concentrations in the water column of the Delaware Estuary (near the Schuylkill River) forecasted into the future. As a point of comparison, the present total PCB water quality criterion of approximately 44 pg/L (Zones 2-5) is also shown. There is some uncertainty about the magnitude of interaction between the water column and sediment bed and also the effective size of the sediment bed reservoir. In order to investigate this uncertainty, the four colored lines in the figure represent various model simulations using high/low estimates of the extent of the sediment bed interaction and small/large estimates of the effective size of the sediment bed reservoir.

![Figure 3. Washout Simulation (from DRBC, 2003).](image)

The model simulations demonstrate that without sediment bed interaction under this future zero-load scenario the estuary would reach the water quality criterion in a very short time (~2 months), as indicated by the almost vertical black line in Figure 3. However with sediment bed interaction, the response time is much longer and depending on the sediment transport scenario, it would take 15-40 years to reach the water quality criterion established in the TMDL.

5. Summary

In this paper we have discussed the dynamics of PCBs in the Delaware Estuary. PCBs that enter the water column of the estuary are subject to water column transport processes. That is, the amount of PCB dilution by freshwater sources increases in the downstream direction due to the cumulative increasing freshwater input along the length of the river. The mixing and dilution also increases in the downstream direction due to increased estuarine mixing in the downstream areas of the estuary. The result is that the assimilative capacity of the
decrease during the 1990s in the tributaries or sludge) cannot be evaluated in this manner due to the lack of data.

Figure 5 – Comparison of loadings trends with (a) tributary concentrations and (b) municipal wastewater treatment plant sludge concentrations. SW/SE and NE refer to different treatment plants of the Philadelphia Water Department. Data were provided by D. Blair (personal communication).

Another check is to compare the total mass discharged to the Delaware Estuary to other water bodies. The total PCB mass discharged to the estuary calculated by back-scaling and integrating the loading trends are compared to other mass estimates in Table 2. This check is useful, because the present analysis is not constrained by the total mass discharged. Some time trends produced a total PCB mass in excess of the global production and this check served as a basis for dismissing those trends. The total global production exceeds 1 million tons of which approximately 650,000 tons were produced in the US. The US air emissions were approximately 8,500 tons. Discharges to major waterbodies (Hudson and Fox Rivers) are in the range of approximately 100 to 600 tons. The two trends used for the Delaware Estuary are in the same range suggesting the time trends are not unreasonable.
The historical water column data for Zone 3 are presented in Figure 6. Data in other zones are insufficient for a useful model-data comparison. The 1980 data point represents two samples. Each sample was analyzed for 7 Aroclor mixtures (e.g. Aroclor1242). One Aroclor mixture was detected and quantified as “1-9 µg/l” and 6 Aroclor mixtures were reported as not detected (USACOE, unknown date). Based on the reported values, the estimated total PCB concentration of the samples ranges from 1,000 (1×1,000+6×0) to 15,000 (1×9,000+6×1,000) ng/L. This data point is plotted at the logarithmic midpoint of that range (4,000 ng/L) in Figure 6. The model results for the Air Trend fall within the range of data (assuming the 1980 data are representative of actual conditions). The results for the Hudson Trend are below the data in the late 1970s. Both trends are in good agreement with the contemporary data in 2001.

6.3.4.2. Historical sediment data

Historical sediment concentrations for Zones 2-6 are presented in Figure 7. The data are highly variable, presumably a result of high spatial variability. Here all samples were lumped by zone. It is possible that a more careful analysis that accounts for differences in sample location (e.g. main channel, nearshore, near tributary mouths, etc.) would reduce some of that variability. The data in all zones are relatively constant in time and a trend of decreasing concentrations is not evident. By comparison the model results for both loading trends are on the high end of the data and decrease in time. Thus the model is not in agreement with the long-term trend seen in the sediment data. This could be the result of error(s) in the model, forcing functions and/or data.
6.3.4.5. Dated core data

The concentrations from the dated core are presented in Figure 10. Measured sediment concentrations on an organic carbon basis are compared to modeled water column concentrations on a particulate organic carbon basis. At first glance it might seem more appropriate to compare the data to sediment concentrations, but that would not be correct. That is because the sediment bed simulated by the model corresponds to the bioturbated sediments present throughout most of the estuary. However, the dated sediment core was collected from a location where there was apparently no significant bioturbation. The concentrations in the dated core are a record of the PCB concentration of depositing solids, and therefore the data are compared to PCB concentrations on organic carbon in the water column corresponding to the time of deposition.

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

![Figure 10 – Historical water column penta-PCB concentrations. Data are from Woodbury Creek core (PC-15; Sommerfield and Madsen, 2003; Eisenreich, 2003). Depth was converted to time using 1.5 cm/yr net deposition rate. Model results are for Segment 44.](image-url)
A stringent test of the model is its ability to predict the presently observed PCB concentrations, using the historical loading. Contemporary sediment data are presented in Figure 9. The data were processed by DRBC by averaging the dry-weight PCB concentrations (µg/kg) by zone. However, sediment bed fraction organic carbon (foc) data were not averaged and therefore the organic carbon-based PCB concentrations (µg/gOC) vary somewhat within each zone.

