaseous PCB concentrations are utilized. Because of uncertainties in historical PCB loadings, it is important to note that the task must be focused on trend evaluations rather than matching individual observed data values. A successful demonstration of the model performance in this section will validate assigned kinetics of the model, especially settling/re-suspension rates which are major mechanisms of exchanging PCBs between the sediment layer and the water column. This step is considered as a 'consistency check' rather than a formal calibration/validation process.

4.4.2 Reconstruction of Historical PCB loading Conditions

To perform 61-year hindcast simulations, reconstructions of historical PCB loading conditions were required. Because of lack of historical PCBs loading data for each of source categories incorporated in the Delaware Estuary water quality model, temporally varying historical loading conditions were developed based on available data. It was determined that PCB loading conditions were well defined for the year 2002 through intensive monitoring efforts for ambient waters including upstream (Delaware River at Trenton and Schuylkill River) and downstream boundaries (Atlantic Ocean and C & D Canal), atmospheric gaseous PCBs, and various external source categories. Given well-defined annual load/concentrations for calendar year 2002, efforts were then focused on the reconstruction of scaling factors for each year for the 61-year simulation period. A temporal scaling factor for each year was developed and multiplied by 2002 loading conditions to develop loading conditions for a given year. The scaling factor for the year 2002 was thus 1.0.

In the Stage 1 modeling effort, a single temporal scaling factor was developed and applied for the 73-year hindcast simulation based on the estimated U.S. penta-PCB air emission (Breivik et al., 2002a and 2002b). Because the emission estimated by Breivik et al. projected up to year 2000, the trend was extended to year 2002 using an exponential curve fit. It was later found that a selection of the methodology of the curve fit to extend to year 2002 had a significant impact on the overall magnitude of the scaling factor. In addition, one of the recommendations from the Stage 1 hindcast evaluation task was the development of the localized scaling factor. Even though Breivik et al. (2007) revised their initial emission estimations to year 2100 with a refined spatial resolution, generalized assumptions were still involved to estimate emission rates. In this study, scaling factors were developed based on information from three spatially distributed sediment cores collected in the Delaware Estuary. Sediment cores collected from the accretionary tidal marsh could be considered as a time capsule for a specific time period as long as the deposited layers were not disturbed by human, high energetic or biological activities. It was then assumed that undisturbed sediment cores contain a temporal record of the PCB loading history to the estuary.

A sedimentological study of Delaware Estuary (Sommerfield and Madsen, 2003) found that none of cores collected from the mainstem of the estuary displayed the ideal radioisotope (Cs-137) profile to develop the sediment layer chronology. Rather, the bottom of the subtidal estuary was disturbed by intense erosion-deposition cycles (high energetic activity) or dredging activities (human activity). Alternatively, eleven sediment cores were collected from the tidal marshes and floodplains fringing the Delaware estuary and analyzed for both Cs-137 for dating and chemical analyses including PCBs. Sites were strategically selected in the low marsh so that the collected cores would preserve time series sediment layers with minimal disturbances. Locations of core collection sites are depicted in Figure 4.4.2-1.

Among those 11 cores, three cores were selected to develop the regional, historical load scaling factors based on two key selection criteria, (1) a reasonable, decent Cs-137 profile so that the vertical disturbances were not significant; and (2) the minimal impact from localized PCB sources. The second criterion was evaluated by comparing temporal changes in the PCB of homolog distributions in the core slices. As shown in the historical PCB homolog distribution from the Dividing Creek marsh core (Figure 4.4.2-2), as an example, the homolog distribution suddenly changed (unusual high nona and deca PCBs signatures) in 1985 (Figure 4.4.2-2). In addition, concentrations in that core slice showed an order of magnitude higher concentration than concentrations found in the rest of the slices, which indicates impacts from a localized source(s).

After the review of Cs-137 and PCB concentration/distribution profiles, three cores collected from Crosswicks Creek marsh, Woodbury Creek marsh and Kelly Island cores were selected to develop scaling factors. Summaries of each core are shown in Figures 4.4.2-3 to 4.4.2-5. In each figure, panel (a) shows homolog distributions of PCBs in each sediment layer; panel (b) shows PCB homolog concentrations in each sediment layer; and panel (c) shows historical load scaling factors with the base year being set at year 2002 for the Crosswicks Creek and Kelly Island cores. Year 2001 was used as a base year for the Woodbury Creek core in this figure.

Figure 4.4.2-1: Locations of sediment core collection in the Delaware estuary

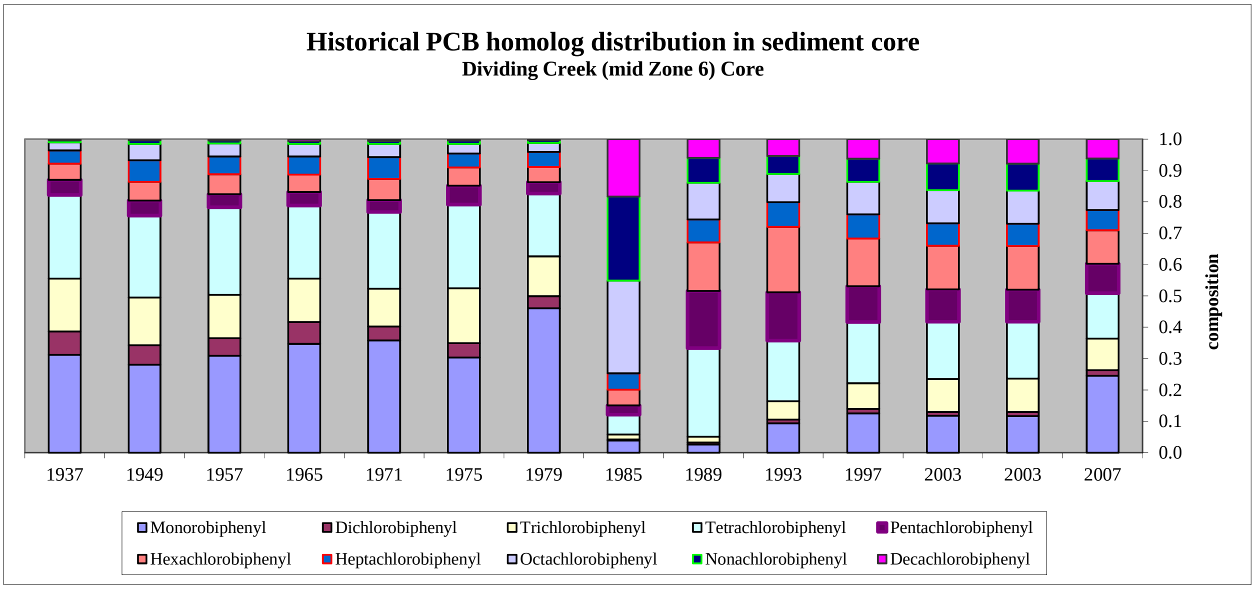


Figure 4.4.2-2: Historical PCB homolog distribution in the Dividing Creek marsh sediment core.

PCB concentrations in the Woodbury creek core are 10 ~ 100 times higher than concentrations measured in the other two cores and it is assumed to represent the influence of an urban environment. The scaling factor derived from the Woodbury creek core was applied to develop historical loadings, boundaries and atmospheric gaseous PCB conditions in Zones 3, 4, and 5. PCB concentrations in the Kelly Island core are relatively low and it is assumed to represent background or rural conditions. Even though there are signs of heavier homolog inputs in 1950s, the overall magnitude is relatively small and four homologs of interest do not appear to be affected by the pulsed inputs. The scaling factor derived from the Kelly Island core was applied to Zone 6. Zone 2 is considered as a suburban area and historical PCB conditions were developed for this Zone using the scaling factor based on the Crosswicks core.

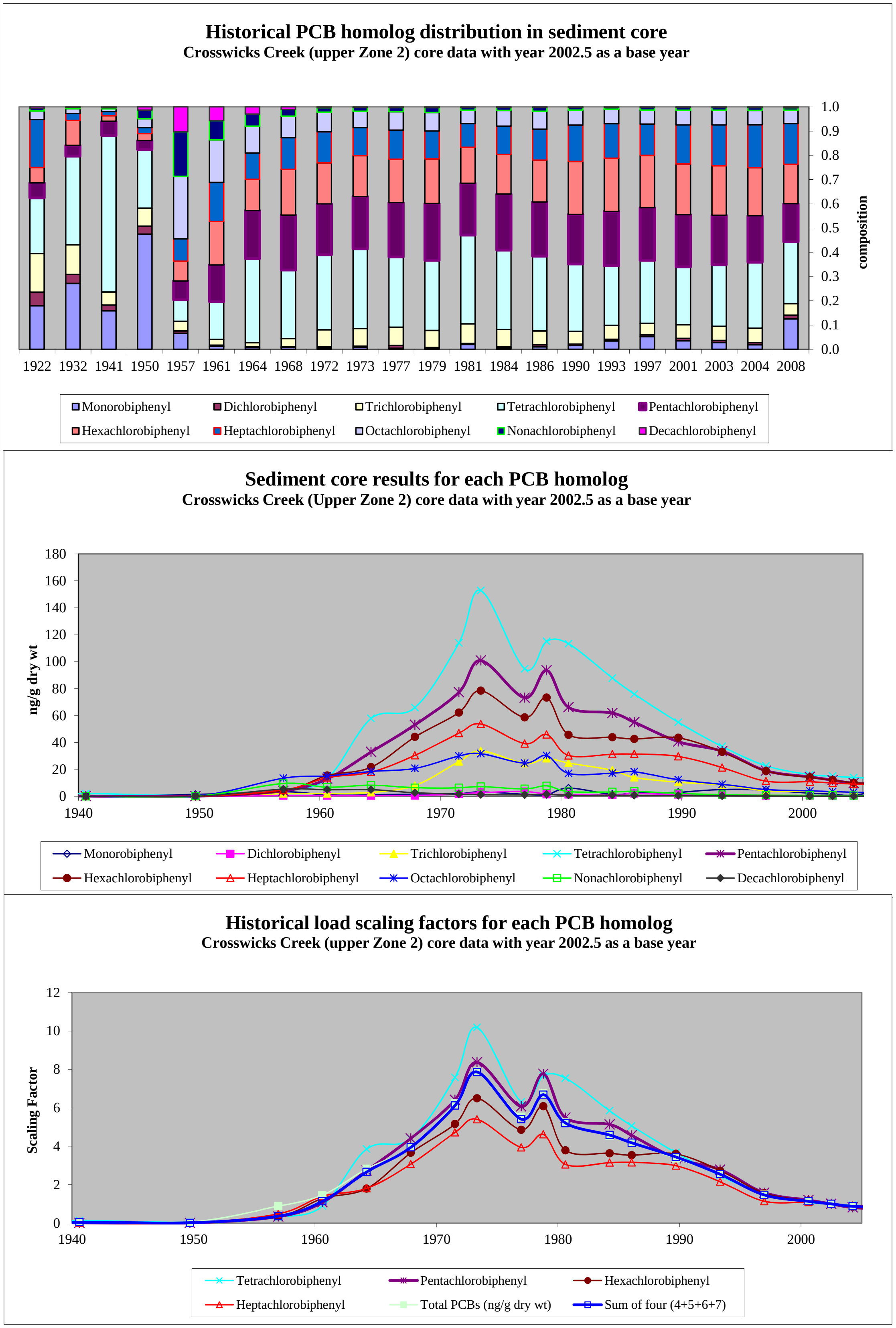


Figure 4.4.2-3: Sediment core data collected from Crosswicks Creek Marsh in Zone 2

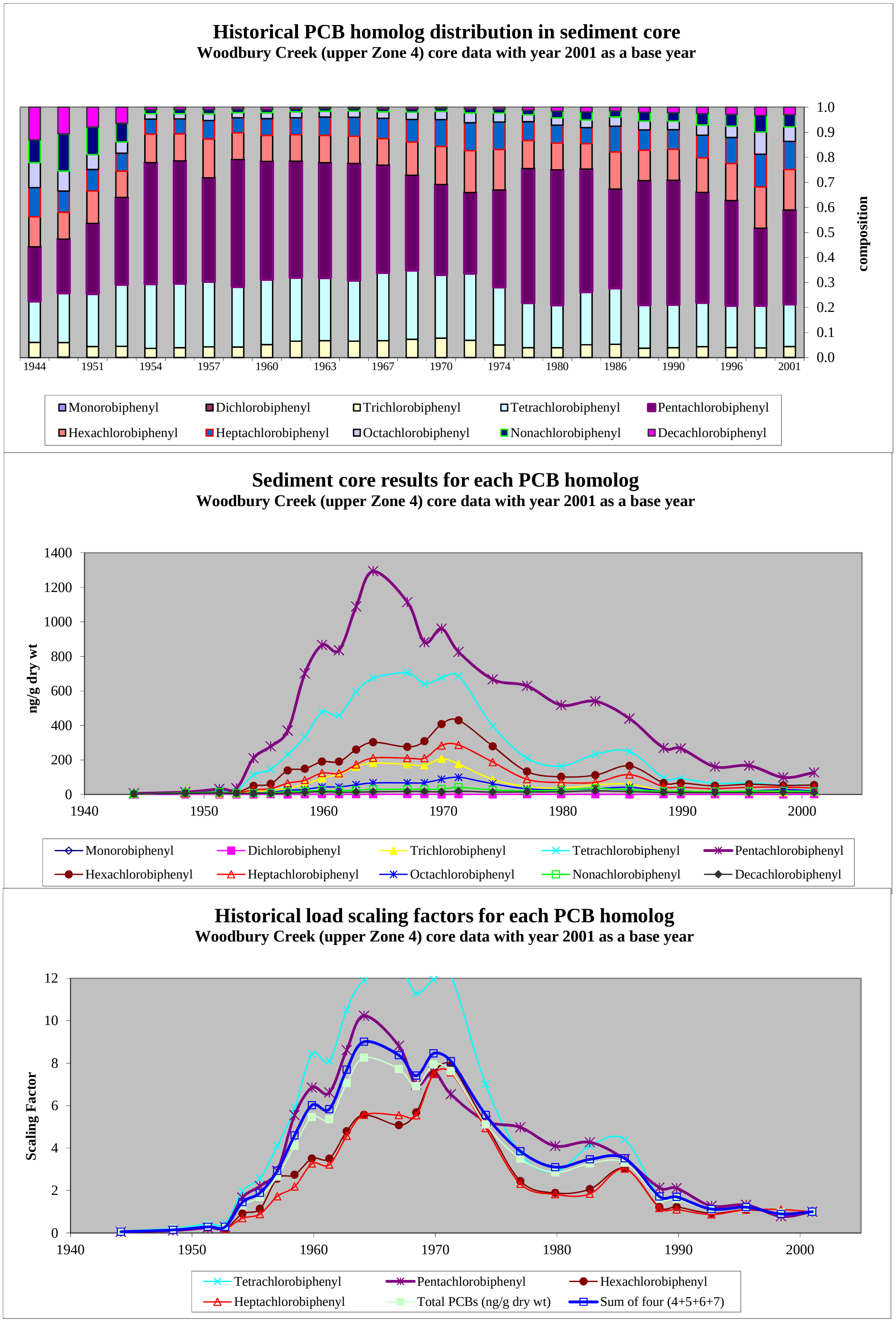
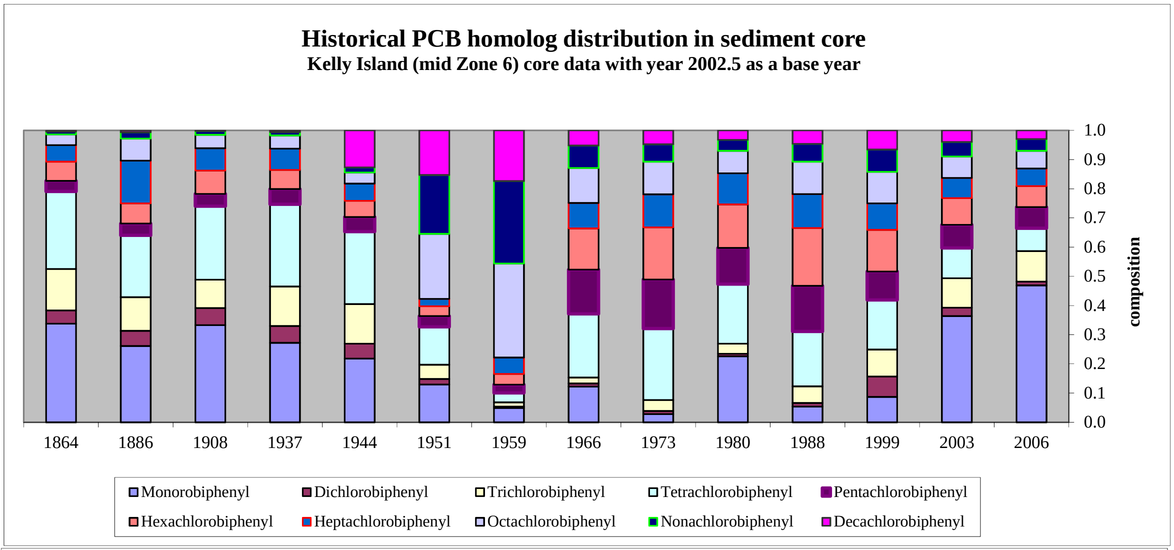
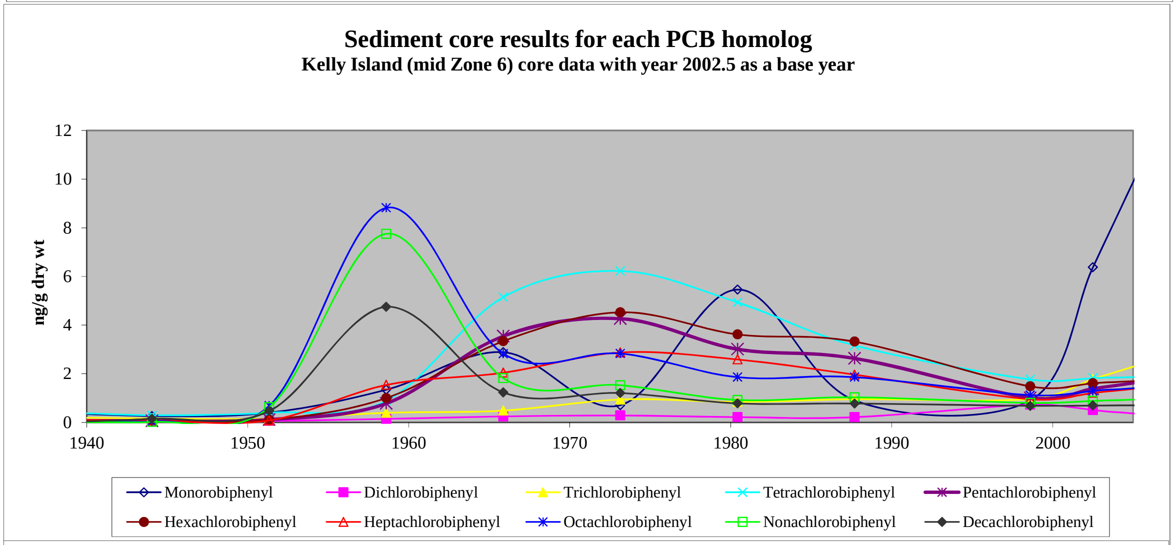


