
PART 4

LM2-TOXIC

Chapter 5. LM2-Toxic Calibration and Confirmation

For diagnosis of system behavior and reasonable prediction of long-term reactions of a water system, it is very important that a water quality model is well-calibrated and confirmed under a conceptually well-constructed solid and toxic chemical dynamics. Two of the main objectives in developing the Level 2 contaminant transport and fate model (LM2-Toxic) were to calibrate and confirm the model using the Lake Michigan Mass Balance Project (LMMBP)-generated data and to apply the model for long-term forecasts of the polychlorinated biphenyl (PCB) concentrations in water and sediment of the lake for different forcing functions and loading scenarios. The advantages of calibrating a coarse spatial grid water quality model like LM2-Toxic are its efficiency and quickness.

LM2-Toxic is a coupled mass balance of organic carbon solids and toxic chemical (PCBs) dynamics. Because of no feedback mechanisms from PCB behavior to organic carbon behavior in the model, the calibration of the LM2-Toxic was done using two separate calibration stages. The first stage was the calibration of organic carbon dynamics without considering any behavior of PCBs in the system and the second stage was the calibration of PCB dynamics without adjusting any parameters associated with organic carbon dynamics.

Prior to the organic carbon and PCB dynamic calibrations, the LM2-Toxic was used as a thermal balance model to calibrate the vertical dispersion coefficients between the water column layers. A

detailed description of inputs used in the thermal balance model can be found in Part 4, Chapter 4, Section 4.4.1.2.

The data collected for the LMMBP were spatially averaged using a volume-weighted averaging algorithm to generate segment-specific cruise mean concentrations (Appendix 4.4.1). The averaging algorithm also computed the statistical standard error that was expressed as error bars related to the mean. The cruise mean concentrations were compared with the predicted concentrations from the LM2-Toxic for the vertical dispersion coefficients calibration, the organic carbon dynamics calibration, and the PCB dynamics calibration.

4.5.1 Vertical Dispersion Coefficients Calibration

Vertical dispersion coefficients at the interfaces between LM2-Toxic water column layers were very important to overall water transport in Lake Michigan. The vertical mixing defined by the vertical dispersion coefficients moves large amounts of mass vertically in the lake and is strongly influenced by water temperature that has a distinct seasonal variation. A thermal balance model was applied to calibrate the predefined vertical dispersion coefficients. The results in Appendix 4.5.1 demonstrate excellent agreement between observed temperature and the model simulation for the LMMBP period. The results from the thermal balance model were also compared to the results from the Princeton Ocean Hydrodynamic Model (POM) (Schwab and Beletsky, 1998) for selected segments (Figure 4.5.1). Both

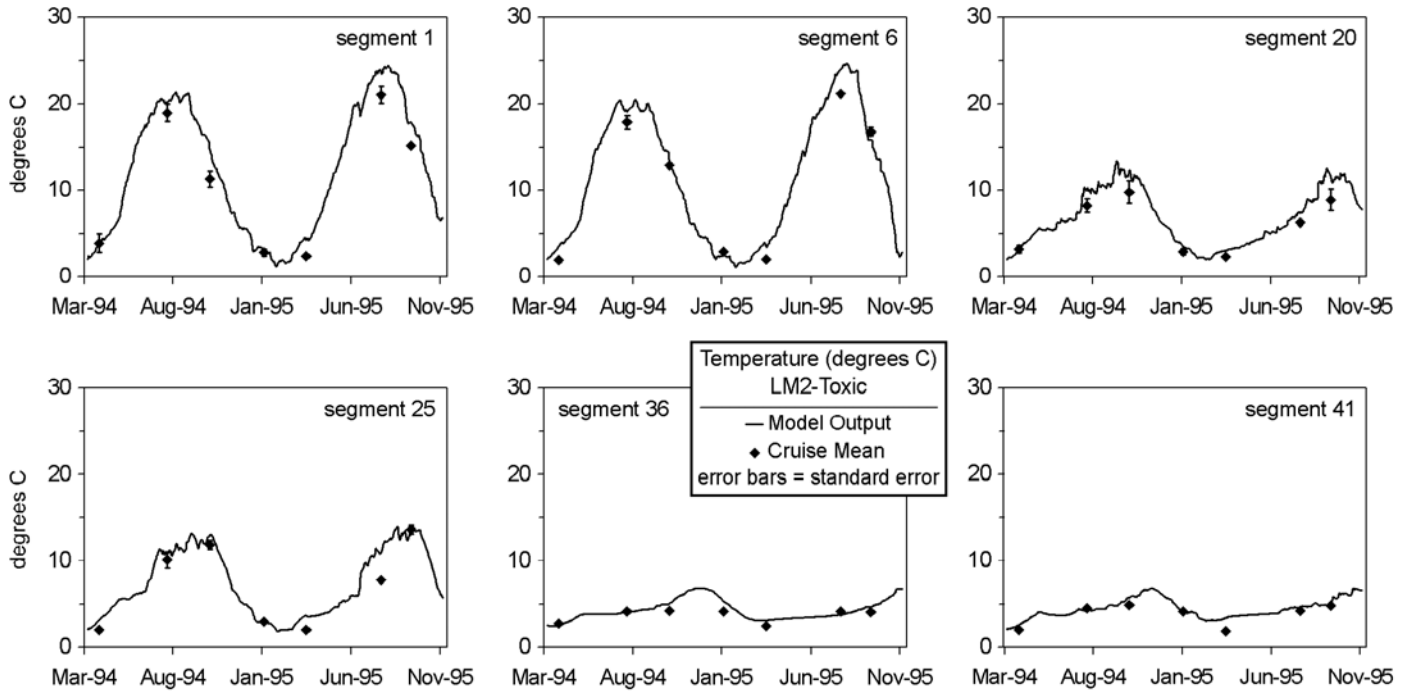


Figure 4.5.1a. Comparison between the temporal profiles for temperature results from the LM2-Toxic.

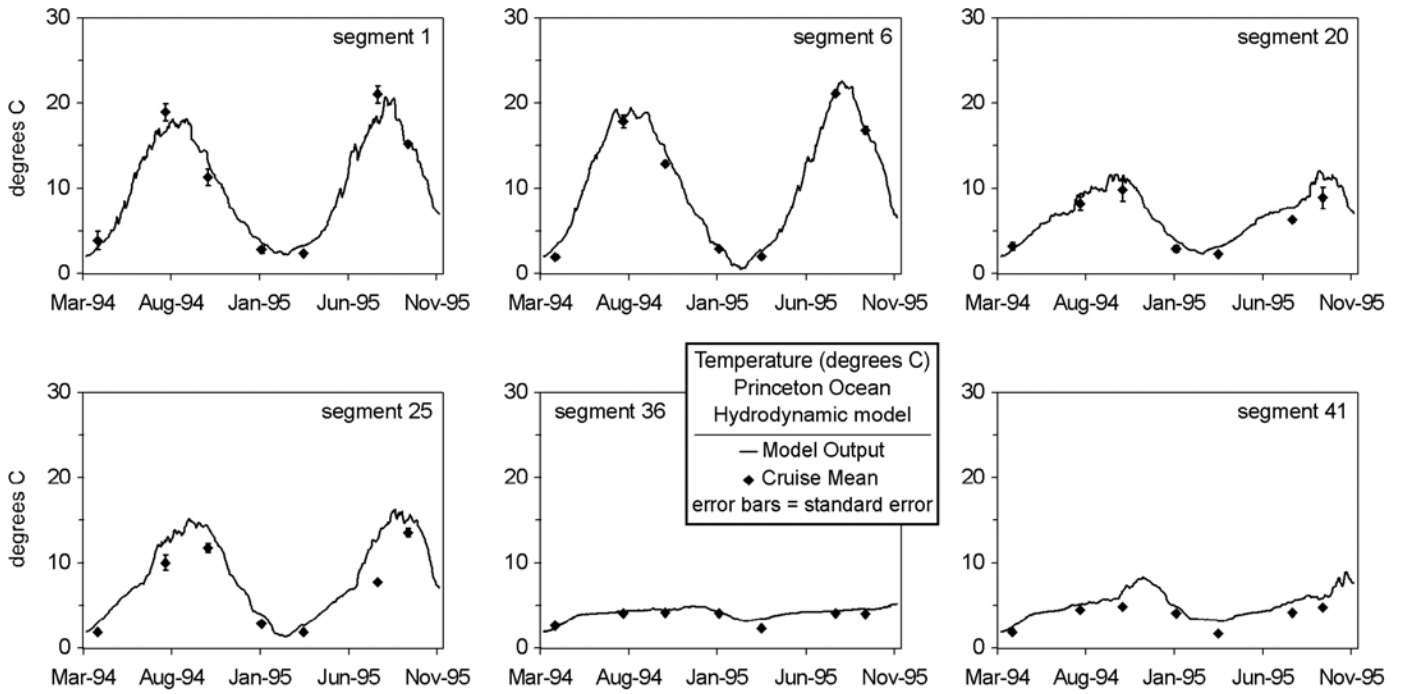


Figure 4.5.1b. Comparison between the temporal profiles for temperature results from the Princeton Ocean Hydrodynamic model.

models did a good job of simulating temperature in the lake.

4.5.2 Organic Carbon Dynamics Calibration

Because the movement of particulate organic carbon (POC) (POC = PDC + BIC, where PDC = particulate detrital carbon, BIC = biotic carbon) dominates the transport and fate of the PCBs in a natural water system, the quality of the calibration of the organic carbon sorbent dynamics was very crucial for a successful subsequent calibration of PCB dynamics. The calibration strategy for the organic carbon dynamics was to 1) fix as many independent parameters used in the model as possible based on literature, field measurements, and analytical results from the field samples, and 2) adjust the parameters considered to be the most uncertain and site-specific without using values exceeding their range constrained by literature.

4.5.2.1 Calibration Process/Procedure

The procedures taken in the organic carbon dynamics calibration for the LM2-Toxic were the following:

1. Fixing segment-specific sediment burial rates (v_b) and thickness of surficial sediment mixing layer based on analyzed results from the LMMBP sediment core measurements (Robbins *et al.*, 1999).
2. Fixing the dissolved organic carbon (DOC) diffusion coefficient between the surficial sediment layer and the overlying water column at $1.73 \times 10^{-4} \text{ m}^2/\text{d}$ (DePinto *et al.*, 1993).
3. Fixing segment-specific critical wave heights using Equation 4.3.12.
4. Assigning initial segment-specific settling velocities for BIC and PDC based on values from the literature (DePinto *et al.*, 1993; Eadie *et al.*, 1990; Baker *et al.*, 1991; Eadie, 1997, Eadie *et al.*, 1984; Thomann and Di Toro, 1983).
5. Estimating segment-specific empirical wave coefficients (α) using Equation 4.3.11.

6. Computing segment-specific daily resuspension rates using procedures described in Sections 4.3.4.2.1 (Steady-State Resuspension Calculation) and 4.3.4.2.2 (Empirical Wave-Induced Resuspension Calculation).
7. Executing the LM2-Toxic, examining model outputs (carbon concentrations), and adjusting segment-specific settling velocities and resuspension rates accordingly by repeating steps 4-6 as necessary.
8. Adjusting biochemical organic carbon transformation rates and yield coefficients listed in Table 4.4.16.

Most of the organic carbon decay rates (transformation rates) and yield coefficients were initially given the same values used in the Green Bay Mass Balance Project (GBMBP) and were adjusted during the LM2-Toxic organic carbon dynamics calibration. The principal parameters adjusted during the organic carbon dynamics calibration were rates related to carbon vertical transport such as settling and resuspension velocities, carbon decay rates, and yield coefficients. The final values for these rates had to be consistent with available literature data and limnological theory.

4.5.2.2 Results and Discussion

The final values for the biochemical transformation rates and yield coefficients are presented in Table 4.4.16. The carbon decay rates and yield coefficients shown in this table are quite consistent with the limnological theory of organic carbon cycling in a natural water system. It was expected that the final carbon decay rates (left-hand side of Equations 4.3.3 - 4.3.5) in pelagic freshwater systems would decrease in the order of BIC, PDC, and DOC. Therefore, the values of substrate saturated decay rates and Michaelis-Menten half-saturation constants for the organic carbon would have the following sequences:

$$\hat{k}_{d(BIC)} > \hat{k}_{d(PDC)} > \hat{k}_{d(DOC)} \text{ and } k_{1/2(DOC)} > k_{1/2(PDC)} > k_{1/2(BIC)}, \text{ respectively.}$$

The lake-wide concentrations (including Green Bay) in surface water layers (epilimnion) for DOC, PDC,

and BIC could be as high as 1.8, 0.30, and 0.20 mg/L, respectively. It is favorable and reasonable to have the value of Michaelis-Menten half-saturation constant for each organic carbon state variable close to double that of its concentration. The final sediment PDC decay rate used in the LM2-Toxic was within the range of the value ($5.7 \times 10^{-5} \text{ d}^{-1}$ at 20°C) used in GBMBP (DePinto *et al.*, 1993) and the value (0.001 d^{-1}) from other literature (Gardiner *et al.*, 1984). The values of yield coefficients ($Y_{(\text{BIC} \rightarrow \text{PDC})}$, $Y_{(\text{PDC} \rightarrow \text{DOC})}$) in Table 4.4.16 indicated less loss to carbon dioxide (CO_2) during the conversion from BIC to PDC than during the conversion from PDC to DOC.

The model results of organic carbon dynamics calibration for the LM2-Toxic are presented in Figures 4.5.2 to 4.5.4 for temporal profiles of all 41 water column segments. The complete set of calibration plots for the organic carbon including temporal profiles in the sediments are provided in Appendix 4.5.2.

Figure 4.5.2 shows slight temporal variation of DOC in the main lake and outer Green Bay (see Figure 4.3.1 for Level 2 segmentation). This temporal change of DOC concentration was closely related to the strong seasonal variation of PDC concentration and was more evident in the epilimnion of the lake. Other than the inner Green Bay area, there was almost no horizontal or vertical spatial variation for DOC.

The temporal profiles based on the model outputs for both BIC and PDC (Figures 4.5.3 and 4.5.4) showed very strong seasonal variation throughout the lake, especially in the epilimnion segments. Excluding the inner shallow water of Green Bay segments where BIC concentration was controlled by its load from the Fox River and very localized algal growth, there was not much horizontal spatial variation for BIC in the lake. The peaks of the BIC temporal profiles for the epilimnion segments resulted from an algal bloom in late spring and early summer. Compared with the epilimnion segments, having a similar temporal variation, the concentration of BIC decreased dramatically in the hypolimnion segments.

The temporal profiles of PDC (Figure 4.5.4) indicated that the main lake and Green Bay were two very different systems. It appeared that the PDC

concentration in Green Bay was more dominated by sediment-water interactions (i.e., resuspension events evidenced by the spikes on the plots) than other components or processes such as tributary loads, decomposition of BIC, and its own decay. In the main lake where water segments were larger and thicker, there was little evidence of resuspension events from the PDC temporal profiles, with the exception of a couple of main lake segments at the end of 1995. Algal primary production and BIC-to-PDC decay were obvious control processes for PDC concentration in the main lake, especially in the epilimnion. An almost constant concentration of PDC (0.12 mg/L) in the large bottom water column segments indicated that, without much contribution from BIC decay to PDC in these segments, there were persistent and substantial PDC fluxes entering these segments by settling from the upper water column layer, resuspension from the surficial sediments, and/or focusing process from the adjacent shallower area (segments) in order to maintain this concentration of PDC.

Figures 4.5.5a to 4.5.5c show a comparison between the model predictions and observed data (cruise-segment mean concentration) of DOC, BIC, and PDC for the entire calibration (i.e., the LMMPB study period). In general, there was good agreement between the data and model predictions for all organic carbons. There was a slight overprediction of BIC concentration indicated by the low slope of the regression line. Though the results from the regression (Figure 4.5.5b) indicated a poorer quality of fit to the observed data and overprediction of BIC, visual examination of temporal profiles of BIC concentration (Figure 4.4.3) suggested the fit was good for most of the segments.

4.5.3 PCB Dynamics Calibration

Because of no feedback mechanisms from PCB dynamics to organic carbon dynamics, only a limited number of parameters associated with PCB dynamics needed to be slightly adjusted. Due to the significant influence of organic carbon movement on the transport and fate of PCBs in Lake Michigan, the PCB partitioning coefficient became one of the very crucial parameters for the LM2-Toxic PCB dynamics calibration. Mass budget analysis for ΣPCBs (see Chapter 6 for details) based on the outputs of the LM-2 Toxic for the two-year LMMPB period indicated

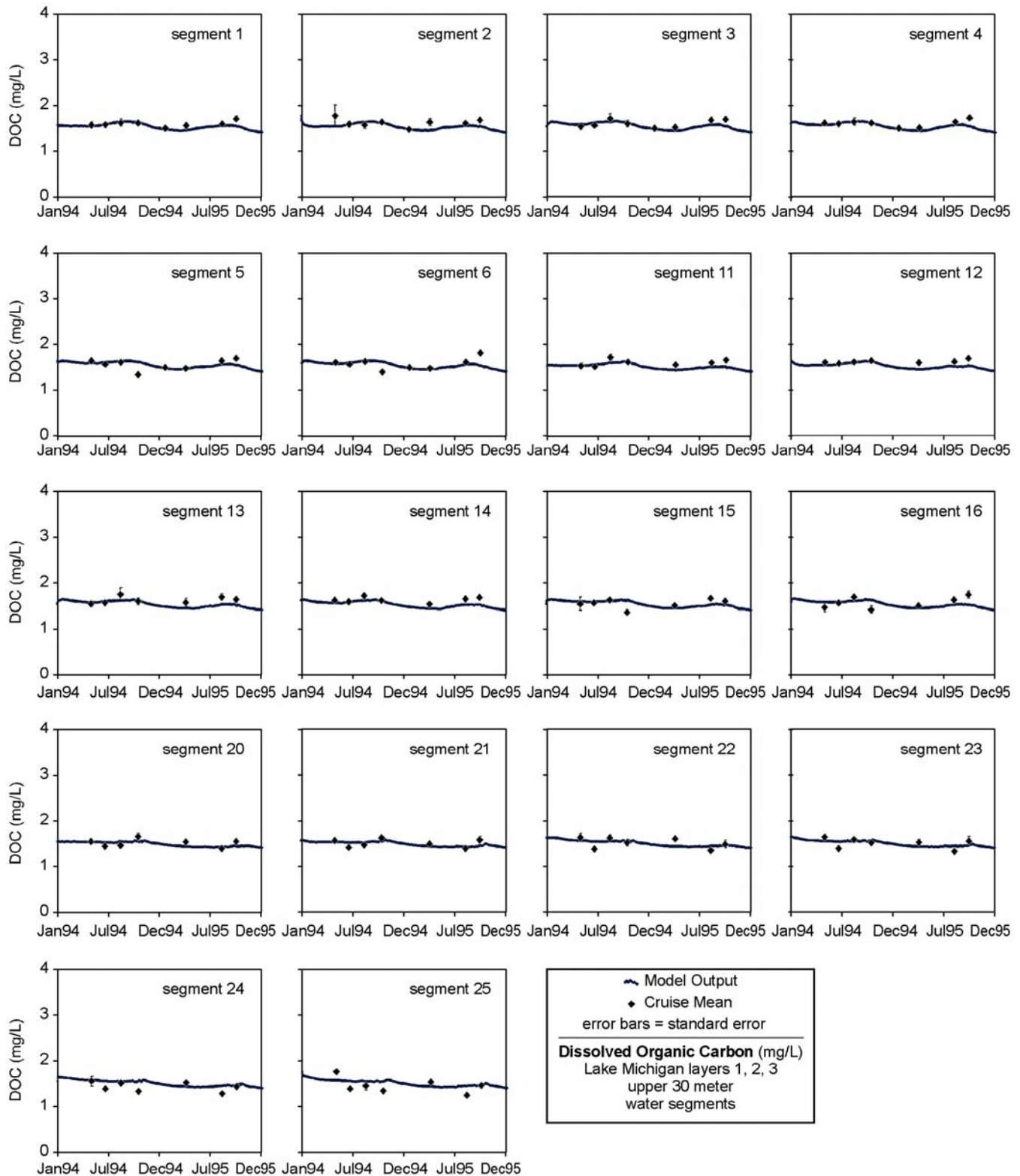


Figure 4.5.2. Temporal profiles of DOC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data.

