HUDSON RIVER PCBs REASSESSMENT RI/FS
RESPONSIVENESS SUMMARY FOR
VOLUME 2A: DATABASE REPORT
VOLUME 2B: PRELIMINARY MODEL CALIBRATION REPORT
VOLUME 2C: DATA EVALUATION AND INTERPRETATION REPORT

DECEMBER 1998

For

U.S. Environmental Protection Agency
Region II
and
U.S. Army Corps of Engineers
Kansas City District

Book 3 of 3

TAMS Consultants, Inc.
Limno-Tech, Inc.
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Menzie-Cura & Associates, Inc.

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Review and Commentary on
General Electric/Quantitative Environmental Analysis, LLC
Thompson Island Pool Sediment PCB Sources, Final Report, March 1998

December 1998

For

U.S. Environmental Protection Agency
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Prepared by
TetraTech, Inc.
and
TAMS Consultants, Inc.

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EXECUTIVE SUMMARY

In March 1998, Quantitative Environmental Analysis, LLC (QEA), on behalf of the General Electric Company (GE), submitted to U.S. EPA Region 2 a report on the Hudson River PCBs NPL site entitled "Thompson Island Pool Sediment PCB Sources, Final Report" (QEA, 1998). This report summarizes, interprets, and refines a number of earlier data analysis and interpretation reports relative to Thompson Island Pool (TIP) PCB dynamics written for GE by HydroQual and O'Brien & Gere. Rather than comment on each of the individual interim reports, this review of the "Final Report", compiled on behalf of EPA Region 2, will serve as a review of all the GE reports submitted to date on the TIP sediment source.The interpretive reports referenced in the final 1998 report are as follows:

- HydroQual, 1995a. Anomalous PCB Load Associated with the Thompson Island pool: Possible Explanations and Suggested Research;
- HydroQual, 1995b. The Erosion Properties of Cohesive Sediments in the Upper Hudson River; and
- HydroQual, 1997. Hudson River PCB DNAPL Transport Study.

QEA raises a number of important and interesting issues regarding the TIP PCB source. In many instances, addressing these issues has required substantial new analyses and careful re-examination of conclusions reached in the Phase 2 Reassessment Remedial Investigation/ Feasibility Study (RRI/FS) Data Evaluation and Interpretation Report (USEPA, 1997). The net result of combining and assessing the interpretations of QEA and the Phase 2 team is an improved understanding of the TIP sediment PCB source. The conclusions presented by QEA are, however, in many cases overstated, and, in some instances, not supported by the data. Numerous other data compilation reports are sited in the 1998 report. See the 1998 QEA report for the complete list of references.

This review addresses primarily the data evaluation and interpretation aspects of the QEA report. QEA's modeling effort, which is not complete, is described in the report, but is addressed here primarily in context of its use in interpretation of PCB loading mechanisms.

The major conclusions of this review are as follows:

- There does appear to be a high sampling bias associated with the GE TID-West station near Thompson Island Dam; however, GE's attempt to compensate for this bias is incorrect and frequently results in an underestimation of the actual load at the TI Dam. Additionally, sampling bias is markedly less for spring high flows, most likely as a result of more energetic mixing conditions.The bias is also less pronounced for trichlorinated and higher congeners relative to total PCBs.

- The analytical bias corrections provided by GE more than compensate for the sampling bias, resulting in load gain estimates for the TIP which are *higher* than those presented in the DEIR (USEPA, 1997).

- The congener signature of the TIP load is consistent with a weathered, partially-dechlorinated PCB source—although not as fully dechlorinated as some buried hot spot sediments. The assumption that pore water flux is the only summer loading pathway appears to be incorrect. Instead, new analyses conducted for this review suggest that the summer TIP load is a mixture of pore water flux and bulk loading of fine sediment, perhaps driven by bioturbation.

- QEA's modeling effort is incomplete, and some aspects of model calibration are unsatisfactory or poorly documented. The QEA PCB fate and transport model is not sufficiently refined to be useful for quantitative analysis of hypotheses of PCB loading sources.

- Analyses of sediment PCB inventory depletion rates presented by QEA are flawed, and do not result in a constraint on interpretation of the TIP load.

- PCB loading occurs throughout the TIP. This loading is consistent with the distribution of known hot spot sediments, and suggests no need to invoke an unknown, "anomalous" PCB source.

- Sediment PCBs both within and downstream of the TIP contribute PCB load to the water column. The presence of a sampling bias at TID-West requires some reanalysis of relative contributions above and below TID. On a load-per-mile basis, however, TIP sediments remain the major concentrated source of loading from sediment. The TIP appears to contribute PCBs at a rate per mile of between two and four times that of downstream sediments.

- Hot spot sediments are a major source of PCB load, although non-hot spot sediments also contribute. QEA's argument that all sediments contribute equally to the PCB load appears incorrect.

- There is no credible evidence for extensive loading of PCB DNAPL or mass flux of highly contaminated sediment bedload into the TIP after the Allen Mill failure. It does appear, however, that elevated water column PCB concentrations entering the TIP in 1991–1993 have resulted in a general increase in surface sediment PCB concentrations in several depositional areas. (See Table 5-2.)

INTRODUCTION

The QEA report (1998, p. 1) presents four major bulleted conclusions, plus a fifth summary conclusion in the text. Each of these will be addressed in turn, and used to organize other comments on the document.

The five conclusions presented by QEA are:

1. *During the 1990's, the amount of PCBs leaving the TIP was significantly overestimated due to a sampling bias at the routine sampling station located at the downstream limit of the TIP.*

2. *The composition of water column PCBs attributed to the TIP sediments indicates that relatively undechlorinated PCBs are the principal source and that surface sediment pore water is the principal point of origin.*

3. *PCB levels in the water column increase in a near linear fashion as water passes through the TIP, indicating a nearly uniform areal flux from sediments within the TIP.*

4. *Sediments downstream of the Thompson Island Dam (TID) contribute PCBs to the water column in a manner consistent with the TIP sediments (i.e., transfer from surface sediment pore water), increasing the water column loading by approximately 50% between TID and Schuylerville.*

5. *Surface sediments within all areas of the river contribute PCBs to the water column, not simply PCBs residing in "hot spot" areas. Comparison of dry weight sediment PCB concentrations, either at depth or at the sediment surface, gives a false impression of the relative importance of various sediments within the river. The surface sediment pore water PCB concentrations, and, hence, the diffusive sediment PCB flux is controlled by PCB concentrations associated with the organic carbon component of the sediments. As these average organic carbon normalized PCB concentrations are similar within "hot spot" and non-"hot spot" areas, these areas contribute similarly to the water column PCB load.*

1.0 PRESENCE OF A SAMPLING BIAS AT TID-WEST

During the 1990's, the amount of PCBs leaving the TIP was significantly overestimated due to a sampling bias at the routine sampling station located at the downstream limit of the TIP. (QEA, 1998, p. 1)

As summarized in QEA (1998), HydroQual (Rhea, 1997) conducted monitoring and produced a memo documenting apparent consistent differences between PCB measurements at the TID-West sampling station and center channel measurements at TIP-18C. Rhea's memo presents results which "indicate that PCB concentrations within TID-west samples are unrepresentative of the average concentration passing the TID. PCB concentrations measured in samples collected from this station consistently exceed those in samples collected in the center channel immediately upstream and downstream of the dam. This bias appears to be responsible for the excess loading observed from the TIP since 1991." The evidence for the "bias" seems strong, at least during some low flow periods. The bias does not, however, account for all the "excess" loading from the TIP.

Most of the observations available from EPA and GE near the Thompson Island Dam were collected at or near the TID-West station, and these data will need to be used in modeling. QEA suggests "correcting" TID-West observations downward to reflect TIP-18C observations, but does not propose a specific correction factor. It should be noted that this sample bias correction factor is more than offset by GE's upward correction for analytical biases (HydroQual, 1997a). Both corrections were proposed after release of the DEIR (USEPA, 1997). The net result of the two corrections is that inferences regarding total PCB load generation from the TIP presented in the DEIR based on analysis of GE data remain appropriate, and may in fact be underestimated; however, estimates of relative loading from the TIP and downstream sediments may need some revision.

QEA's initial examination of the apparent bias in TID-West sample observations estimated that center-channel and downstream concentrations were only about 63 percent of concentrations observed at the TID-West station. These results were based on analysis of the ratio of TID-Center to TID-West samples collected from 9/18/96 through 10/16/97. Subsequently, QEA determined that TID-Center samples were essentially equivalent to samples obtained downstream of the dam ("TIDPRW" samples), and has continued to collect samples at TID-West and TIDPRW for comparison. Samples through 9/15/98 (total of 51 samples) are now available in the most recent (10/13/98) update to the GE database. Some significant revisions have occurred in the first few data points through 6/17/97; only minor differences were detected in later data. Note that the earliest data points do not have a TID Center (TIP-18C) result reported in the database, but equivalent samples are available as float survey (FS) or TIP samples. One data point which was non-detect at TID-West (12/29/97) was omitted from calculations. For the period of 8/13 through 10/16/97 in which both TIP-18C and TIDPRW samples are available, the TIP-18C results have been used.

Over the full set of 1996-1998 samples, the average ratio of TID-Center or TIDPRW total PCB results to TID-West total PCB results is 0.86, much closer to unity than the original ratio of 0.62 proposed in J. Rhea's memo of 9/30/97 (Rhea, 1997). Samples collected in 1996-1997 had an average ratio of 0.72 (including samples after 9/30/97), while samples collected in 1998 had an average ratio of 0.92. A wide range of ratios is seen in individual sample pairs, including results where the ratio is greater than 1 (*i.e.*, the TID-West result is less than center channel result).

1.1 *Bias Corrections for Total PCBs*

In revisiting this analysis, it is first appropriate to enquire why the ratio in the GE 1998 results is higher than in 1996-1997 results. Two important characteristics distinguish this sampling period from the full set of samples: First, flows were low (less than 5,000 cfs), whereas higher flows occur in the 1998 sampling. Second, the 1996-1997 samples all were taken during a period in which the upstream concentrations at Fort Edward were very low or non-detect, whereas increased upstream loads reoccurred during the 1998 sampling. Figures 1-1 and 1-2 show the relationship between observed ratios and (1) flow, and (2) total PCB concentration at Fort Edward.