Figure 4.4.2-4: Sediment core data collected from Woodbury Creek Marsh in Zone 4





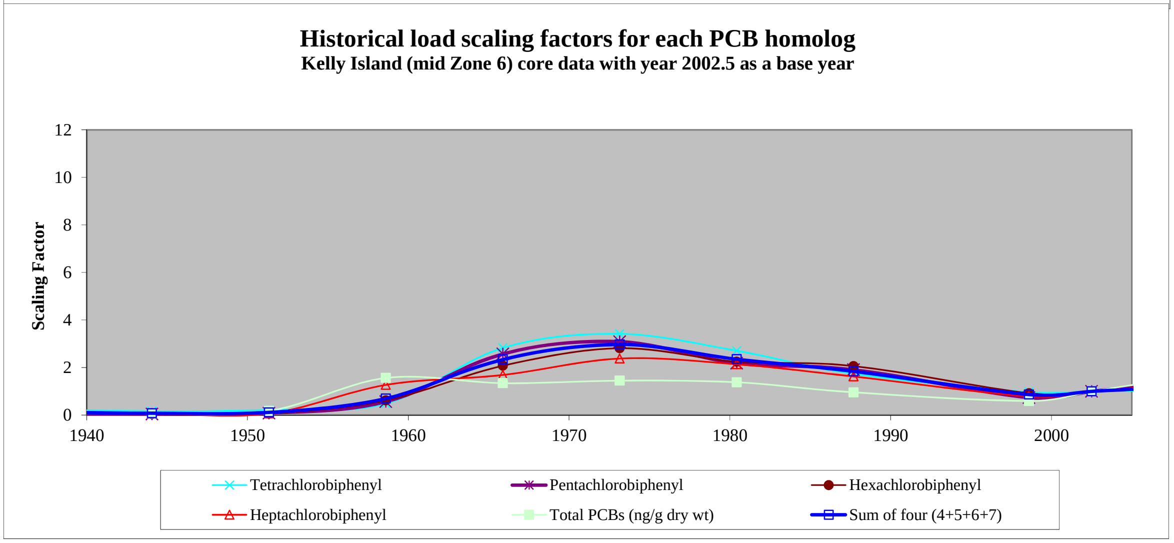


Figure 4.4.2-5: Sediment core data collected from Kelly Island Marsh in Zone 6

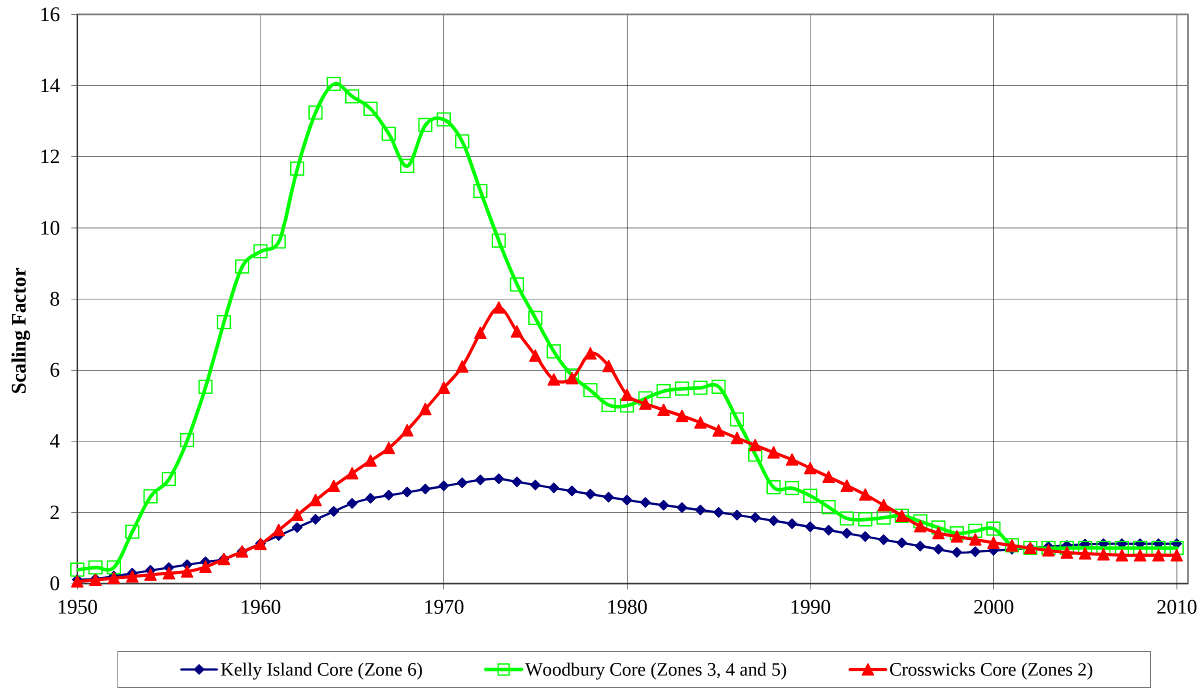


Figure 4.4.2-6: Zone specific scaling factors based on PCB concentrations in sediment cores

The concentration of each slice was divided by the concentration of 2002 to obtain the scaling factor for the slice or for the corresponding date of the slice. Since the temporal gaps between slices ranged a few years to tens of years, a linear interpolation was performed using the nearby two data points to obtain the concentration for every year from 1950 to the last slice. Dates for the last slice (top of the core or surface) of each core were different since all three cores were collected in different years. Dates for the last slices were 2001, 2006 and 2008 for Woodbury Creek, Kelly Island and Crosswicks Creek Cores, respectively. Since the latest date from the Woodbury Creek core was 2001, an extrapolation was performed using an exponential curve fit to 13 data points to estimate the concentration in 2002. It was assumed that PCB concentrations remain constant in each core from the last data point to year 2010. For an example, the yearly scaling factor for the Crosswicks Creek core from 2007 to 2010 was set at 0.796. Scaling factors were developed for each of four homologs (tetra, penta, hexa and hepta-PCBs), total PCBs and the sum of four homologs. Even though some differences were observed for scaling factors among homologs, especially tetra PCBs in the Crosswicks and Woodbury Creek cores, sensitivity simulation results indicated that differences were negligible especially post 1980s since scaling factors were within a narrow range. Therefore, a single scaling factor derived from the sum of four homologs was used. Three, spatially varying PCB scaling factors were developed and are depicted in Figure 4.4.2-6.

Derived temporal (yearly) scaling factors were uniformly applied to (1) PCB external loads, (2) PCB concentrations for four major boundaries, and (3) gaseous PCB concentrations for each model segment during the one year cycling period for each of the four homolog models.

4.4.3 Historical and Contemporary PCB Data

4.4.3.1 Sediment Data

To evaluate the consistency of the model performance, 61-year hindcast simulation results for four homologs, tetra, penta, hexa and hepta PCBs were compared with monitoring data collected in multiple matrixes: water column, sediment layer, and fish tissue. Historical PCB data were compiled from multiple sources during the Stage 1 PCB TMDL modeling effort and detailed descriptions of sources of data were provided in the Stage 1 model calibration report (DRBC, 2003c). Data collected/analyzed by DRBC since 2003 were added in this study and are discussed in this section.

4.4.3.1 Water Column Data

Three water column measurements were identified for pre-1999 in previous modeling reports. All three data points were located in Zone 3 of the Estuary and had values of 340, 180, 3,873 nanograms per liter (ng/l) of total PCBs for 1974, 1975 and 1980, respectively. DRBC launched a spatially and temporally intensive PCB monitoring program for the ambient waters of the estuary in 2001 utilizing the EPA HRGC/HRMS Method 1668A (U.S. EPA, 1999). Samples were analyzed for 148 congeners which contribute approximately 95 percent of the total concentration. All water column samples collected since 2005 were analyzed for all 209 congeners using the 1668A to eliminate any uncertainties. All data presented here are neither blank-corrected nor adjusted to compensate un-analyzed congeners.

4.4.3.2 Sediment Data

PCBs data in sediment layers are summarized in two formats, solid normalized mass base (ug-PCBs per kilogram of solids) and carbon normalized mass base (ug-PCBs/g-organic carbon). Even though large variations exist in the concentrations and homolog distributions across the estuary, it is believed that there is much less analytical uncertainty in the sediment data collected since 2000. This is attributable to the larger spatial scales of the surveys that were conducted and the use of the more sensitive Method 1668A rather than the Aroclor-based Method 8082A. Using sediment data collected from 2000 to 2010, Zone by Zone homolog distributions for the solid normalized mass data set are summarized in Figure 4.4.3-1. Analytical results revealed that penta- and hexa- PCBs are the dominant homologs followed by tetra- and hexa- PCBs. Nona- and deca- PCBs contributions are noticeably elevated in sediment samples collected in Zone 5.

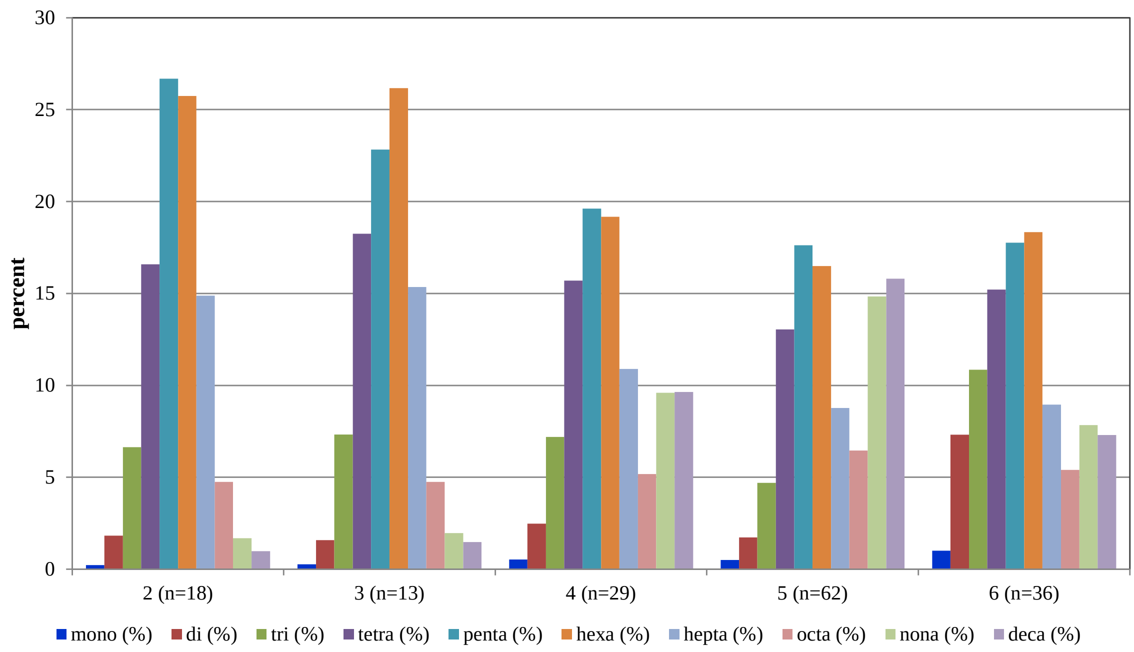


Figure 4.4.3-1: Averaged PCB Homolog distribution in surface sediment layer by Zone in the Delaware River Estuary (2000 - 2010).

To obtain homolog concentrations for historical (pre-2000) data, each total PCB concentration was multiplied by the fraction contributed by each homolog from the contemporary data set (2000 to 2010). PCB homolog contributions are summarized by Zone in Table 4.4.3-1. Average contributions from four PCB homologs, tetra-, penta-, hexa-, and hepta-PCBs were 15.8, 20.9, 21.2, and 11.8 percent, respectively.

Table 4.4.3-1: Average PCB homolog distribution in surface sediment layer by Zone in the Delaware River Estuary (2000 – 2010).

Zone	mono (%)	di (%)	tri (%)	tetra (%)	penta (%)	hexa (%)	hepta (%)	octa (%)	nona (%)	deca (%)	Count
2	0.2	1.8	6.6	16.6	26.7	25.7	14.9	4.8	1.7	1.0	18
3	0.3	1.6	7.3	18.3	22.8	26.2	15.4	4.8	2.0	1.5	13
4	0.5	2.5	7.2	15.7	19.6	19.2	10.9	5.2	9.6	9.6	29
5	0.5	1.7	4.7	13.0	17.6	16.5	8.8	6.5	14.8	15.8	62
6	1.0	7.3	10.9	15.2	17.8	18.3	9.0	5.4	7.8	7.3	36
average	0.5	3.0	7.3	15.8	20.9	21.2	11.8	5.3	7.2	7.0	158

Carbon-normalized PCB concentrations in the surficial sediment layer are summarized in Figure 4.4.3-2 to compare with the simulated results for year 2000-01 and 2008-10. Even though samples from the 2008-2010 survey seem to have lower concentrations than samples from the 2001 survey in Zones 2 and 6, it is difficult to identify general trends because of large variability.

This indicates that either the external PCB loadings into the Delaware Estuary have not been significantly changed over the 7 year period or the 7 year period is too short for the sediment layer to respond to changes of external PCB loadings.

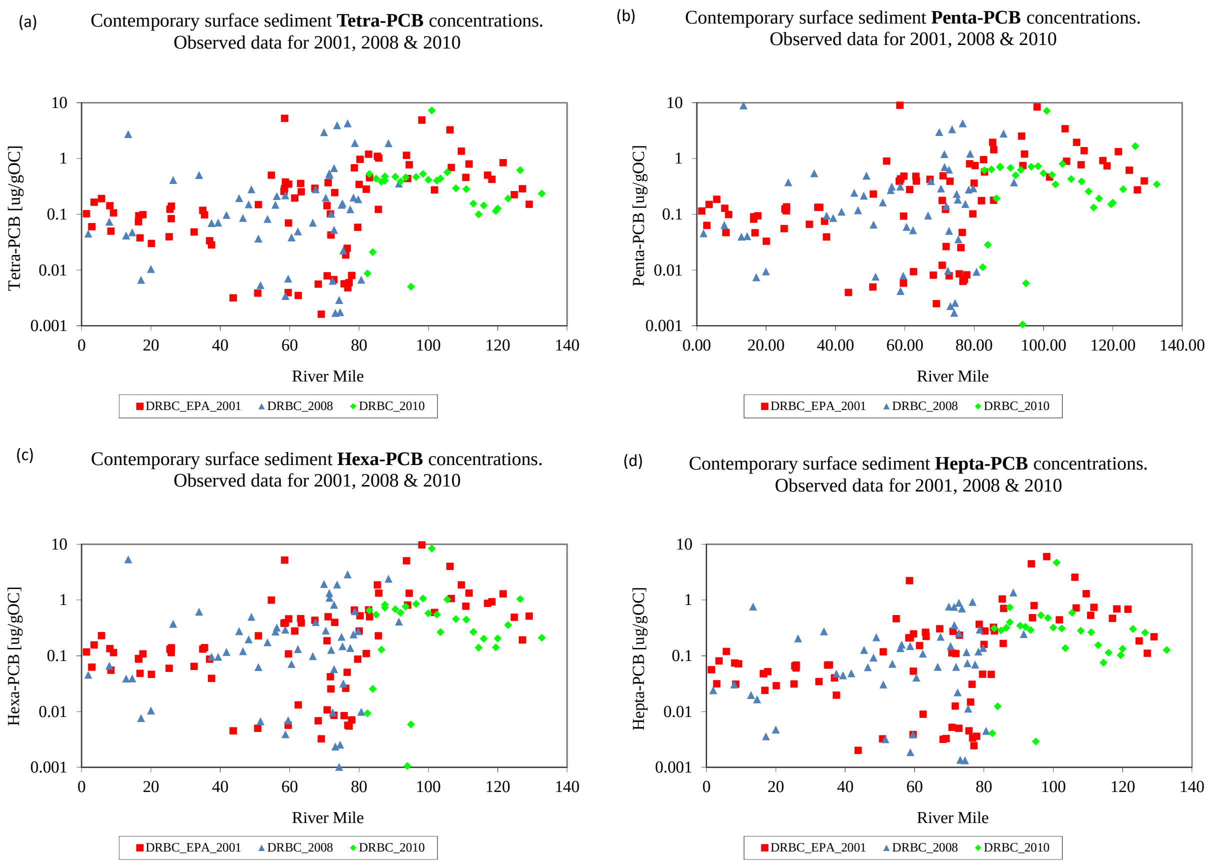


Figure 4.4.3-2: Organic carbon normalized PCBs in surface sediment layer: (a) tetra PCB; (b) penta PCB; (c) hexa PCB; (d) hepta PCB.