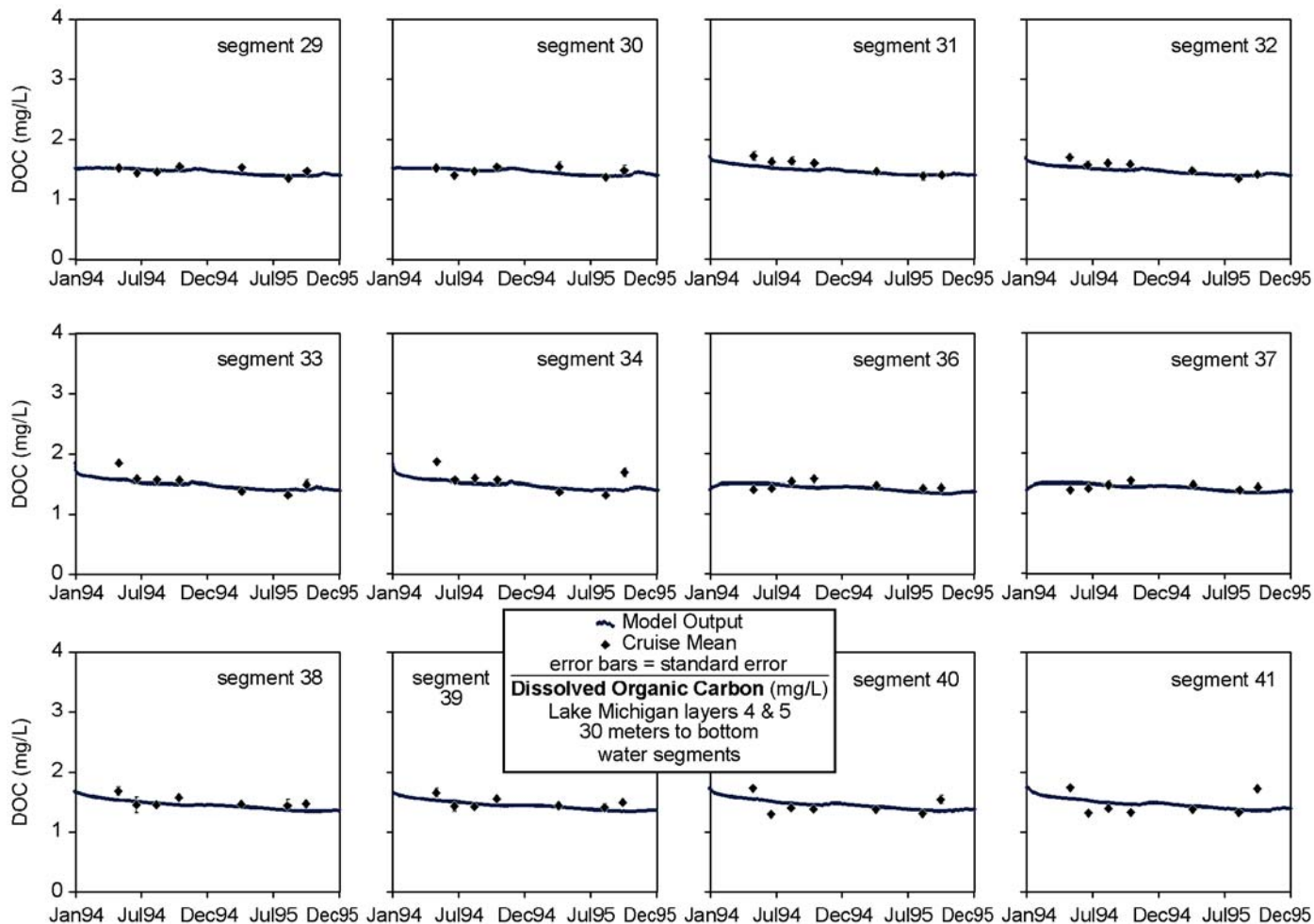


Figure 4.5.2. Temporal profiles of DOC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

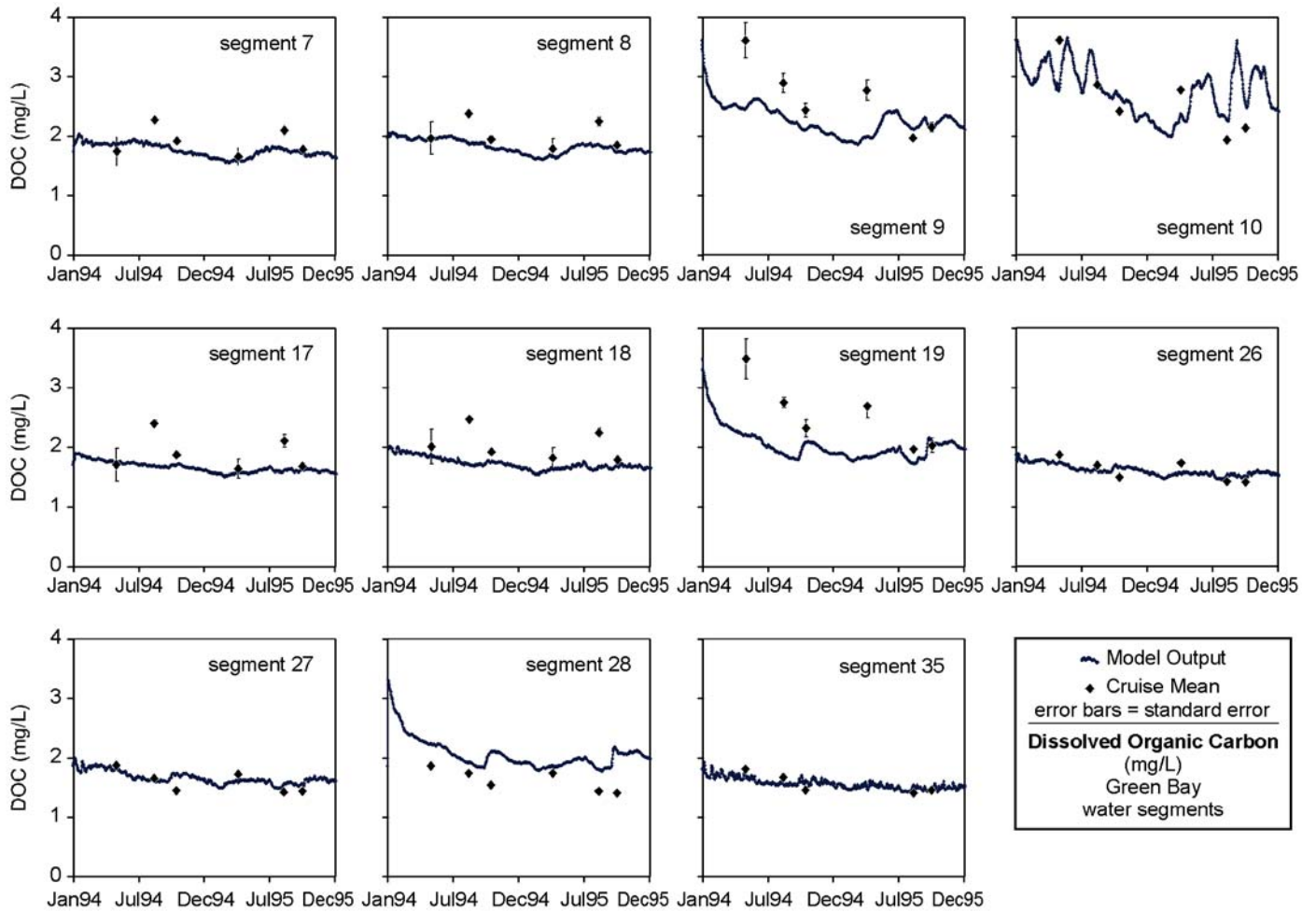


Figure 4.5.2. Temporal profiles of DOC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

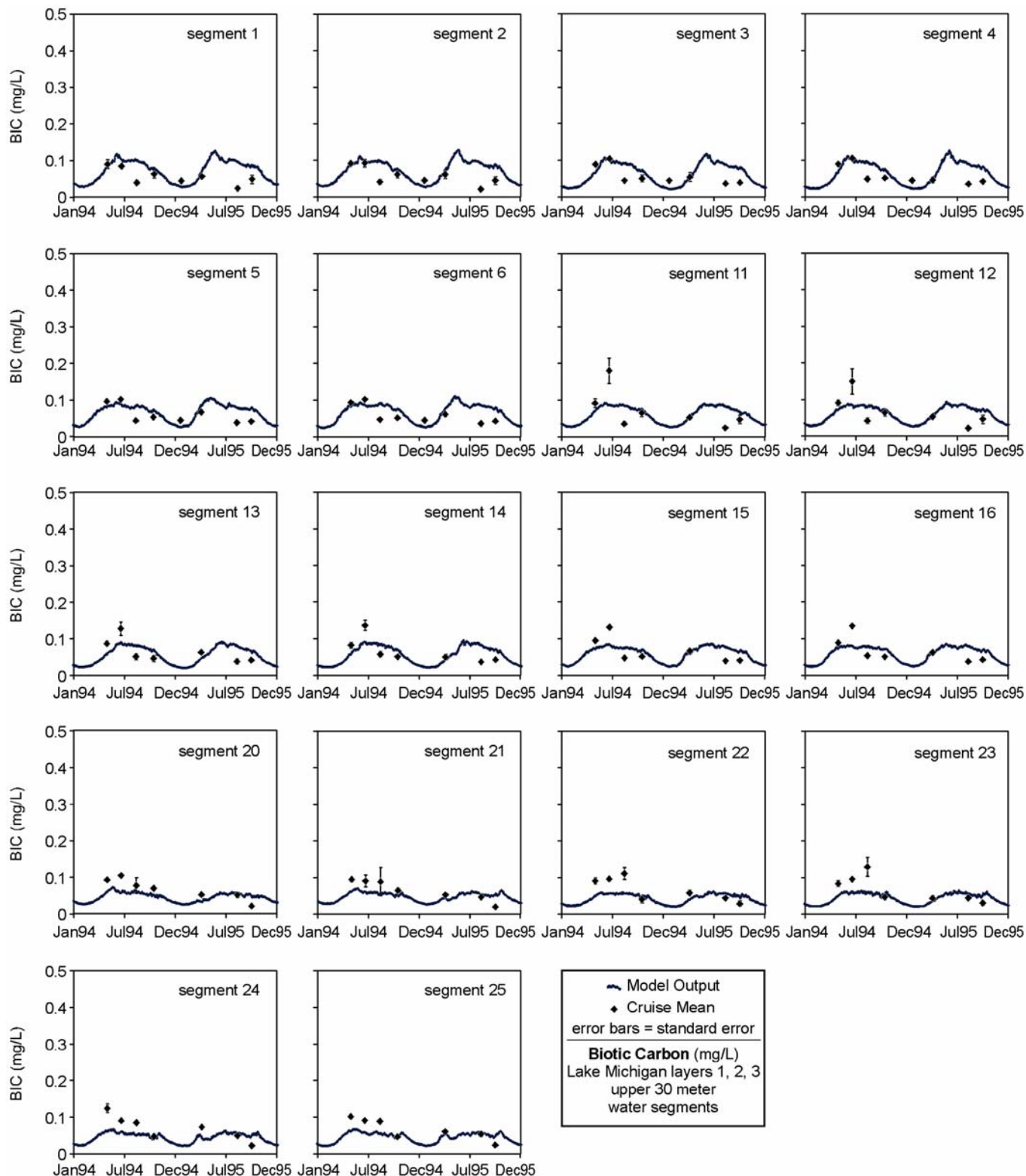


Figure 4.5.3. Temporal profiles of BIC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data.

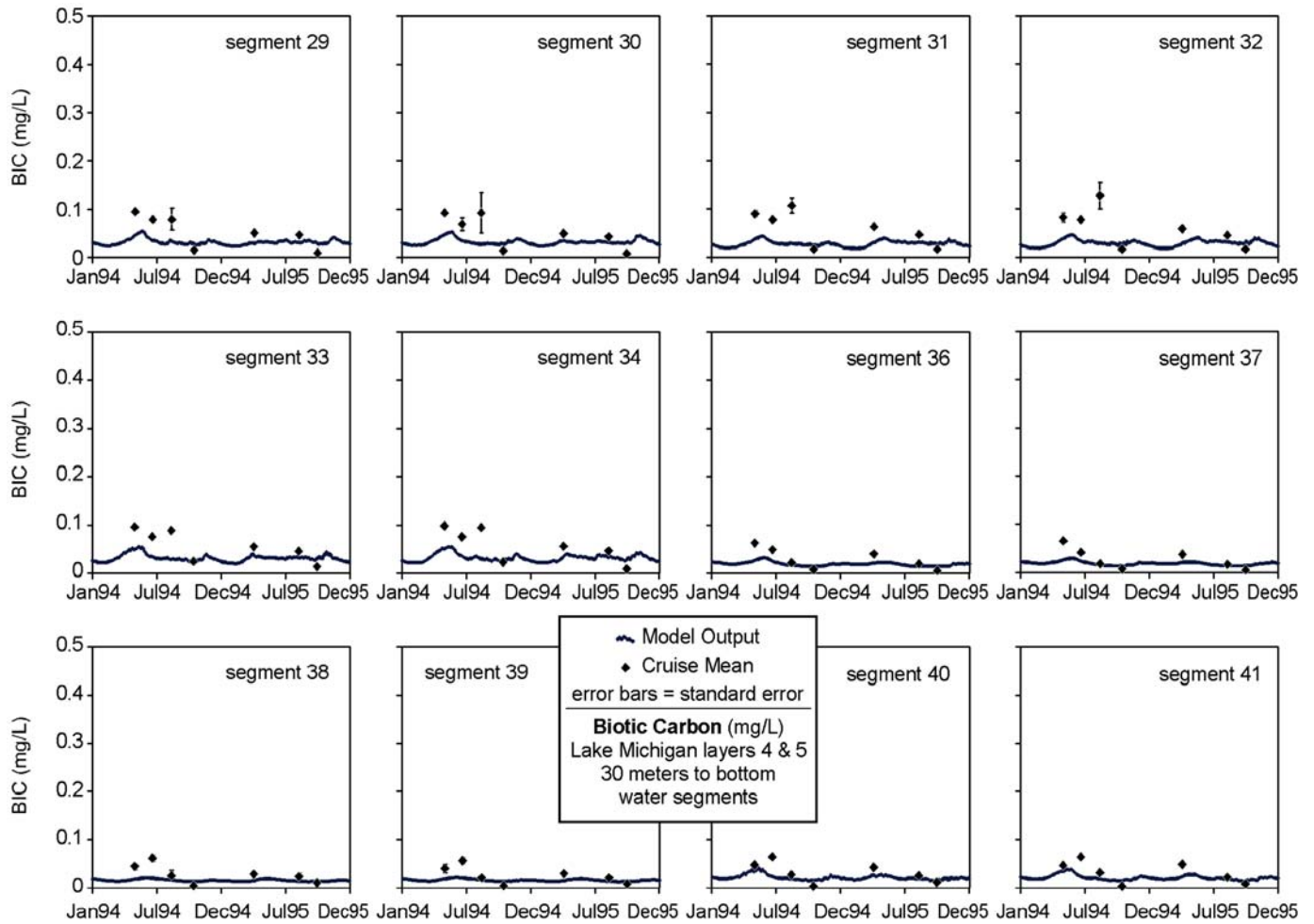


Figure 4.5.3. Temporal profiles of BIC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

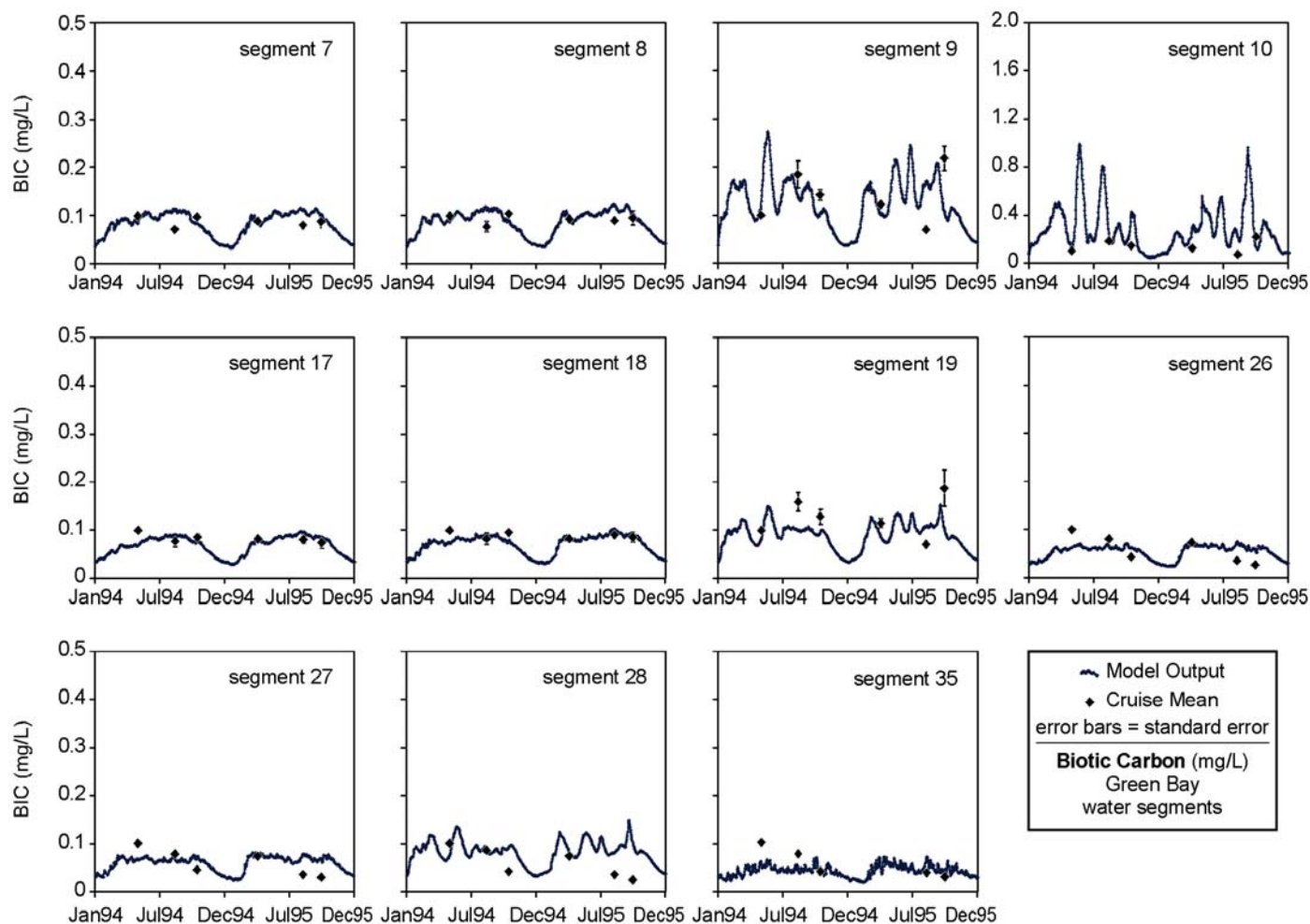


Figure 4.5.3. Temporal profiles of BIC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

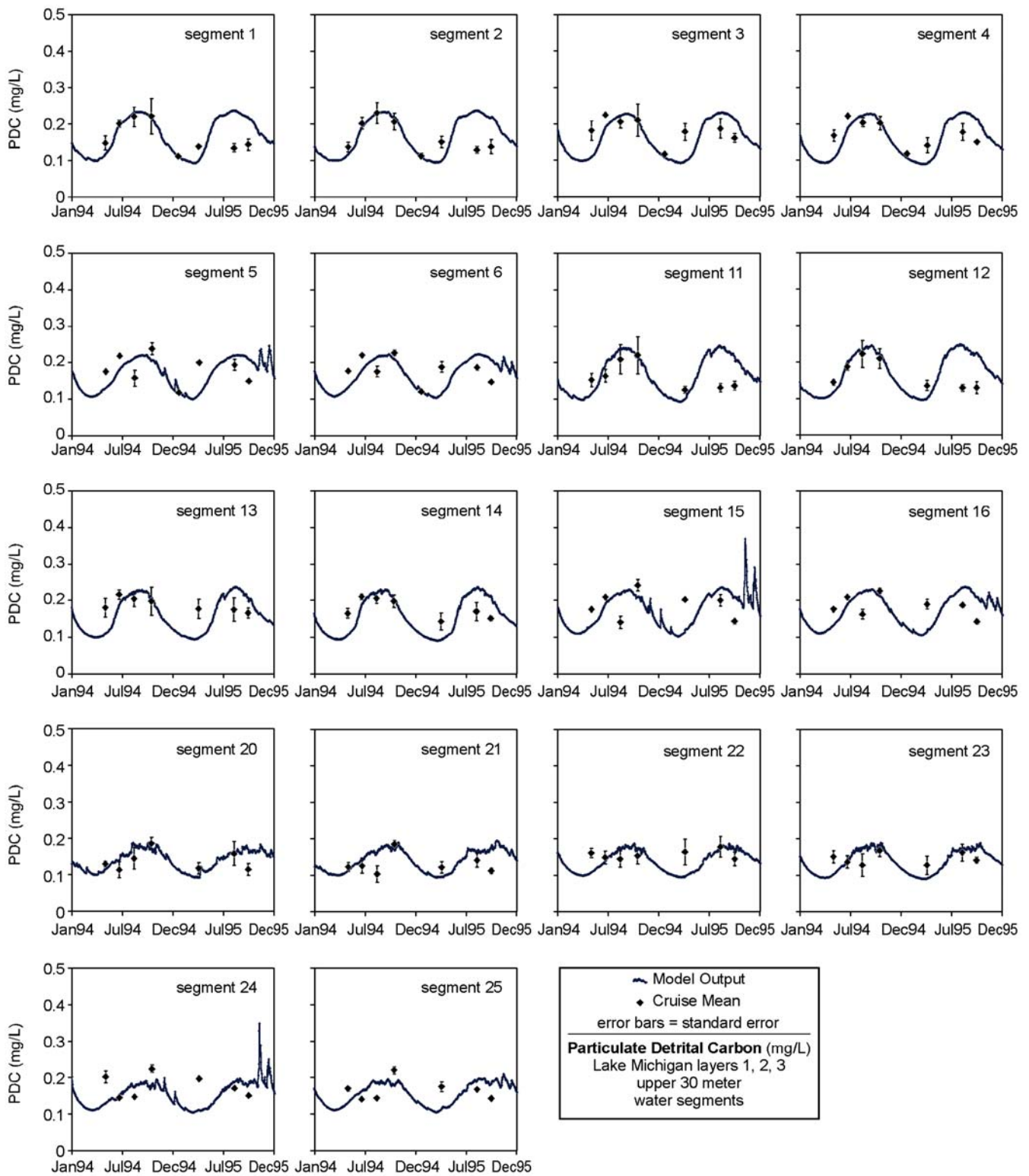


Figure 4.5.4. Temporal profiles of PDC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data.