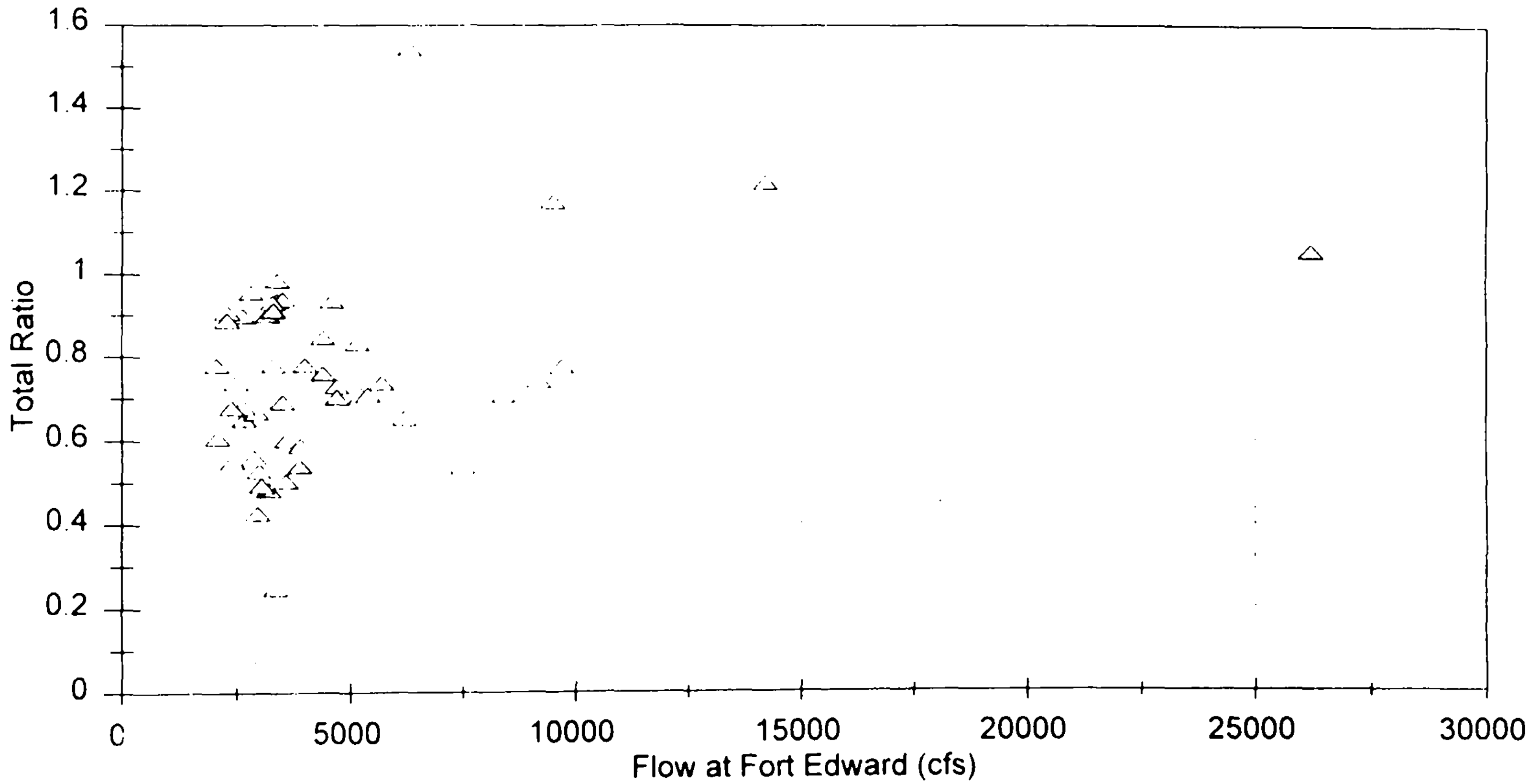

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Figure 1-1 Relationship Between Ft. Edward Flow and the Ratio of TID-West/TID-Center for Total PCBConcentrations

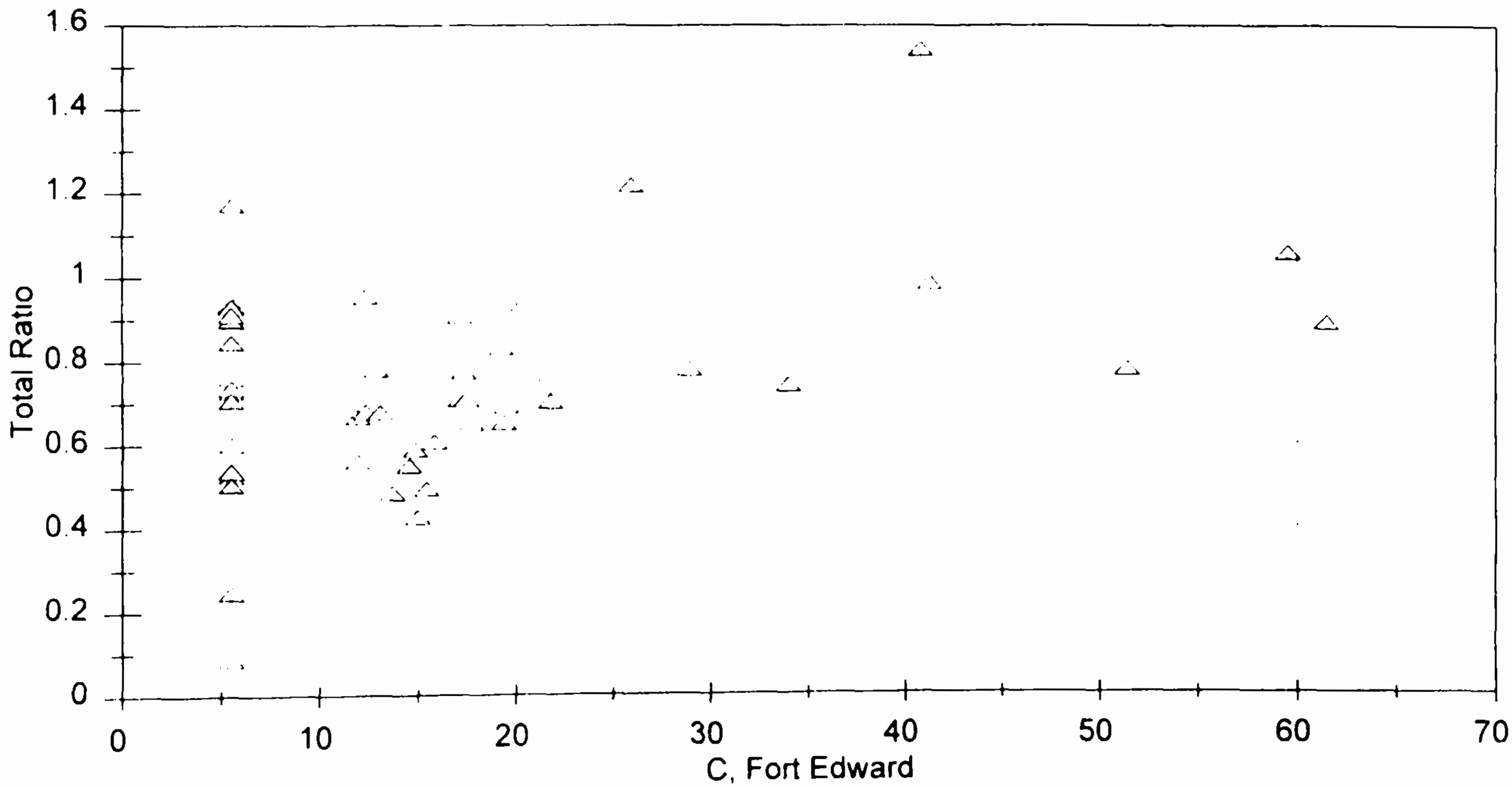

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Figure 1-2 Relationship Between the Ft. Edward PCB Concentration and the Ratio of TID-West/TID-Center for Total PCBConcentrations

From these figures, it will be noted that the ratio between center channel and TID-West observations appears to approach unity as either flow or upstream concentration increases. The relationship to flow is fairly obvious: increased flow implies greater lateral mixing potential, which should make concentrations more uniform across a channel section.

To understand the relationship to upstream concentration, consider the extremely simplified conceptual mode shown in Figure 1-3, in which downstream flow through the TIP is indicated by arrows. Discrepancy between shore concentrations (C_1) and mixed concentrations at the dam (C_2) presumably arises because there is an additional load in the nearshore area (L), which is not immediately mixed laterally. Consider a case in which transport is laterally mixed at some point (say, the end of Griffin Island). At this point, there is a flow of magnitude Q_0 with a concentration of C_0. Downstream (i.e., in the areas of the TID-West sampling station) full lateral mixing does not occur, and an additional load, L, is introduced. For simplicity, assume that the flow is split into two portions, with a flow of Q_1 going through the nearshore portion, and a flow of Q_0-Q_1 going through the main channel. These flows then mix and recombine at the dam. It is important to realize that the concentration in the nearshore area is determined by both the upstream concentration and the local loading, L. Under these conditions, the concentration in the nearshore area (TID-West) would be given by

$$C_1 = C_0 + L/Q_1$$

while the mixed center channel concentration at the dam would be given by

$$C_2 = C_0 + L/Q_0$$

The ratio would then be

$$C_2/C_1 = \frac{C_0 + L/Q_0}{C_0 + L/Q_1}$$

This ratio depends on the relative magnitude of Q_1 to Q_0, indicating that lateral mixing intensity presumably increases with the magnitude of Q_0. As Q_1 increases toward Q_0 (implying instant lateral mixing of L), the ratio should approach 1. The ratio also depends on the relative magnitude of C_0 versus L. As the upstream concentration increases, the ratio should again increase toward 1 because the contributions from the nearshore area are swamped by upstream loads.

Thus, the high bias seen in initial GE sample comparisons is a joint result of low flows and low upstream concentrations. The bias results from incomplete lateral mixing of what is likely (to a first approximation) a fixed local load. If this load is small relative to the upstream load, or if mixing is high, the bias is reduced. Thus, it is entirely inappropriate to apply the apparent bias correction observed in 1996–1997 to the entire observed time series at TID-West. In particular, a much smaller bias correction should apply during conditions prior to 1995 in which much higher upstream loads were observed.

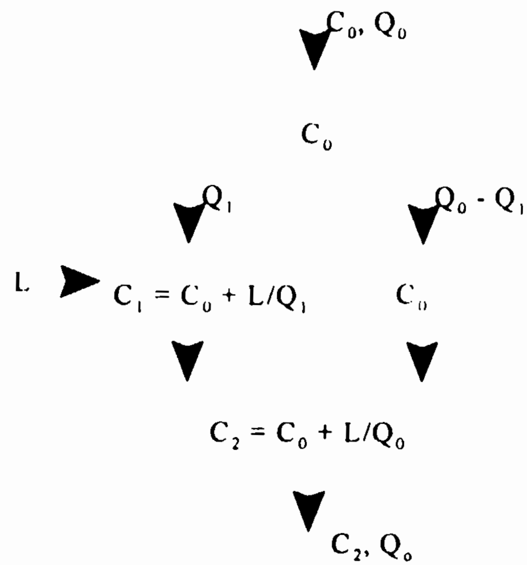

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Figure 1-3 Conceptual Model Of PCB Loads Near the TI Dam

Note that the mixed upstream concentration relative to TID-West, C_0, is presumably the concentration near Griffin Island, which is not known for most sampling events. This concentration includes the load at Fort Edward plus any incremental load within the pool above Griffin Island. Nonetheless, a high load at Fort Edward would tend to reduce the ratio between TID-West and center channel observations.

The graphs presented above suggest that high bias for total PCB measurements at TID-West occurs at conditions of flow less than about 4,000 cfs at Fort Edward and concentrations less than about 17 ng/l at Fort Edward. If we segregate the observations based on these criteria, using the full set of GE data through 9/15/98, the following results are obtained for the ratio of center channel to TID-West observations:

Table 1-1
Summary Statistics for Total PCB Loads at the TI Dam

Total PCB Results		Flow at Fort Edward	
		< 4,000 cfs	≥ 4,000 cfs
Concentration at Fort Edward	< 17 ng/l total PCBs	average = 0.64 median = 0.60 count = 23 average significantly different from 1	average = 0.78 median = 0.75 count = 8 average significantly different from 1
	≥ 17 ng/ total PCBs	average = 0.80 median = 0.78 count = 8 average significantly different from 1	average = 0.90 median = 0.77 count = 11 average not significantly different from 1

In three of the four cells the average ratio is significantly less than 1 at the 95% confidence level. As predicted, the ratio increases with both increasing upstream flow and increasing upstream concentration. At high flow and high concentration, the average is not significantly different from 1, and no bias correction should be used.

1.2 *Bias Corrections for ΣTri+*

The bias was also analyzed for the ΣTri+ parameter, that is the sum of trichlorinated and higher homologues. The ratio for ΣTri+ also shows relationships to upstream concentration and flow, as shown in Figures 1-4 and 1-5. Based on these figures, a flow of 4,000 cfs at Fort Edward was again selected as a breakpoint, while a ΣTri+ concentration of 15 ng/l at Fort Edward was selected as the concentration breakpoint. Results of the analysis are shown in Table 1-2.