4.4.3.2 Fish Tissue Data

Historical (pre-2000) fish tissue data were typically reported as total PCBs based upon analysis for PCB Aroclors or a small subset of PCB congeners. Data were reported with lipid data and also without lipid data. Those data sets without lipid data were corrected with an assumed lipid content of 3.15 percent to calculate lipid-normalized total PCBs in fish tissue. Then, the fraction of the average contribution of each homolog obtained from 2004 to 2010 data (Table 4.4.3-3) was multiplied to the historical data sets to calculate the observed PCB homologs in those samples (see discussion below).

Fish tissue samples collected at five locations in the estuary in 2000 and 2001 were analyzed using Method 1668A for 129 congeners while samples collected from 2004 to 2010 at the same locations were analyzed using Method 1668A for 209 congeners. Table 4.4.3-2 presents the lipid-normalized PCB homolog concentrations in White Perch from 2000 to 2010 for the five sites. Using the subset of data for 209 congeners for the period from 2004 to 2010, lipid-normalized PCB homolog distributions by zone and overall are summarized in Table 4.4.3-3. Fish tissue PCB concentrations on a wet weight basis and lipid-normalized basis; and PCB homolog distributions are presented in Figure 4.4.3-3.

Overall, distributions of lipid-normalized PCB homologs are relatively consistent among zones except for the higher contributions from heavier homologs for samples collected in Zone 5. This was also observed with homolog distributions found in the water column and sediment data. Average contributions of lipid-normalized PCBs in White Perch from four PCB homologs, tetra-, penta-, hexa-, and hepta-PCBs are 11.3, 26.4, 34.0, and 16.1 percent, respectively. The sum of those four homologs comprises approximately 87.8 percent of the total PCBs. Controlling these four homologs is important if the fish consumption advisories in the Delaware Estuary are to be relaxed or lifted.

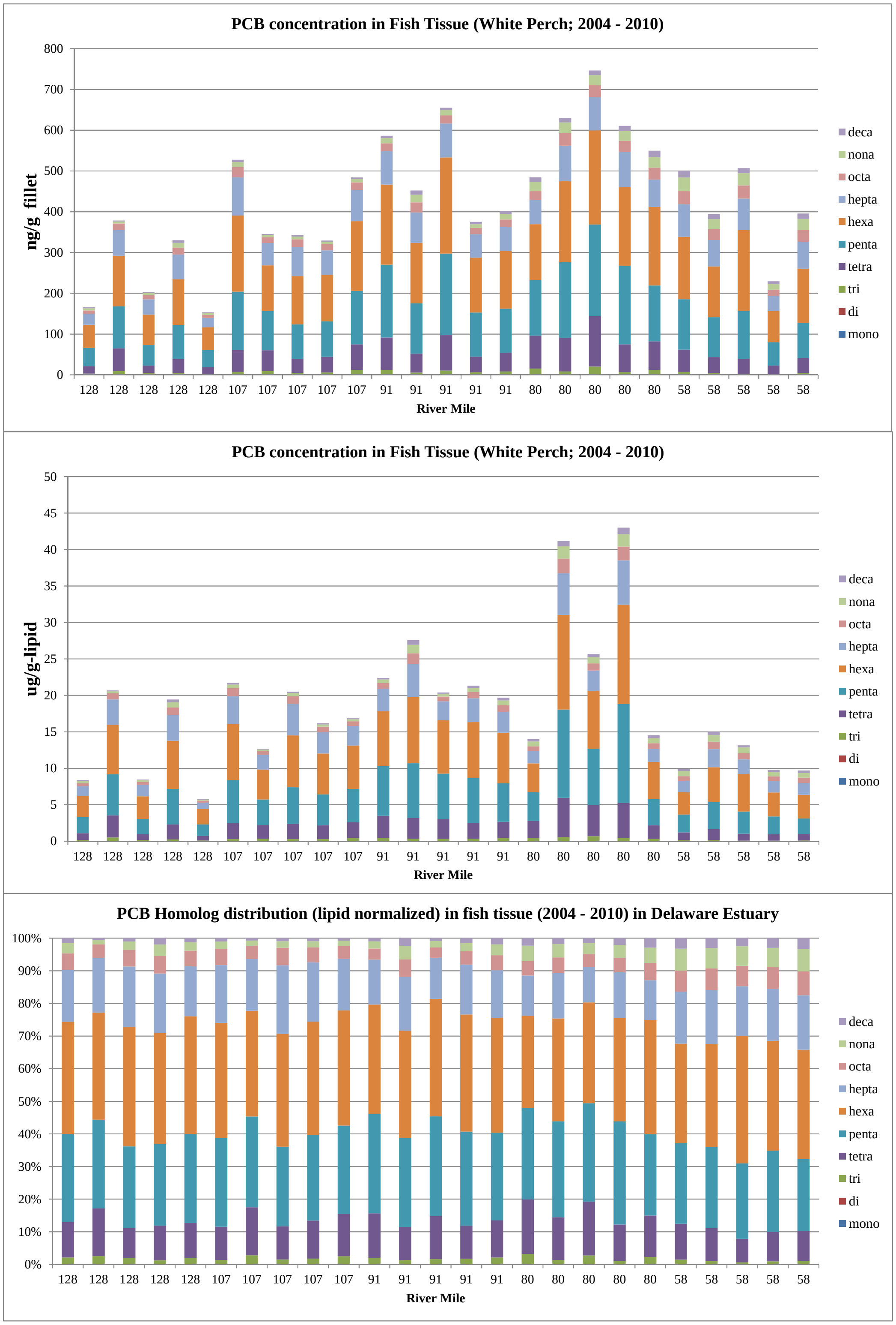


Figure 4.4.3-3: PCB concentrations in fish (White Perch) tissue (a) in fish fillet (ng/g-fillet), (b) lipid normalized (ug/g-lipid), (c) homolog distribution of lipid-normalized PCBs.

Table 4.4.3-2: Lipid normalized PCB concentrations in ug/g-lipid in fish tissue (White Perch)

Year	River Mile	DRBC Zone	mono-	di-	tri-	tetra-	penta-	hexa-	hepta-	octa-	nona-	deca-	Total PCBs
2000	128	2	0.08	0.07	0.51	2.65	3.29	3.14	3.73	0.47	0.18	0.09	14.23
2004	128	2	0.00	0.01	0.17	0.92	2.25	2.88	1.33	0.43	0.26	0.13	8.37
2005	128	2	0.00	0.02	0.51	3.02	5.64	6.78	3.46	0.86	0.28	0.11	20.69
2006	128	2	0.00	0.02	0.16	0.78	2.11	3.10	1.56	0.44	0.21	0.09	8.46
2007	128	2	0.00	0.01	0.23	2.07	4.86	6.61	3.55	1.04	0.68	0.38	19.43
2010	128	2	0.00	0.01	0.11	0.62	1.58	2.10	0.88	0.28	0.15	0.07	5.80
2001	107	3	0.02	0.12	0.62	7.53	12.00	13.11	9.23	1.87	0.95	0.61	46.08
2004	107	3	0.00	0.01	0.28	2.22	5.89	7.68	3.85	1.08	0.49	0.22	21.71
2005	107	3	0.00	0.02	0.34	1.86	3.53	4.10	2.01	0.52	0.20	0.09	12.66
2006	107	3	0.00	0.02	0.29	2.08	5.02	7.11	4.30	1.11	0.40	0.20	20.52
2007	107	3	0.00	0.02	0.27	1.88	4.25	5.60	2.93	0.75	0.30	0.15	16.16
2010	107	3	0.00	0.02	0.41	2.19	4.57	5.96	2.67	0.65	0.29	0.12	16.87
2004	91	4	0.00	0.03	0.42	3.05	6.82	7.50	3.10	0.76	0.48	0.22	22.39
2005	91	4	0.01	0.05	0.31	2.83	7.52	9.06	4.55	1.48	1.15	0.64	27.58
2006	91	4	0.00	0.03	0.29	2.71	6.23	7.35	2.58	0.64	0.40	0.17	20.41
2007	91	4	0.00	0.04	0.32	2.17	6.15	7.65	3.28	0.86	0.53	0.32	21.32
2010	91	4	0.00	0.02	0.40	2.24	5.29	6.94	2.86	0.91	0.65	0.37	19.69
2001	80	4	0.08	0.07	0.37	4.78	6.99	7.70	5.51	1.13	0.63	0.36	27.63
2004	80	4	0.00	0.03	0.42	2.34	3.93	3.96	1.73	0.62	0.66	0.32	14.01
2005	80	4	0.00	0.03	0.53	5.40	12.10	12.97	5.73	1.99	1.69	0.73	41.17
2006	80	4	0.00	0.05	0.65	4.25	7.72	7.93	2.79	1.00	0.86	0.38	25.65
2007	80	4	0.00	0.02	0.46	4.78	13.59	13.61	6.06	1.89	1.69	0.89	43.00
2010	80	4	0.00	0.02	0.30	1.86	3.62	5.09	1.78	0.77	0.68	0.42	14.54
2001	63	5	0.04	0.13	0.59	5.47	6.21	5.69	3.38	1.03	0.92	0.71	24.16
2000	58	5	0.03	0.11	0.43	4.37	6.18	7.33	5.03	1.15	0.71	0.41	25.74
2004	58	5	0.00	0.01	0.14	1.09	2.45	3.03	1.58	0.64	0.67	0.32	9.92
2005	58	5	0.00	0.01	0.15	1.53	3.73	4.74	2.48	1.01	0.94	0.45	15.04
2006	58	5	0.00	0.01	0.07	0.95	3.05	5.15	2.01	0.83	0.78	0.33	13.18
2007	58	5	0.00	0.00	0.09	0.88	2.43	3.28	1.56	0.66	0.57	0.29	9.76
2010	58	5	0.00	0.01	0.11	0.89	2.13	3.25	1.62	0.71	0.66	0.33	9.70

Table 4.4.3-3: Lipid-normalized PCB homolog distributions in White Perch in the Delaware River Estuary (2004 – 2010).

DRBC Zone	mono (%)	di (%)	tri (%)	tetra (%)	penta (%)	hexa (%)	hepta (%)	octa (%)	nona (%)	deca (%)	Count
2 (n=5)	0.00	0.14	1.86	11.21	26.26	34.82	16.92	4.93	2.61	1.25	5
3 (n=5)	0.00	0.11	1.89	11.94	26.56	34.48	17.69	4.60	1.86	0.86	5
4 (n=10)	0.01	0.14	1.79	12.90	28.80	33.08	13.63	4.34	3.50	1.80	10
5 (n=5)	0.00	0.06	0.99	9.31	23.90	33.65	16.07	6.71	6.31	3.00	5
6 (n=0)											
average	0.00	0.11	1.63	11.34	26.38	34.01	16.08	5.14	3.57	1.73	25

4.4.4 Hindcast simulation results

Results of the 61-year (1950 to 2010) hindcast simulation results for four homologs, tetra-, penta-, hexa- and hepta- PCBs were compared with the observed data collected from the three matrixes: water column, surficial sediment layer, and fish tissue. A description of the model setups are is found in Section 4.4.1. The development of historical loadings is discussed in Section 4.4.2. Sources and treatment of the observed data are discussed in the Section 4.4.3 and the previous model calibration report (DRBC, 2003c).

Simulated results for each of the four homologs are graphically compared for each zone in three matrixes: water column PCBs in ng/L, surface sediment layer PCBs in ug/kg-solid, and fish tissue PCBs in ug/g-lipid. The current DELPCB model computes water column and PCB concentrations in the three sediment layers, but does not simulate PCBs concentrations in fish tissue. To calculate simulated PCB concentrations in the fish tissue (White Perch), the sum of the simulated, DOC bound and truly dissolved water column PCB concentrations were multiplied with the bioaccumulation factor (BAF) of 10^7 (L/kg) which was obtained from a study by Ashley et al, 2004. Finally, the observed contemporary PCB concentrations in the surface sediment layer in ug/g-organic carbon are compared with the simulated results. The model was initiated with a clean sediment condition at the beginning of the simulation (i.e., zero PCB concentrations for the year 1950 were assigned as an initial condition). The simulated results were extracted for spatially to make graphical comparison for years 2000-2001 and 2008-2010. The graphical comparisons of the simulated and the observed are presented in Figures 4.4.4-1 through 4.4.4-16. All four homolog models are in good agreement with the observed PCBs in the water column and in the fish tissue (see Figures 4.4.4-1, 4.4.4-5, 4.4.4-9 and 4.4.4-13 for water column comparisons and Figures 4.4.4-3, 4.4.4-7, 4.4.4-11 and 4.4.4-15 for the fish tissue comparisons).

Because of the large variability in the observed PCBs in the sediment layer, it is difficult to draw conclusions on the performance of the model. The tetra-PCB model underestimates PCB sediment concentrations for a portion of the simulation period in the upper portions of estuary (Zones 2 and 3). In Zone 2, this occurs between 2000 and 2010. In Zone 3, this occurs between 1990 and 2010. In Zone 6, this occurs 1985 and 1995 with reasonable agreement after 2000. As noted earlier, the scaling factor derived from the tetra PCB, alone, yielded greater magnitude in 1960s and 1970s. However, a sensitivity simulation result revealed that the scaling factor would not be the sole cause of the underestimation.

The penta PCB model also underestimates PCBs in the sediment layer in Zones 2 and 3, particularly in the period after 2000 while the model is in good agreement with observed data in the rest of zones (Figure 4.4.4-6).

Both the hexa- and hepta-PCB models are in good agreement with the respective observed PCB homolog concentrations in the surficial sediment layers (see Figures 4.4.4-10 and 4.4.4-14).

To investigate the underestimation for the two lighter homologs, tetra- and penta-PCBs, additional model sensitivity simulations were conducted. These sensitivity analyses indicated that gaseous exchanges between the water column and the atmosphere play a critical role in the modeling of the four PCB homologs, but particularly the lighter homologs. Without the volatilization process, the tetra PCB model predicts up to three times higher concentrations of tetra-PCBs in the water column in Zone 2 and up to 20 times in Zone 6. On an average basis, the tetra-PCB model predicts 1.3 times higher tetra-PCBs in the water column in Zone 2 and approximately 5.2 times higher in Zone 6 without the volatilization process. The difference is much greater since the surface area for Zone 6 is much greater than that of Zone 2. This indicates that PCBs in the water column are a source of PCBs in the atmosphere. In addition to the gaseous exchanges, unaccounted sources, especially episodic events, and the unaccounted de-chlorination of PCBs may contribute underestimations of lighter homolog PCBs.
This indicates that the need for a site-specific scaling factor for the Philadelphia area, identification of undocumented active or historical sources, and/or the limitation of the current one-dimensional model to properly simulate sediment trapping in upper estuary.