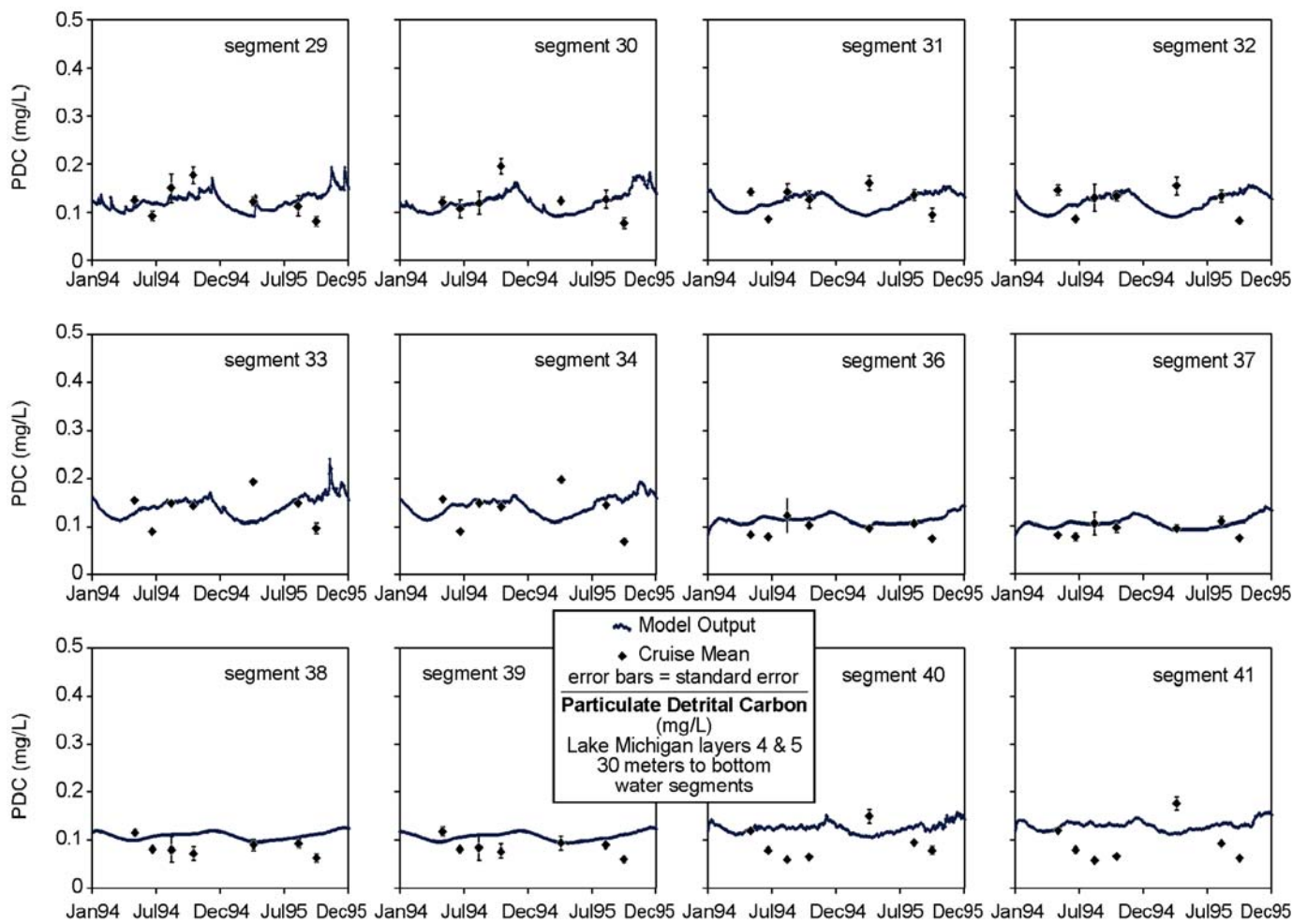


Figure 4.5.4. Temporal profiles of PDC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

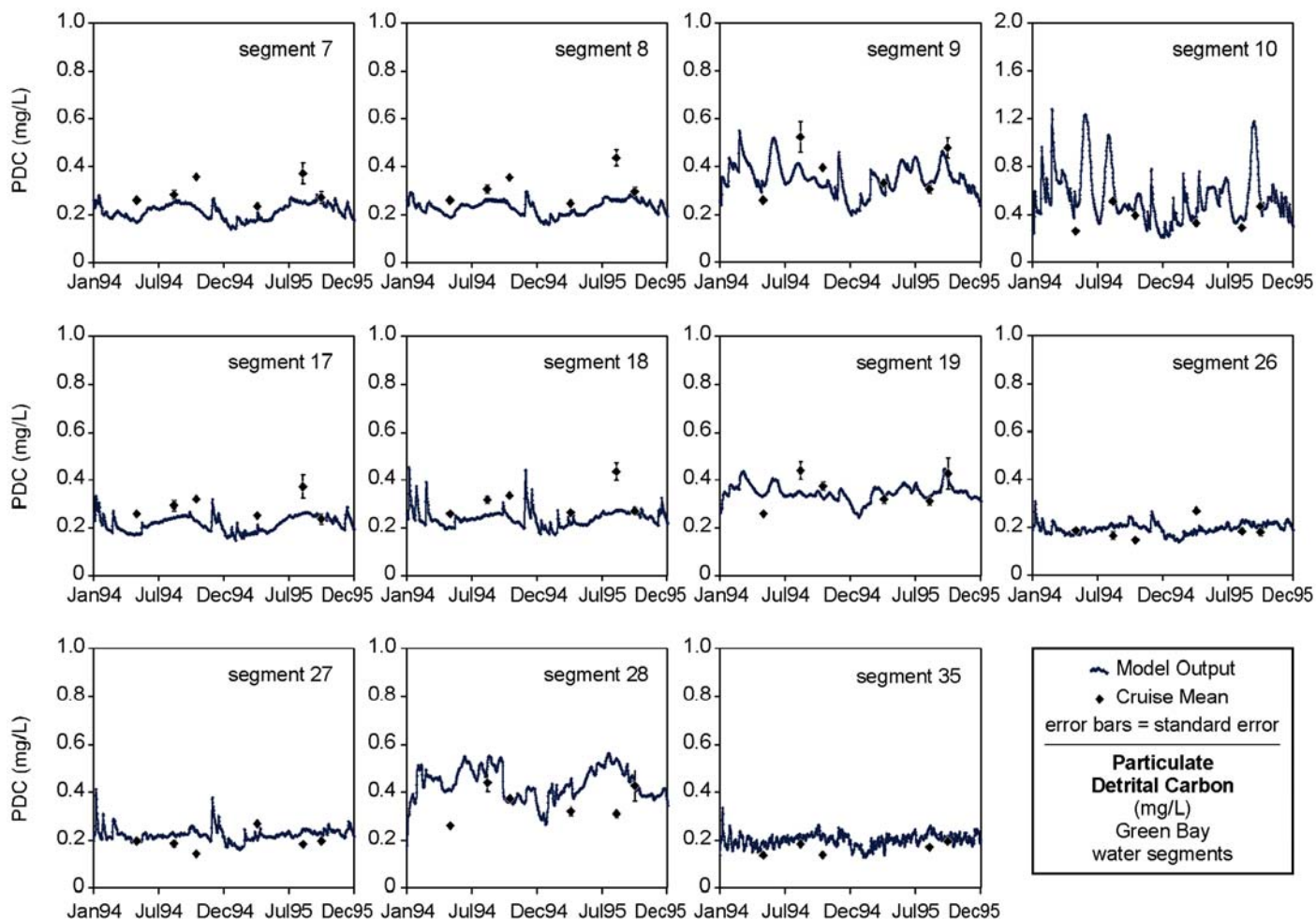


Figure 4.5.4. Temporal profiles of PDC in the Lake Michigan water column segments for the organic carbon dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

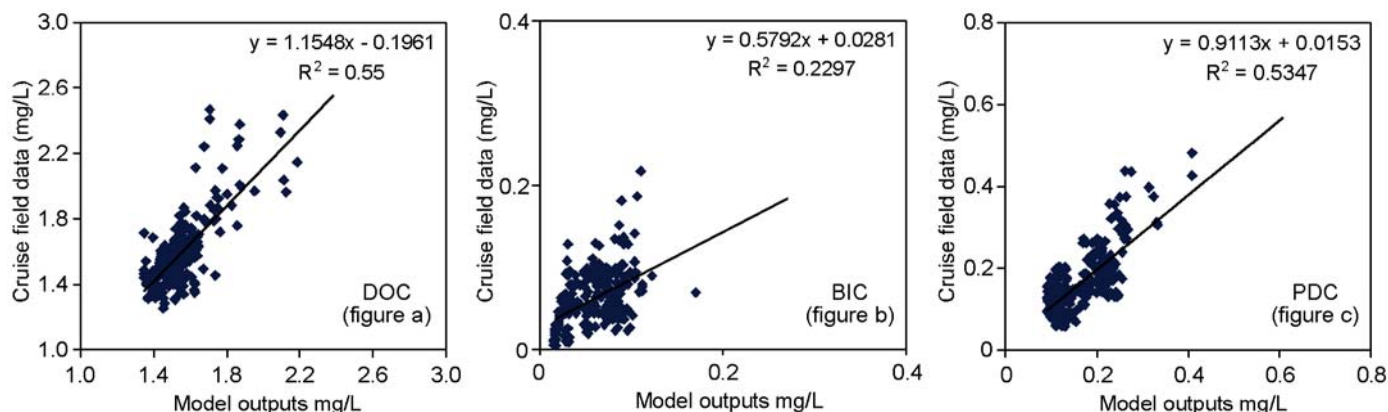


Figure 4.5.5. Observed data versus the LM2-Toxic predictions for DOC, BIC, and PDC for the LMMBP period.

Michigan. Enthalpy in Equation 4.3.24 was one of the volatilization parameters to which the PCB concentrations in the main lake were very sensitive to, and it was slightly adjusted during the PCB dynamics calibration. In addition to adjustments of these two parameters, the initial conditions in some of the Green Bay sediment segments were adjusted for some of the PCB congeners. This was considered acceptable because PCB concentrations initially used in the LM2-Toxic for both the water column and the sediment segments of Green Bay were very questionable. Previous studies (Bierman *et al.*, 1992, DePinto *et al.*, 1993) of the Green Bay system have shown that strong PCB gradients exist in both the water column and the sediments. Small number of samples of that system would not, therefore, be able to capture the details of these gradients. Also, the system is vulnerable to resuspension events that can contribute to high variability in observed PCB concentrations in the water column. The initial PCB concentrations for the Green Bay water column segments were derived from interpolations based on samples from only two water stations (GB17 and GB24M). The initial PCB concentrations for the Green Bay sediment segments were arithmetic averages of samples collected at only four sediment stations (two Ponar sampling locations: SD89P and SD106P; two gravity core sampling locations: 95GI and 113GI) during the LMMBP period.

The segment-specific cruise mean concentrations for each PCB congener were generated using the same inverse distance and volume-weighted averaging algorithm (Appendix 4.4.1) based on the 1994-1995 LMMBP samples collected during the eight cruises. These mean concentrations were then used for the LM2-Toxic PCB dynamics calibration and comparison with the LM2-Toxic outputs.

4.5.3.1 Calibration Procedures

The specific procedures taken in PCB congener dynamics in the lake for the LM2-Toxic were the following:

1. Fixing the PCB diffusion coefficient between the surficial sediment layer and the overlying water column at $1.73 \times 10^{-4} \text{ m}^2/\text{d}$ (DePinto *et al.*, 1993).
2. Assigning estimated initial partition coefficients for each PCB congener computed by using a two-phase partitioning model based on data from the LMMBP collected field samples.
3. Assigning volatilization-related parameters such as enthalpy and entropy of each PCB congener as derived by Bamford *et al.* (2002).
4. Slightly adjusting, within the bounds of literature values and/or acceptable variation in field observations, sediment PCB initial conditions for the Green Bay sediment segments, partition

coefficients, and enthalpy for the PCB congeners as necessary to improve the fit between observed data and model outputs.

4.5.3.2 Results and Discussion

The values for the final set of partition coefficients ($\log K'_{\text{POC},a}$ and $\log K_{\text{DOC}}$ in Table 4.4.28) for the LMMBP selected individual and co-eluting PCB congeners were close to the octanol-water partition coefficient (K_{OW}) calculated by Hawker and Connell (1988). As shown in Figure 4.4.15, the partition coefficients for some of the low and high chlorinated PCB congeners were adjusted the most during the LM2-Toxic PCB calibration. Based on the PCB dynamics calibration procedure outlined in the previous section along with the parameters listed in Tables 4.4.28 and 4.4.29, the PCB congener dynamics in the LM2-Toxic were calibrated for the two-year LMMBP period. Due to the extremely large amount of output from the model on a congener basis, the results and discussion in this section will be focused on only one PCB congener (PCB_{28+31}) and the sum of all the LMMBP modeled PCB congeners (ΣPCBs) for the purpose of demonstrating the calibration outcomes. PCB_{28+31} had the highest external loads, and its concentration in the Lake Michigan system was easily double that of the next closest PCB congener. The mass of ΣPCBs accounted for approximately 70-75% of total PCB mass.

Figures 4.5.6 and 4.5.7 show that temporal calibration profiles of all 41 water column segments for PCB_{28+31} and ΣPCBs (dissolved phase + particulate phase). Appendix 4.5.3 provides a complete set of calibration plots for PCB_{28+31} and ΣPCBs , including temporal profiles in sediments, total dissolved phase (unbound and DOC bound), and particulate phase (sorbed to PDC and BIC).

Although complete sets of calibration plots for each PCB congener are available, it is impossible to put all of them in this report.

Based on cruise mean data and model outputs in Appendix 4.5.3, PCB concentration in the dissolved phase was approximately double its concentration in the particulate phase in the main lake. The temporal profiles (Figures 4.5.6 and 4.5.7) show some degree of temporal variation controlled by a combination of

seasonal variation of external loads, atmospheric concentration, and sediment resuspension events. The separate dissolved and particulate PCB temporal plots (Appendix 4.5.3) also illustrate that the seasonal variation of particulate PCBs was much more prominent than the seasonal variation of dissolved PCBs.

The temporal profiles (Figures 4.5.6 and 4.5.7) indicate that there was a slight longitudinal concentration gradient throughout the main lake. The highest concentrations were found in the southern segments due to higher PCB atmospheric deposition (dry + wet) and much higher PCB atmospheric concentrations observed in the area close to Chicago. There was little vertical gradient found based on main lake cruise mean data. This indicated that vertical transport such as vertical advective flows, vertical mixing, and resuspension strongly influenced the PCB concentrations in Lake Michigan water column. On the other hand, the model output predicted higher concentrations in the bottom layer of the main lake. Possible explanations of this difference between predicted and observed include: 1) segment-specific resuspension rates for the depositional area were not setup properly for the model, 2) the initial average PCB concentrations in surficial sediments were too high, or 3) there should be a bottom layer with a large pool of resuspended materials (benthic nepheloid layer, BNL) containing PCBs added into the model segmentation (Baker *et al.*, 1991; Eadie *et al.*, 1984; Eadie *et al.*, 1990; Eadie, 1997). The BNL, with much higher carbon and PCB concentrations, could serve as a buffer between the hypolimnion layer and the surficial sediment. The LM2-Toxic PCB dynamics calibration was conducted on the PCB congener level. Therefore, the calibration was a tedious and very time-consuming task. The PCB calibration strategy was to adjust only those parameters that definitely needed to be adjusted. The PCB concentrations in the water column, especially the hypolimnion, were very sensitive to the PCB initial conditions in the sediments. Sediment samples collected by box coring may be biased on the high side due to the selection of sites that could be cored (fine-grained sediment). In the deep depositional areas of the lake, it is unlikely that resuspension occurs. To avoid controversy and excessive effort on the model calibration, the segment-specific resuspension rates were not adjusted independently during the

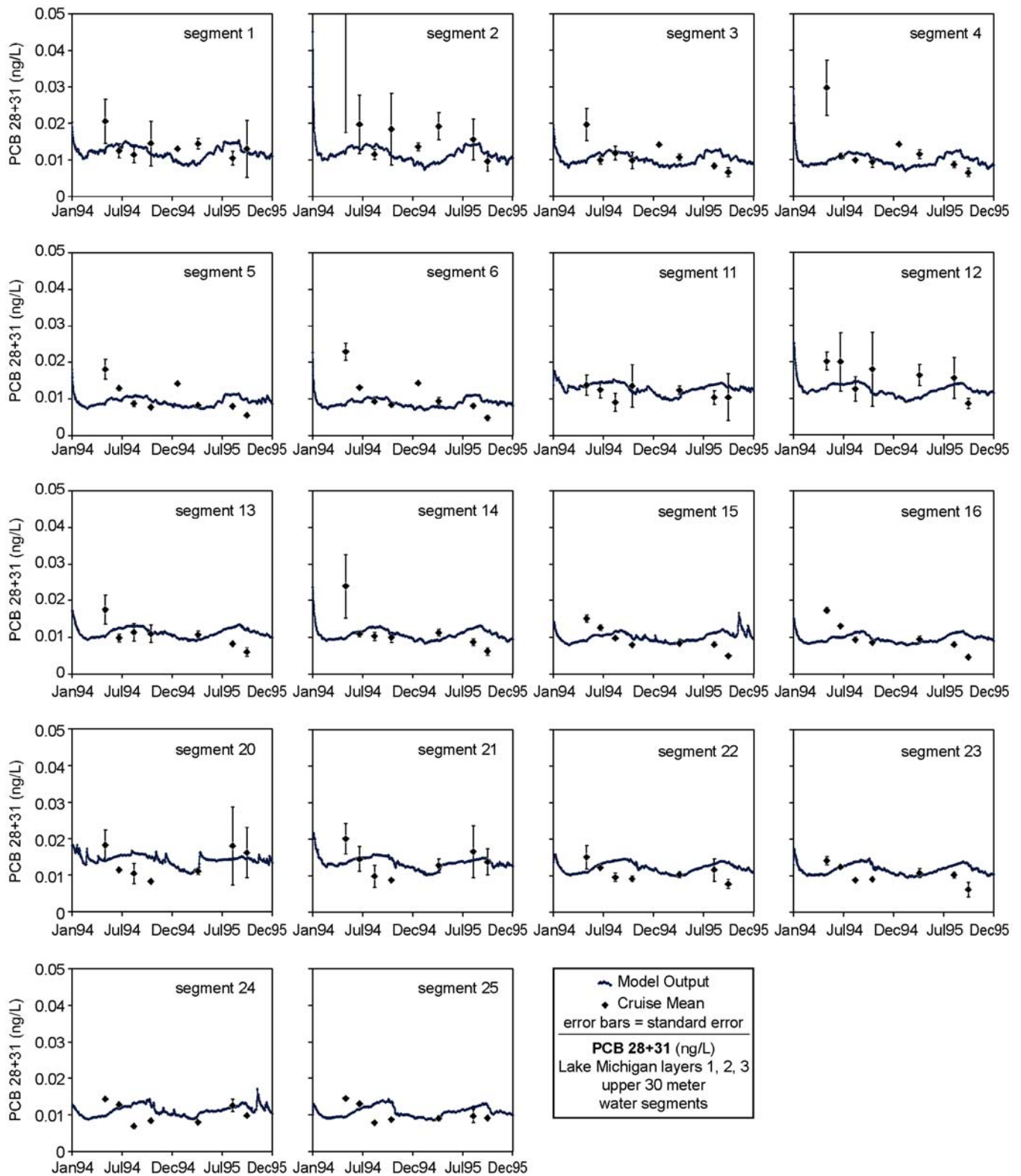


Figure 4.5.6. Temporal profiles of PCB₂₈₊₃₁ (dissolved phase + particulate phase) in Lake Michigan water column segments for PCB dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data.