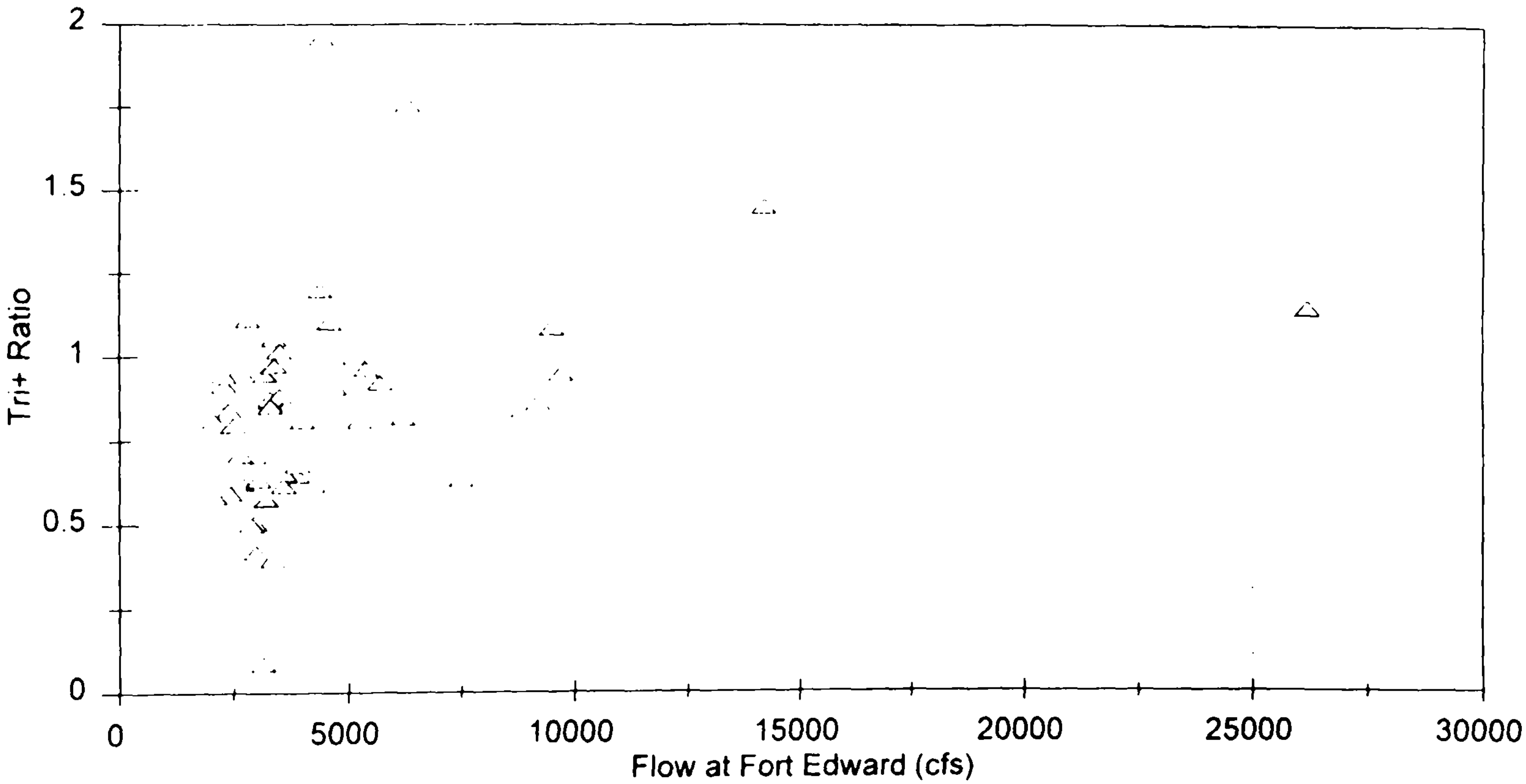

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Figure 1-4 Relationship Between Ft. Edward Flow and the Ratio of TID-West/TID-Center for ΣTri+Concentrations

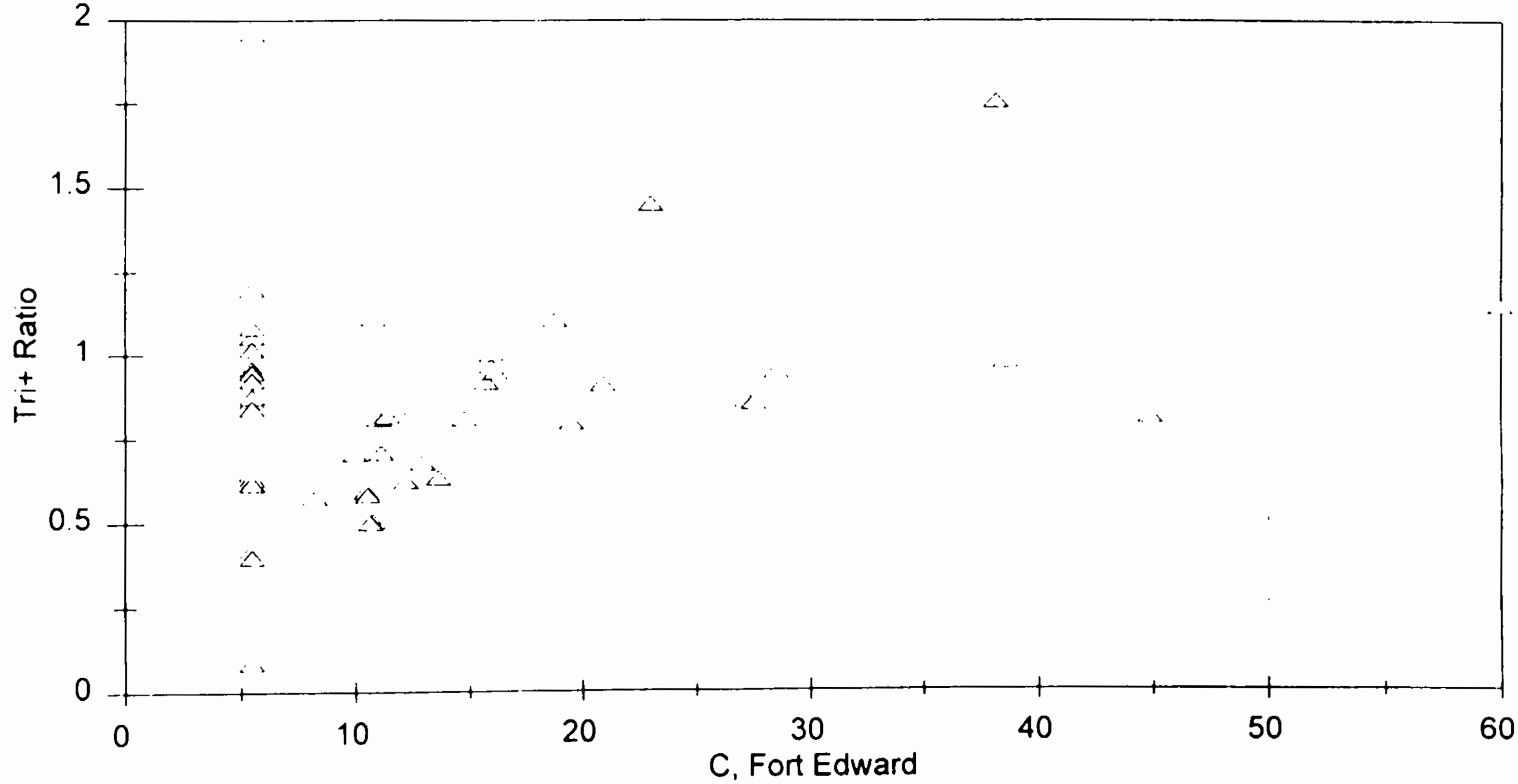

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Figure 1-5 **Relationship Between the Ft. Edward ΣTri+ Concentration and the Ratio of TID-West/TID-Center for ΣTri+Concentrations**

Table 1-2
Summary Statistics for ΣTri+ Loads at the TI Dam

ΣTri+		Flow at Fort Edward	
		< 4,000 cfs	≥ 4,000 cfs
Concentration at Fort Edward	< 15 ng/l ΣTri+	average = 0.69 median = 0.65 count = 24 average significantly different from 1	average = 0.97 median = 0.83 count = 10 average not significantly different from 1
	≥ 15 ng/ ΣTri+	average = 0.88 median = 0.88 count = 7 average significantly different from 1	average = 1.13 median = 1.00 count = 9 average not significantly different from 1

In two of the four cells, the average is significantly less than 1—but only in the low flow, low upstream concentration cell does the average approach the large bias correction factor which has previously been proposed.

1.3 Summary of Bias Estimates

An empirical analysis of the full set of comparisons between TID-West and TIP-18C or TIDPRW samples shows that the observed bias is dependent on both flow and upstream concentration. When upstream concentration is high (as was the case in the early 1990's), the bias will be small. The bias will also be small or non-existent at high flows. As a result, the apparent bias should have only a small effect on calculations of annual load.

Stratifying the analysis by flow and concentration removes much of the apparent seasonal component of the bias. While there does appear to be a seasonal cycle of load generation in the nearshore sediments, peaking around June, this may have little effect on the ratio between nearshore and center channel concentrations. These results indicate that any bias correction of TID-West observations must be conditional on both concentration and flow at Fort Edward. Estimated empirical bias correction factors are summarized in Table 1-3:

Table 1-3
Correction Factors for the TI Dam PCB Loads

Empirical Bias Correction Factors		Total PCBs	ΣTri+
Low Flow, Low Upstream Concentration	Fort Edward Flow < 4000 cfs Fort Edward Concentration < 17 ng/l total PCBs *or* ≤ 15 ng/l ΣTri+	0.64	0.69
Low Flow, High Upstream Concentration	Fort Edward Flow < 4000 cfs Fort Edward Concentration ≥ 17 ng/l total PCBs *or* ≥ 15 ng/l ΣTri+	0.80	0.88
High Flow, Low Upstream Concentration	Fort Edward Flow ≥ 4000 cfs Fort Edward Concentration < 17 ng/l total PCBs *or* ≤ 15 ng/l ΣTri+	0.78	1.0
High Flow, High Upstream Concentration	Fort Edward Flow ≥ 4000 cfs Fort Edward Concentration ≥ 17 ng/l total PCBs *or* ≥ 15 ng/l ΣTri+	1.0	1.0

1.4 Interpretation of the Apparent Bias

While evidence of a *difference* in concentrations between the TID monitoring stations under various conditions is clear, the interpretation is not. These correction factors serve to match the center and west station at the TI Dam but do not indicate which value is more correct. A more careful examination of the data leads to the following conclusions:

- Even if the estimate of bias is correct, this does not account for all the "excess loading" observed from the TIP; instead, the evidence continues to suggest that there is a summer gain of *at least* 0.5 kg/d (and more likely 0.7 to 1 kg/day) total PCBs from the Thompson Island Pool.

- While there is a difference between summer concentrations at stations near the Thompson Island Dam, the conclusion that TID-West observations are biased high, and that this constitutes the entire difference, is only one among a number of possible explanations.

- HydroQual observations on lateral variability of PCB concentrations in the Thompson Island Pool appear to provide evidence that near-shore contaminated sediments *are* a significant source of PCB load to the Pool.

While there are consistent differences in low-flow concentrations between TID-West and TIP-18C, homologue patterns at the two stations are generally similar and reflect an increase in mono-, di-, and trichlorobiphenyl loads relative to the Rogers Island station. Concentrations in the center channel just downstream of the Thompson Island Dam (available for August through October 1997 only) are similar to those at TIP-18C, suggesting that TIP-18C (rather that TID-West) provides a good estimate of load exiting the TIP. These observations are consistent with a theory that the PCB load exiting the TIP represents a simple dilution of concentrations originating in nearshore hot spot areas, as discussed in Section 1.1 above.

There are also alternative explanations, other than simple bias in TID-West observations, which may account for part or all of the difference between TID-West and center channel observations at TIP-18C: The difference between TIP-18C and TID-West samples might suggest that TID-West is biased high relative to the average concentration leaving the TIP, or that TIP-18C is biased low, or some combination of the two. During four of the sampling events, HydroQual also sampled PCB concentrations at TID-East and at several stations below the Thompson Island Dam. During each of these events, TID-East concentrations were similar to those at TIP-West and greater than those at TIP-18C, indicating that either both wing-wall stations are biased high, or TIP-18C is biased low. Samples 200 feet downstream of the dam were generally within 10 ng/l of TIP-18C samples, although higher than TIP-18C in three out of four summer events despite any volatilization losses during transport over the dam, suggesting that TIP-18C was approximately representative of concentrations going over the dam at the time of observations. However, on the one occasion (8/13/97) on which samples were also taken two miles further downstream at Fort Miller a different picture emerges. On 8/13, total PCB concentration at TID-West was 90.2 and TIP-18C 49.6 ng/l. Concentration at Fort Miller on this date was 76 ng/l, or a little greater than the average of TID-West and TIP-18C concentrations, while concentration at Schuylerville was 74.2 ng/l. Measurements at Fort Miller and Schuylerville presumably average out short-term diurnal and lateral variability in TIP loads relative to observations just above or below the dam. This suggests the possibility that the actual daily load transported downstream may be an average of TID-West and TIP-18C observations.