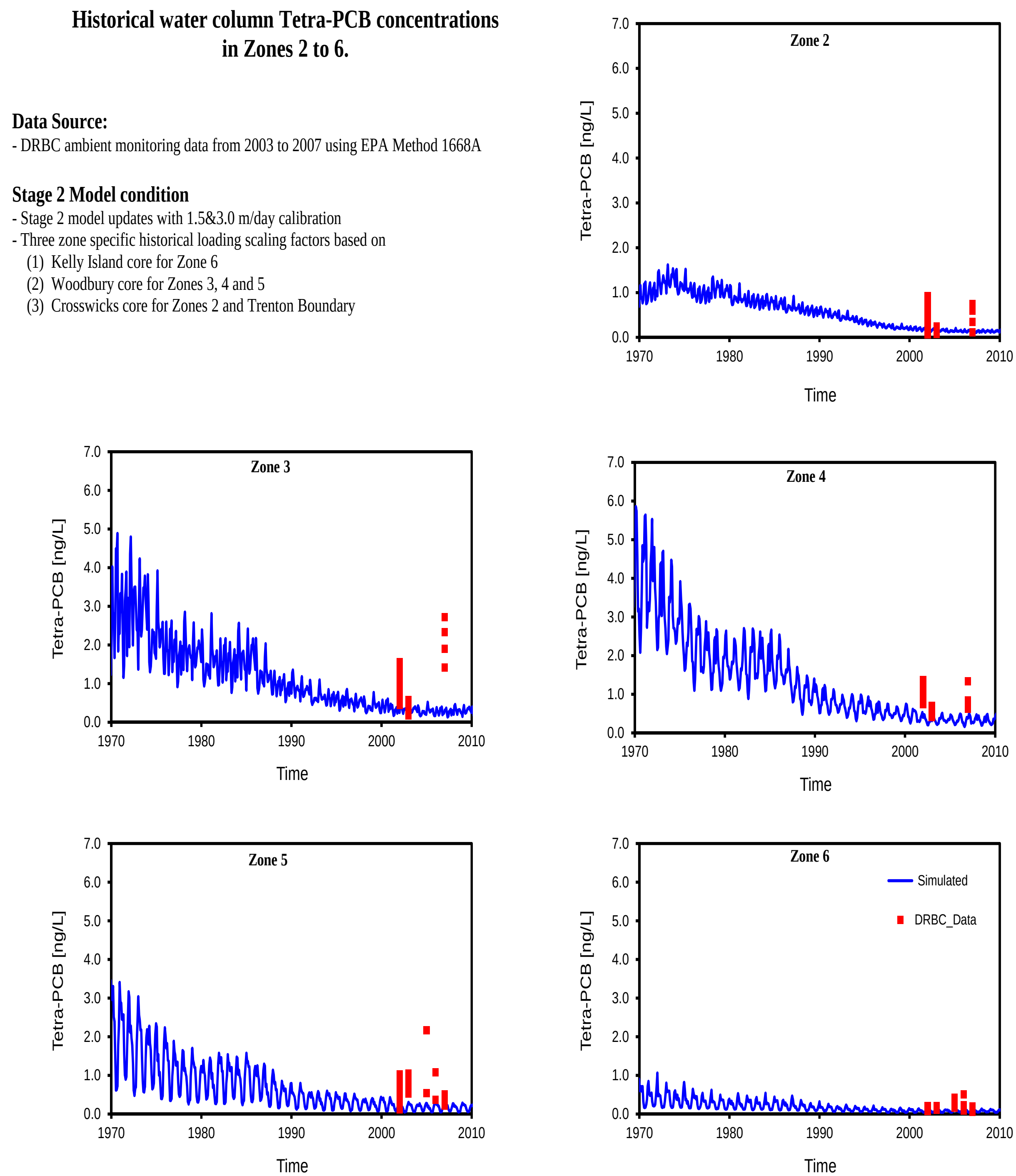


Figure 4.4.4-1: Simulated and observed Tetra PCBs in water column

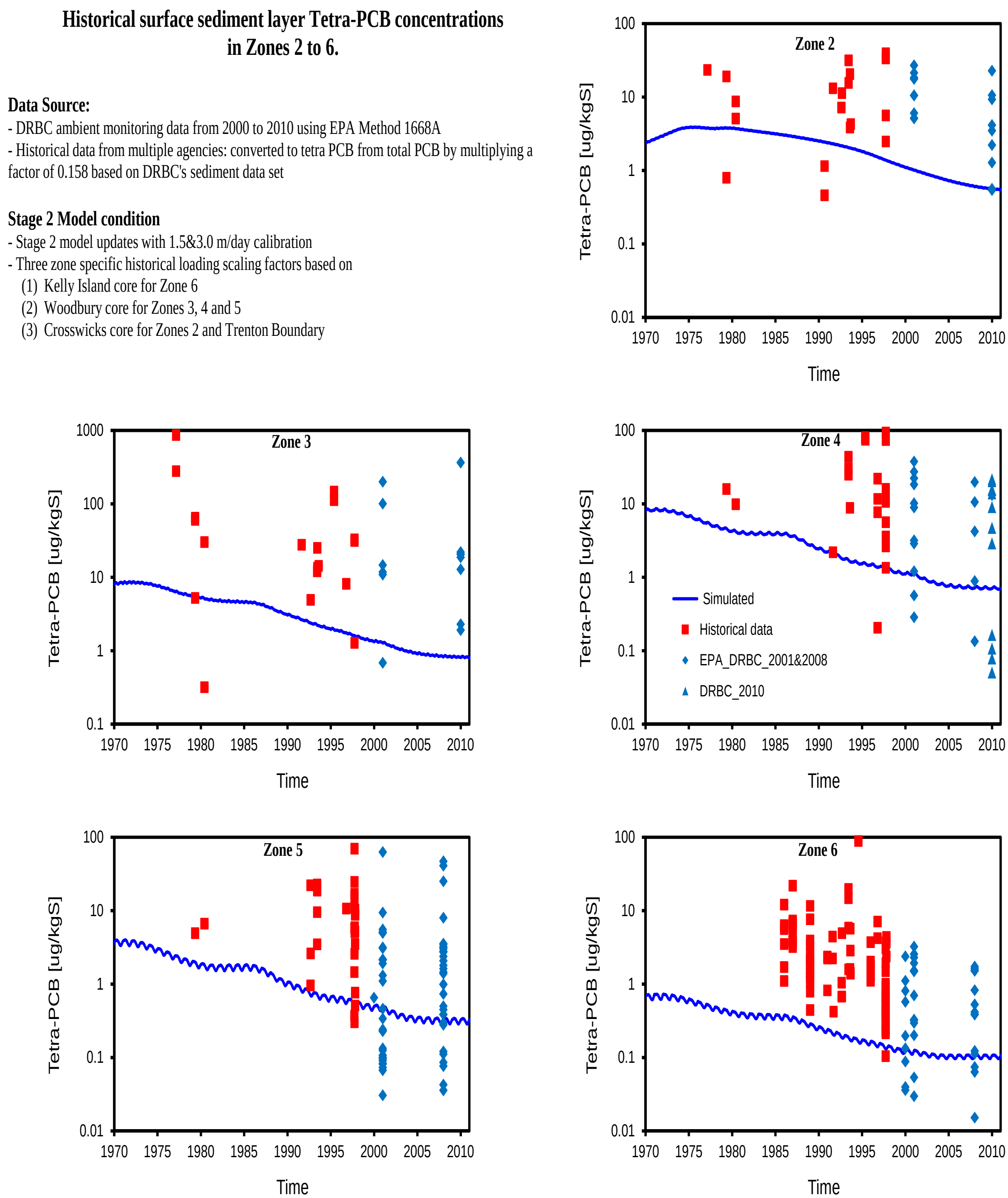


Figure 4.4.4-2: Simulated and observed Tetra PCBs in surface sediment layer. Note that the y-axis scale for Zone 3 is different from the scales of the rest of the plots for other zones.

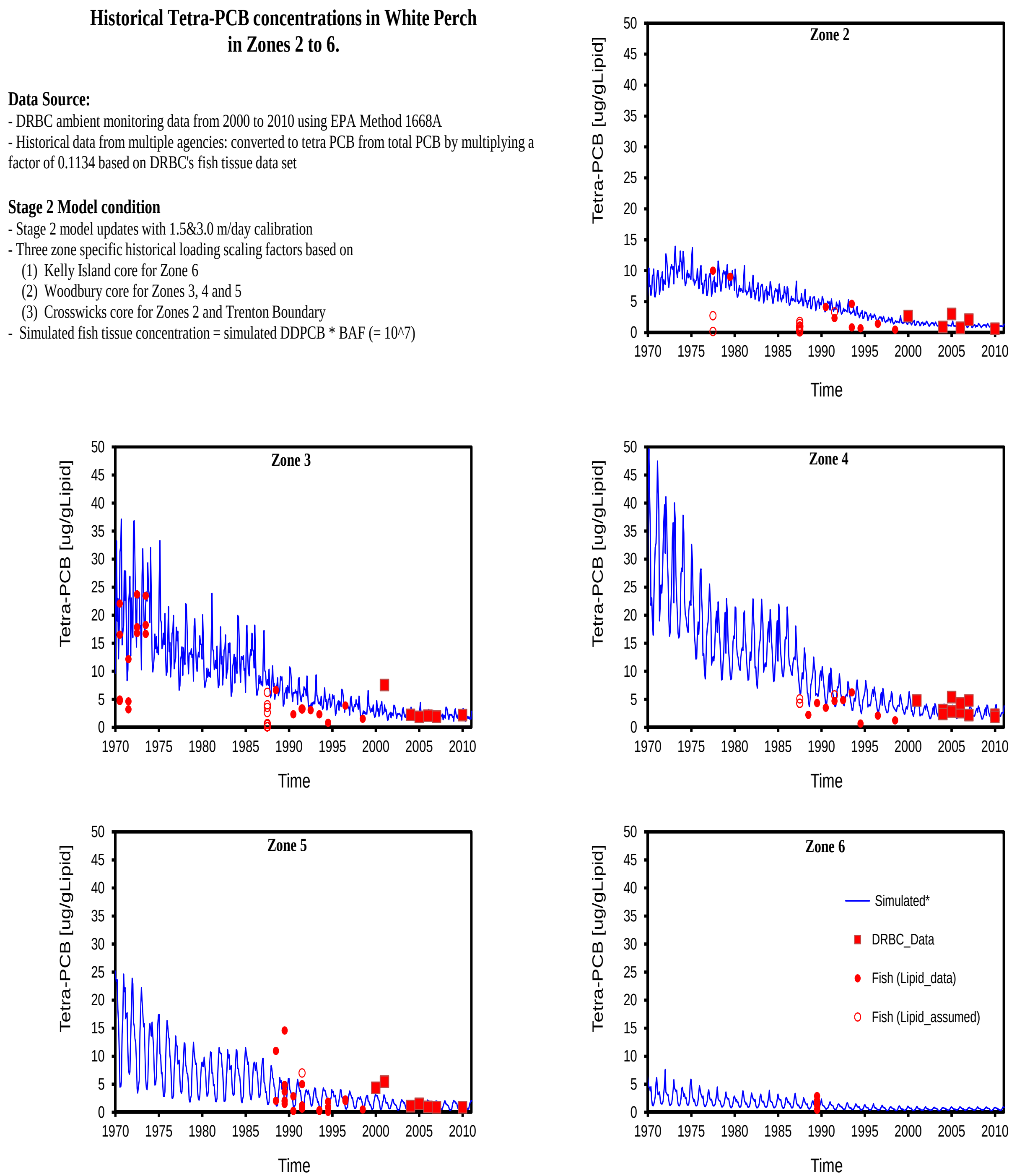


Figure 4.4.4-3: Simulated and observed Tetra PCBs in fish tissue (white perch). Simulated* results were obtained by multiplying simulated dissolved and DOC bound PCBs (DDPCBs) and a bioconcentration factor (BCF) of 10^7.

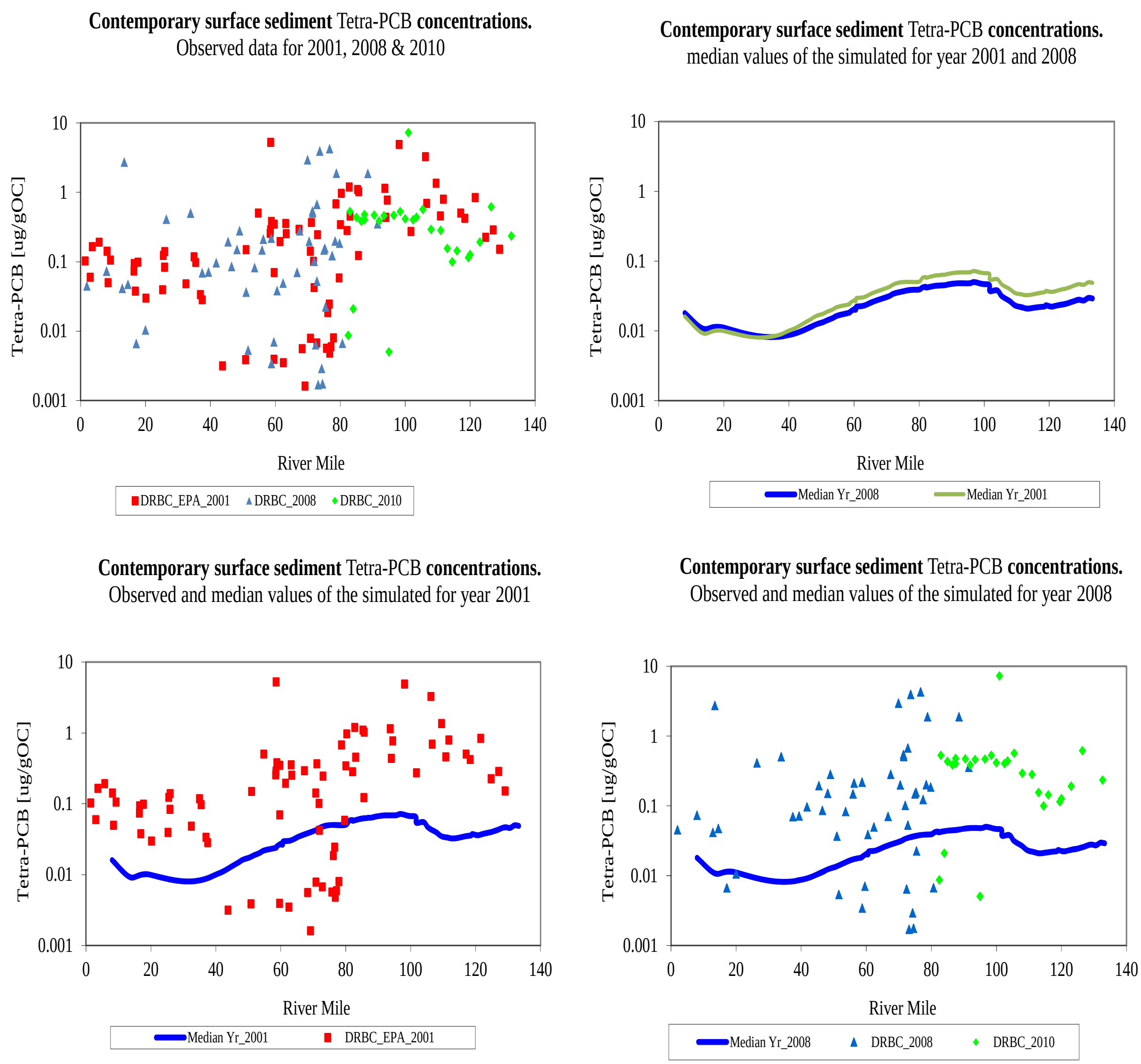


Figure 4.4.4-4: Organic carbon normalized tetra-PCBs in surface sediment layer: (a) observed data collected 2000 – 2010; (b) simulated results of median values for year 2001 and year 2008; (c) the observed and the simulated for the year 2001; (d) the observed and the simulated for the year 2008.

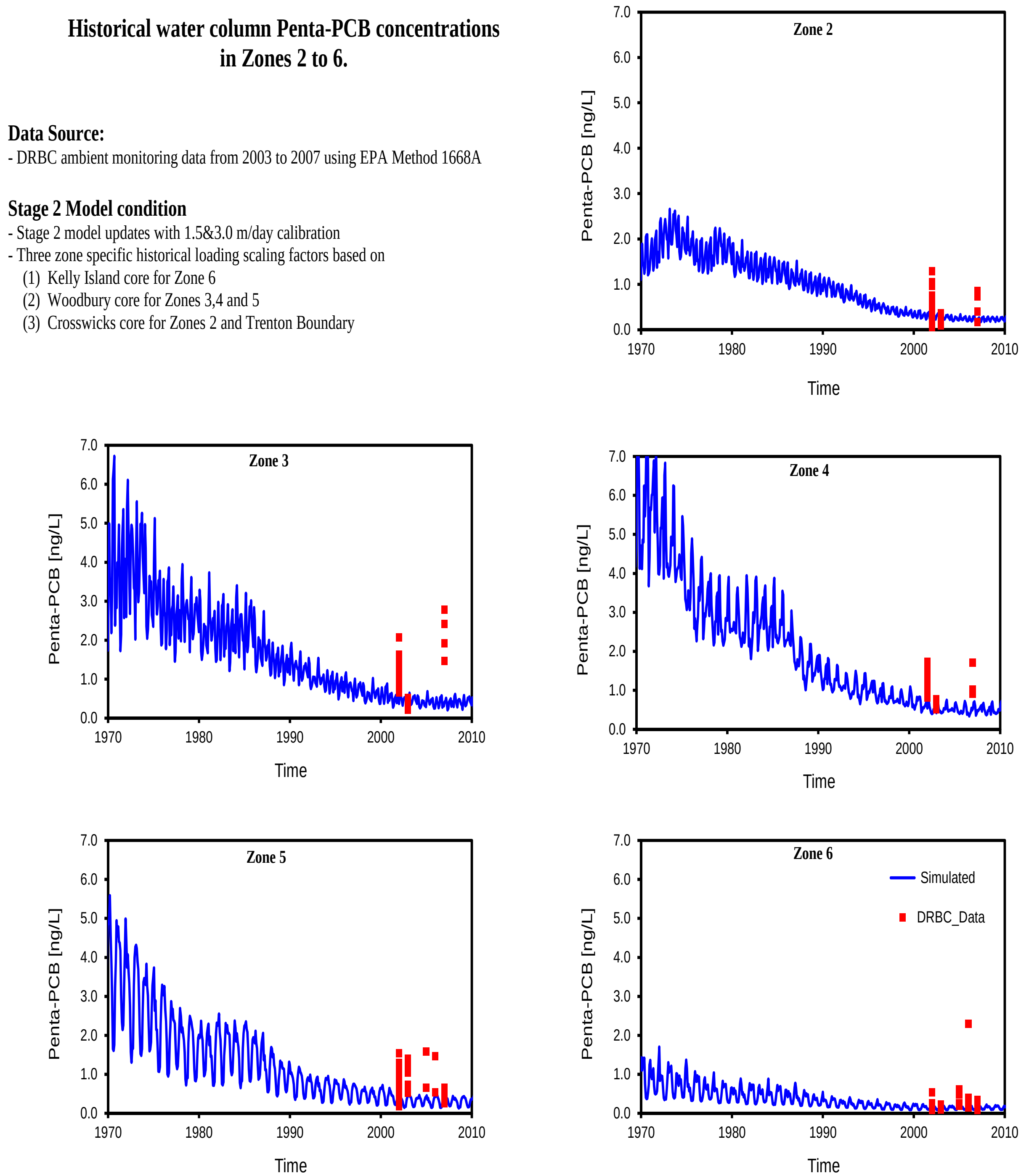


Figure 4.4.4-5: Simulated and observed Penta-PCBs in water column.