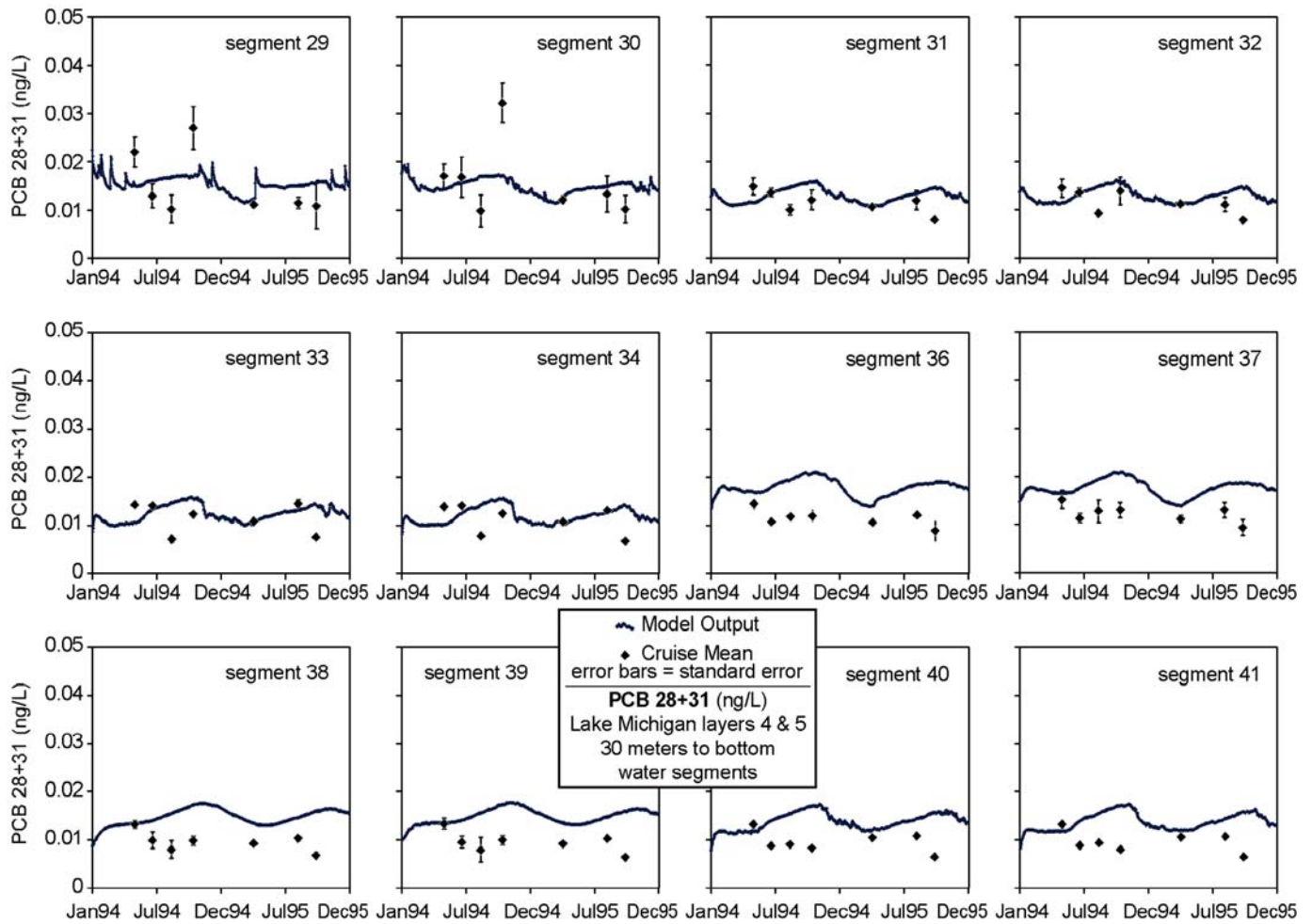


Figure 4.5.6. Temporal profiles of PCB₂₈₊₃₁ (dissolved phase + particulate phase) in Lake Michigan water column segments for PCB dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

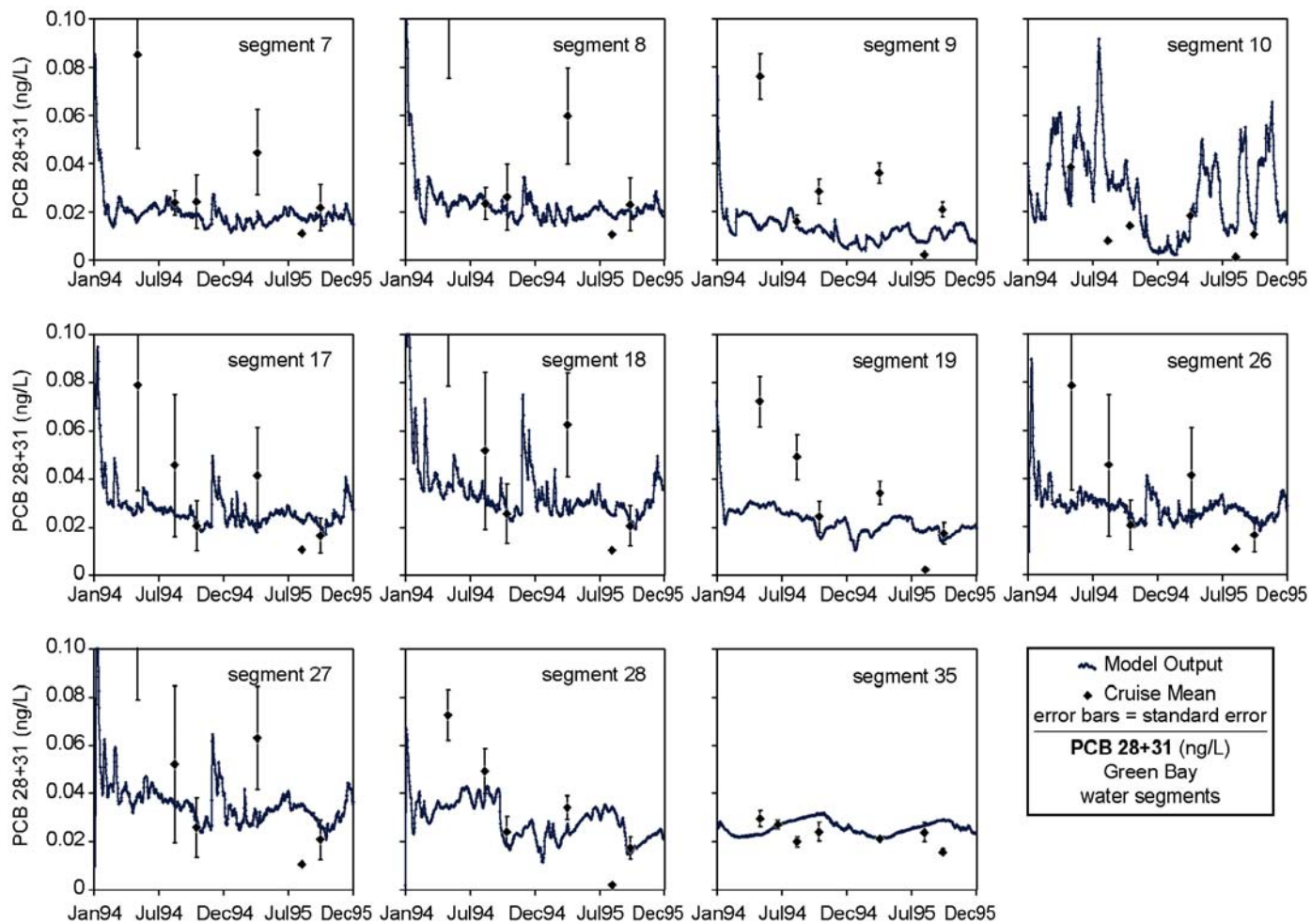


Figure 4.5.6. Temporal profiles of PCB₂₈₊₃₁ (dissolved phase + particulate phase) in Lake Michigan water column segments for PCB dynamics calibration of the LM2-Toxic and the LMMPBP cruise mean data (Continued).

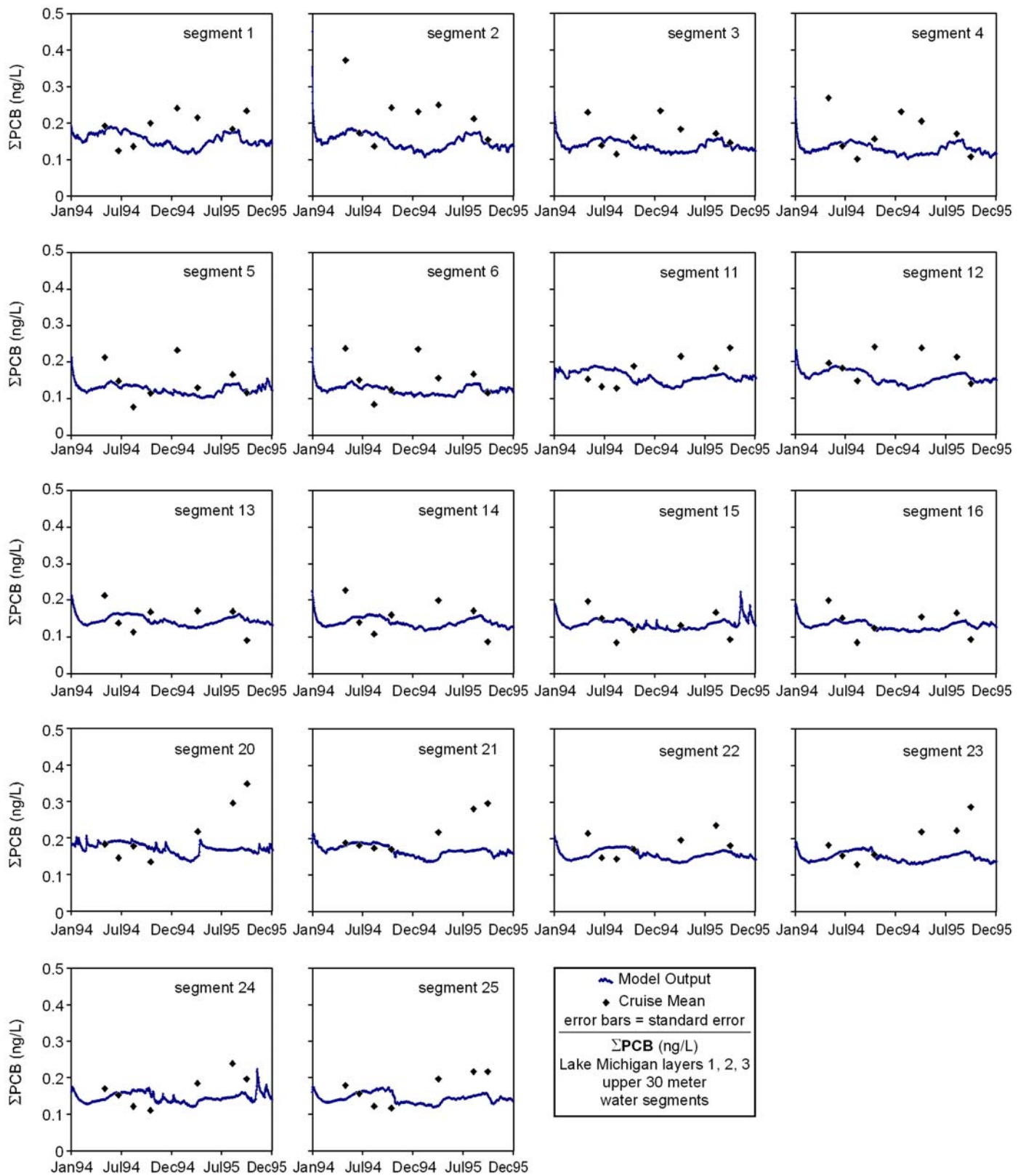


Figure 4.5.7. Temporal profiles of ΣPCBs (dissolved phase + particulate phase) in Lake Michigan water column segments for PCB dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data.

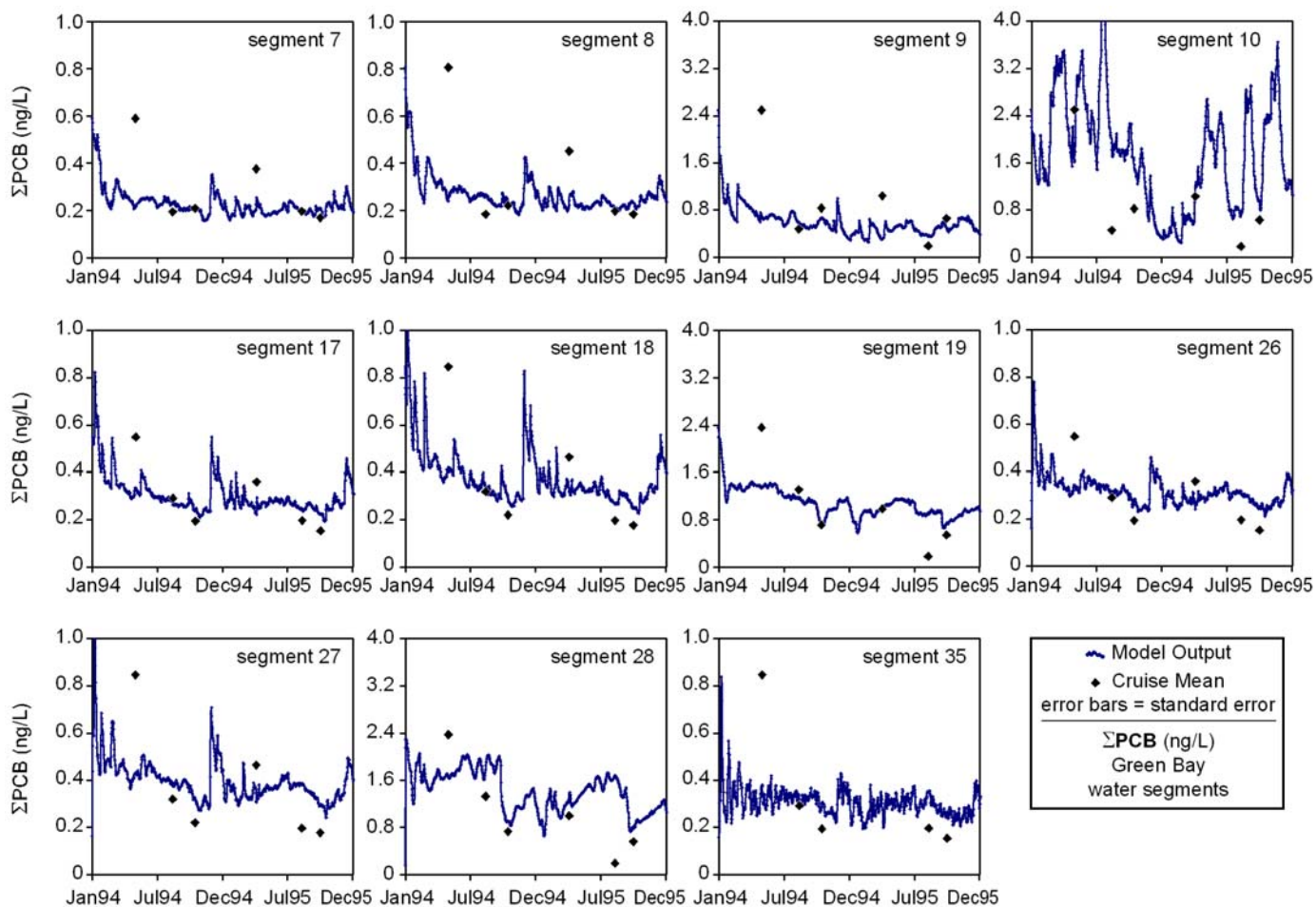


Figure 4.5.7. Temporal profiles of ΣPCBs (dissolved phase + particulate phase) in Lake Michigan water column segments for PCB dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

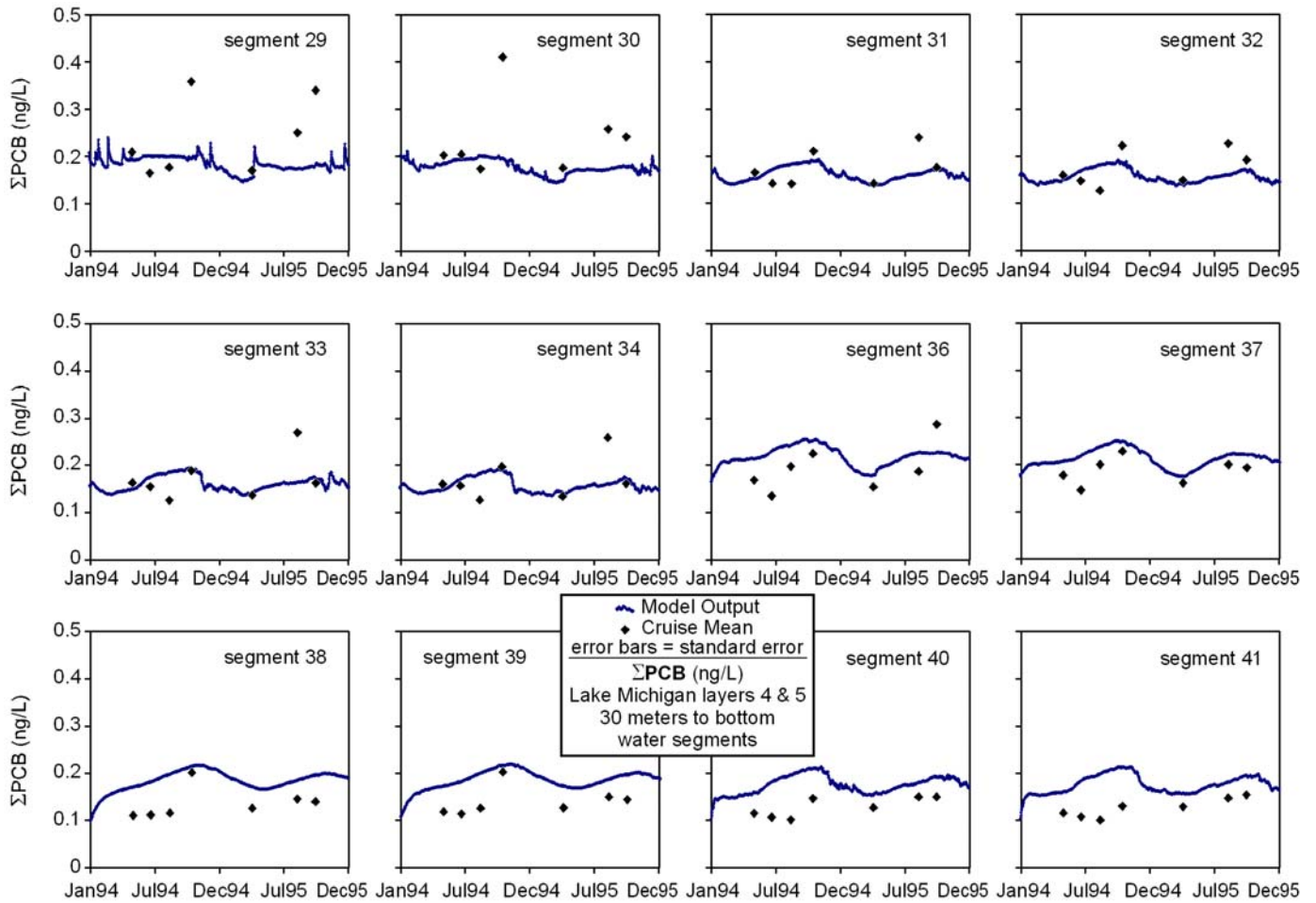


Figure 4.5.7. Temporal profiles of Σ PCBs (dissolved phase + particulate phase) in Lake Michigan water column segments for PCB dynamics calibration of the LM2-Toxic and the LMMBP cruise mean data (Continued).

calibration, and the PCB initial sediment concentrations in the main lake were kept as the original results of the interpolation based on surficial sediment field data.