1.5 Evidence of Loading from TIP Sediments

The QEA bias study results demonstrate that, under some conditions, PCB concentrations are higher in shallow nearshore areas above Thompson Island Dam than in the main channel. The strong concentration differential suggests that the increased PCB concentrations nearshore must arise from nearby sources (e.g., hot spots 15 through 20), thus allowing limited time for lateral mixing. An unintended consequence of the bias study would thus appear to be a demonstration that these hot spots do indeed constitute a significant source of PCBs to the water column. Even if the nearshore concentrations are biased high relative to total load, it is these shallow nearshore concentrations which are most relevant to biological exposure.

1.6 Re-evaluation of Thompson Island Pool Load

Since the release of the DEIR (USEPA, 1997), GE has released corrections for analytical bias in their PCB analyses, and proposed a correction for sampling bias. Revised estimates of load from the TIP need to account for both factors. The re-evaluation below first considers the effect of the analytical bias corrections, without any correction for sampling bias, on the estimates of load gain between the station at Rogers Island and TID-West, then adds the effect of potential sampling bias.

1.6.1 Analytical Bias

GE's recent analytical corrections resulted in a significant increase in the apparent load gain between the Rogers Island (Rt. 197) and the TID-West stations. The older, uncorrected data led to an estimate of approximately 0.56 kg/d load gain across the TIP (USEPA, 1997, Table 3-21); using the corrected data gives an estimate of about 0.82 kg/d over the 1991-1997 period of record. During summer (June–August) of 1996 and 1997 the re-calculated gain from Rogers Island to TID-West after analytical corrections *appears* to have been about 1.26 kg/d. As shown in Figure 1-6, the estimates of load at Rogers Island (River Mile 197) and TID-West (River Mile 188.5) diverge, showing a consistent increase in apparent load between the two sampling stations. Over 90% of this apparent load gain is in mono-, di-, and trichlorobiphenyls, with the largest load gain in dichlorobiphenyls. Note that the load estimates are not corrected for the apparent sampling bias.

1.6.2 Sampling Bias

If the QEA conclusion that the center channel observation is more representative of transport through the Pool is assumed to be correct, and the correction factors developed above are applied, this would still not eliminate the load gain. Instead, the apparent load gain for 1991–1997 (after correction for both analytical and sampling biases) would be a value of about 0.62 as an annual average (note that the value exceeds the DEIR estimate of 0.56 kg/d) by 10 percent. This value assumes the 1991 - 1997 bias correction is based on five years with Rogers Island concentratins greater than 17 ug/L (1991 - 1995) (correction factor = 0.8) and two years with concentrations less than 17 ug/L (1996 - 1997) (concentration factor = 0.64). This yields a correction factor of 0.75. This correction factor assumes that all TIP loads are generated at low flow conditions, thereby yielding maximum correction and minimum estimate of the 0.82 average annual TIP load. It is very important to note that the application of the proposed sample bias correction would still <u>not</u> cancel out the increase in estimated load which resulted from GE's analytical recalculation—and would continue to identify the Thompson Island Pool as a significant source of PCB load.

1.7 Implications of Alleged Sample Bias

QEA (p. 11) states that the DEIR "concluded that PCBs passing the TID during low flow conditions were the major source of PCBs to the freshwater Hudson", and implies that this conclusion is incorrect in light of the sample bias. However, the DEIR did not claim that low flow conditions dominated load or that TIP sediments were dominant source of total PCBs during 1993 observations (USEPA, 1997, pp. 3.90–91):

> ...the GE Hudson Falls source contributes the majority of the PCBs to the water column on an annual basis due to its large contribution during the spring runoff period. The TI Pool source is estimated to be the primary source of PCBs to the water column for 11 months of the year (*i.e.*, the low flow period) and it contributes approximately 32 percent of the annual PCB load.

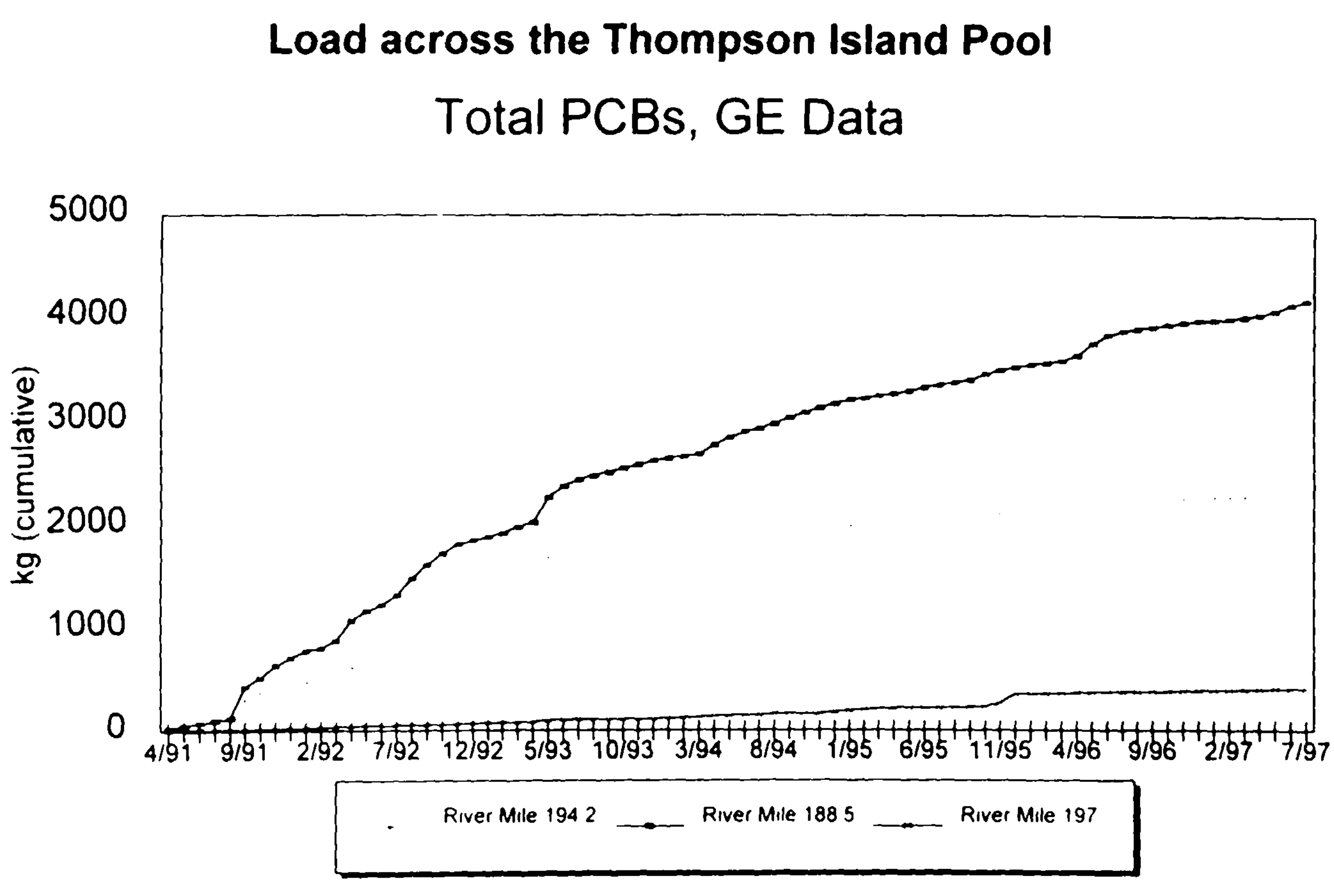

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Figure 1-6. Apparent PCB Load Gain across the Thompson Island Pool using GE Data with Corrections for Analytical Bias Only

The presence of a sampling bias in USEPA Phase 2 data would, however, require a reassessment of the relative percent contribution of TIP loads. If a sample bias correction factor of 0.80 is applied only to low flow load estimates at the Thompson Island Dam, the net effect would be a revision downward of the percent contributed by the TIP in 1993 from 32 percent to approximately 27 percent of total load. The value of 0.8 is used since the Ft. Edward concentration never fell below 17 ng/L during the 1993 sampling events. Because of the high total loads seen in 1993 this still represents a significant PCB loading source. A more accurate estimate of the TIP's contribution is expected from the upcoming Baseline Modeling Report. Nonetheless, it is clear that the load revisions serve to re-emphasize (and not detract from)the importance of the TIP load.

One major topic for which the sample bias would have a major effect is on the estimation of relative loads from the TIP and from downstream segments. This is because the analytical bias corrections apply to all GE measurements, whereas the sample bias correction would apply only to estimates at Thompson Island Dam. This topic is covered in Section 4. The issue of relative loads is also affected by the revised flow estimates discussed in the corrections to Chapter 3.

As to load estimates based on GE data, the net effect of analytical corrections and the suggested corrections for sampling bias result in a higher estimate of total PCB load generation from the TIP relative to that estimated in the DEIR based on the earlier version of the GE data. The apparent sampling bias does not appear to affect the homologue pattern of the TIP load gain, only its magnitude.

2. Signature and Origin of the TIP Load

The composition of water column PCBs attributed to the TIP sediments indicates that relatively undechlorinated PCBs are the principal source and that surface sediment pore water is the principal point of origin. (QEA, 1998, p. 1)

QEA's summary statement is misleading and not strongly supported by the evidence. The statement contains two parts. It is first concluded "*that relatively undechlorinated PCBs are the principal source.*" This is misleading. It is true that the TIP load is *relatively* undechlorinated compared to buried, more highly dechlorinated sediments. However, the load is strongly dechlorinated relative to raw Aroclor 1242, and, indeed, the surface sediments in the TIP on average show significant dechlorination. It is secondly stated "*that surface sediment pore water is the principal point of origin.*" This conclusion is not fully supported by the data; indeed, the congener pattern of the TIP load shows consistent differences relative to the congener composition from surface sediment pore water. Reanalysis of the available data suggest that the TIP load most likely originates from a mixture of pore water flux and resuspension of fine sediment.

2.1 Characteristics of TIP Summer Load and TIP Surface Sediments

GE monitoring of summer water column PCB homologue concentrations from 1991 through 1997 shows a consistent shift in homologue pattern between Rogers Island and Thompson Island Dam (as measured at the TID-West station). In all years monitored, average summer homologue patterns shift from a tri- and tetrachlorobiphenyl dominated pattern at Rogers Island to a mono-, di-, and tri-chlorobiphenyl dominated pattern at TID-West. A similar shift is seen in the Phase 2 data. The significance of the apparent shift in the GE data was strengthened by GE's recent "corrections for analytical biases" (HydroQual, 1997a), and is greater than was reported in the Phase 2 DEIR (USEPA, 1997). Based on data collected in 1997, the pattern shift is also immune to any potential spatial biases in the TID-West versus TIP-18C (center channel) sampling stations.