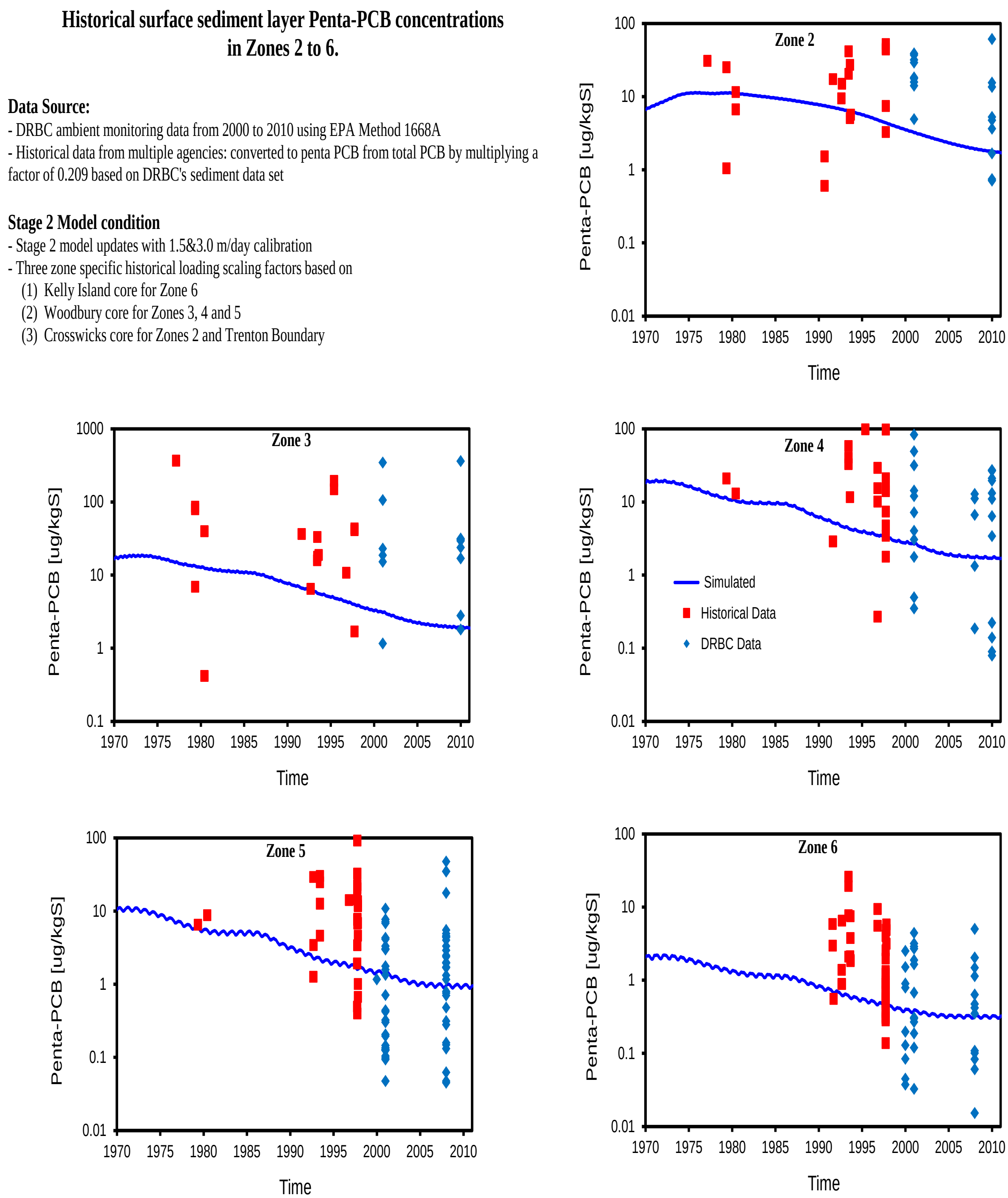


Figure 4.4.4-6: Simulated and observed Penta-PCBs in surface sediment layer. Note that the y-axis scale for Zone 3 is different from the scales of the rest of the plots for other zones.

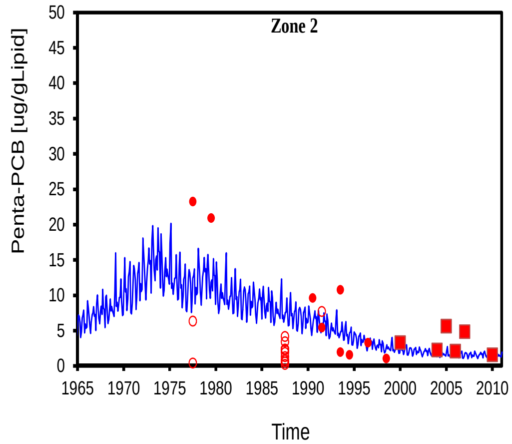
Historical Penta-PCB concentrations in White Perch in Zones 2 to 6.

Data Source:

- DRBC ambient monitoring data from 2000 to 2010 using EPA Method 1668A
- Historical data from multiple agencies: converted to penta PCB from total PCB by multiplying a factor of 0.264 based on DRBC's fish tissue data set

Stage 2 Model condition

- Stage 2 model updates with 1.5&3.0 m/day calibration
- Three zone specific historical loading scaling factors based on
  (1) Kelly Island core for Zone 6
  (2) Woodbury core for Zones 3 , 4 & 5
  (3) Crosswicks core for Zone 2 and Trenton Boundary
- Simulated fish tissue concentration = simulated DDPCB * BAF (= 10^7)



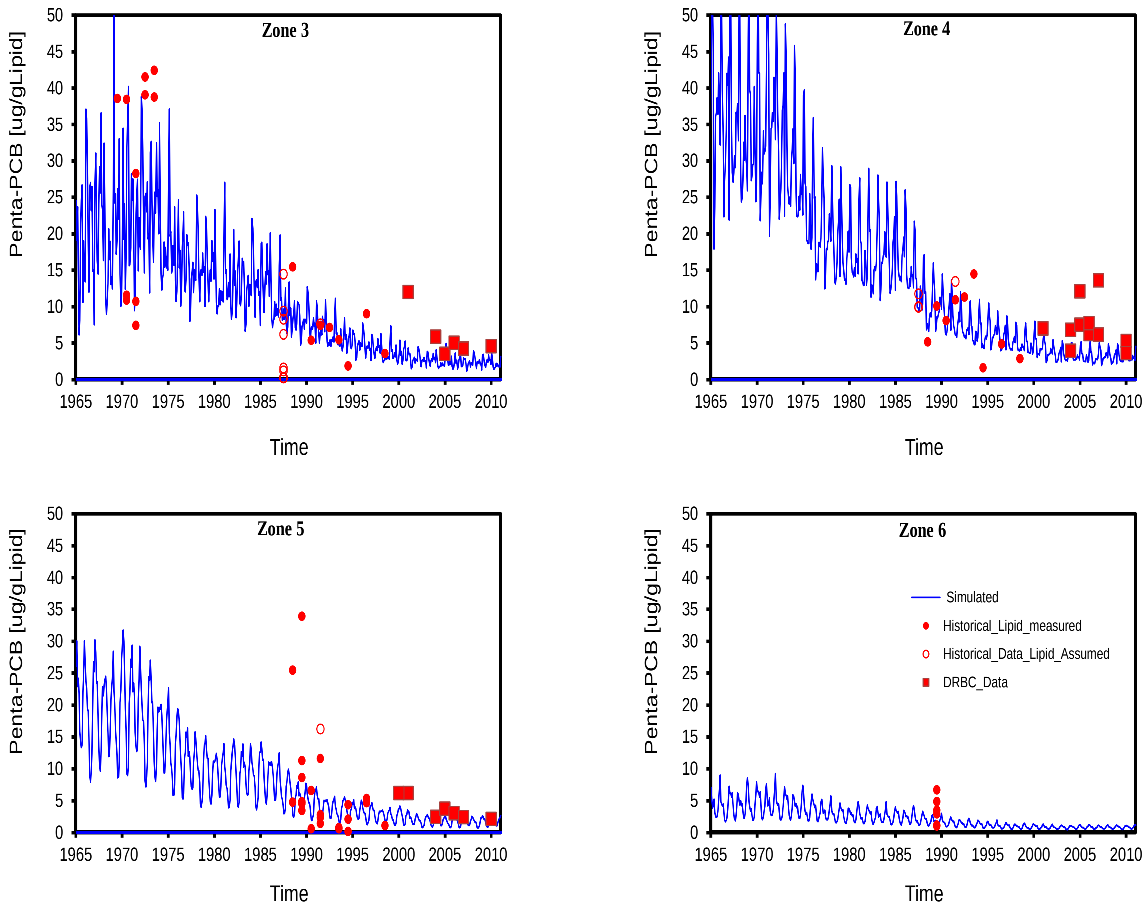


Figure 4.4.4-7: Simulated and observed Penta PCBs in fish tissue (white perch). Simulated* results were obtained by multiplying sum of simulated dissolved and doc bound penta PCBs (DDPCBs) and bioaccumulation factor (BAF) of 10^7.

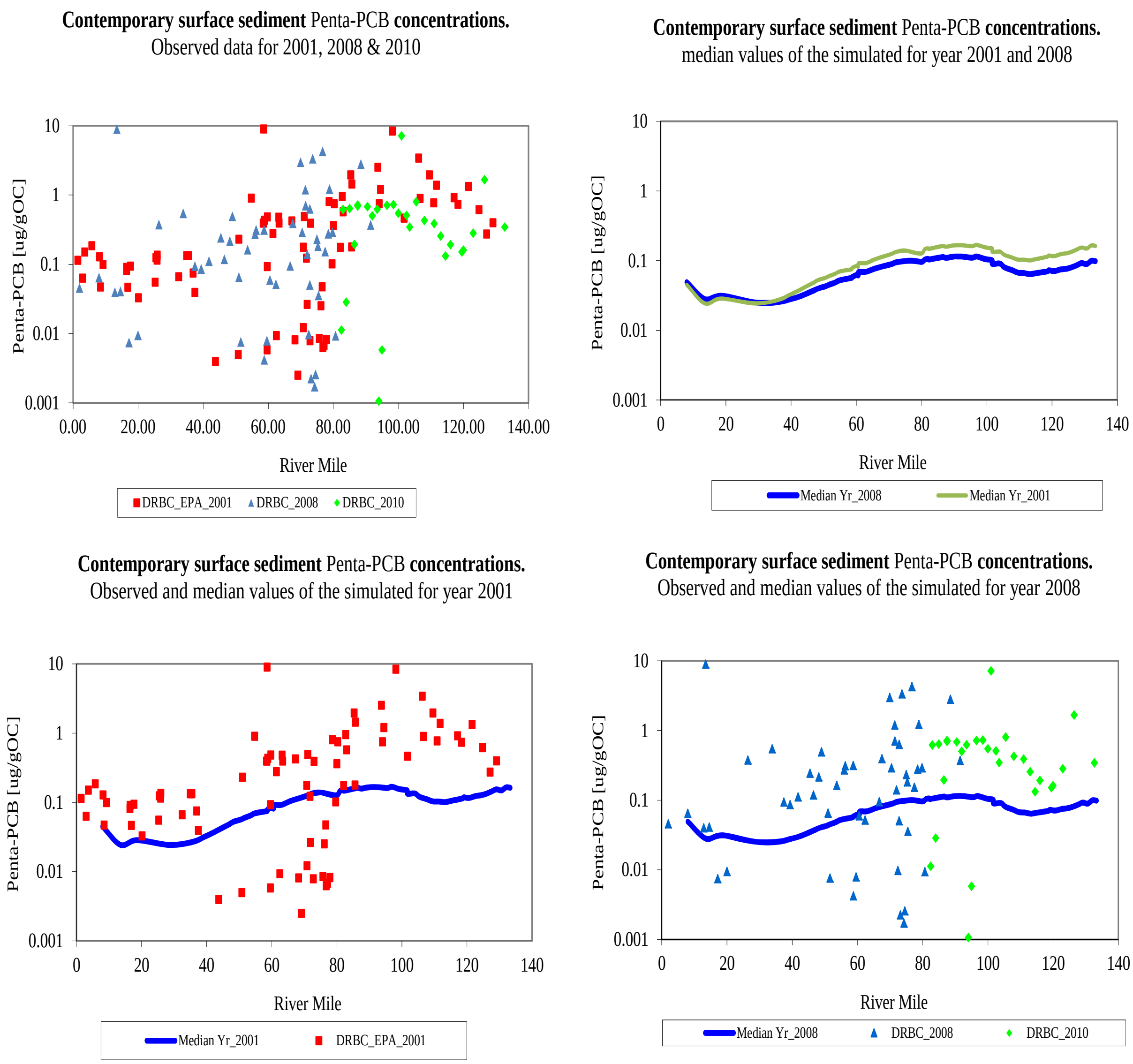


Figure 4.4.4-8: Organic carbon normalized penta-PCBs in surface sediment layer: (a) observed data collected 2000 – 2010; (b) simulated results for year 2001 and year 2008; (c) the observed and the simulated for the year 2001; (d) the observed and the simulated for the year 2008.

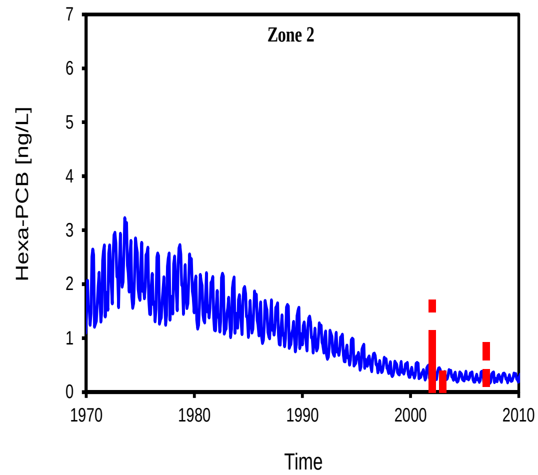
Historical water column Hexa-PCB concentrations in Zones 2 to 6.

Data Source:

- DRBC ambient monitoring data from 2003 to 2007 using EPA Method 1668A

Stage 2 Model condition

- Stage 2 model updates with 1.5&3.0 m/day calibration
- Three zone specific historical loading scaling factors based on
  (1) Kelly Island core for Zone 6
  (2) Woodbury core for Zones 3 , 4 & 5
  (3) Crosswicks core for Zone 2 and Trenton Boundary



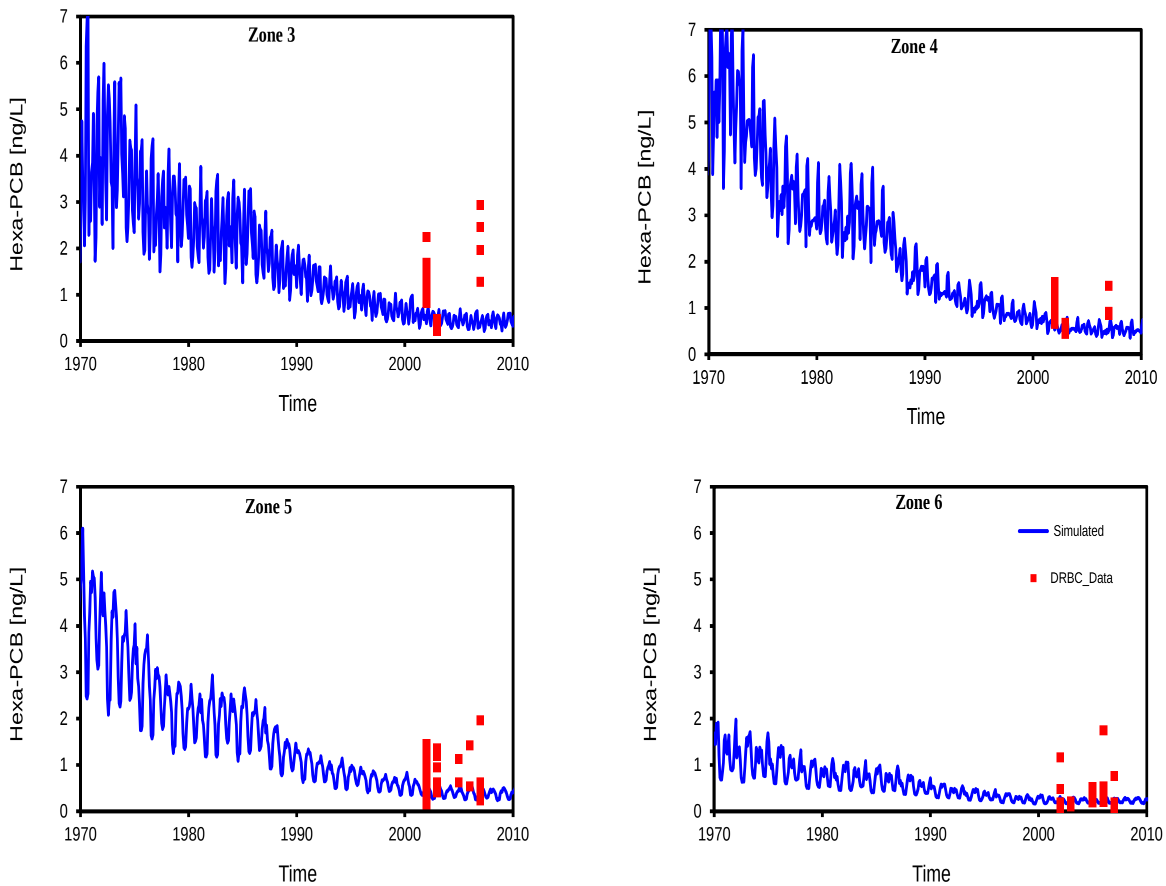


Figure 4.4.4-9: Simulated and observed Hexa PCBs in water column.