Temporal variations of PCBs in Green Bay were much different from those in the main lake. PCB concentrations in Green Bay were dominated by the particulate phase (Appendix 4.5.3), especially for the water column segments in the inner bay. Dissolved PCBs were about 1.5 to 2.0 times higher than the particulate PCBs for the water column segments in the main lake. From visual examination of the temporal profiles (Figures 4.5.6 and 4.5.7), calibration results for Green Bay segments were better than those for the main lake. This was unexpected because observational data for the Green Bay water segments were based on only two water stations (GB17 and GB24M). The PCB concentrations in Green Bay were about 5 to 10

times higher than that in the main lake. It appears that it was much easier for a water quality model to simulate and get a good fit with observed data for a chemical constituent with a much higher concentration than for cases when the concentration was close to the detection limit.

The distribution of PCBs between dissolved and particulate phases during the PCB calibration was very sensitive to the adjustment of the POC partition coefficients ($K_{POC,\alpha}$). This distribution was not sensitive to the DOC partition coefficient due to its value being two orders of magnitude lower, even though the DOC concentration was about 5 to 10 times higher than the POC concentration in the main lake. Figures 4.5.8a and 4.5.8b show a comparison between the cruise mean concentrations and model simulation results for PCB_{28+31} and $\Sigma PCBs$ for the calibration period. The plots illustrate that there was

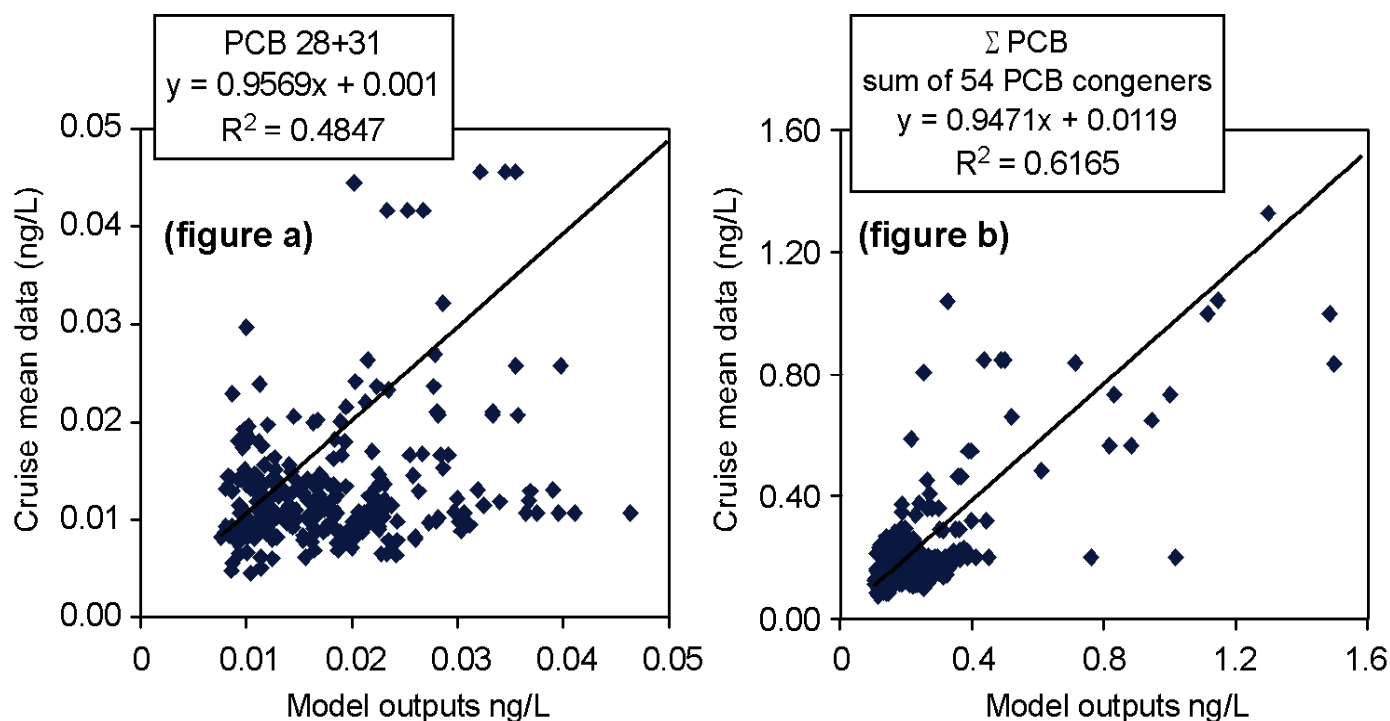


Figure 4.5.8. Observed data versus the LM2-Toxic predictions for PCB_{28+31} and ΣPCB for the LMMBP period.

a good correspondence between model simulation results and cruise mean data. Most of the overpredictions were for segments in the bottom layer of the main lake.

Table 4.5.1 presents the coefficients (slope, intercept, and R squares) of the regression equations based on the results of a comparison between cruise mean concentration and the LM2-Toxic simulated concentration for all the LMMBP selected PCB congeners. In general, the results from the regression for the PCB congeners were reasonably good. The results would be much better if the original initial conditions in the Lake Michigan sediment segments for the PCB congeners were slightly adjusted (initial conditions were adjusted down to maximum of 20%). The calibration strategy was to devote only limited effort to fine-tune the calibration and to adjust as few parameters as possible during the calibration.

4.5.4 The LM-2 Toxic Confirmation

As for any mass balance model, the results of the LM2-Toxic calibration and the outcomes of long-term model prediction have some degree of uncertainty. As the framework of a water quality model becomes more complex, the credibility of the model does not necessarily increase. When the model complexity increases, the dimensions of the associated uncertainties will increase, and the ability to describe model performance will also become increasingly difficult. Other than the uncertainties associated with the numerical algorithms and equations used to describe physical and biochemical processes in the model, data entered into the model are subject to a certain error, and this error propagates into the model results. Due to time constraints, qualitative evaluation of the model was the focus for the LM2-Toxic verification. The following modeling effort was made for the LM2-Toxic confirmation in order to reduce uncertainties associated with water transport, settling and resuspension, and sedimentation. These processes are crucial to long-term projections using any water quality model.

4.5.4.1 Mass Balance Checking

It is important to check the mass balance on an individual segment basis for a state variable simulated in a model. This can ensure that there is

no excessive mass increase or decrease in a segment due to programming error(s) and error(s) associated with the numerical method used in the model. The task was completed very successfully. Three organic carbon solids (BIC, PDC, and DOC) and a conservative tracer (any assumed conservative tracer) were designated as the only state variables. With initial and boundary concentrations of the conservative tracer set equal to 1 mg/L in both the water column and sediment segments and with no external loads, gas exchange, partitioning processes, or any kinetic processes, LM2-Toxic was run for short-term (two years) and long-term (62 years) simulations. The results from the short-term run showed almost no change in all media. For the long-term run, an extremely small change was found in water segments, and a maximum change of 1% was found in a couple of the sediment segments. Table 4.5.2 shows the mass balance checking results for the long-term model run in each segment. Considering the small volumes of surficial sediment segments (average thickness about 1-2 cm), a one percent change in concentrations over 62 years is an acceptable variation in terms of conserving mass.

4.5.4.2 Chloride Model

A chloride model was applied as another confirmation step to ensure that the overall water transport components, including both advection and dispersion, used in the LM2-Toxic were reasonably accurate. With the same model input structure as the temperature balance model, chloride was simulated as a state variable without adjusting any parameter. The resulting temporal profiles in Appendix 4.3.2 confirmed the credibility of the water transport used in LM2-Toxic.

4.5.4.3 ¹³⁷Cs and ^{239,240}Pu Simulation and Results

Based on particle (PDC) net burial in sediments using Pb-210 core dating results (Robbins *et al.*, 1999), a set of settling and resuspension velocities were adjusted simultaneously to maintain the net burial during the LM2-Toxic carbon dynamics calibration. The best-fit values were selected for BIC and PDC. These rates yielded a rate of cycling of particulate matter between the sediments and overlying water. Errors in specifying the settling and resuspension rates can have a significant impact on the model calibrations and the resulting long-term predictions.

Table 4.5.1. Results of the Regression Between the LM2-Toxic Calibration Results and the Cruise Mean Data for the LMMBP Selected PCB Congeners

Congener	Slope	Intercept	R ²
PCB8+5	0.9512	0.0022	0.1845
PCB15+17	0.6072	0.0034	0.3995
PCB16+32	0.9255	0.0122	0.0628
PCB18	0.6271	0.0023	0.4112
PCB26	0.5238	0.0009	0.4188
PCB28+31	0.9569	0.001	0.4847
PCB33	0.4931	0.0054	0.2811
PCB37+42	0.7625	0.0041	0.3332
PCB44	0.8514	0.0012	0.5210
PCB49	1.1693	0.0006	0.3165
PCB52	0.8729	0.0042	0.4145
PCB56+60	0.5822	0.0008	0.5976
PCB66	0.8250	- 0.002	0.5896
PCB70+76	0.7159	- 5E-05	0.5146
PCB74	0.6659	0.0008	0.5769
PCB77+110	0.5593	0.0018	0.4219
PCB81	0.4079	0.0013	0.0160
PCB87	0.5492	0.0020	0.4007
PCB92+84	0.4801	0.0087	0.1896
PCB89	0.0825	0.0012	0.0029
PCB99	0.3746	0.0055	0.1153
PCB101	0.8253	0.0006	0.4186
PCB118	0.4403	0.0020	0.4540
PCB123+149	0.5762	0.0011	0.4723
PCB105+132+153	0.7421	0.0002	0.6205
PCB151	0.4629	9E-05	0.5125
PCB163+138	0.5649	0.0028	0.4258
PCB170+190	0.5879	4E-05	0.3735
PCB172+197	0.3501	0.0001	0.2309
PCB180	0.4372	8E-05	0.3545
PCB187+182	0.7757	0.0012	0.2425
PCB195+208	0.1696	9E-05	0.4053
PCB196+203	0.2402	0.0007	0.1035
PCB201	0.0911	0.0046	0.0004
PCB85	0.5099	0.0006	0.5194
PCB146	0.3329	0.0013	0.2261
ΣPCBs ^a	0.9471	0.0119	0.6165

^aSum of all the LMMBP selected PCB congeners.

Table 4.5.2. Results of the LM2-Toxic Mass Balance Checking for a 62-Year Simulation of an Assumed Conservative Tracer (Set the Model Initial Conditions and Boundary Concentrations of the Conservative Trace = 1)

Water Column Segment	Initial Concentration (mg/L)	Concentration at the End of Simulation (mg/L)	Change (%)
1	1.00000	1.00003	0.003
2	1.00000	1.00003	0.003
3	1.00000	1.00002	0.002
4	1.00000	1.00002	0.002
5	1.00000	1.00002	0.002
6	1.00000	1.00002	0.002
7	1.00000	1.00002	0.002
8	1.00000	1.00003	0.003
9	1.00000	1.00004	0.004
10	1.00000	1.00007	0.007
11	1.00000	1.00003	0.003
12	1.00000	1.00003	0.003
13	1.00000	1.00001	0.001
14	1.00000	1.00002	0.002
15	1.00000	1.00002	0.002
16	1.00000	1.00002	0.002
17	1.00000	1.00002	0.002
18	1.00000	1.00004	0.004
19	1.00000	1.00001	0.001
20	1.00000	1.00003	0.003
21	1.00000	1.00003	0.003
22	1.00000	1.00001	0.001
23	1.00000	1.00001	0.001
24	1.00000	1.00002	0.002
25	1.00000	1.00002	0.002
26	1.00000	1.00002	0.002
27	1.00000	1.00002	0.002
28	1.00000	1.99999	-0.001
29	1.00000	1.00003	0.003
30	1.00000	1.00003	0.003
31	1.00000	1.00001	0.001
32	1.00000	1.00001	0.001
33	1.00000	1.00001	0.001
34	1.00000	1.00002	0.002
35	1.00000	1.00001	0.001
36	1.00000	1.00002	0.002
37	1.00000	1.00002	0.002
38	1.00000	1.00000	0.000
39	1.00000	1.00000	0.000
40	1.00000	1.00001	0.001
41	1.00000	1.00001	0.001
42	0.99959	0.99616	-0.343

Table 4.5.2. Results of the LM2-Toxic Mass Balance Checking for a 62-Year Simulation of an Assumed Conservative Tracer (Set the Model Initial Conditions and Boundary Concentrations of the Conservative Trace = 1) (Continued)

Water Column Segment	Initial Concentration (mg/L)	Concentration at the End of Simulation (mg/L)	Change (%)
43	0.99955	0.99496	-0.459
44	0.99944	0.99362	-0.582
45	0.99947	0.99387	-0.560
46	0.99939	0.99064	-0.876
47	0.99958	0.99103	-0.856
48	0.99965	0.98954	-1.011
49	0.99980	0.99263	-0.717
50	0.99979	0.99258	-0.721
51	0.99964	0.99187	-0.778
52	0.99953	0.99359	-0.594
53	0.99963	0.99585	-0.379
54	0.99958	0.99525	-0.433
55	0.99971	0.99772	-0.200
56	0.99979	0.99737	-0.242
57	0.99963	0.99603	-0.361
58	0.99955	0.99330	-0.626
59	0.99962	0.99160	-0.802
60	0.99977	0.99252	-0.725
61	0.99974	0.99215	-0.759
62	0.99979	0.99245	-0.734
63	0.99969	0.99430	-0.539
64	0.99960	0.99566	-0.394
65	0.99922	0.99102	-0.820
66	0.99926	0.99158	-0.768
67	0.99938	0.99318	-0.621
68	0.99950	0.99447	-0.504
69	0.99952	0.99442	-0.511
70	0.99977	0.99356	-0.621
71	0.99980	0.99317	-0.664
72	0.99963	0.99561	-0.402
73	0.99967	0.99563	-0.404
74	0.99964	0.99566	-0.398
75	0.99972	0.99711	-0.261
76	0.99970	0.99688	-0.282
77	0.99943	0.99359	-0.585
78	0.99980	0.99163	-0.817
79	0.99981	0.99284	-0.697
80	0.99982	0.99136	-0.846
81	0.99980	0.99035	-0.945
82	0.99982	0.99137	-0.845
83	0.99982	0.99134	-0.849
84	0.99982	0.99112	-0.870

Table 4.5.2. Results of the LM2-Toxic Mass Balance Checking for a 62-Year Simulation of an Assumed Conservative Tracer (Set the Model Initial Conditions and Boundary Concentrations of the Conservative Trace = 1) (Continued)

Water Column Segment	Initial Concentration (mg/L)	Concentration at the End of Simulation (mg/L)	Change (%)
85	0.99979	0.99032	-0.947
86	0.99979	0.99072	-0.907
87	0.99981	0.99184	-0.798
88	0.99983	0.99389	-0.595
89	0.99983	0.99146	-0.837
90	0.99980	0.98917	-1.063
91	0.99982	0.99063	-0.920
92	0.99979	0.99097	-0.883
93	0.99982	0.99202	-0.780
94	0.99982	0.99233	0.749

To confirm the settling and resuspension rates selected for the LM2-Toxic, a radionuclide model was developed. The radionuclides, ^{137}Cs and $^{239,240}\text{Pu}$, were used as state variables in the LM2-Toxic, and a 46-year hindcast (1950-1995) simulation was executed. Figure 4.5.9 presents cesium and plutonium lake-wide water column concentrations resulting from the radionuclide model 46-year hindcast simulation. The profiles of both ^{137}Cs and $^{239,240}\text{Pu}$ indicate that the water column concentration of the radionuclides decreased at a rate faster than the one suggested by the data. There are quite a few factors that can contribute to this discrepancy. Among them, loading history of total suspended solids, internal primary production history, partitioning coefficients, coarse segmentation, and the settling and resuspension rates could have a strong influence in the level of ^{137}Cs and $^{239,240}\text{Pu}$ concentration in the water column of the lake.

To determine the representativeness of the rate of sediment-water solids cycling used in the LM2-Toxic, the total sediment ^{137}Cs predicted and observed inventories were compared. There was a very good agreement in total sediment ^{137}Cs inventory for those sediment segments where the sediment core samples were collected (Figure 4.5.10). There was a large discrepancy in the comparison for segment 52. The model underestimated total sediment ^{137}Cs inventory in that segment. This underestimation may

be caused by the location of segment 52. It is a very narrow transitional area along the southeast shoreline of the lake with a steep slope. The LM2-Toxic, with a very coarse spatial resolution for the water column, was unable to predict the radionuclide sediment inventory in such a narrow transitional band. In general, the results from the LM2 ^{137}Cs and $^{239,240}\text{Pu}$ model imply that the combination of the settling, resuspension, and burial rates used in the LM2-Toxic were a reasonable representation of the rate of cycling of particulate matter between the sediments and overlying water column of the lake.