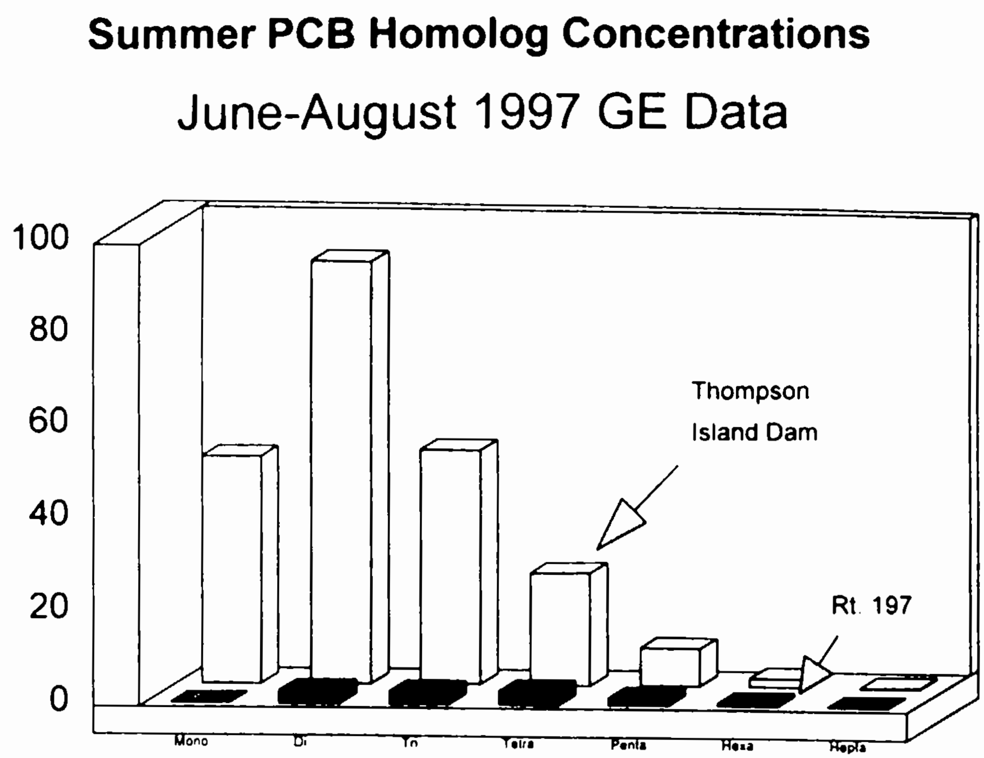
QEA chose to base their analysis on summer 1997 data (June through August), in part because the 1997 data contain observations from both TID-West and TIP-18C, allowing them to choose to use the supposedly unbiased center-channel observations. The choice of summer 1997 data is also fortuitous because upstream loads and concentrations at Rogers Island were very low during this period, enabling a more direct interpretation of the TIP signal. Homologue patterns at Rogers Island (Rt. 197) and TID-West (Thompson Island Dam) during summer 1997 are shown in Figure 2-1, and show the usual strong shift to a mono-, di-, tri-chlorobiphenyl dominated pattern.

A more informative comparison can be made by examining the relative percent composition of a set of key congeners. For this and subsequent analyses the following GE/NEA capillary column peaks and associated congeners were chosen for comparison because (1) they are environmentally significant, and (2) three-phase partition coefficient estimates are available. For each peak the congener of most environmental significance in upper Hudson River sediments is listed first.

Table 2-1. NEA Peaks and Associated Congeners Used in Pattern Analysis

NEA Peak	Homologue Group	Congeners
Peak 2	Monochlorobiphenyl	BZ #1
Peak 5	Dichlorobiphenyl	BZ#4, BZ#10
Peak 8	Dichlorobiphenyl	BZ#8, BZ#5
Peak 14	Di/Trichlorobiphenyl	BZ#15, BZ#18
Peak 24	Tri/Tetrachlorobiphenyl	BZ#28, BZ#50
Peak 23	Trichlorobiphenyl	BZ#31
Peak 37	Tetra/Pentachlorobiphenyl	BZ#44, BZ#104
Peak 31	Tetrachlorobiphenyl	BZ#52, BZ#73
Peak 47	Tetrachlorobiphenyl	BZ#70, BZ#76, BZ#61
Peak 48	Penta/Tetrachlorobiphenyl	BZ#95, BZ#66, BZ#93
Peak 53	Pentachlorobiphenyl	BZ#101, BZ#90
Peak 69	Penta/Hexachlorobiphenyl	BZ#118, BZ#149, BZ#106
Peak 82	Hexachlorobiphenyl	BZ#138, BZ#163
Peak 75	Hexachlorobiphenyl	BZ#153

Across this set of peaks, the congener pattern at the TID is remarkably similar during summer 1997 whether we examine raw concentrations at TID-West, concentrations at the "unbiased" center



TetraTech/TAMS

Figure 2-1. PCB Homologue Shift Across the TIP, Summer 1997 channel station TIP-18C. the difference in concentration between Rogers Island and TIP-18C (TIPC-Gain), or the concentration at TID-West normalized to solids concentration (Figure 2-2). The pattern, however, is distinctly different from that of unaltered Aroclor 1242 (based on Aquatec analyses). The similarity between the different water column measures, when evaluated as relative percentages, coupled with the near lack of upstream load, removes a number of confounding issues (such as whether the TIP represents a net addition or a replacement of the upstream load) and greatly simplifies the analysis.

Measures of congener concentration in the TIP sediments are also available in a number of variations. Figure 2-3 compares, for the selected GE peaks, the congener pattern found in the surface 0–2 cm layer of Phase 2 cores 18, 19, and 20 (analyzed as sum of quantitated congeners associated with each GE/NEA peak); the pattern found in the top 0–5 cm layer of the GE 1991 composite sediment samples; and, as an example of a more extensively dechlorinated pattern, the 8–12 cm layer of Phase 2 core 18. The unweathered Aroclor 1242 pattern is also shown in this figure.

In this figure, the patterns in the Phase 2 and GE surface sediments are similar, except that the relative contribution of BZ#4+BZ#10 appears elevated in the GE results. This probably reflects the much more extensive spatial coverage of the 1991 GE data, plus potential re-contamination of surface sediments prior to the collection of Phase 2 cores in fall 1992 (see Section 5.4). The 8–12 cm layer of Core 18 is clearly more dechlorinated, as shown by the depletion of BZ#5+BZ#8, BZ#15+BZ#18, and BZ#28 relative to BZ#1 and BZ#4+BZ#10. More noticeable, however, is the fact that all the sediment patterns appear to be significantly dechlorinated relative to unweathered Aroclor 1242.

2.2 QEA Analysis of Sediment Source

QEA undertook a modeling approach to estimate the characteristics of a sediment which would result in the observed PCB gain across the TIP. The results of this analysis, although credible, are largely determined by the initial assumptions, which are not fully constrained by available data. Further, although this is stated to be a "Final Report", the modeling which is presented is preliminary and clearly in the process of further development.

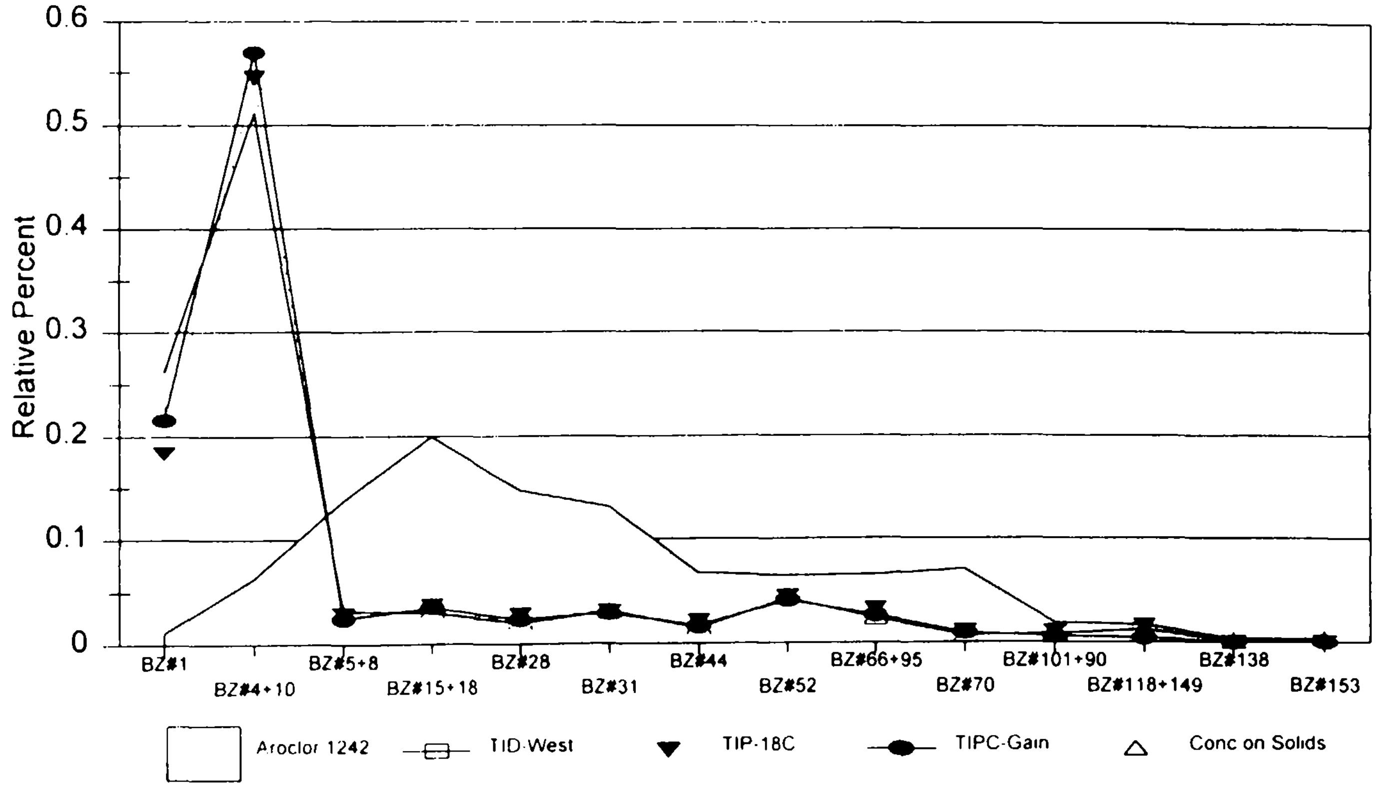
2.2.1 Modeling Framework

It is not the intention of this review to provide a detailed critique or commentary on GE's evolving PCB modeling framework. This modeling framework is still under development, and is not fully documented in QEA's (1998) report. Brief comments are, however, appropriate related to the ability of the modeling framework to represent and assess sources of PCB load.

The modeling framework consists of four linked components: hydrodynamic models, sediment transport models, PCB fate models, and PCB bioaccumulation models. Of these, the bioaccumulation component is not relevant to the topics of this review. The other three components are summarized below.