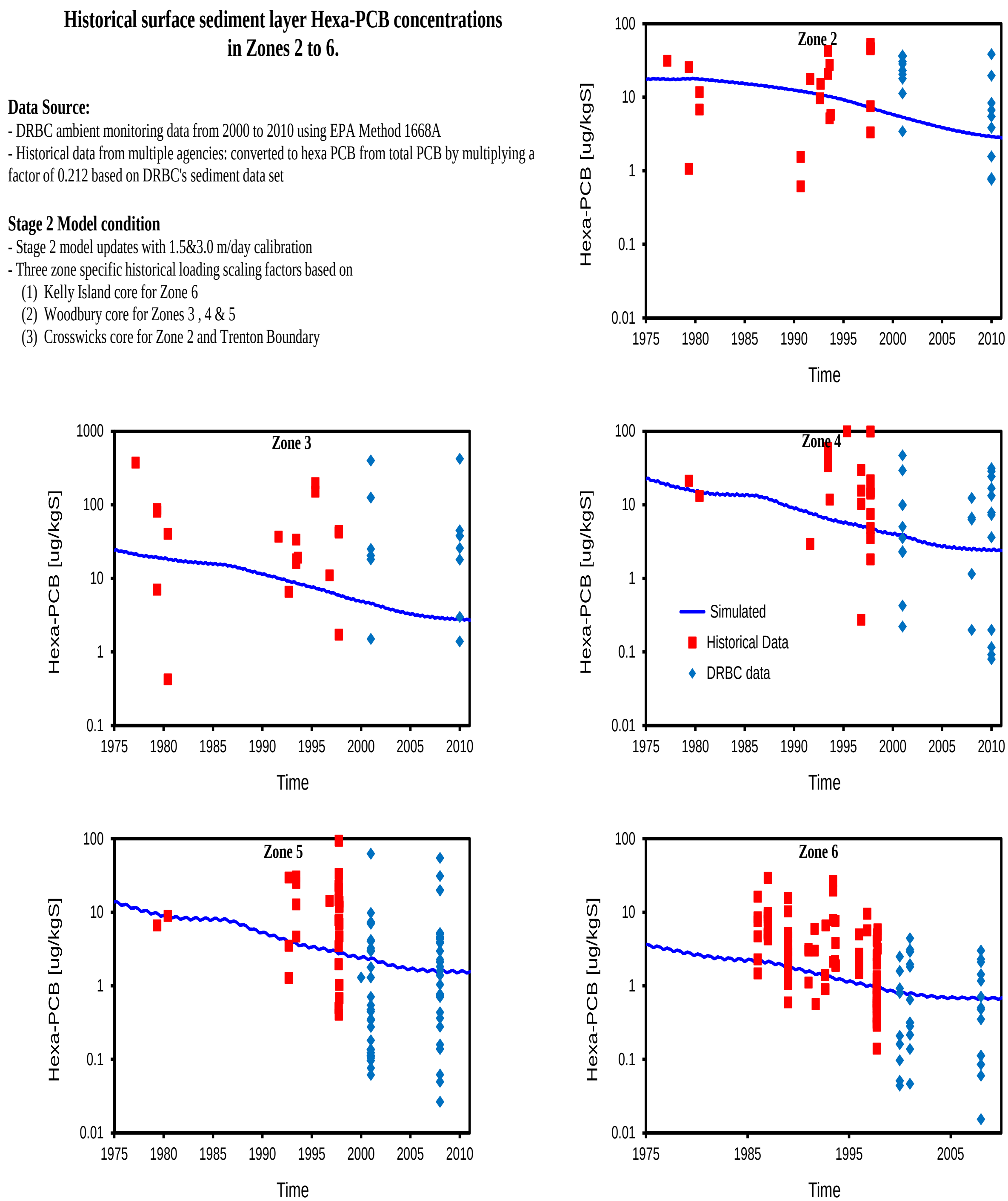


Figure 4.4.4-10: Simulated and observed Hexa PCBs in surface sediment layer. Note that the y-axis scale for Zone 3 is different from the scales of the rest of the plots for other zones.

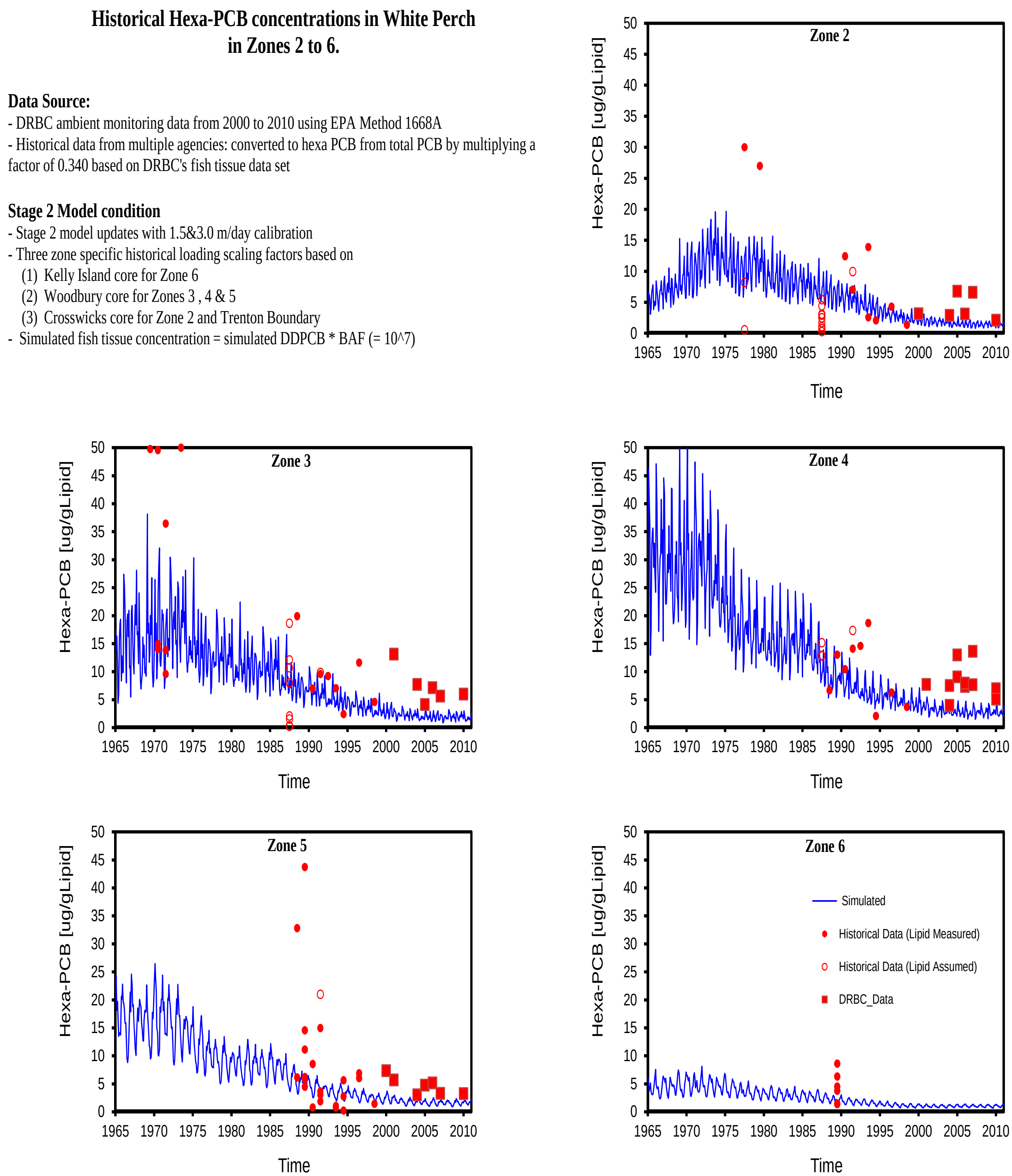


Figure 4.4.4-11: Simulated and observed Hexa PCBs in fish tissue (white perch). Simulated* results were obtained by multiplying sum of simulated dissolved and doc bound hexa PCBs (DDPCBs) and bioaccumulation factor (BAF) of 10^7.

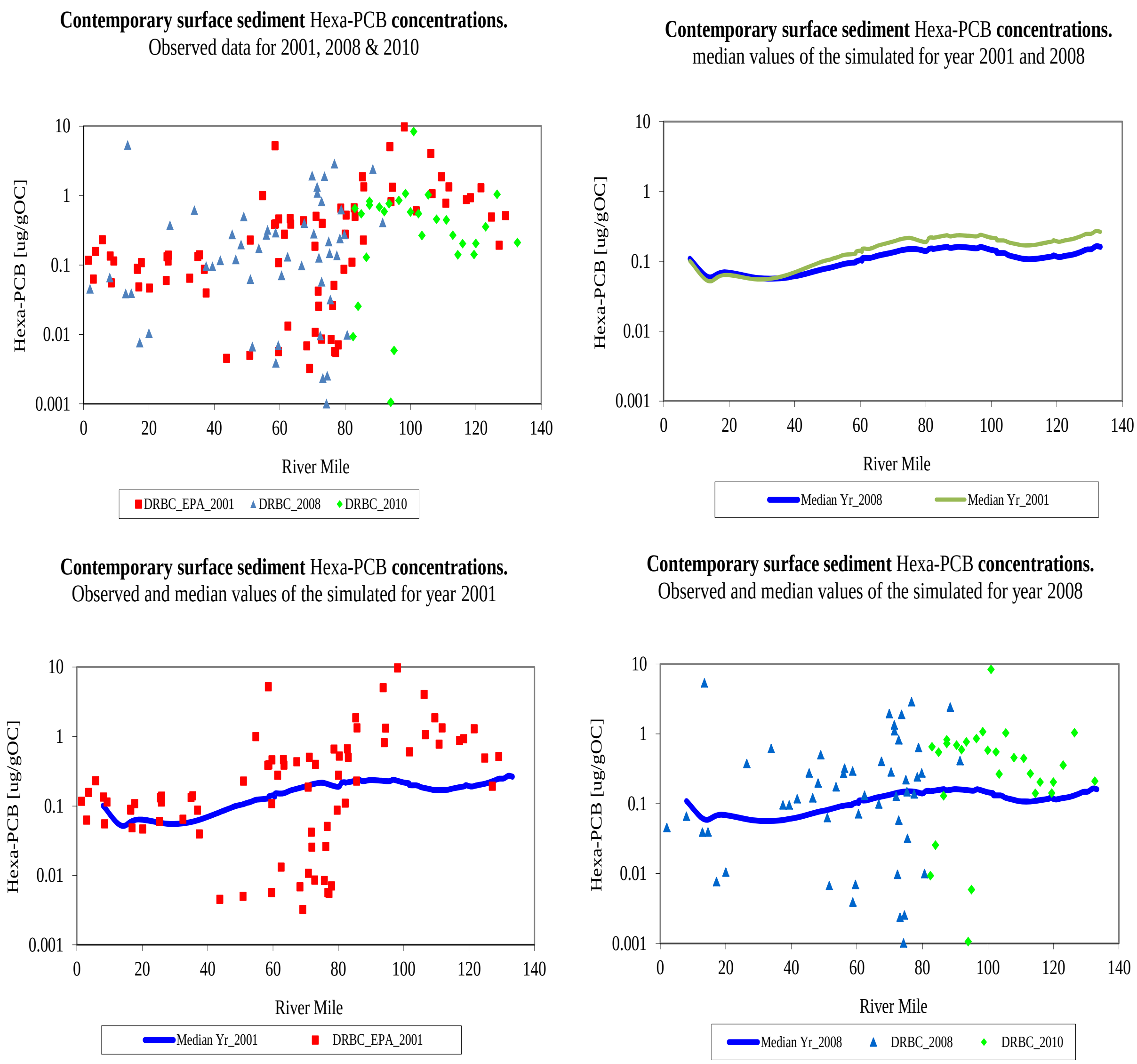
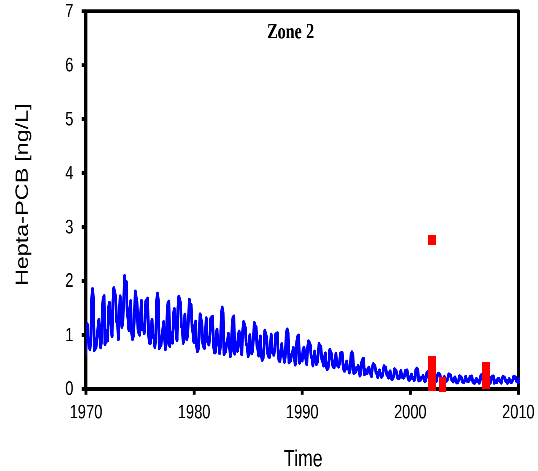


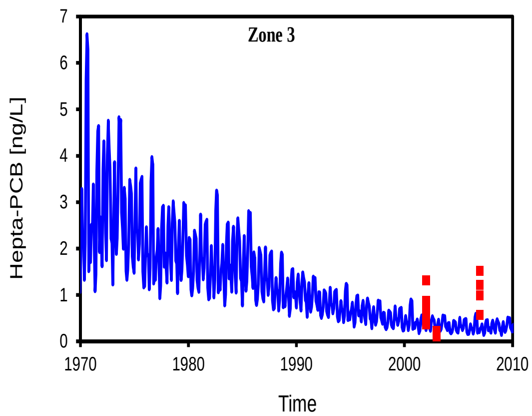
Figure 4.4.4-12: Organic carbon normalized hexa-PCBs in surface sediment layer: (a) observed data collected 2000 – 2010; (b) simulated results for year 2001 and year 2008; (c) the observed and the simulated for the year 2001; (d) the observed and the simulated for the year 2008.

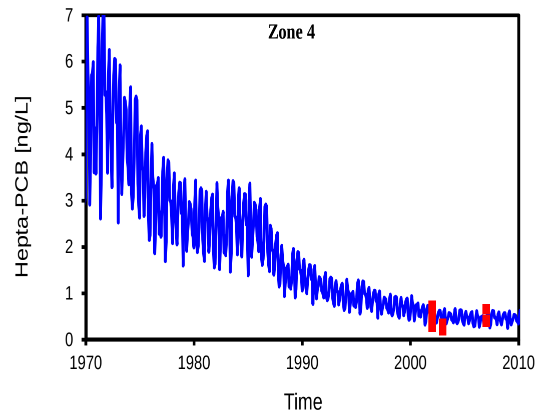
Historical water column Hepta-PCB concentrations in Zones 2 to 6.

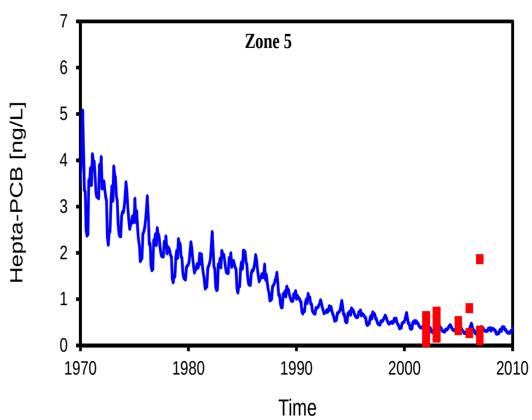
Data Source:
- DRBC ambient monitoring data from 2003 to 2007 using EPA Method 1668A

Stage 2 Model condition
- Stage 2 model updates with 1.5&3.0 m/day calibration
- Three zone specific historical loading scaling factors based on
  (1) Kelly Island core for Zone 6
  (2) Woodbury core for Zones 3 , 4 & 5
  (3) Crosswicks core for Zone 2 and Trenton Boundary









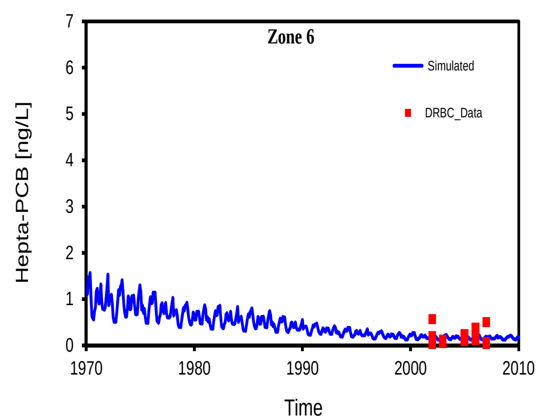


Figure 4.4.4-13: Simulated and observed Hepta PCBs in water column.