4.5.4.4 Long-Term Organic Carbon Simulations

For the purpose of providing another dimension of LM2-Toxic confirmation, a 40-year long-term organic carbon simulation was executed to produce the total sediment accumulation over the simulation period. Using the model, total sediment thickness (cm) accumulated over 40 years was calculated. It was converted to sediment accumulation rate (cm/year) by dividing by 40 years and comparing to the measured sediment accumulation rate. The three organic carbons (DOC, BIC, PDC) were the only state variables in the LM2-Toxic for the simulation. The set of sediment accumulation rates at each box core sampling location (Robbins *et al.*, 1999) were interpolated using a natural-neighbor interpolation algorithm (Appendix 4.4.1) to generate segment-

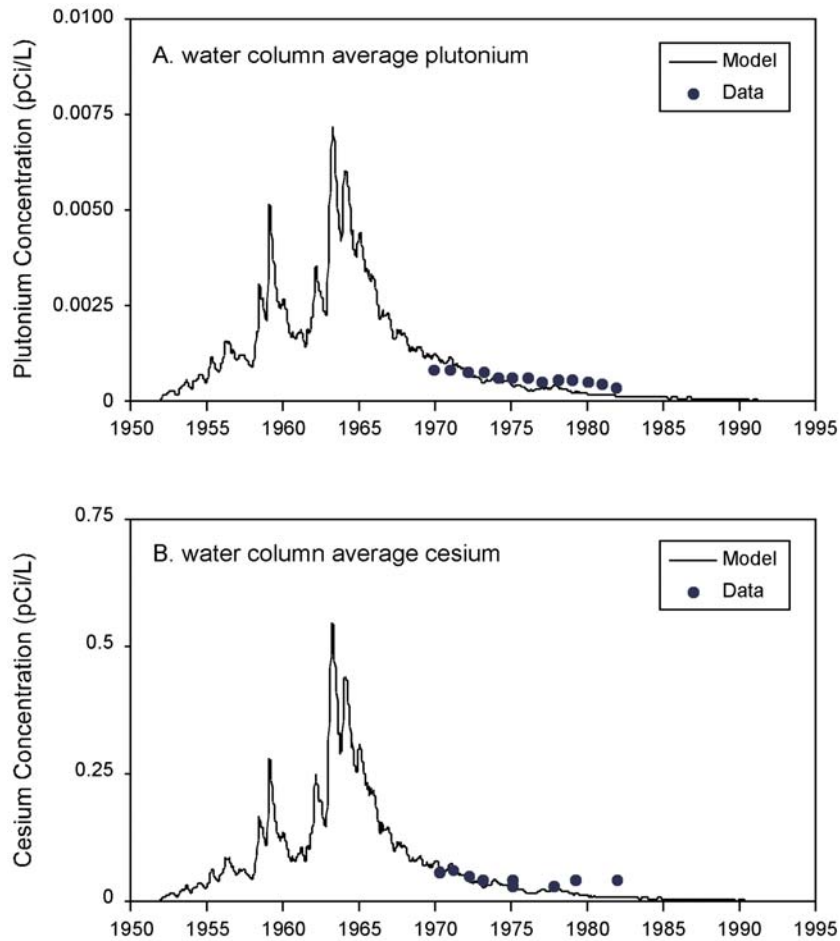


Figure 4.5.9. Lake-wide average concentrations of (a) ^{137}Cs and (b) $^{239,240}\text{Pu}$ computed by the LM2 radionuclide model over 46 years (1950-1995).

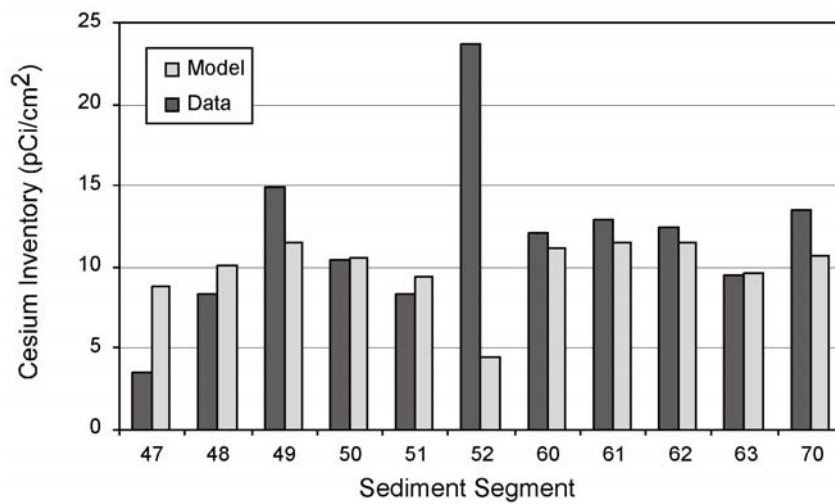


Figure 4.5.10. Sediment ^{137}Cs inventory comparison between the observed data (see Appendix 4.8 for details) and the LM2 radionuclide model outputs.

specific accumulation rates (cm/year). Table 4.5.3 presents comparisons between 1) the segment – specific sediment accumulation rates generated based on the data (Robbins *et al.*, 1999) and the segment-specific accumulation rates computed by the LM2-Toxic and 2) lake-wide average sediment accumulation rates generated from the data (Robbins *et al.*, 1999) and computed by the LM2-Toxic. The discrepancy between the field data and model output on a lake-wide basis was about 30%. A large portion of this difference was contributed by sediment segments under water columns 5 and 6 (segments 65-77) where the bottom geometry is complicated and by Green Bay sediment segments. Because there was only one sediment box core sample collected in the sediment segments under water columns 5 and 6 and no box core sample was taken in Green Bay, the interpolation of the LMMBP-generated accumulation rates could create substantial uncertainty in the interpolated segment-specific accumulation rates for the sediment segments under water columns 5 and 6 and in Green Bay. In general, the results in Table 4.5.3 showed reasonably good match between the field data and model predicted accumulation rates, especially in areas where a large number of box cores were collected.

4.5.4.5 PCB Hindcast

A hindcast used as either a calibration or a confirmation of a mathematical model is considered an important and preferred approach to assess the credibility of a model. It has been used for models such as MICHTOX (Endicott, 2002), LOTOX (DePinto *et al.*, 2003), HUDTOX (U.S. Environmental Protection Agency, 2000), and the Delaware River model (Delaware River Basin Commission, 2003). To gain confidence in the prediction of a toxic chemical model, a PCB hindcast is conducted to confirm the suitability of the processes conceptualized in the model and of the associated parameters used in the model.

A PCB hindcast was not one of the confirmation components proposed in the original LMMBP modeling work plan (U.S. Environmental Protection Agency, 1997). This modeling task was done in response to a suggestion from the 2004 peer review panel (summarized by Rygwelski in Part 7, Appendix 1). Because LM2-Toxic went through a very

thorough and successful short-term (two-year project period) calibration and a series of model confirmation efforts detailed in the previous sections, the main purpose of the LM2-Toxic PCB hindcast simulation was to confirm the representativeness of the calibration parameters determined from the short-term calibration and to check the consistency of the estimated historical PCB load with the available sediment core profiles and historical inventory data. A description of data and procedure used for the LM2-Toxic PCB hindcast and a discussion of the results and findings from the PCB hindcast are presented in the following sections.

4.5.4.5.1 Data and Procedure for the PCB Hindcast

In order to run the LM2-Toxic PCB hindcast, the following data were required: 1) PCB loading history; 2) historical atmospheric vapor phase PCB concentrations; 3) historical primary productivity; 4) the date when PCBs started being loaded into Lake Michigan; 5) physical conditions such as temperature, wind speed, and carbon and PCB transport and kinetic parameters; and 6) the estimated long-term carbon solid concentrations on which the resuspension rates should be adjusted to keep solid cycling rates balanced (see Section 4.3.4.2.1 – Steady-State Resuspension Calibration for details).

The minimum data needed to reasonably assess the performance of the LM2-Toxic PCB hindcast were 1) continuous long-term historical annual averaged water column observed PCB concentrations; 2) sediment PCB core profiles representative of the depositional area, and 3) the sediment total PCB inventory.

Among the data necessary for a successful PCB hindcast and to assess model performance, PCB loading history, historical PCB vapor phase concentrations, and a reliable estimation of sediment inventory are the most critical. PCB loading history and historical PCB vapor phase concentrations control in-flux and out-flux of PCB mass for the Lake Michigan system. Historical concentrations in the system are controlled by these fluxes. When compared to a reliable estimate of sediment PCB inventory, the model generated lake-wide sediment inventory can provide the confidence that there is no

Table 4.5.3. Comparison Between the LMMBP Field-Generated and the LM2-Toxic-Generated Sediment Accumulation Rates (cm/year)

Segment	Field Data^a (cm/year)	Model Output (cm/year)
42	0.0000	0.0000
43	0.0000	0.0000
44	0.0002	0.0000
45	0.0058	0.0000
46	0.0181	0.0650
47	0.0495	0.0900
48	0.1135	0.1250
49	0.3630	0.3875
50	0.2662	0.2900
51	0.1444	0.1900
52	0.2324	0.1800
53	0.0497	0.0000
54	0.0466	0.0250
55	0.0068	0.0000
56	0.0000	0.0000
57	0.0036	0.0000
58	0.0276	0.1300
59	0.1059	0.1900
60	0.2213	0.2800
61	0.2726	0.3250
62	0.2768	0.3100
63	0.1847	0.3200
64	0.1372	0.0250
65	0.0013	0.0000
66	0.0032	0.0000
67	0.0004	0.0000
68	0.0176	0.0000
69	0.0543	0.2750
70	0.1165	0.2400
71	0.1938	0.3000
72	0.0000	0.3000
73	0.0153	0.3575
74	0.0033	0.3250
75	0.0054	0.0000
76	0.0123	0.0000
77	0.0180	0.0000
78	0.0496	0.0000
79	0.0496	0.0000
80	0.0496	0.1000
81	0.0496	0.1000
82	0.0496	0.1000
83	0.0496	0.1000
84	0.0496	0.0000
85	0.0496	0.0000
86	0.0496	0.0000

Table 4.5.3. Comparison Between the LMMBP Field-Generated and the LM2-Toxic-Generated Sediment Accumulation Rates (cm/year) (Continued)

Segment	Field Data ^a (cm/year)	Model Output (cm/year)
87	0.0496	0.0000
88	0.0993	0.0000
89	0.0993	0.0000
90	0.0993	0.6000
91	0.0993	0.4000
92	0.0947	0.3000
93	0.0947	0.4000
94	0.0947	0.4000
Lake-Wide Average	0.1337	0.1742

^aSediment segment-specific accumulation rates computed based on sediment accumulation rates at each sediment box core sampling location estimated by John Robbins (Robbins *et al.*, 1999).

significant overestimation or underestimation by the LM2-Toxic for the total PCB mass in the lake sediments. The major challenge for the PCB hindcast was that these data are very limited for Lake Michigan. The following subsections provide the references for data sources and a brief description of each major data set used in the LM2-Toxic PCB hindcast.

4.5.4.5.1.1 PCB Loading Reconstruction – As is the case for most large water bodies, there is no long-term historical PCB load record available for the lake. Endicott *et al.* (2005) and Endicott (2005) are the only researchers who attempted to reconstruct the long-term PCB loading history of Lake Michigan using an approach similar to that applied to Lake Ontario by Mackay (1988) and Gobas *et al.* (1995). Endicott (2005) conducted three 55-five year total PCB hindcast simulations using MICHTOX and concluded that the results from Scenario B had the best-fit with the available historical PCB data. The year when PCB contamination began was assumed to be 1940. The PCB loading function of Scenario B peaked in 1961 and declined after 1963. The rates of increase in the loads including tributary and atmospheric loads were the same as the rates of decrease. Based on observations of the past 25 years, the rates of increase and decrease were

defined as 0.115/year and 0.0535/year for atmospheric loads and tributary loads, respectively.

In contrast to the procedure of reconstructing the historical PCB total loading function used in the MICHTOX (Endicott, 2005), the historical PCB loading estimation used in the LM2-Toxic PCB hindcast simulations was done by relating it to the results obtained from the analysis of a highly resolved sediment core (LM94-15A) collected during the LMMBP period (Details are in Part 1, Chapter 7 of this report). In doing so, some assumptions and professional judgments were made. One important assumption was that the total PCB inventory and the shape of the total PCB profile obtained from the sediment core represented the PCB loading history from all sources. Consequently, the following key elements that were used in reconstructing a historical PCB loading function were derived based on the core LM94-15A profile: 1) the starting date of the PCB loading time function (January 01, 1949); 2) the year in which the PCB loading function reached its peak which was determined to be 1967; and 3) the slopes on both the inclining and declining sides of the core profile curve were linear. The historical PCB loading time function was then back-projected based on the above elements and variations of the LMMBP estimated loads for 1994 reported by the United

States Geological Survey (USGS) (Hall and Robertson, 1998) for tributary loads and the LMMBP atmospheric working group (McCarty *et al.*, 2004; Miller *et al.*, 2001) for atmospheric loads. Details on the determination of the key elements and the procedure in reconstructing the PCB load history are further discussed in Part 1, Chapter 7. Figure 4.5.11 shows the final reconstructed total PCB historical loading function (January 01, 1949 – December 31, 1995) and the PCB profile from the sediment core (LM94-15A). The monthly variation pattern in the reconstructed long-term historical PCB load functions used in the LM2-Toxic model for each PCB congener followed the same monthly pattern established by the LMMBP estimated loads.

4.5.4.5.1.2 PCB Atmospheric Vapor Phase Concentration Reconstruction – Recent studies (Thomann and Di Toro, 1983; Rodgers *et al.*, 1988; Jeremiason *et al.*, 1994; DePinto *et al.*, 2003; Part 3 of this report; Part 4.6.2 of this report) have shown that the air-water exchange between dissolved PCBs in surface water and overlaying vapor phase PCBs is a very important and possibly the most significant loss/gain process, especially in recent years, for PCBs in the Great Lakes region. The gross volatilization and absorption fluxes transport large amounts of PCB mass in and out of the lakes due to the gradient of PCB concentrations between the air and surface water. These individual fluxes were usually greater than the sum of the external loads (tributary, atmospheric wet and dry deposition). Therefore, a reasonable representation of a reconstructed historical PCB atmospheric vapor phase concentration is critical to the success of the LM2-Toxic PCB hindcast for Lake Michigan. Following a similar approach used in the reconstruction of the loading time function, the starting date of the PCB vapor phase time function was January 01, 1949, the year for which the PCB vapor concentration reached its peak was 1967, and the slope on the inclining side of the time function is the same as the one indicated from the core LM94-15A profile. The only difference is that the vapor concentration on the declining side of the time function was back-projected based on the LMMBP (1994-1995) generated PCB vapor concentration and the decline rate that was carefully selected *via* a thorough review of research studies conducted on PCB vapor phase concentration and the data

collected within the Lake Michigan watershed for the 25 years prior to 1996.

The estimation of the declining rate in the vapor phase PCB concentrations is very subjective to the data set and number of data points used in the derivation of the rate. The half-life of the declining rate published in the literature ranges from 6 to 20 years for PCB vapor phase concentrations over Lake Michigan (Hillery *et al.*, 1997; Schneider *et al.*, 2001; and Buehler *et al.*, 2002, 2004). The individual data sets used by researchers to determine the PCB vapor concentrations declining rate were usually a subset of the historical PCB vapor concentrations measured between 1977 and 2001. Hillery *et al.* (1997) and Schneider *et al.* (2001) calculated a declining rate of six-year half-life based on the measurements collected before 1997, while a rate of half-life as high as 20 years was estimated by Buehler *et al.* (2002, 2004) using only the data from the Integrated Atmospheric Deposition Network (IADN), 1992-2001. In this study, a declining rate of 0.115/year, which corresponds to a six-year half-life, was chosen because the simulation period of the LM2-Toxic PCB hindcast was from 1949 through 1995 and overlapped the post-peak declining period used by Hillery *et al.* (1997) and Schneider *et al.* (2000). Similar to the PCB load reconstruction, the reconstructed PCB vapor phase concentration time function maintains the same monthly pattern observed during the LMMBP period. Figure 4.5.12 shows the reconstructed historical time function of total PCB vapor phase concentrations (January 01, 1949 – December 31, 1995) along with the reconstructed total loading function for Lake Michigan.

4.5.4.5.1.3 Estimation of Historical Primary Productivity – PCBs are hydrophobic organic chemicals and are closely associated with organic carbon in natural water systems. The movement and fate of organic carbon mass are very important to the distribution of PCBs in the Lake Michigan system. Therefore, a historical organic carbon loading function was necessary for a LM2-Toxic PCB hindcast. The carbon solid loads to the lake are primarily from tributaries (external loads) and primary production of phytoplankton (internal load). Both the measurements and outputs from the LM3-Eutro for the two-year project period (1994-1995) indicated that the internally-generated organic carbon load

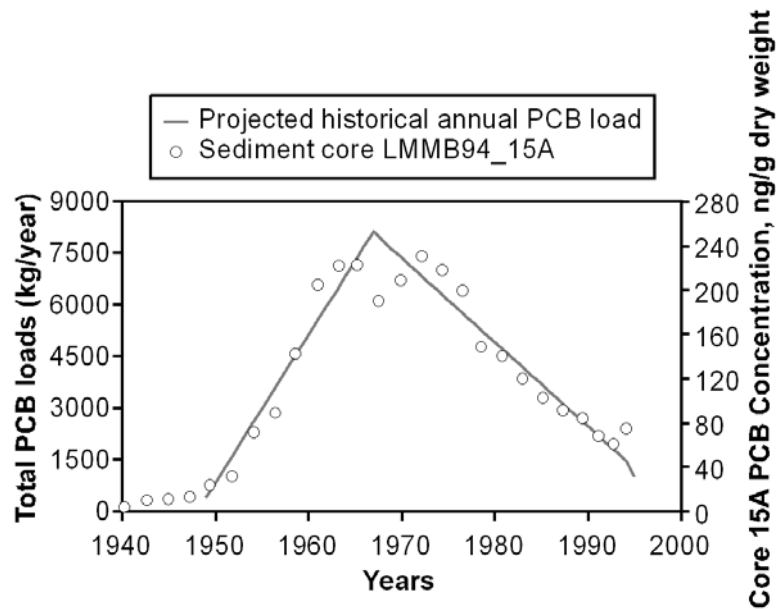


Figure 4.5.11. Reconstructed historical total PCB loading time functions and sediment core LM94-15A total PCB concentration profiles for Lake Michigan. Note: The total PCB loading time function was back-projected based on the estimated PCB load for 1994. The last data point of the load time function represents the estimated PCB load for 1995.

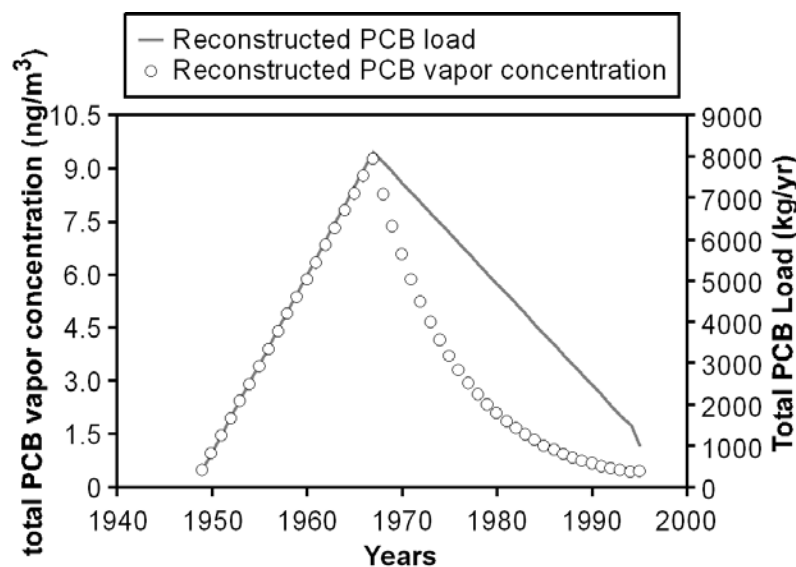


Figure 4.5.12. Reconstructed total PCB vapor phase concentrations and total PCB loading time functions for Lake Michigan. Note: The total PCB loading time function was back-projected based on the estimated PCB load for 1994. The last data point of the load time function represents the estimated PCB load for 1995.

(primary production) accounted for approximately 90% of the total carbon solid loads for Lake Michigan (details are in Part 4, Section 4.4.2). Consequently, it would be an adequate representation of the historical carbon solid loading function if the primary production history for Lake Michigan could be reasonably reconstructed. However, there are too few primary production data for Lake Michigan in the literature to permit creation of an organic carbon loading history. Due to time constraints, a simple relationship was established by correlating primary productivity with available historical total phosphorus loads (Appendix 4.5.5).

By establishing a relationship between total phosphorus loads and primary productivity, an estimation of historical primary productivity was constructed for Lake Michigan using an approach similar to the one by Vollenweider *et al.* (1974). Figure 4.5.5.1 in Appendix 4.5.5 shows the relationship between total phosphorus loads and lake area normalized primary productivity. Figure 4.5.13 presents the reconstructed total carbon solids loading time function used for the LM2-Toxic PCB hindcast simulations.