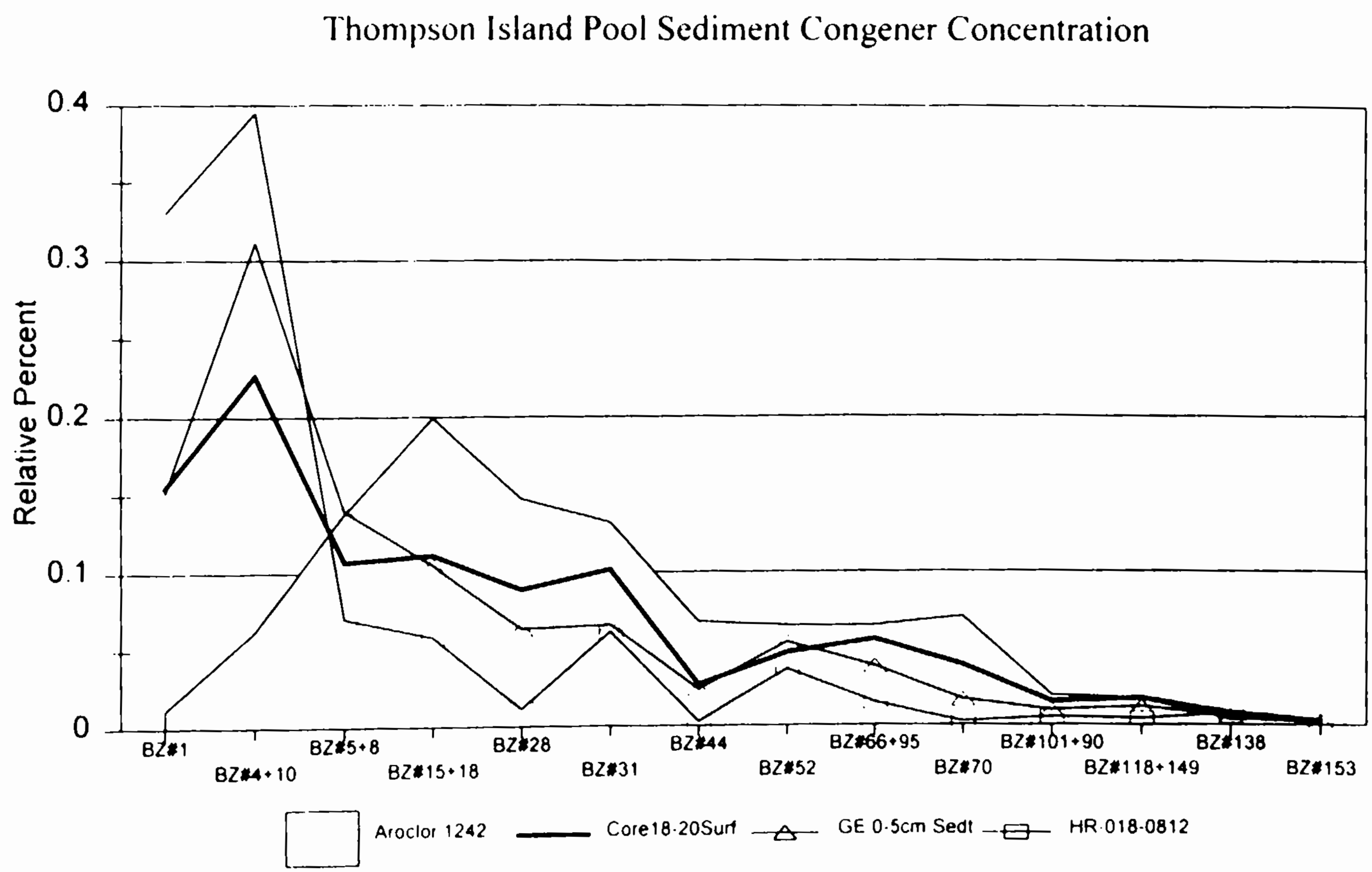
To represent hydrodynamics in the upper Hudson River, QEA has developed two separate models: A finely-segmented two-dimensional vertically-integrated model which is used to estimate

Summer 1997 Water Column Concentrations



TetraTech/TAMS

Figure 2-2. Summer 1997 Water Column Relative PCB Congener Concentrations near the Thompson Island Dam Compared to Aroclor 1242



TetraTech/TAMS

Figure 2-3. Congener Pattern in TIP Sediment Compared to Aroclor 1242

shear stress at the sediment-water interface, and a simpler one-dimensional model designed to drive long-term PCB fate simulations.

Sediment resuspension, deposition, and transport is also addressed by two separate model components, one for cohesive sediment and one for non-cohesive sediment. There are two significant limitations to the sediment component of the model, as currently configured, which may limit its usefulness as a tool to evaluate the Thompson Island Pool PCB load. First, the model used for the report does not consider resuspension of non-cohesive sediment, which constitutes a majority of the surface area in the TIP. Preliminary results developed for USEPA (LTI, 1996) indicate, as we would generally expect, that the non-cohesive sediments are subject to greater shear stress and, potentially, greater amounts of erosion and potential loading of PCBs to the water column than the relatively stable cohesive sediment areas.

A second limitation of the QEA approach to sediment modeling is that hydrodynamic shear stress is the only mechanism considered for mobilization of cohesive sediments. Given the low rates of predicted resuspension from shear stress acting on cohesive sediment surfaces, other mechanisms may be more important in mobilizing or freeing sediment mass from cohesive areas. Mechanisms that might cause large-scale disturbances of cohesive sediment beds include destabilization of undercut areas adjacent to the canal channel; mechanical abrasion by bedload and other debris; and ice scour at spring ice breakup. Other localized, non-hydrodynamic scour disturbances which may introduce sediment into the water column from cohesive sediment areas include: bioturbation by benthic organisms, bioturbation by demersal fish, mechanical scour by boats (prop wash) and floating debris in shallow/nearshore areas, and uprooting of macrophytes by flow, ice, wind, or biological action.

QEA's PCB fate and transport model is generally similar to the approach used by USEPA: It considers three-phase partitioning (water, POC, DOC) and models PCB transport from the sediment to water column via diffusion, advective seepage, and sediment resuspension. It should be noted that the QEA approach contains only a weak and indirect linkage between the PCB model and the hydrodynamic and sediment models. Typically, calibration constraints are placed on the solids and PCB models simultaneously, a process made much mre difficult by weak linkage. Additionally, sediment resuspension is used by the PCB model only on a reach-averaged basis (QEA, 1998, p. 18): "The calibrated sediment transport model was used to generate a relationship between the mass of sediment resuspended and flow rate for each of the eight reaches from Fort Edward to the Troy Dam. These relationships were then used in the PCB fate model to determine erosion rate in each model segment for a specified flow rate." It is not stated how non-cohesive sediment scour or bedload movement were accounted for in these relationships. Further, QEA has emphasized the importance of lateral variations in flow velocity and hence shear stress, but any lateral variability represented in their sediment transport model is essentially lost when the results are laterally averaged within each reach. Applying a reach average sediment flux to a reach average PCB concentration will yield incorrect results, as the highest PCB concentrations are found in depositional areas which, by definition, tend to experience lower shear stress.

Diffusive flux is similarly spatially aggregated across model reaches (p. A-9): "...the diffusive loading equation can be used with area-weighted averages for organic carbon normalized PCB concentrations to calculate the net TIP flux." This spatial aggregation implies that the model is only appropriate for making inferences about net fluxes at the reach scale, and should not be used to make inferences about loading patterns within a model reach. Further, the approach of applying a reach-average flux rate (of sediment or pore water) to a reach-average PCB concentration is likely to yield biased estimates of loading if there is any correlation between PCB concentration and rate of sediment or pore water flux. It is important to note that the model calculates resuspension from cohesive sediments only, but surface concentration averages are apparently obtained over the whole Thompson Island Pool. As PCB concentrations are likely to be higher in fine-grained cohesive sediments, use of the average concentration with a sediment flux rate from cohesive sediments will underestimate the total PCB flux by cohesive sediment erosion.

2.2.2 Model Calibration

The hydrodynamic model was calibrated to observations of 28–29 November, 1990, at which time the flow at Fort Edward was steady at around 7,860 cfs. A validation test was performed using data from the May 1983 flood, with a peak flow at Fort Edward of 34,100 cfs, using stage heights reported at Champlain Canal staff gauges. (These were the same data used for calibration of a one-dimensional hydrodynamic model in USEPA's Phase I effort (USEPA, 1991)). The hydrodynamic calibration provides a reasonable fit, but is only matched to water surface elevation at two locations. True calibration of hydrodynamics should include comparison to stage and velocity at multiple stations. QEA emphasizes lateral variability in flow velocity in their interpretations of model results, but provides no information to show that this lateral variability is correctly represented in the model.

For the sediment model, QEA presents only a calibration to April 1982 USGS data, with no validation results. This is not a very satisfactory data set for calibration because data are not available on the loads from many tributaries, nor are data available from the TIP or below Thompson Island Dam. In addition, only limited information is available on size class distributions during this event. Neither the basis for assigning particle size classes to tributary loads nor the assumed settling velocities are adequately documented. The sediment model described by QEA addresses erosion of cohesive sediment only, yet the calibration data would include scour from both cohesive and non-cohesive sediments. Model results appear to underpredict, by about one-third, peak suspended solids concentrations at Waterford, while concentrations at Stillwater were also underpredicted by a small, but consistent amount. QEA suggests that the under prediction "is likely due to an underestimation of solids loading from the Hoosic River", and states, without providing details, that "More recent calibrations of the sediment transport model using new tributary solids loading data confirm this assessment of the preliminary model calibration." Note that calibration with incorrectly specified tributary solids loads may lead to an incorrect estimate of the rate of resuspension of sediment within the river. It is not clear why calibration/validation to more detailed solids data collected by USEPA in the Phase 2 effort or to the 1991 Thompson Island Pool suspended solids data collected by GE (O'Brien & Gere, 1993b) are not presented.

The PCB model was applied for long term simulation over the period 1977 to 1996. The approach taken here is cause for considerable concern. First, the state variable was taken as total PCBs, and assigned a single partition coefficient to organic carbon (in a three phase model) of 40,000 L/kg (log K_{OC} = 5.4), based on analysis of total PCB data in the Phase 2 data collection. The same value was assumed for partitioning in both the water column and sediment. In fact, PCB congeners show a wide range of partitioning behavior. Estimates of log(K_{POC}) in the water column for a subset of 15 congeners range from 5.19 (BZ#4) to 6.55 (BZ#151) (*i.e.*, more than an factor of 20). An estimate obtained for total PCBs from the Phase 2 data will be strongly weighted to the partitioning behavior of mono-, di-, and tri-chlorobiphenyls, which dominate water column concentrations in the TIP and downstream. This would not present a major problem as long as the congener composition remained relatively constant in space and time. Observations from the 1990's show, however, that there is a strong shift in congener pattern across the Thompson Island Pool under low flow conditions, with the mono- and di-chlorobiphenyl components largely absent at Rogers Island. Modeling total PCBs with a single partition coefficient will reduce accuracy of the model in predicting PCB fate and transport across the Thompson Island Pool. The major source of error would come from lumping mono- and dichlorobiphenyls, which generally show weaker partitioning, with more highly chlorinated homologues. The approach proposed by USEPA of modeling the sum of tri- and higher-chlorinated homologues, instead of the sum of all congeners, is both more consistent with historical analytical methods and reduces the influence of variability in partitioning behavior among congeners. There is also a strong possibility that congener patterns have changed over time, although little or no data to resolve this issue are available for the earlier time periods.

Application of the same partition coefficients to water column particulates and the sediment matrix is also questionable, as the physical availability of binding sites may be very different within a compacted sediment. As presented in Section 2.3, the effective K_{OC} for the lightest congeners (BZ#1, BZ#4+10) may be significantly lower in the sediment than in the water column.

For K_{DOC}, QEA assumed a value equal to 10 percent of K_{OC}. This is supposedly based on analysis of the 1991 field data for Hudson River sediment (O'Brien & Gere, 1993a). Our reanalysis of the sediment data (Section 2.3) suggest that K_{DOC} may be, on average, somewhat less than 10 percent of K_{OC}. Once again, effective partitioning appears to differ in the water column and sediment. Analysis of the Phase 2 water column data (USEPA, 1997, Table 3-8) suggested that K_{DOC} values for BZ#1, 4, and 8 were greater than 30% of K_{POC}. Burgess *et al.* (1996) have also reported that sediment K_{OC} and K_{DOC} values generally differ by less than a factor of 10 in New Bedford Harbor sediments.

PCB volatilization is stated to be based on the O'Connor-Dobbins reaeration equation (QEA, 1998, pp. 18-19), but a constant mass transfer coefficient is documented (100 m/d) and indicated by equation (A-8). If the O'Connor-Dobbins method was used, the mass transfer coefficient should be a function of flow, instead of a constant.

The QEA PCB transport model runs from Fort Edward to Waterford. Predictions of the model are strongly determined by assumptions regarding initial sediment and upstream boundary conditions. Prior to the start of intensive monitoring in 1991, determination of upstream boundary loads presents a significant problem, as only sparse USGS total PCB measurements are available. QEA approached this problem by estimating "a correlation of PCB concentration with flow at Fort Edward based upon USGS data." Daily PCB concentrations are then estimated based on flows. The exact form of the "correlation" is not documented, although earlier authors (e.g., Turk and Troutman, 1981) have suggested a bimodal relationship to flow, with PCB concentration peaks at both high and low flows. Information presented in the Phase I report (USEPA, 1991, Figure B.4-12) demonstrates, however, that there is little if any direct correlation between flow and PCB concentration at the Fort Edward station, although a slightly stronger multivariate relationship can be established by (1) stratifying observations into high and low flow periods, and (2) including a declining trend with time in the model. Use of such an approach to "reconstruct" a surrogate series of daily PCB concentrations is likely to miss the point for long term modeling, however. What the long term model really needs is an accurate representation of upstream seasonal mass loading, not daily concentrations. It would therefore appear advisable to establish the upstream boundary condition by forming a best estimate of PCB mass load (see USEPA, 1997, Section 3.3.5), then apportioning this load based on the flow volume over a time-scale that is appropriate to the mass balance model application.