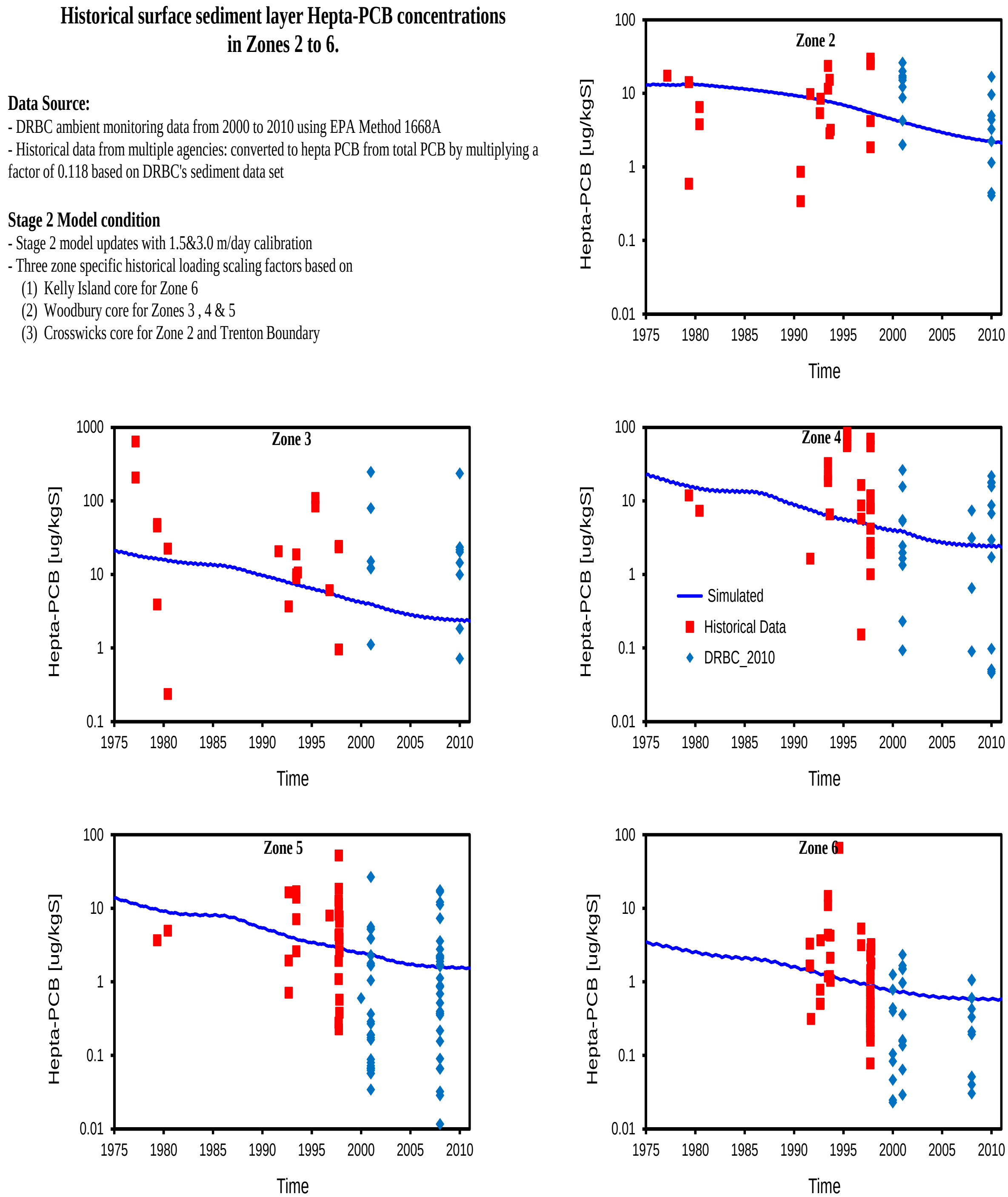


Figure 4.4.4-14: Simulated and observed Hepta PCBs in surface sediment layer. Note that the y-axis scale for Zone 3 is different from the scales of the rest of the plots for other zones.

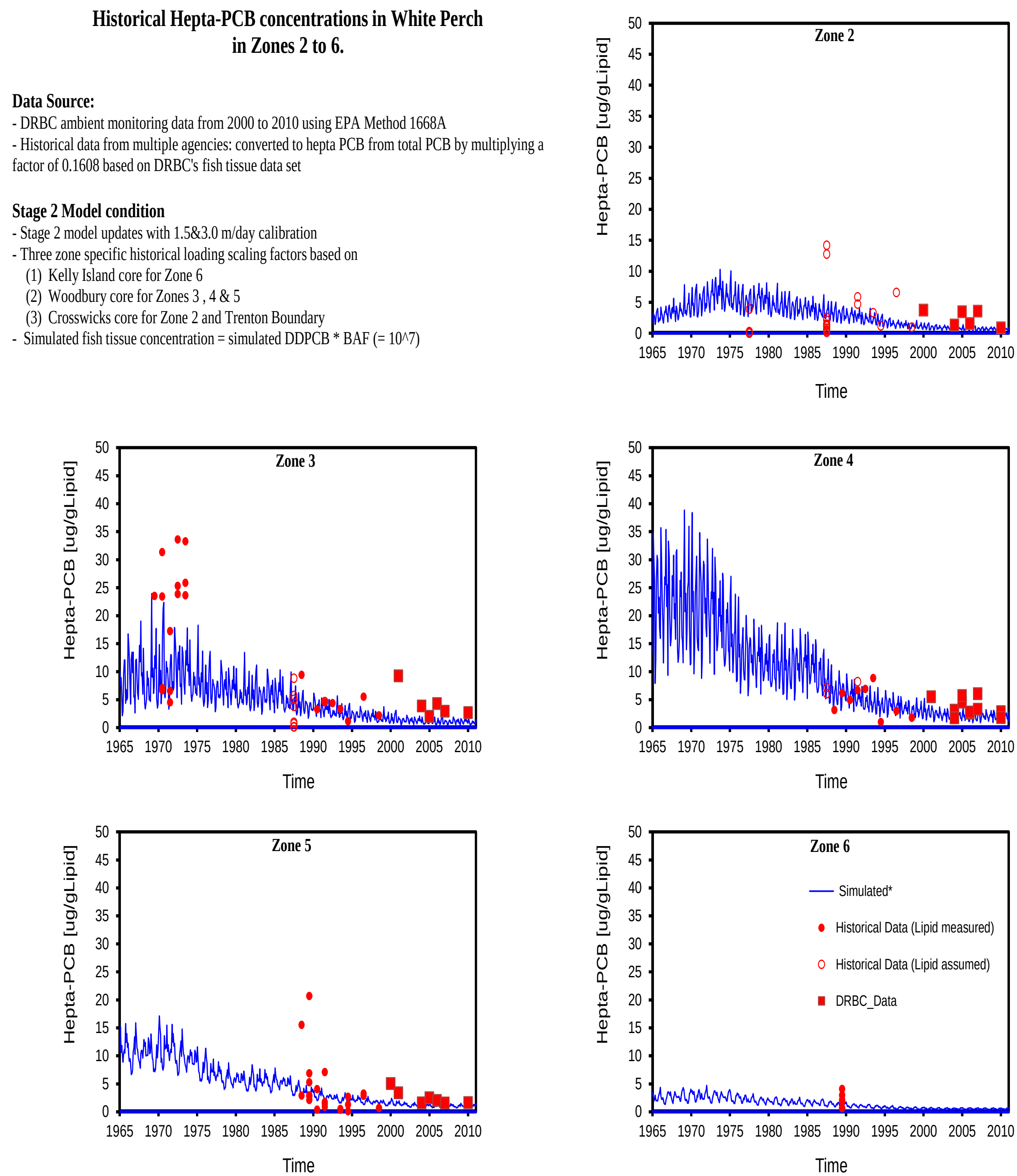


Figure 4.4.4-15: Simulated and observed Hepta PCBs in fish tissue (white perch). Simulated* results were obtained by multiplying sum of simulated dissolved and doc bound hepta PCBs (DDPCBs) and bioaccumulation factor (BAF) of 10^7.

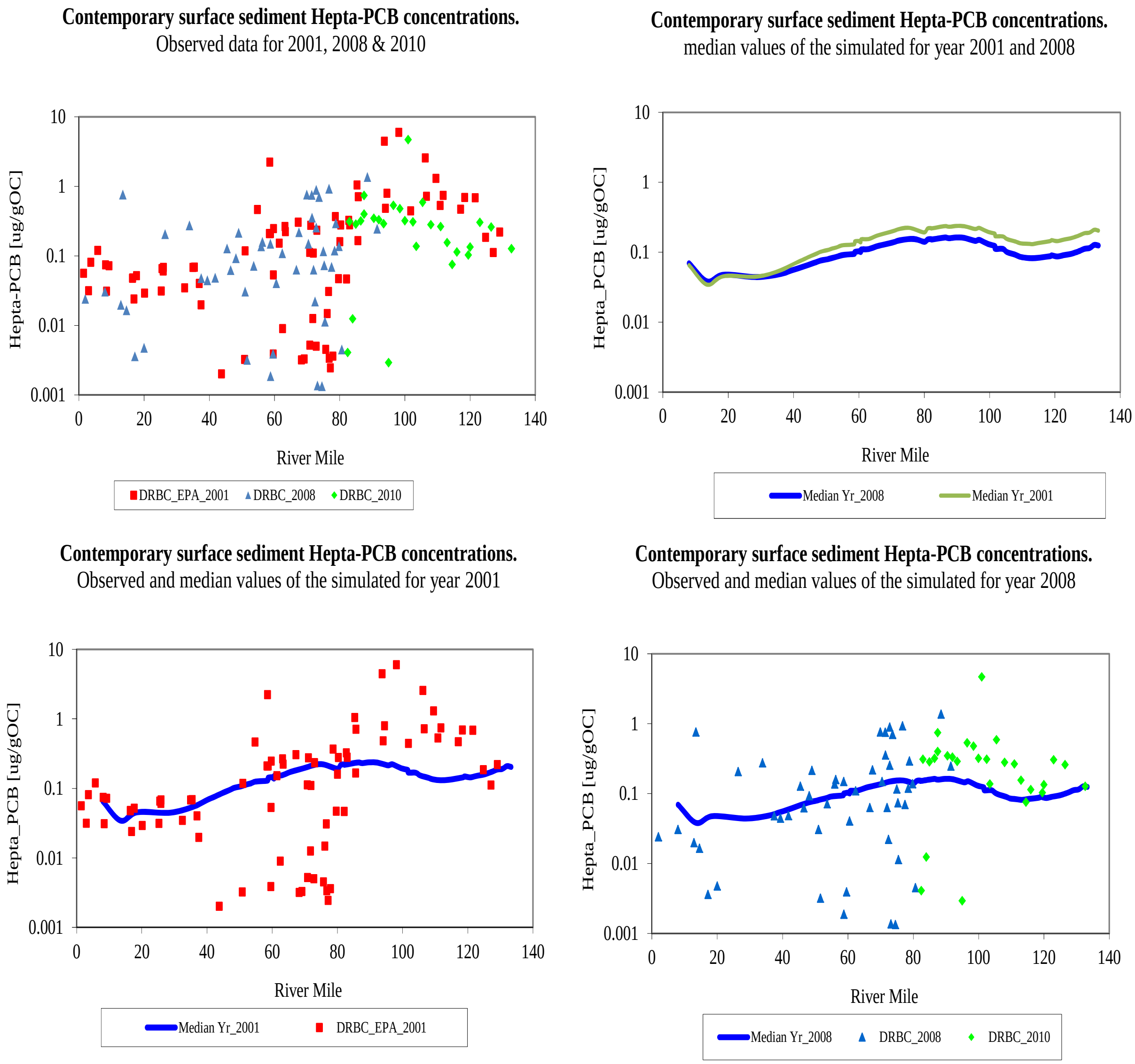


Figure 4.4.4-16: Organic carbon normalized hepta-PCBs in surface sediment layer: (a) observed data collected 2000 – 2010; (b) simulated results for year 2001 and year 2008; (c) the observed and the simulated for the year 2001; (d) the observed and the simulated for the year 2008.

4.5 Summary

4.5.1 Short-term Model Calibration Summary

The approach to calibrating the updated DELPCB model for the four homologs involved the specification of 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 component of the calibration strategy was that parameters determined through model calibration were held spatially and temporally constant unless there was supporting information to the contrary. During the calibration process, no model parameters were assigned arbitrary values (i.e., used as tuning parameters) in order to obtain the best "curve fits" of the predicted concentrations to the observed data. 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.

A combination of spatial and temporal plots, bivariate plots and cumulative frequency diagrams for biotic carbon (BIC), particulate detrital carbon (PDC), total-dissolved (a sum of the truly-dissolved and the dissolved organic carbon bounded), particulate and total penta-PCBs were used to evaluate the performance of the four homolog models in predicting each of the variables. The penta-PCB homolog model is presented first since much of the calibration effort utilized this homolog model. For tetra-, hexa- and hepta-PCBs, only total PCBs are presented in the spatial and temporal plots.

Spatial plots of BIC indicated good agreement for most of the sampling dates. The Stage 2 model showed improved agreement over the Stage 1 model. Bivariate plots confirmed the agreement between observed and simulated values. Analytical variability in the low range of observed values (1.0 mg/L) contributed to the observed variability in these plots.

Incorporation of upstream transport of biotic carbon and particulate detrital carbon from Zone 6 to lower Zone 5 in the Stage 2 model resulted in higher predicted PDC concentrations than the Stage 1 model around the area of the estuarine turbidity maximum (ETM). Improved agreement between observed and predicted concentrations was evident in the spatial plots of PDC in some ambient surveys, but not all surveys. Bivariate plots confirmed this observation particularly in Zones 3 and 4. Several factors may contribute to this lack of agreement including limited sediment quality data particularly in Zone 3, the limited areal extent of the geophysical mapping effort due to the technology and vessel utilized to obtain the data, and the heterogeneity of the sediment data in general. The bivariate plot for all Zones combined did indicate reasonable agreement between observed and simulated concentrations across the entire model domain.

Penta-PCB spatial plots of all three phases indicated good agreement for most sampling dates. Some underestimate of the particulate PCB concentrations was evident in some Zones. Spatial plots of total PCBs for the tetra- and hexa-PCB homologs indicated that most data points fell within the range of predicted values on all sampling dates. Spatial plots of hepta-PCBs suggested overestimation by the model for a few surveys.

Bivariate plots of total-dissolved PCBs for all four homologs indicated good agreement. Particulate PCBs were generally in agreement with observed values but the tetra- and penta-PCB homolog models underestimated particulate PCB concentrations. Total PCB concentrations for three homologs, penta-, hexa- and hepta-PCBs, exhibited good agreement with observed values. Predicted total tetra-PCBs tended to underestimate observed values in all Zones.

Cumulative frequency diagrams (CFD) are very useful in evaluating the fit if the data since they compare the frequency distributions of the simulated and observed values for each of the state variables. These diagrams indicate that model predictions are in good agreement with observed values over the range of observations, particularly for the penta-, hexa- and hepta-PCB homologs. The tendency of the tetra-PCB model to underestimate observed concentrations is also evident in the CFD plots. Probable causes of the underestimation are under assignment of the upstream boundary PCB condition, unaccounted tetra-PCB loads, reduced exchange of PCBs between the sediment and water column due to masking, kinetic processes not included in the current model, and/or over prediction of the volatilization which is a major sink for tetra-PCB, especially in Zone 6.

4.5.2 Hindcast Simulation Summary

Hindcast simulations with all four PCB homolog models demonstrate that the models are in good agreement with the observed PCBs in the water column and in the fish tissue, while the hexa- and hepta-PCB models are in good agreement with the respective observed PCB homolog concentrations in the surficial sediment layers.

The tetra-PCB model underestimates PCB sediment concentrations for a portion of the simulation period in the upper portions of estuary (Zones 2 and 3) and in Zone 6. Factors contributing to this include the use of a single scaling factor derived from the sum of four homologs rather than a homolog-specific scaling factor, uncertainty in the current loading estimates which translate into uncertainties in the historical loadings, and the large surface area of Zone 6 which increases the influence of gaseous exchange between the water column and the atmosphere. It should be noted, however, that the underestimation by the tetra-PCB model are not consistent, and are limited to portions of the 61 year hindcast simulation period, particularly the latter portions of the period.

The penta-PCB model also underestimates PCBs in the sediment layer in Zones 2 and 3, particularly in the period after 2000 while the model is in good agreement with observed data in the rest of zones.