The model-simulated concentrations for the two loading trends bracket the data in the upstream portion of the estuary (Zones 2 and 3). Below that the agreement is worse with the model progressively overpredicting concentrations with distance downstream. At the downstream end (Delaware Bay, Zone 6) the model overpredicts PCB concentrations for both loading trends by almost an order of magnitude. This is consistent with the model-data comparison for historical sediment concentrations presented in Section 6.3.4.2.

Although the model is within the range of the historic sediment data (which has ~2-order of magnitude variability) at the end of the simulation period, it clearly tends to overpredict the observed sediment concentrations. This could be related to the inability of the model to simulate the estuarine turbidity maximum and associated effect on PCB fate and transport. On the other hand, a unit load simulation (results not presented here) demonstrated that the PCB mass in that part of the estuary is predominantly from the Atlantic Ocean. It is possible that the loading trends are not applicable to the Atlantic Ocean concentration. Due to the large volume the Atlantic Ocean responds slowly to changes in input. It is expected that applying the loading trend to the Atlantic Ocean resulted in an overestimation of the historical boundary concentration. The inability of the model to reproduce the data is therefore not necessarily a shortcoming of the model, but could be a shortcoming of the method used to develop the historical ocean boundary condition.

Figure 9 – Contemporary surface sediment penta-PCB concentrations. Model results are for sediment layer 1.
Figure 7(a) – **Historical sediment bed total-PCB concentrations** in Zone 2. Model results are average of layers 1 and 2.

Figure 7(b) – **Historical sediment bed total-PCB concentrations** in Zone 3. Model results are average of layers 1 and 2.
Figure 7(c) – **Historical sediment bed total-PCB concentrations in Zone 4.** Model results are average of layers 1 and 2.

Figure 7(d) – **Historical sediment bed total-PCB concentrations in Zone 5.** Model results are average of layers 1 and 2.
Figure 7(e) – **Historical sediment bed total-PCB concentrations in Zone 6.** Model results are average of layers 1 and 2.

6.3.4.3. Historical fish data

Observed PCB concentrations in fish, compiled by Greene (2002), are presented in Figure 8 for Zones 2-6. For this comparison fillet and whole body results are not differentiated and when no lipid data are available it is assumed the lipid content is the average of the samples in the database (fillet = 2.7%, whole body = 6.8%, White Perch). Those data points are represented by different symbols on the plots.

The model does not include a fish compartment and a direct model-data comparison is therefore not possible. Fish concentrations on a $\mu$g/gLipid basis are compared to water column and sediment bed concentrations on a $\mu$g/gOC basis. The validity of this method depends on the assumptions that the partitioning of PCBs between water and organic carbon, and water and fish lipid is similar. For hydrophobic chemicals (like PCBs), this is known to be the case (Di Toro et al., 2000). The comparison is complicated by biomagnification, however, which will tend to increase the fish concentrations relative to the water column and sediment concentrations. Also, it is expected that the time trend of fish tissue concentration lags that of the water column and/or sediment bed concentrations, because it takes some time for the PCBs to move up the food chain. Whether the fish concentrations should reflect the water column or sediment bed concentration depends on the source of PCBs for the fish. The reasoning for presenting model results for both compartments is that depending on the base of the food web (benthic or pelagic) the fish concentration should equilibrate with the water column or sediment bed or some combination of them. The data shown in Figure 8 are for White Perch whose feeding habits vary with age and are not well defined (opportunistic). Data for other biota (American Eel, Striped Bass, Channel/White Catfish, Weakfish, Osprey eggs) are presented in Appendix B.
Figure B.3 – Historical Weakfish total-PCB concentration in Delaware Bay (Zone 6).

Figure B.4 – Historical Channel/White Catfish total-PCB concentration in the Delaware Estuary.
The data show a decrease in fish tissue concentration from ~1970 to ~1990. However, over the past ~10 years, from 1990 to 2002 no decrease in concentration is evident. This is roughly consistent with the relatively constant sediment concentrations (Figure 7). The last two years show an increasing trend in fish tissue concentrations. This recent increase is seen in the White/Channel Catfish data as well (Appendix B). The model sediment concentrations for the Air Trend are at the high end of the data. If any biomagnification is accounted for the agreement worsens. The sediment concentrations for the Hudson Trend are at the low end of the data, which is more consistent when biomagnification is assumed to occur. Neither trend captures the constant concentration over the past ~10 years or increase over the last two years. This is an important discrepancy between the model and historical data. This could be the result of error(s) in the model, forcing functions and/or data.

Figure 8(a) – **Historical fish total-PCB concentration in Zone 2.** Data are for White Perch. Model sediment results are for layer 1.
Figure 8(b) – **Historical fish total-PCB concentration in Zone 3.** Data are for White Perch. Model sediment results are for layer 1.

Figure 8(c) – **Historical fish total-PCB concentration in Zone 4.** Data are for White Perch. Model sediment results are for layer 1.
Figure 8(d) – **Historical fish total-PCB concentration in Zone 5.** Data are for White Perch. Model sediment results are for layer 1.

Figure 8(e) – **Historical fish total-PCB concentration in Zone 6.** Data are for White Perch. Model sediment results are for layer 1.

6.3.4.4. Contemporary sediment data