The reconstructed carbon solids loading history (Figure 4.5.13) indicated that the annual average internal carbon loads for Lake Michigan reached a peak value of approximately 3.5×10^9 kg/year in 1980 and then decreased to the current level (1994-1995) of 2.1×10^9 kg/year used in the LM2-Toxic model. The annual average carbon concentrations were expected to follow the same trend as the historical carbon solids loading function.

4.5.4.5.1.4 Other Physical and Kinetic Parameters – In terms of physical processes, one of the main assumptions made for the LM2-Toxic PCB hindcast was that the time functions for water transport, wind speed, wave heights, and temperature constructed for the two-year LMMBP period were representative of annual average conditions (see Part 1, Chapter 4 for details) that existed in the lake for the entire hindcast simulation period. Values of the kinetic parameters used in the model calibration were kept the same during the hindcast simulation.

Resuspension rate is a function of organic carbon concentration in the water column, assuming the other parameters in Equation 4.3.8 are constant (see

Part 4, Chapter 3 for details). By using the carbon concentration data generated during the LMMBP and the reconstructed carbon solids loading history, the annual average organic carbon concentrations in the water column were estimated (Appendix 4.5.5). The resuspension rates for each year throughout the hindcast simulation period were adjusted with the estimated annual organic carbon concentrations (see Section 4.3.4.2.1 – Steady-State Resuspension Calibration for details). The adjusted resuspension time function maintained the same monthly pattern that was derived from the observations made during the LMMBP period.

4.5.4.5.1.5 Historical Water Column PCB Concentrations and Sediment Core Profiles – Historical PCB concentrations in the water column and sediments are essential data to evaluate the results of a water quality model hindcast simulation. The available Lake Michigan water column data are listed in Table 4.5.4 together with their sources. Measurements made before 1994 LMMBP were taken at a very limited number of locations, within short-time periods and at depths less than 10 m in the water column. Thus they are biased and may not truly represent annual average water column PCB concentrations.

Table 4.5.5 provides the sediment PCB core profiles with depth and temporal information at three LMMBP sediment sampling locations (LM94-015A, LM95-061A, and LM95-086A). Two of the sediment cores (LM95-061A and LM95-086A) were taken within depositional zones as defined in Figure 4.3.2. Core LM94-015A was collected in the transitional zone. Figure 4.5.14 shows the locations of the three sediment cores taken during the LMMBP period. For more details about these three sediment cores, see section Part 1, Chapter 7.

4.5.4.5.1.6 PCB Inventory in Lake Michigan Sediments – An estimate of PCB inventory in the lake sediments is the final information needed to ultimately confirm the outcomes of the LM2-Toxic PCB hindcast and the applicability of the model for future predictions. Table 4.5.6 lists the available PCB sediment inventory data for Lake Michigan. The most recent estimate from Eadie and Van Hoof (see Part 1, Chapter 7 for details) showed that the PCB inventory for the lake is about 60,998 kg.

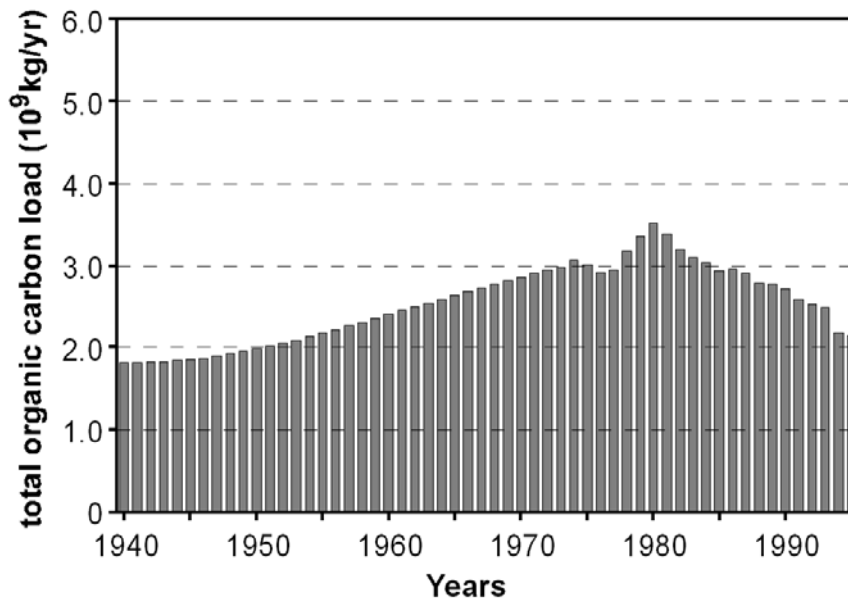


Figure 4.5.13. Reconstructed total organic carbon load (primary production + LMMBP tributary loads) for Lake Michigan.

Table 4.5.4. Available Historical Water Column Total PCB Concentrations for Lake Michigan

Year	Concentration (ng/L)	Standard Error/ Deviation (ng/L)	Depth (m)	Reference
1976	7.2	3.1		Chambers and Eadie, 1980
1979	2.88	3.37	1	Rice <i>et al.</i> , 1982
1980	5.66	1.12	1	Rice <i>et al.</i> , 1982
1980	6.36	1.3	1	Rice <i>et al.</i> , 1982
1980	1.2	0.5	5	Swackhamer and Armstrong, 1987
1981	0.28		1	Filkins <i>et al.</i> , 1983
1986	1.1	0.2		Lefkovitz, 1987
1991	0.64	0.43	8	Pearson, 1996
1992	0.424	0.058		Bicksler, 1996
1993	0.22	0.04	5	Anderson, 1999
1994-1995	0.259	0.172		LMMBP

Table 4.5.5. Sediment PCB Concentration Vertical Profiles Analyzed for Three Sediment Box Cores Taken During the LMMPB

LM94-015A			LM95-061A			LM95-086A		
Interval cm	Total PCBs ng/g Dry	Mid-Interval Date	Interval cm	Total PCBs ng/g Dry	Mid-Interval ng/g Dry	Interval cm	Total PCBs ng/g Dry	Mid-Interval Date
0-1	73.7	1994.16	0-0.5	91.1	1995.37	0-0.5	78.3	1994.90
1-2	60.7	1992.78	0.5-1	111	1994.78	0.5-1	64.6	1993.30
2-3	67.6	1991.16	1-1.5	110	1994.28	1-1.5	66.6	1991.40
3-4	83.7	1989.45	1.5-2	127	1993.89	1.5-2	75.7	1989.30
4-5	91.1	1987.37	2-2.5	117	1993.37	2-2.5	77.2	1987.10
5-6	102	1985.17	2.5-3	120	1992.63	2.5-3	77	1984.60
6-7	119	1983.07	3-3.5	122	1991.90	3-3.5	80.1	1982.00
7-8	140	1980.81	3.5-4	136	1991.12	3.5-4	76.6	1979.00
8-9	148	1978.61	4-5	100	1989.61	4-5	77.7	1974.20
9-10	199	1976.55	5-6	106	1987.43	5-6	102	1968.10
10-11	217	1974.43	6-7	103	1985.08	6-7	101	1961.90
11-12	230	1972.21	7-8	117	1982.53	7-8	97.2	1955.70
12-13	208	1969.91	8-9	119	1979.84	8-9	82	1949.50
13-14	190	1967.54	9-10	117	1977.08	9-10	34.6	1942.00
14-15	222	1965.35	10-11	144	1974.34	10-11	14.5	1933.80
15-16	221	1963.31	11-12	164	1971.69	11-12	7.84	1925.00
16-17	204	1961.05	12-13	159	1968.97	12-13	3.54	1916.50
17-18	142	1958.70	13-14	128	1966.30	13-14	2.61	1908.60
18-19	88.8	1956.47	14-15	86.9	1963.55	14-15	1.51	1900.50
19-20	71	1954.23	15-16	65	1960.58	15-16	0.893	1891.60
20-21	31.4	1951.82	16-17	50.4	1957.68			
21-22	23.5	1949.47	17-18	29.2	1954.65			
22-23	12.5	1947.27	18-19	17.6	1951.57			
23-24	10.5	1945.07	20-22	7.02	–			
24-25	9.52	1942.78	22-24	4.51	–			
25-26	3.58	1940.30	24-26	4.22	–			
26-27	2.19	1937.73	26-28	2.62	–			
27-28	1.37	1934.83	28-30	1.51	–			
28-30	1.62	1930.81						

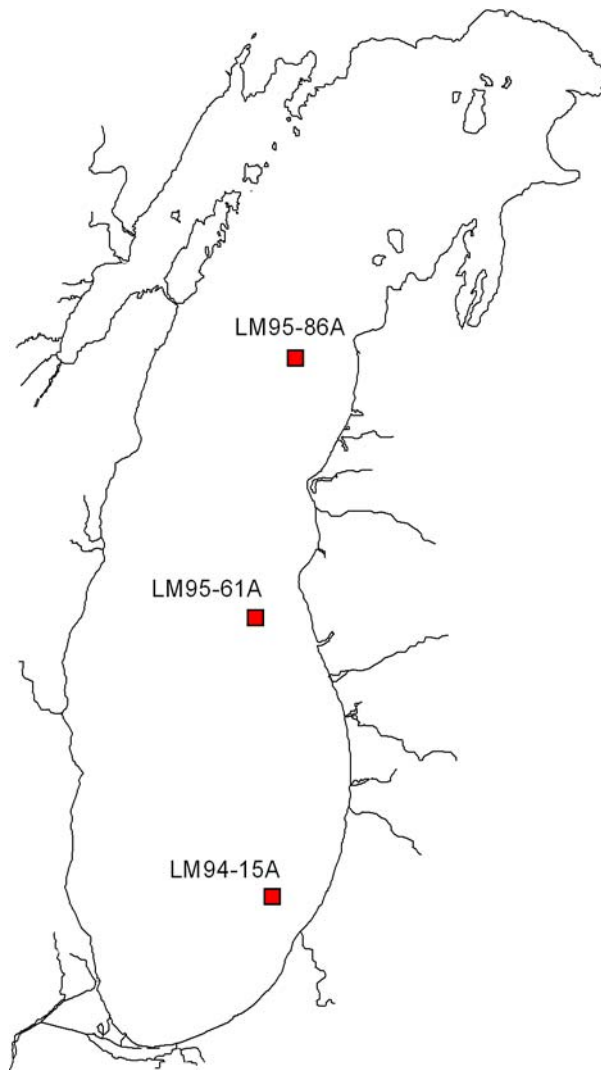


Figure 4.5.14. The sampling sites of the sediment box core samples (LM94-15A, LM95-61A, LM95-87A) taken during the LMMBP for which vertical PCB concentration profiles were analyzed and available.

Table 4.5.6. Available Inventories of PCBs in Lake Michigan Sediments

System	Inventory (kg)	Source
Lake Michigan	75,000	Golden <i>et al.</i> , 1993
Green Bay	14,565	Wisconsin Department of Natural Resources, 2003
Lake Michigan + Green Bay	60,000	Eadie and Van Hoof (personal communication, 2006)

4.5.4.5.2 Results From the LM2-Toxic PCB Hindcast

As mentioned previously, in order to ensure the predictability of a water quality model, a long-term PCB hindcast has conventionally been used for either confirming a set of key model parameters defined by the combination of literature sources and short-term model calibration or directly as a long-term calibration tool if a short-term model calibration has not been conducted. LM2-Toxic went through a very comprehensive and data intensive short-term calibration using LMMBP-generated field data. The PCB hindcast for this report is to confirm the model parameters defined by the short-term calibration and to provide confidence in modeling long-term predictions.

Results from the LM2-Toxic PCB hindcast presented and discussed in this section include 1) water column PCB concentrations from the hindcast versus available historical data, 2) sediment PCB concentrations from the hindcast versus sediment core profiles, 3) mass budget checking for the hindcast simulation period, and 4) a comparison between model-generated PCB sediment inventory and available sediment inventory estimations made by other researchers. In general, the results demonstrate the LM2-Toxic PCB hindcast is reasonably successful for reproducing PCB concentrations in both the water column and the sediments of Lake Michigan.

The results of the LM2-Toxic PCB hindcast are presented in Figures 4.5.15 through 4.5.17 for annual and monthly average concentrations in the water column and annual average concentrations in the sediments. In general, the results from the hindcast are reasonably good for both the water column and the sediment relative to the available historical water column field data and the three LMMBP sediment cores. The results demonstrate that the model is able to generate the temporal trends of PCB concentrations which closely match the observed trends.

Some of the historical data derived before and during 1980 (Chambers and Eadie, 1980; Rice *et al.*, 1982) are not shown in Figures 4.5.15 and 4.5.16. Due to the limitation of the analytical method, the objective of the research studies, and the water depth (≤ 1

meter below the water surface), the representativeness of these early measurements for the lake as a whole is questionable. Taking account of the possible variation in PCB concentrations with water depth, the open lake value of $1.2 \text{ ng/L} \pm 0.46$ (for surface water only - five meters) for 1980 from Swackhamer and Armstrong (1987) was considered to be more appropriate comparison with the lake-wide annual or monthly average concentration generated from the model hindcast.

It is important to consider temporal variation when comparing model results with historical data. For most of the historical data, sampling occurred during a two-week or less period during the year (usually summer). Compared to the annual lake-wide average water column concentration in Figure 4.5.15, the monthly lake-wide average concentration in Figure 4.5.16 demonstrates significant variation in the water column PCB concentrations for any given year. The monthly variation in the lake PCB concentrations becomes most intense in the top layer of the water column (within 10 meter depth) with the highest concentrations occurring in the summer months (July to September) and lowest concentrations in the winter months (December to February).

The vertical profile of PCB sediment concentrations assembled based on the LM2-Toxic PCB hindcast outputs for the depositional area of the lake was compared to the three sediment core profiles (LM94-015A, LM95-061A, and LM95-086A) measured and analyzed for the LMMBP. The concentration profile from the model is porosity normalized. Considering the fact that the model-generated vertical PCB sediment concentration profile is a lake-wide average vertical profile and based on the outputs of the model with a very coarse spatial segmentation, the model did a fairly good job of matching the general trend of the vertical profiles from the three sediment cores and had the closest match with core LM95-061.

There are certainly unmatched portions between the model-generated profile and the profiles from the sediment cores. But it is very important to understand that the common purpose of a hindcast is to provide confirmation of the general conceptualization and parameterization of a model. The successfulness of a model hindcast should not be judged only on whether the model output can match field

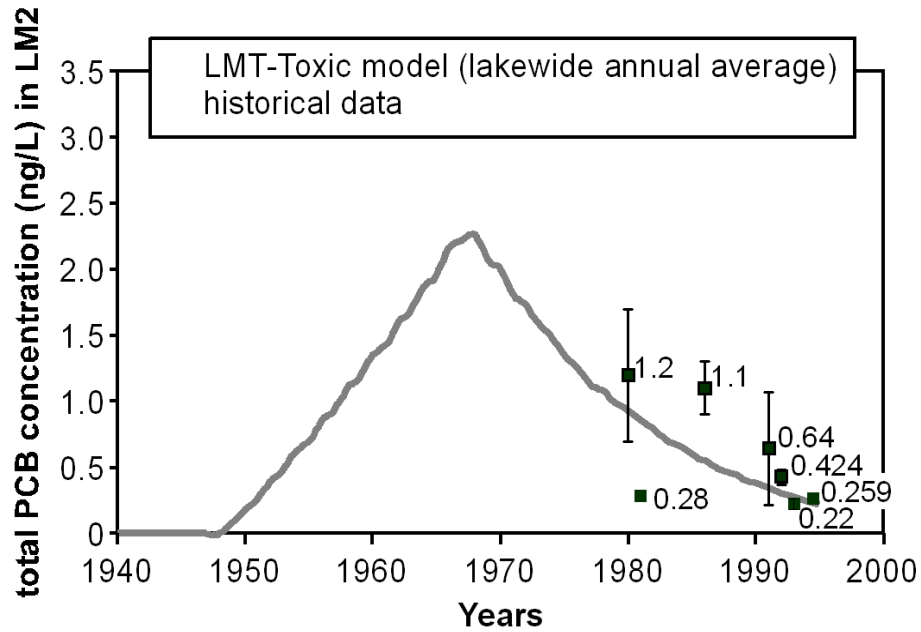


Figure 4.5.15. Annual lake-wide average total PCB water column concentrations from the LM2-Toxic PCB hindcast simulation.

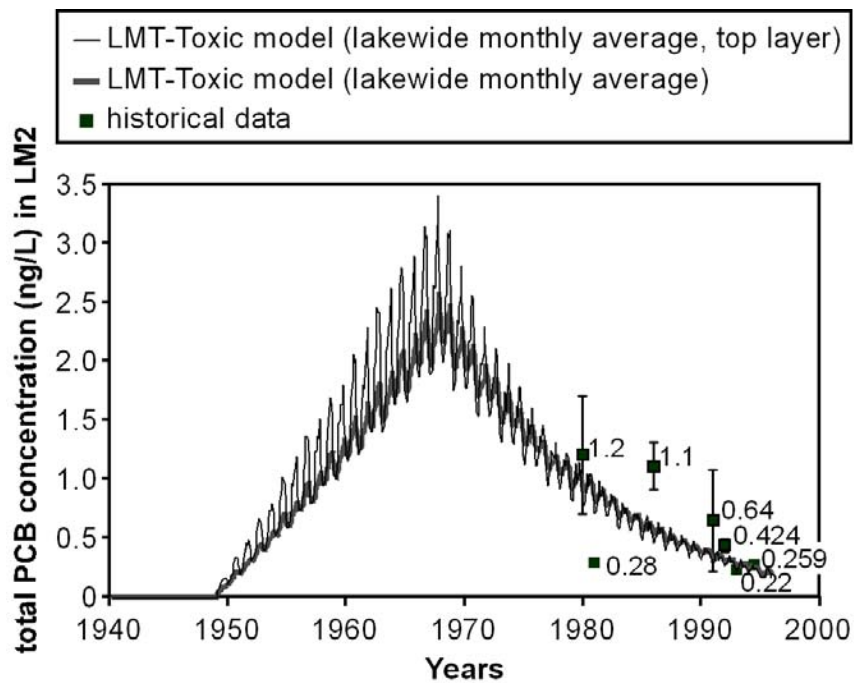


Figure 4.5.16. Monthly lake-wide average total PCB water column concentrations from the LM2-Toxic PCB hindcast simulation. High concentration in the summer months and low concentration in the winter months.

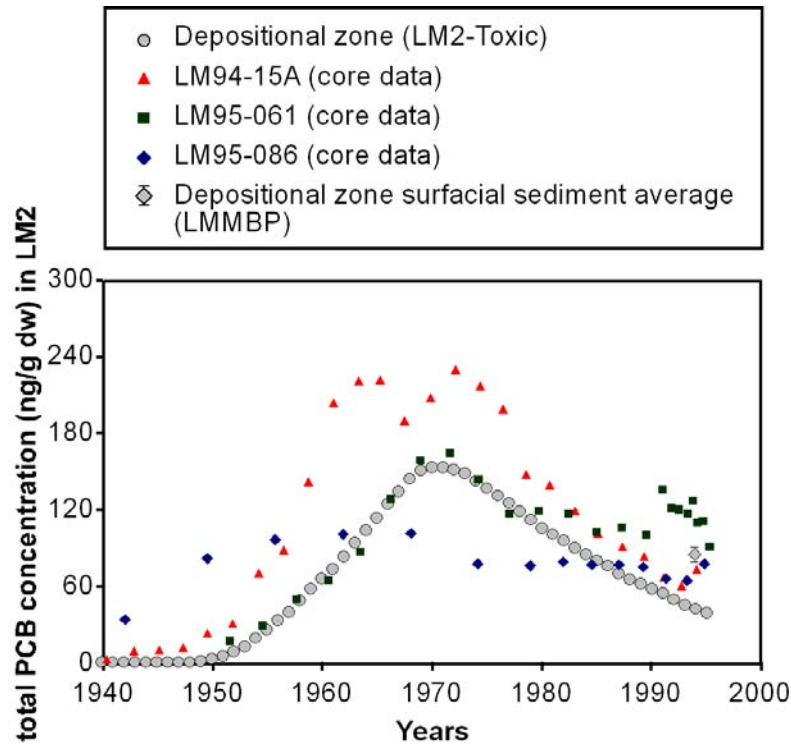


Figure 4.5.17. Annual average total PCB concentration profiles in the sediment depositional zone from the LM2-Toxic PCB hindcast simulation.

observation at one point or a short portion of the temporal profile.