The hindcast simulations are considered a ‘consistency check’ rather than a formal calibration/validation of each of the four PCB homolog models. The process utilizes the weight of the evidence since a high level of uncertainty exists in a development of historical conditions including analytical methodology differences, available information on sources and variability of PCB loadings, and hydrodynamic conditions. Hydrodynamic conditions of the Delaware Estuary have also changed significantly over the hindcast simulation period (Walsh, 2004) due to a number of dredging projects that resulted in spatial and temporal changes in hydraulic geometry variables including the depth, width, and cross-sectional area. These changes are not incorporated in the model and likely contribute to the variability in the agreement between the predicted and observed values.

The hindcast model simulations demonstrate that the four homolog models reasonably predict water column, sediment and fish tissue concentrations. Given the variability inherent in measured concentrations and model predictions, the assigned kinetics of the model, especially the settling/re-suspension rates, result in acceptable predictions of PCB concentrations for the tetra-, penta-, hexa- and hepta-PCBs.

5 Conclusions

5.1 General conclusions

In 2001, the Delaware River Basin Commission initiated development of a water quality model for organic carbon and PCB homologs (DELPCB). DELPCB has two organic carbon (biotic carbon or BIC) and particulate detrital carbon (PDC) state variables, four state variables for an individual PCB homolog, and one inorganic solid (IS) as a pseudo-state variable linked with the one-dimensional DYNHYD5 hydrodynamic model. The time-variable model includes three types of mass balances: (1) a water balance; (2) an organic carbon (OC) balance; and (3) a PCB homolog balance. The sediment processes in DELPCB are a simplified version that includes (1) depositional flux of organic carbon (BIC and PDC), (2) degradation of such flux (BIC and PDC), (3) resuspension of PDC and (4) the resulting sediment (PDC) flux. The PCB mass balance tracks all sources, losses and internal transformations of PCBs in the river and consists of four state variables: truly dissolved PCB, particulate PCB, DOC-bound PCB and total PCB. During the modeling process, upon receiving the information of physical transport from DYNHYD5, DELPCB simulates the spatial and temporal distributions of the carbon and PCB in the water colum and sediment layer. PCBs are then transported and transformed by advection, dispersion, pore water diffusion, organic carbon partitioning, and gaseous exchanges. DELPCB was originally established as a penta-PCB model in view of the time constraints imposed by a court-ordered deadline of December 15, 2003 for establishment of the TMDLs for PCBs. In 2006, the penta-PCB homolog version of DELPCB was recalibrated by the Commission staff to update model loadings and forcing functions, and utilize a revised model code. Following the recalibration, further enhancement was deemed necessary to better simulate particulate BIC and PDC in the region of the estuarine turbidity maximum or ETM, to incorporate additional data and new analytical approaches for estimating model inputs and parameters, and to develop and calibrate three additional PCB homolog models: tetra-PCB, hexa-PCB and hepta-PCB.

The model enhancements included:

1. Externalized assignment and revised coefficients for gas phase PCB processes including the use of six different subareas,
2. Upstream water column transport for BIC and PDC in lower Zones 5 and Zone 6,
3. Masking of sediment layers based on sediment type to limit interactions between the water column and sediment layer,
4. Direct incorporation of dredging and its impact on removal of PCB homologs,
5. Updating of sediment initial conditions,
6. Updating of external loads from contaminated sites, point sources, minor tributaries and air deposition,
7. Updating of boundary conditions for the Delaware River at Trenton, the Schuylkill River at Philadelphia, the C&D Canal and the ocean boundary,
8. Parameter/constant specifications for the tetra-PCB, hexa-PCB and hepta-PCB homologs, and

9. The use of sediment cores collected in marshes bordering all 5 water quality management zones (Zones 2 - 6) to provide scaling factors for historical loadings for hindcast simulations.

Following incorporation of these enhancements, the model was recalibrated using the penta-PCB homolog version of the model, followed by subsequent extension of the model to three other homologs. Despite these enhancements, significant uncertainty inherent in both the available data and model limits the ability of the model to accurately predict PCB concentrations in the ambient waters of the Delaware River and Bay. One source of uncertainty is the use of a one-dimensional hydrodynamic model to drive the carbon and PCB homolog submodel. Use of a three-dimensional hydrodynamic model will permit better simulation of organic carbon transport and fate, particularly in Zone 5 and 6. Uncertainty in the ambient data (air, water, sediment, fish tissue) and the PCB forcing functions (point and non-point source loadings) for both contemporary and historical conditions limit the ability of the model to simulate observed conditions. While this uncertainty has been reduced or evaluated during this and the previous recalibration effort, it cannot be eliminated.

The general approach used to calibrate the updated DELPCB model for the four homologs involved the specification of 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 component of the calibration 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 with due consideration of the uncertainty in the available data and model components.

5.2 Short-term calibration

A combination of spatial and temporal plots, bivariate plots and cumulative frequency diagrams for biotic carbon (BIC), particulate detrital carbon (PDC), total-dissolved (a sum of the truly-dissolved and the dissolved organic carbon bounded), particulate and total PCBs were used to evaluate the performance of the four homolog models in predicting each of the variables.

Spatial plots of observed and simulated BIC were in good agreement for most of the sampling dates, with the Stage 2 model showing improved agreement over the Stage 1 model. Incorporation of upstream transport of biotic carbon and particulate detrital carbon from Zone 6 to lower Zone 5 in the Stage 2 model resulted in higher predicted PDC concentrations than the Stage 1 model around the area of the estuarine turbidity maximum (ETM). Improved agreement between observed and predicted concentrations was evident in the spatial plots of PDC in some ambient surveys, but not all surveys. While improved, the simulation of PDC in the region of the ETM should improve substantially when a three-dimensional hydrodynamic submodel is linked to the PCB homolog models in the future.

Spatial, bivariate and CFD plots indicated that the model was in reasonable agreement with the observed data for dissolved PCB phase of all four homologs in all Zones. Particulate PCBs were generally in agreement with observed values for the hexa- and hepta-PCB homologs, but the tetra- and penta-PCB homolog models appear to underestimate particulate PCB concentrations. Total PCB concentrations for three homologs, penta-, hexa- and hepta-PCBs, exhibited good agreement with observed values. Predicted total tetra-PCBs tended to underestimate observed values in all Zones, particularly in the upper end of the distribution of observed concentrations. PCB homologs in the fish tissue of resident fish species (channel catfish and white perch) in the Delaware Estuary consist almost entirely of the tetra through hepta-PCB homologs (~86 to 89%), with the tetra-PCB homolog contributing approximately 10% of the total PCBs. In addition, the reasonable agreement for all four homologs in long-term model simulations is consistent with the 70 year exposure duration used in establishing the PCB human health criterion and the principle exposure route for PCBs of fish consumption.

5.3 Hindcast Simulations

Hindcast simulations with all four PCB homolog models demonstrate that the models are in good agreement with the observed PCBs in the water column and in the fish tissue, while the hexa- and hepta-PCB models are in good agreement with the respective observed PCB homolog concentrations in the surficial sediment layers. Several factors may be contributing to the underestimation by the model of tetra- and penta-PCB concentrations in the sediments of Zone 2 and 3, and are discussed in detail in Section 4.5.2. This is a significant improvement over the Stage 1 model where some discrepancies were noted in the agreement of the model with the observed sediment and fish tissue concentrations (Fikslin et al, 2006).

The hindcast model simulations demonstrate that the four homolog models reasonably predict water column, sediment and fish tissue concentrations. Given the variability inherent in measured concentrations and model predictions, the assigned kinetics of the model, especially the settling/re-suspension rates, result in acceptable predictions of PCB concentrations for the tetra-, penta-, hexa- and hepta-PCBs.

5.4 Recommendations

Model refinement is a continuing process in which new data or research may be incorporated into the DELPCB model to improve the model simulations. While most of the recommendations in the 2006 model recalibration report were implemented in the development and recalibration of the four PCB homolog models, the following refinements of DELPCB are suggested to improve the predictive ability of the model:

- To be used as a tool for the development of PCB TMDLs and for the evaluation of the progress of implementation of the Pollution Minimization Plan, the DELPCB model needs to be continuously validated with longer-term data sets. Intense monitoring of PCBs in ambient waters, sediment layers, atmosphere, and fish tissue every 10 years is recommended.

- Identification, development and use of a three dimensional hydrodynamic model with a sediment (carbon) transport module is critical to replace the current one-dimensional DYNHYD model. Several candidate modeling frameworks are available including the U.S. Army COE Curvilinear Hydrodynamics in 3 Dimensions - Z- Plane (CH3D-Z) model of the Delaware Estuary (Johnson, 2007) and the Regional Ocean Modeling System (ROMS) framework which has recently been extended to the Delaware River and Bay.

- Continue to refine the PCB forcing functions at the model boundaries, particularly the Delaware River at Trenton, NJ and the ocean boundary. PCB loadings at these two boundaries have a significant effect on ambient water concentrations in Zones 2-5 and Zone 6, respectively.

- Collect additional data on sediment characteristics and PCB concentrations in Zones 2 and 3 to better parameterize the sediment masking incorporated in this study. Given the heterogeneity evident in the sediment data and the large area of these Zones that were not characterized as to sediment characteristics, the number and spatial extent of this data collection effort should reflect a finer scale than previous studies.

- Other enhancements that should be considered include use of alternative Henry's Law constants for all 209 PCB congeners, incorporation of additional model segments in Delaware Bay (Zone 6), reanalysis of the available air monitoring data to resolve issues with coelution and extrapolation to the homolog level, and development of a deca-PCB homolog model for use as a tracer for transport and sediment-water interactions.

5.5 Summary

The overall objective of this effort was to assess the predictive capability of the coupled hydrodynamic, organic carbon and PCB homolog models in representing the principal environmental processes that influence the transport and fate of four PCB homologs in the Delaware River and Estuary: tetra-PCB, penta-PCB, hexa-PCB and hepta-PCB.

Comparisons of simulated to measured water quality concentrations indicate generally good agreement and no consistent bias of the estimates for organic carbon and the four PCB homologs during the model calibration period.

Spatial, bivariate and CFD plots indicated that the model was in reasonable agreement with the observed data for dissolved PCB phase of all four homologs in all Zones. Particulate PCBs were generally in agreement with observed values for the hexa- and hepta-PCB homologs, but the tetra- and penta-PCB homolog models appear to underestimate particulate PCB concentrations. Total PCB concentrations for three homologs, penta-, hexa- and hepta-PCBs, exhibited good agreement with observed values.

The hindcast model simulations demonstrate that the four homolog models reasonably predict water column, sediment and fish tissue concentrations. Given the variability inherent in measured concentrations and model predictions, the assigned kinetics of the model, especially the settling/re-suspension rates, result in acceptable predictions of PCB concentrations for the tetra-, penta-, hexa- and hepta-PCBs.

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.

6 REFERENCES

Ashley, J.T.F., D.J. Velinsky, M. Wilhelm, J.E. Baker, D. Secor and M. Toaspern. 2004. Bioaccumulation of polychlorinated biphenyls in the Delaware River Estuary. Report No. 03-03F submitted to the Delaware River Basin. January 15, 2004.

Bamford, H.A., D.L. Poster and J.E. Baker. 2000. Henry's Law constants of polychlorinated biphenyl congeners and their variation with temperature. Jour. Chem. & Eng. Data 45:1069-1074.

Bamford, H.A., D.L. Poster, R.E. Huie and J.E. Baker. 2002. Using extrathermodynamic relationships to model the temperature dependence of Henry's Law constants of 209 PCB congeners. Envir. Sci, & Tech. 36:4395-4402.

Hansen, B.G., Ana B. Paya-Perez, Mohammed Rahman, and Bo R. Larsen. 1999. QSARs for Kow and Koc of PCB congeners: A Critical examination of Data, assumptions and statistical approaches. Chemosphere 39(13):2209-2228.

Breivik, K., A. Sweetman, J. M. Pacyna, and K. C. Jones, 2002a. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. 1. Global production and consumption. The Science of the Total Environment 290: 181-198.

Breivik, K., A. Sweetman, J. M. Pacyna, and K. C. Jones, 2002b. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. 2. Emissions. The Science of the Total Environment 290: 199-224.

Breivik, K., A. Sweetman, J.M. Pacyna and K.C. Jones. 2007. Towards a global historical emission inventory for selected PCB congeners - A mass balance approach 3. An update. Science of the Total Environment 377:296-307.

Cohen, R.A. 1999. An Introduction to PROC LOESS for Local Regression. Proceedings of the 24th Annual SAS Users Group International Conference. Paper 273. April 1999. Miami Beach, FL.

Cleveland, W.S. 1979. Robust locally weighted regression and smoothing scatterplots. Jour. Amer. Stat. Asso. 74(368):829-836.

Cleveland, W.S. and S.J. Devlin. 1988. Locally weighted regression: An approach to regression analysis by local fitting. Jour. Amer. Stat. Asso. 83(403):596-610.

Cook T.L., C.K. Sommerfield and K. Wong. 2007. Observations of tidal and springtime sediment transport in the upper Delaware Estuary. Estuarine, Coastal and Shelf Sci.72:235-246.

Delaware River Basin Commission. 1998. Study of the Loadings of Polychlorinated Biphenyls from Tributaries and Point Sources Discharging to the Tidal Delaware River. Delaware River Basin Commission. West Trenton, NJ. June 1998.

Delaware River Basin Commission. 2003a. PCB Water Quality Model for the Delaware Estuary (DELPCB). Delaware River Basin Commission. West Trenton, NJ. September 2003.

Delaware River Basin Commission. 2003b. DYNHYD5 Hydrodynamic Model (Version 2.0) and Chloride Water Quality Model for the Delaware Estuary. Delaware River Basin Commission. West Trenton, NJ. September 2003.

Delaware River Basin Commission. 2003c. Calibration of the PCB Water Quality Model of the Delaware Estuary for Penta-PCBs and Carbon. Delaware River Basin Commission. West Trenton, NJ. September 2003.

Fikslin, T.J., V.J. Bierman, J. Yagecic, R.A. MacGillivray, G.J. Cavallo, D. Liao, N.S. Suk S.C. Hinz, F.L. Hellweger and D.M. DiToro. 2006. Revised Calibration of the Water Quality Model of 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. West Trenton, NJ. September 2006.

Frame, G.M. 1996. spreadsheet (aroclor_frame.xls) condensed from research results reported in: Frame, G. M., Cochran, J. W., and Boewadt, S.S. Complete PCB congener distributions for 17 Aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. J. High Resol. Chromatogr., 19:657-668.

Hansen, B.G., Ana B. Paya-Perez, Mohammed Rahman, and Bo R. Larsen. 1999. QSARs for Kow and Koc of PCB congeners: A Critical examination of data, assumptions and statistical approaches. Chemosphere 39(13):2209-2228.

Hawker, D.W. and D.W. Connell. 1988. Octanol-water partition coefficient of PCB congeners. Environ Sci. Technology 22:382-387.

Johnson, B.H. 2007. User's manual for CH3D-Z with the Delaware Deepening Model as an Example. Report prepared for the U.S. Army Corps of Engineers, Philadelphia District. Philadelphia, PA

Karickoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10(8):833-846.

National Oceanic and Atmospheric Administration. 1989. National Status & Trends Program for Marine Environmental Quality , Progress Report, A Summary of Data on Tissue

Contamination from the First Three Years (1986-1988) of the Mussel Watch Project Technical Memorandum NOS OMA 49.

National Oceanic and Atmospheric Administration. 2001. Magnitude and Extent of Contaminated Sediment and Toxicity in Delaware Bay. NOAA technical memorandum NOS NCCOS CCMA, 148.

National Oceanic and Atmospheric Administration. Mussel Watch Database. Retrieved January 2003 from http://nsandt.noaa.gov/data_description_nsandt.htm.

Soil Conservation Service. 1986. Urban Hydrology for Small Watersheds, Technical Release 55. June 1986.

Hurvich, C.M. and J.S. Simonoff. 1998. Smoothing parameter selection in nonparametric regression using an improved Akaike information criterion. Jour. Royal Stat. Soc. B60:271-293.

Sommerfield C.K. 2009 Mechanisms of sediment flux and turbidity maintenance in the Delaware River Estuary. Final Report to the Delaware River Basin Commission. October 2009.

Sommerfield, C.K. and Madsen, J.A., 2003. Sedimentological and Geophysical Survey of the Upper Delaware Estuary. Final report to the Delaware River Basin Commission, 124 pp.

Sommerfield, C.K. and K. Wong. 2011. Mechanisms of sediment flux and turbidity maintenance in the Delaware Estuary. Jour. Geophys. Res. 116, C01005, doi:10.1029/2010JC006462.

Thomann R.V. and J.A. Mueller. 1987. *Principles of Surface Water Modeling and Control*. Harper & Row Publishers. New York, NY.

U.S. Environmental Protection Agency. 1999. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS. Office of Water. EPA-821-R-00-002. December 1999.

Walsh, D.R. 2004. Anthropogenic influences on the morphology of the tidal Delaware River and Estuary: 1877–1987. Master of Science Thesis. University of Delaware. Newark, DE.

Wong, K. and C.K. Sommerfield. 2009. The variability of currents and sea level in the upper Delaware Estuary. Jour, Mar. Res. 67:479-501.