An additional problem in using the USGS data is that what was measured is not equivalent to total PCBs determined by modern capillary column methods, resulting in a disjunction between model input data coincident with the start of the GE monitoring effort in 1991. Instead, the packed column results appear to approximate the sum of tri- and higher-chlorinated PCB homologues. NEA conducted split sample experiments to compare the USGS packed column method results (based on the description in Schroeder and Barnes, 1983) to capillary column analyses, using individual or mixed standards composed of Aroclor 1242, 1254, and 1221. A regression of split sample results for USGS-method total PCBs on the capillary column sum of tri- and higher-chlorinated homologues results in a good linear fit, with an intercept not significantly different from zero and a slope not significantly different from one. Thus the USGS packed-column results can be used as a measure of the tri- and higher-chlorinated sum, but not as a measure of total PCBs.

The USGS laboratory switched to a capillary column analysis beginning in November 1987 (personal communication from Ken Pearsall, USGS/Troy, based on letter received from Brooke Connor at USGS Denver laboratory). USGS capillary column results are also believed to approximate the sum of tri- and higher-chlorinated PCB homologues, rather than total PCBs, although this issue is still under investigation by QEA and TAMS.

QEA (1998, p. 20) recognizes the issue of "analytical bias" in the USGS monitoring data, but has not incorporated any correction into their modeling effort. The resulting discontinuity in the upstream boundary condition associated with the switch to GE capillary column results in 1991 suggests the existing calibration of the PCB model should be regarded with a high degree of scepticism.

QEA does not present any attempt to match the PCB model predictions to water column observations. Instead, their "calibration" of the long-term PCB model is based on matching "observed surface sediment (0-5 cm) PCB concentrations in TIP and downstream in the vicinity of Schuylerville, Stillwater, and Waterford." Data for 1991 are available for each of these locations (O'Brien & Gere, 1993a). Relatively sparse data for the whole upper Hudson were also collected in 1977 (O'Brien & Gere, 1978). Finally, detailed sediment sampling for 1984 is available from the Thompson Island Pool only (Brown *et al.*, 1988). The result is that three separate sediment sampling events are available for "calibration" in the Thompson Island Pool, while only two are available for each of Schuylerville, Stillwater, and Waterford. It is not hard to fit a curve through two points, but it is difficult to guarantee that the fit represents a realistic and unique interpretation of the data. To obtain the results presented in the report, QEA also found it necessary to add "an empirically defined, exponentially decreasing load...to the TIP in the period between 1977 and 1983."

Similar to the water column data, additional problems are occasioned by the fact that total PCB measurements by the methods used in 1977, 1984, and 1991 are not equivalent. The 1991 sediment data (O'Brien & Gere, 1993a) were analyzed by modern capillary column methods and represent an estimate of the sum of all PCB congeners for an 0-5 cm depth. The 1977 and 1984 analyses generally do not have a 5 cm slice. Indeed, in the 1984 analyses the "surface" core section has an average length of about 10 inches, and concentration in the top 5 cm can only be guessed at. The 1977 and 1984 analyses were also by packed column methods which are believed to miss most mono- and di-chlorobiphenyls. Our analysis of the 1984 sediment data suggests that these results approximate the sum of tri- and higher-chlorinated congeners (representing on average 93.4% of this sum). The 1977 sediment data are also suspected to approximate a sum of tri- and higher-chlorinated congeners, but may have a small upward bias relative to the 1984 results due to the use of an Aroclor 1016 standard rather than an Aroclor 1242 standard. The 1977 sediment data also serve as initial conditions for sediment in the model. Unfortunately, surviving documentation of this analytical effort does not appear to be sufficient to definitively establish exactly what was measured in 1977.

QEA also compared its model predictions to estimates of annual PCB load derived from the USGS data for 1977–1991, and imply a general agreement, although QEA's predicted loads at Waterford are overestimated in the early 1980's, and loads from 1983 through 1991 show only limited variability. QEA's estimates of annual loads, however, appear to differ significantly from those presented in the DEIR (USEPA, 1997, Table 3-23). For instance, the QEA estimate of 1983 calendar year loading is about 2300 lbs, while the Phase 2 estimate is about 3200 lbs. QEA does not document how their annual mass load estimates were obtained for Figure 3-7; however, the method was presumably that described on p. 27 for estimation of load across the TIP. This method calculates annual loads based on the average daily load in observations. As demonstrated by Preston *et al.* (1991), this is not an advisable approach to estimating annual loads from sparse data. The problem is that load is typically correlated with flow (even if concentration is not). Therefore, if the available data do not constitute an unbiased sample of annual flows calculating annual load from observed daily loads will result in a biased estimate. Estimators which take into account the relationship between loads and flows usually provide better results. As documented in the DEIR (USEPA, 1997, pp. 3-132 through 3-133) a stratified version of a ratio estimator of annual loads (Cochran, 1977) appears to be a good choice for PCBs in the Hudson, while a seasonal averaging method (Dolan *et al.*, 1981) can be used as a check.

QEA also compared its PCB model predictions to weekly water column monitoring at the Thompson Island Dam and found that the model underpredicted observed loads by 300 to 500 percent. Apparently, the Thompson Island Dam estimates were not corrected for the presumed sampling bias at the TID-West station, but this would appear likely to account for only a small portion of the under-prediction, because the correction factor is no more than 20 percent (0.8) for the period prior to 1996.

The net result of these data issues is that neither the upstream boundary conditions, the sediment initial conditions, nor the calibration targets are correctly specified in the existing QEA PCB model. Further, the model calibration was not successfully validated against recent Thompson Island Dam loads. It thus appears that the existing QEA PCB model should be considered an incomplete experimental tool, and should not be used to test quantitative hypotheses regarding PCB load from the Thompson Island Pool or other areas of the Hudson River.

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2.2.3 Depletion Rate of TIP PCB Inventory

QEA (1998, Section 4.1.1) uses mass balance calculations to "test the hypothesis that the anomalous PCB loading could be attributed to sediment surface PCB transport processes", and concludes that "the PCB loadings observed from the TIP between 1993 and 1996 cannot be representative of long-term surface sediment-water exchange processes" because they would result in rapid depletion of the observed mass of monochlorobiphenyls (by 1995), dichlorobiphenyls (by 1996), and trichlorobiphenyls (by 2000). The analysis does not depend on the long-term PCB mass transport model, but rather is based on simple mass balance calculations. Flux rates of PCB homologues from TIP sediments were calculated from GE monitoring and compared to estimated 1984 surface layer concentrations to estimate time to depletion.

This analysis is flawed on a number of grounds, and should not be regarded seriously. Key issues include the following:

1. The estimates of load generation from the TIP are based on uncorrected TID-West concentration observations. According to QEA, these estimates are biased high, and the estimates of TIP load generation, and rate of depletion, should be correspondingly lower. In fact, it is likely that the actual loads are higher than those estimated by QEA, as discussed in Section 1.

2. The analysis assumes that the monochlorobiphenyl and dichlorobiphenyl fractions of the 1984 sediment inventory may be estimated by application of the observed fraction in USEPA 1994 data to the 1984 total PCB estimate. In fact, as noted above, the 1984 quantitations substantially do not account for the mono- and dichlorobiphenyl fractions, and instead provide an approximation of the sum of tri- and higher-chlorinated homologues. No evidence is available as to the inventory of monochlorobiphenyls and dichlorobiphenyls in 1984. Further, assuming that part of the 1984 inventory consists of monochlorobiphenyls and dichlorobiphenyls results in an under-estimation of the surface sediment inventory of higher-chlorinated congeners.

3. The analysis assumes that there is no replenishment of surface sediment PCB homologue inventories. In fact, diffusion and pore water advection would both move dissolved and DOC-bound PCBs into surface sediment from deeper, more highly contaminated sediment reservoirs (see Section 2.3.3). Further, no accounting is made for erosive and mass wasting processes which may mechanically move buried PCBs to the surface, particularly in unstable non-cohesive sediments. Finally, there is some evidence suggesting replenishment of surface sediment inventories by the Bakers Falls source during the early 1990's (see Section 5.4).

4. Estimates of loading are based on an average of observed loads. As noted in the previous section, this is not an appropriate method for estimating annual loads from sparse point-in-time data, and may result in significantly biased estimates of load.

In sum, the analysis of depletion rates is not supported by the data, and does not represent a constraint on possible mechanisms of PCB load generation within the TIP.

2.2.4 Analysis of Ground Water Seepage Flux

In Section 4.1.2, QEA provides an analysis of PCB loading by ground water seepage (advective) flux, and concludes that this represents an insignificant source of PCB loading to the TIP. This analysis also is flawed and cannot be used to draw firm conclusions.

The analysis presented by QEA involves estimation of an average seepage rate, and application of this rate to mean surficial pore water PCB concentrations calculated from total PCB concentrations in the 0-5 cm layer in 1991 (O'Brien & Gere, 1993a) by application of equilibrium partitioning assumptions. A single K_{OC} estimate of $10^{5.4}$ L/kg was applied to total PCBs, and K_{DOC} was assumed equal to 10% of K_{OC}, which may result in inaccurate predictions, as described above in Section 2.2.2. The seepage rate was estimated as 0.04 L/m^2-hr, and the estimated seepage flux was 11 kg/yr total PCBs (0.03 kg/d). However, analysis on a congener basis, with congener-specific partition coefficients, would likely result in a greater estimate of ground water seepage flux. As a check on QEA's rough estimates, the seepage rate can also be applied directly to pore water concentrations observed in 1991. This provides a similar order of magnitude estimate of 6.4 kg/yr. It thus appears that seepage advection could not be an important PCB loading source, *if* the assumptions used by QEA are appropriate.

QEA's analysis of seepage rate is based on observations obtained from two replicate seepage meters deployed at five locations within the TIP and one location downstream in May–June, 1997. Such seepage meters have been used with considerable success in lake environments. Their use to draw inferences within riverine environments is, however, fraught with difficulty. It is well known that sediment texture within the TIP is highly heterogeneous, while the sediment is underlain by fractured rock. In such circumstances, ground water seepage can be expected to flow via preferential, localized pathways. Deployment of seepage meters at five locations is likely to miss these preferential outlets, and thus underestimate total seepage rate. This is one of the reasons that USEPA decided against deploying seepage meters during the Phase 2 sampling effort. In addition, the seepage meter results were highly variable, and apparently subject to large uncertainties. A better estimate of total gain from ground water flow across the Thompson Island Pool could be obtained from careful monitoring of flow in the mainstem and tributaries. In addition, localized seepage outlet springs or boils could provide a mechanism for resuspension of fine sediment during quiescent low flow conditions.

A focus on ground water seepage may also miss important components of advective loading from sediment, including interflow and drainage of exposed nearshore sediments. Interflow refers to the fact that a portion of the total flow in a river may proceed through lateral flow within permeable surface sediments. This could provide a mechanism for PCB advection from non-cohesive sediments, but is unlikely to be significant in clays or other cohesive sediments. In nearshore sediments there is a seasonal cycle of saturation and drainage, in which spring high stages pump water into the sediment, which is subsequently drained, by both surface and subsurface pathways, as stage recedes. Unfortunately, the PCB inventory in shallow nearshore areas is very poorly characterized due to limitations on boat accessibility.

In fact, empirical evidence suggests that advective flux may constitute a significant portion of PCB loading within the TIP. During every year from 1991 through 1997, GE data suggest that the rate of PCB load gain across the TIP declines from early to late summer. Because the hydraulic gradient between near-river ground water and the river also typically declines across this time period, one possible explanation is that the seasonal decline in PCB gain is attributable to seasonal variations in advective flux.

Figure 2-4 shows the average loads and concentrations of monochlorobiphenyls observed at the TID-West station from 1991 through 1997. Monochlorobiphenyls were selected because loads of this homologue group appear to arise almost entirely within the TIP, avoiding the difficulty of calculating gain. Concentration peaks after the spring high flows, then declines across the summer months. Monochlorobiphenyl load peaks during the spring flow, but also shows a similar decline across the summer. Such a pattern would be consistent with a significant advective flux, which would be highest immediately after spring flows and would decline over the summer. A second peak is seen in the early fall, which is a period in which flows typically increase, and might be associated with flushing of PCBs out of senescent macrophyte beds and other nearshore areas.