The discrepancy between the LM2-Toxic PCB hindcast generated sediment profile and the profiles from the sediment cores becomes most noticeable for the portion after 1990. This is the part of the profiles that represents the unconsolidated portion – the surficial sediment mixed layer. The explanations for the discrepancy could be:

- 1) The model does not have adequately reconstructed historical physical conditions such as wave, water circulation, and temperature time functions. These time functions can dictate organic carbon and PCB concentrations in the lake and the solids cycling rates such as resuspension, burial, and settling. For example, a severe weather event could create a major localized resuspension event in the lake and, therefore, could elevate PCB concentrations in the local water column and surficial sediments along the path impacted by water transport. The

elevated concentrations could also remain for a long time after the major event. The recorded maximum wave heights from the southern National Oceanic and Atmospheric Administration’s (NOAA) buoy 45007 indicate that a major storm event occurred on September 23, 1989 which induced a maximum wave height of 5.6 meters. The sediment profile from core LM95-061A shows a step increase in PCB concentrations just after the event. The step increase would very likely be caused by re-depositing the sediments with higher PCB concentrations resuspended from a nearby area.

- 2) The unit for the sediment PCB concentration output from the LM2-Toxic is ng/L. In order to compare it with the PCB sediment profiles (ng/g dw) from the cores, porosity is used to convert the model-generated PCB sediment concentration from the unit of ng/L to ng/g dw. The converted PCB sediment concentration is extremely sensitive to the porosity used in the conversion. The value (0.953) for the porosity

used in the conversion is the average of the porosities at the sediment sampling sites located within the depositional area of the lake. The range of the porosities at these sediment sampling sites is between 0.943 and 0.966.

- 3) Some physical-chemical processes such as the BNL and its associated transport were not built in the LM2-Toxic model. A seasonal persistent BNL with high total suspended solid is not an uncommon phenomenon in the Great Lakes and has been observed and documented by numerous researchers (Chambers and Eadie, 1980, 1981; Eadie *et al.*, 1984; Baker and Eisenreich, 1985; Baker *et al.*, 1991; Eadie, 1997; Hawley, 2003). The BNL is usually formed in a large lake such as a Great Lake during summer stratification. The thickness of the BNL is from a few meters up to 10 meters above the bottom of the lake (Chambers and Eadie, 1980, 1981; Eadie *et al.*, 1984). Total suspended solids and associated chemicals in both particulate and dissolved phases increase exponentially from the top to the bottom of the BNL. The suspended solids in the hypolimnion with less attached pollutant will adsorb more PCBs when the solids settle through this layer to the lake bottom. The existence of the BNL and the physical-chemical processes associated with this layer could elevate the concentration of PCBs in the sediments. Compared to the hypolimnion, samples collected in the BNL during the LMMBP (August 1994, August 1995, and September 1995 cruises) show a 4 to 20 times higher particulate PCB concentrations and 1.5 times higher dissolved PCB concentrations. Because the BNL and the associated processes are not built in the LM2-Toxic, the PCB hindcast could underpredict PCB concentrations in certain areas of the lake sediments.
- 4) There are uncertainties associated with the derived historical primary production, PCB loading, and vapor-phase time functions.
- 5) The uncertainties related to model parameters including calibration parameters could also propagate through the model to the predicted sediment PCB concentrations.

Mass budget checking is a necessary step to ensure that a water quality model does not generate or lose mass through the entire simulation period. Figure 4.5.18 shows the mass budget of Σ PCB (sum of 54 PCB congeners for Lake Michigan during the simulation period of the LM2-Toxic PCB hindcast (1949-1995). The inventories in the mass budget diagram represent the Σ PCB masses left in both the water column and sediment at the end (last time step) of the model simulation. Each mass component with an arrow in Figure 4.5.18 indicates a mass flux in or out of the system during the entire simulation period. A simple mass budget check was done based on the numbers in Figure 4.5.18. Table 4.5.7 lists the Σ PCB inventories, the mass fluxes, and the calculation of the mass budget checking. The result of the mass budget checking shows that there is only about 0.66% of mass not being accounted for over the 47 years of the hindcast simulation period. This small amount of uncounted mass over the entire hindcast period should not have much of an impact on the accuracy of PCB concentrations computed by the LM2-Toxic.

The most reliable confirmation of the LM2-Toxic model comes from the comparison between the total PCB sediment inventory (total PCB = Σ PCB x 1.1668 = 52,278 kg x 1.1668 = 60,998 kg) calculated from the LM2-Toxic PCB hindcast and the latest estimation of the total PCB sediment inventory (about 60,000 kg) provided by Eadie and Van Hoof (personal communication, see Part 1, Chapter 7). The factor 1.1668 used to convert the Σ PCBs to the total PCBs was derived from the LMMBP data (Part 1, Chapter 3). The latest sediment inventory estimate from Eadie and Van Hoof was based on a large quantity of information collected during the LMMBP for Lake Michigan sediment, including more than 60 box core PCB sediment profiles and also roughly 60 ponar and gravity core samples. A few previous and most recent studies listed in Table 4.5.6 indicate that the lake-wide sediment inventory is likely between 60,000 kg and 75,000 kg. The sediment PCB inventory (60,988 kg) computed from the LM2-Toxic PCB hindcast is within the range provided in the literature.

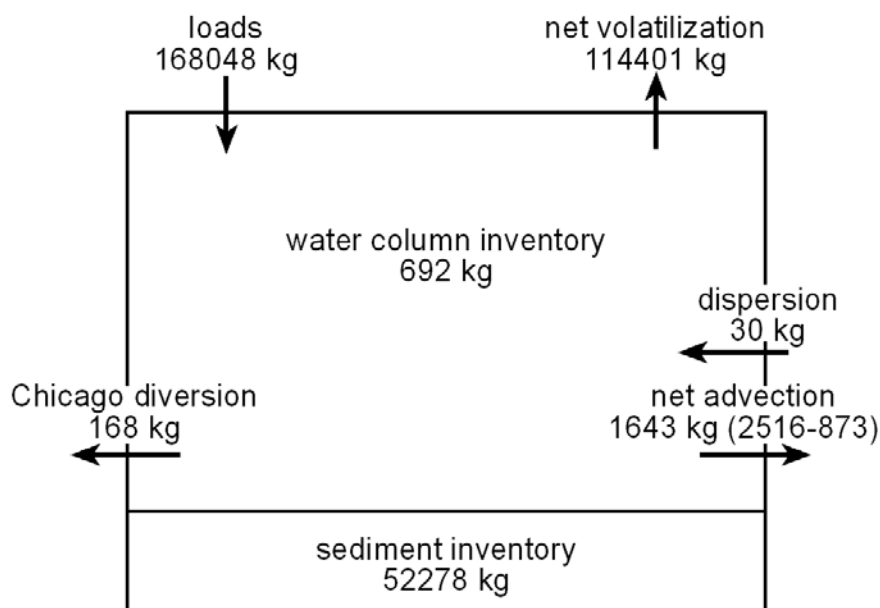


Figure 4.5.18. ΣPCB mass budget of Lake Michigan during the period of the LM2-Toxic PCB hindcast (1949-1995).

Table 4.5.7. Calculations in PCB Mass Budget Checking for the LM2-Toxic PCB Hindcast

Mass of In-Flux (kg)		Mass of Out-Flux (kg)		Inventory (Kg)	
Loads	16,048	Net Volatilization	114,401	Water Column	692
Dispersion	30	Net Advection	1,643	Sediment	52,278
		Chicago Diversion	168		

Difference in PCB mass over the hindcast simulation period (47 years) = (Inventory + Mass of out-flux) - (Mass of in-flux) = (692 + 52,278 + 114,401 + 1,643 + 168) - (168,048 + 30) = 169,182 - 168,078 = 1,104 kg

Percentage of the difference in PCB mass over the PCB total input into Lake Michigan = difference in PCB mass over the hindcast simulation/mass of in-flux = 1,104 kg/168,078 kg = 0.657%

Given the adequate level of reconstructed historical forcing functions including loading and vapor phase concentrations, the overall results from the LM2-Toxic PCB hindcast demonstrate that the model is able to generate PCB concentrations in both the water column and sediment that compare reasonably well with the available historical data and estimated sediment total PCB inventories.

References

- Anderson, D.J., T.B. Bloem, R.K. Blankenbaker, and T.A. Stanko. 1999. Concentrations of Polychlorinated Biphenyls in the Water Column of the Laurentian Great Lakes: Spring 1993. *J. Great Lakes Res.*, 25(1):160-170.
- Baker, J.E. and S.J. Eisenreich. 1985. Chlorinated Hydrocarbon Cycling in the Benthic Nepheloid Layer of Lake Superior. *Environ. Sci. Technol.*, 19(9):854-861.
- Baker, J.E., S.J. Eisenreich, and B.J. Eadie. 1991. Sediment Trap Fluxes and Benthic Recycling of Organic Carbon, Polycyclic Aromatic Hydrocarbon, and Polychlorobiphenyl Congeners in Lake Superior. *Environ. Sci. Technol.*, 25(3):500-509.
- 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. *Environ. Sci. Technol.*, 36(20):4395-4402.
- Bicksler, J. 1996. PCBs in the Spring-Time Water Column of the Great Lakes. M.S. Thesis, University of Minnesota, Minneapolis, Minnesota. 160 pp.
- Bierman, V.J., J.V. DePinto, T.C. Young, P.W. Rodgers, S.C. Martin, and R. Raghunathan. 1992. Development and Validation of an Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan. U.S. Environmental Protection Agency, Office of Research and Development, ERL-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. 381 pp.
- Buehler, S.S., I. Basu, and R.A. Hites. 2002. Gas-Phase Polychlorinated Biphenyl and Hexachlorocyclohexane Concentrations Near the Great Lakes: A Historical Perspective. *Environ. Sci. Technol.*, 36(23):5051-5056.
- Buehler, S.S., I. Basu, and R.A. Hites. 2004. Causes of Variability in Pesticide and PCB Concentrations in Air Near the Great Lakes. *Environ. Sci. Technol.*, 38(2):414-422.
- Chambers, R.L. and B.J. Eadie. 1980. Nearshore Chemistry in the Vicinity of the Grand River, Michigan. National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan. NOAA Technical Memorandum ERL GLERL-28, 28 pp.
- Chambers, R.L. and B.L. Eadie. 1981. Nepheloid and Suspended Particulate Matter in Southeastern Lake Michigan. *Sedimentology*, 28(3):439-447.
- Delaware River Basin Commission. 2003. Calibration of the PCB Water Quality Model for the Delaware Estuary for Penta-PCBs and Carbon. Delaware River Basin Commission, West Trenton, New Jersey. 147 pp. (Website: http://www.epa.gov/reg3wapd/tmdl/pa_tmdl/delaware%20river/ModelCalibrationReport.pdf).
- DePinto, J.V., R. Raghunathan, P. Sierzenga, X. Zhang, V.J. Bierman, Jr., P.W. Rodgers, and T.C. Young. 1993. Recalibration of GBTOX: An Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan. Final Report. U.S. Environmental Protection Agency, Office of Research and Development, ERL-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. 132 pp.
- DePinto, J.V., W.M. Larson, J. Kaur, and J. Atkinson. 2003. LOTOX2 Model Documentation - In Support of Development of Load Reduction Strategies and a TMDL for PCBs in Lake Ontario. Submitted to New England Interstate Water Pollution Control Commission, Boott Mills South, Lowell, Massachusetts. 122 pp.

-
- Eadie, B.J., R.L. Chambers, W.S. Gardner, and G.L. Bell. 1984. Sediment Trap Studies in Lake Michigan: Resuspension and Chemical Fluxes in the Southern Basin. *J. Great Lakes Res.*, 10(3):307-321.
- Eadie, B.J., H.A. Vanderploeg, J.A. Robbins, and G.L. Bell. 1990. Significance of Sediment Resuspension and Particle Settling. In: M.M. Tilzer and C. Serruya (Eds.), *Large Lakes: Ecological Structure and Function*, pp. 196-209. Springer-Verlag, New York, New York.
- Eadie, B.J. 1997. Probing Particle Processes in Lake Michigan Using Sediment Traps. *Water, Air, and Soil Pollut.*, 99:133-139.
- Endicott, D.D. 2005. 2002 Lake Michigan Mass Balance Project: Modeling Total PCBs Using the MICHTOX Model. In: R. Rossmann (Ed.), *MICHTOX: A Mass Balance and Bioaccumulation Model for Toxic Chemicals in Lake Michigan, Part 2*. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, MED-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. EPA/600/R-05/158, 140 pp.
- Endicott, D.D., W.L. Richardson, and D.J. Kandt. 2005. 1992 MICHTOX: A Mass Balance and Bioaccumulation Model for Toxic Chemicals in Lake Michigan. In: R. Rossmann (Ed.), *MICHTOX: A Mass Balance and Bioaccumulation Model for Toxic Chemicals in Lake Michigan, Part 1*. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, MED-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. EPA/600/R-05/158, 140 pp.
- Filkins, J.C., J.M. Townsend, and S.G. Rood. 1983. Organochlorines in Offshore Waters of the Great Lakes, 1981. U.S. Environmental Protection Agency, Office of Research and Development, ERL-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. 12 pp.
- Gardiner, R.D., M.T. Auer, and R.P. Canale. 1984. Sediment Oxygen Demand in Green Bay (Lake Michigan). In: M. Pirbazari and J.S. Devinny (Eds.), *Proceedings of the 1984 Specialty Conference on Environmental Engineering*, pp. 514-519. American Society of Civil Engineers, New York, New York.
- Gobas, F.A.P.C., M.N.Z. Graggen, and X. Zhang. 1995. Time Response of the Lake Ontario Ecosystem to Virtual Elimination of PCBs. *Environ. Sci. Technol.*, 29(8):2038-2046.
- Golden, K.A., C.S. Wong, J.D. Jeremiason, S.J. Eisenreich, G. Sanders, J. Hallgren, D.L. Swackhamer, D.R. Engstrom, and D.T. Long. 1993. Accumulation and Preliminary Inventory of Organochlorines in Great Lakes Sediments. *Water Sci. Technol.*, 29(8-9):19-31.
- Hall, D. and D. Robertson. 1998. Estimation of Contaminant Loading from Monitored and Unmonitored Tributaries to Lake Michigan for the USEPA Lake Michigan Mass Balance Study. Quality Systems and Implementation Plan. Submitted October 23, 1998. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, Illinois. 19 pp.
- Hawker, D.W. and D.W. Connell. 1988. Octanol-Water Partition Coefficients of Polychlorinated Biphenyl Congeners. *Environ. Sci. Technol.*, 22(4):382-387.
- Hawley, N. 2003. Observations of the Intermediate and Benthic Nepheloid Layers in Southern Lake Michigan During the Summer of 1995. National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan. NOAA Technical Memorandum ERL GLERL-124, 30 pp.
- Hillery, B.L., I. Basu, C.W. Sweet, and R.A. Hites. 1997. Temporal and Spatial Trends in a Long-Term Study of Gas-Phase PCB Concentrations Near the Great Lakes. *Environ. Sci. Technol.*, 31(6):1811-1816.

-
- Jeremiason, J.D., K.C. Hornbuckle, and S.J. Eisenreich. 1994. PCBs in Lake Superior, 1978-1992: Decreases in Water Concentrations Reflect Loss by Volatilization. *Environ. Sci. Technol.*, 28(5):903-914.
- Lefkovitz, L.F. 1987. The Particle Mediated Fractionation of PCBs in Lake Michigan. M.S. Thesis, University of Wisconsin, Madison, Wisconsin. 238 pp.
- Mackay, D. 1988. A Model of PCB Behaviour in Lake Ontario. In: Report on Modeling the Loading-Concentration Relationship for Critical Pollutants in the Great Lakes, Appendix V. Task Force on Chemical Loadings, Water Quality Board, International Joint Commission, Windsor, Ontario, Canada. 275 pp.
- McCarty, H.B., J. Schofield, K. Miller, R.N. Brent, P. Van Hoff, and B. Eadie. 2004. Results of the Lake Michigan Mass Balance Study: Polychlorinated Biphenyls and *trans*-Nonachlor Data Report. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, Illinois. EPA/905/R-01/011, 289 pp.
- Miller, S.M., M.L. Green, J.V. DePinto, and K.C. Hornbuckle. 2001. Results from the Lake Michigan Mass Balance Study: Concentrations and Fluxes of Atmospheric Polychlorinated Biphenyls and *trans*-Nonachlor. *Environ. Sci. Technol.*, 35(2):278-285.
- Miller, S.M. 2003. The Effects of Large-Scale Episodic Sediment Resuspension on Persistent Organic Pollutants in Southern Lake Michigan. Ph.D. Thesis, The University of Iowa, Iowa City, Iowa. 194 pp.
- Pearson, R.F., K.C. Hornbuckle, S.J. Eisenreich, and D.L. Swackhamer. 1996. PCBs in Lake Michigan Water Revisited. *Environ. Sci. Technol.*, 30(5):1429-1436.
- Rice, C.P., B.J. Eadie, and K.M. Erstfield. 1982. Enrichment of PCBs in Lake Michigan Surface Films. *J. Great Lakes Res.*, 8(2):265-270.
- Robbins, J.A., N.R. Morehead, R.W. Rood, D.N. Edgington, and S. Meyer. 1999. Accumulation and Near-Surface Mixing of Sediments in Lake Michigan as Determined for the Lake Michigan Mass Balance Program, Volumes 1 and 2. Project Report. U.S. Environmental Protection Agency, Office of Research and Development, ERL-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. 503 pp.
- Rodgers, P.W., T.A.D. Slaweki, J.V. DePinto, and W. Booty. 1988. LTI Toxics Model Application: PCBs in Lake Ontario - An Exploratory Application. In: Report on Modeling the Loading-Concentration Relationship for Critical Pollutants in the Great Lakes, Appendix III. Task Force on Chemical Loadings, Water Quality Board, International Joint Commission, Windsor, Ontario, Canada. 275 pp.
- Rygwelski, K.R. (Ed.). 2005. Lake Michigan Mass Balance Project (LMMBP) PCB Peer Review Report. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, MED-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. 31 pp.
- Schneider, A.R., H.M. Stapleton, J. Cornwell, and J.E. Baker. 2001. Recent Declines in PAH, PCB, and Toxaphene Levels in the Northern Great Lakes as Determined from High Resolution Sediment Cores. *Environ. Sci. Technol.*, 35(19):3809-3815.
- Schwab, D. and D. Beletsky. 1998. Lake Michigan Mass Balance Study: Hydrodynamic Modeling Project. National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan. NOAA Technical Memorandum ERL GLERL-108, 53 pp.
- Swackhamer, D.L. and D.E. Armstrong. 1987. Distribution and Characterization of PCBs in Lake Michigan Water. *J. Great Lakes Res.*, 13(1):24-36.
- Thomann, R.V. and D.M. Di Toro. 1983. Physico-Chemical Model of Toxic Substances in the Great Lakes. *J. Great Lakes Res.*, 9(4):474-496.

U.S. Environmental Protection Agency. 1997. Lake Michigan Mass Balance Project Modeling Work Plan. Final Report. U.S. Environmental Protection Agency, Office of Research and Development, ERL-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. 30 pp.

U.S. Environmental Protection Agency. 2000. Hudson River PCBs Reassessment RI/FS Phase 3 Report: Feasibility Study, Books 1-6. U.S. Environmental Protection Agency, Region 2, New York, New York. 2,095 pp.

Vollenweider, R.A., M. Munawar, and P. Stadelmann. 1974. A Comparative Review of Phytoplankton and Primary Production in the Laurentian Great Lakes. J. Fish. Res. Board Canada, 31(5):739-762.

Wisconsin Department of Natural Resources. 2003. Estimates of PCB Mass, Sediment Volume, and Surface Sediment Concentrations in Operable Unit 5, Green Bay Using an Alternative Approach. Wisconsin Department of Natural Resources, Madison, Wisconsin. White Paper Number 19, 23 pp.