2.3 Reanalysis of Thompson Island Pool Sediment Source Congener Signature

A reanalysis of the potential characteristics of a sediment source to account for the summer 1997 TIP load was undertaken for this review. This reanalysis used three-phase partitioning in the sediment, based on *in situ* partition coefficient estimates obtained from the GE 1991 data (O'Brien & Gere, 1993a). Because of the analytical corrections made to the GE congener data in mid-1997 (HydroQual, 1997a), the three phase sediment partition coefficient estimates reported in the DEIR (USEPA, 1997) are no longer valid, and were re-estimated for this work. Three different methods of fitting these coefficients were used in the DEIR. For application to the TIP sediment pattern matching it appeared desirable to use estimates obtained by a consistent method. Accordingly, optimization method 3 (USEPA, 1997) was applied for all congeners (conditional optimization based on estimated two-phase $K_{OC,a}$). The resulting estimates are shown in Table 2-2. As has been noted previously, three-phase sediment partition coefficient estimates from the GE data are highly uncertain, due to problems with the sample handling and compositing procedures. It is believed, however, that the estimates of *in situ* partitioning provide the best available basis for attempting to match water column concentrations to sediment.

These partition coefficients can be used to estimate absolute and relative concentrations of congeners in pore water given a total sediment concentration. They also may be used to back-calculate a total sediment concentration from water column gain, given assumptions about the transfer mechanism from sediment to the water column. Results are presented below for (1) source originating from pore water, and (2) source originating from a mix of pore water and bulk sediment transfer to the water column.

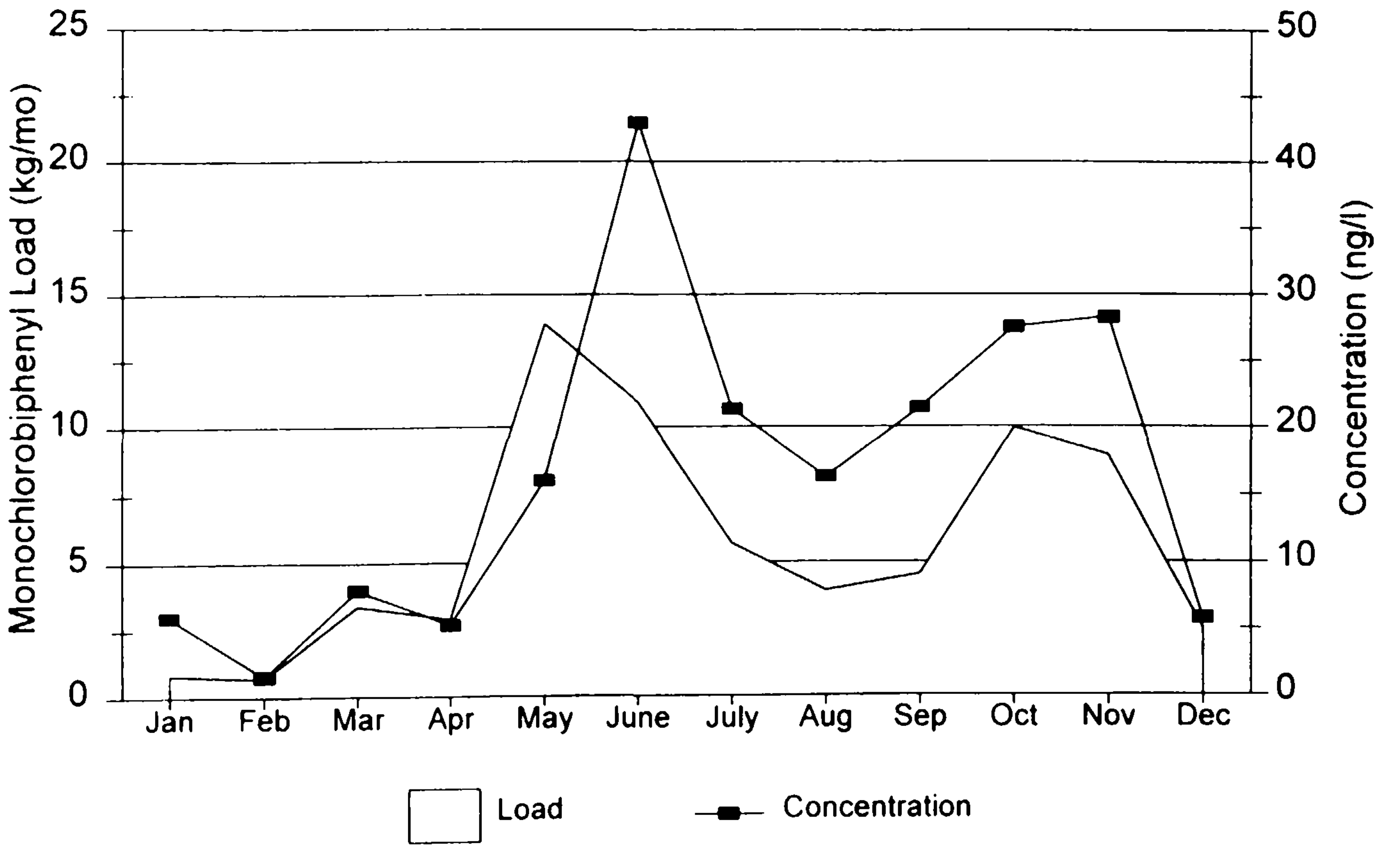

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Figure 2-4. Average Monthly Load and Concentration of Monochlorobiphenyls at the TID-West Station, 1991–1997

2.3.1 Pore Water Source

QEA has focused on diffusive transfer from sediment pore water as the main source of PCB loading from TIP sediments. Using the partition coefficient approach and pattern matching, the case of a pure pore water source, whether loaded to the water column via diffusion or advection, is readily examined.

At first glance, the relative concentration gain measured at TIP-18C looks quite similar to the relative concentrations in surface sediment pore water (Figure 2-5). The apparent agreement is, however, largely due to the fact that both patterns are dominated by BZ#4+10. For other congeners, there is much less agreement, as there is a substantially higher proportion of BZ#1 in pore water than in surface water, while the more highly chlorinated congeners have a relative percent of 21% in the TIP-18C gain, but only 5% in pore water. Further, the tetra- and higher-chlorinated congeners show a pattern which looks more like sediment than pore water.

As noted above, congener concentration in pore water consists of both a truly-dissolved and a DOC-complexed phase. Together these represent the *apparent* dissolved phase, denoted $C_{PW,a}$. For a pure pore water source, the congener pattern in the water column should be equivalent to the pattern in $C_{PW,a}$. Equation (3-29) in the DEIR (USEPA, 1997) states the equilibrium relationship between $C_{PW,a}$ and the particulate concentration, C_P—which is a close approximation to the total concentration within the sediment matrix:

Table 2-2. Revised Three-Phase Partition Coefficient Estimates for PCBs in Sediment in the Freshwater Portion of the Hudson River

PCB Congeners (BZ#)	log K_{OC} (L/kg)	log K_{DOC} (L/kg)
1	4.46	3.63
4+10	4.73	3.60
5+8	5.78	4.03
15+18	5.95	4.23
22+51	6.14	4.48
28+50	6.49	4.36
31	6.17	4.33
44+104	6.98	5.78
52+73	5.98	4.32
66+93+95	6.09	4.53
61+70+76	6.01	4.10
101+90	5.98	4.68
118+149+106	6.10	4.91
138+163	6.31	5.12
153	6.28	5.25

$$C_P = \frac{f_{OC}\, K_{OC}\, C_{PW,a}}{\theta\left(1 + m_{DOC} K_{DOC}\right)}$$

where

f_{OC} is the fraction of organic carbon in the solid phase;
K_{OC} is the partition coefficient to organic carbon;
θ is the saturated porosity, or volume of water per volume of wet sediment,
m_{DOC} is the mass of DOC per volume of pore water; and
K_{DOC} is the partition coefficient to dissolved organic carbon.

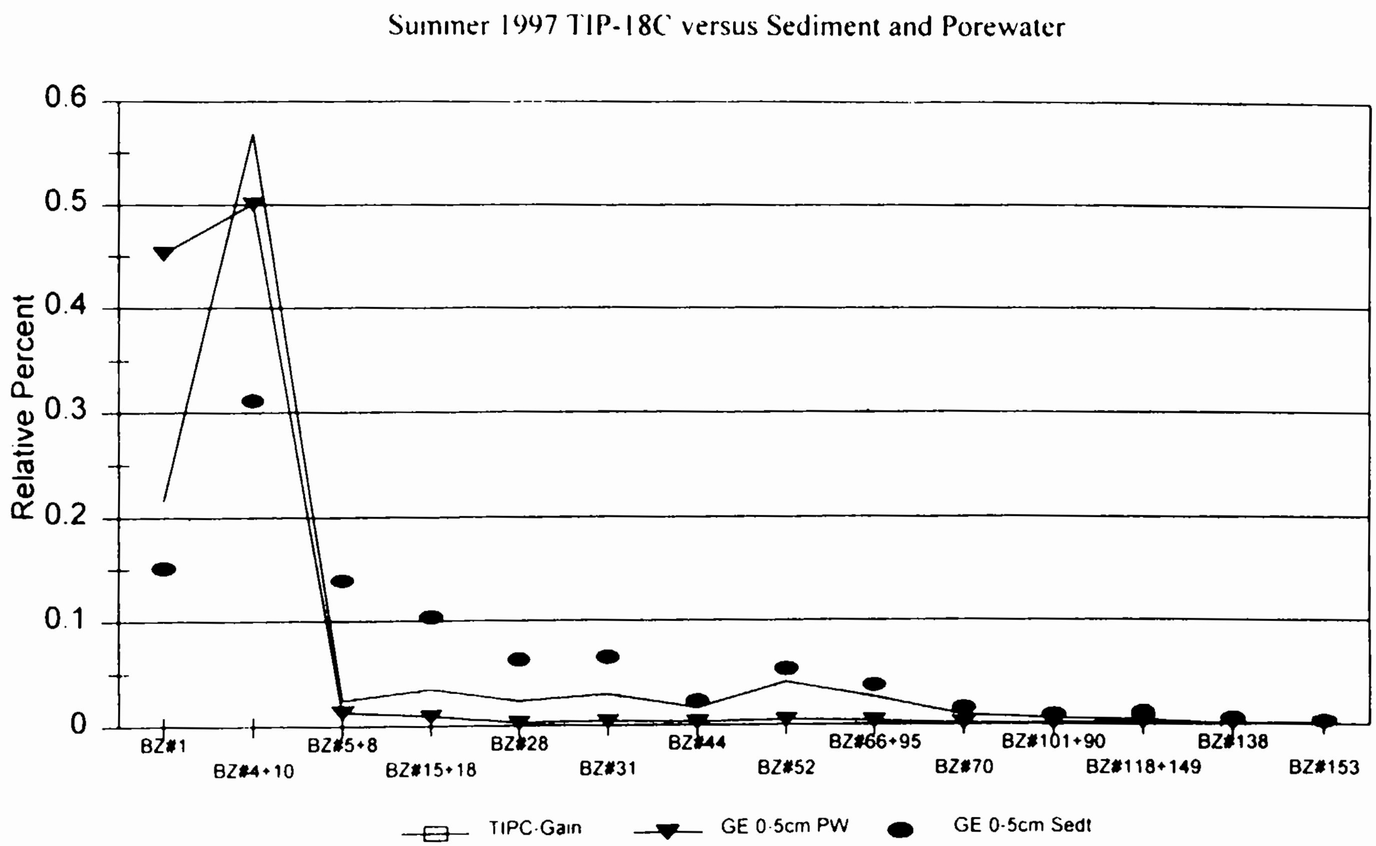

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Figure 2-5. Relative Percent Patterns in Water Column Gain at TIP-18C, Surface Sediment, and Surface Sediment Pore Water

This equation may be used to calculate a congener pattern in a sediment source given a congener pattern in the assumed pore water flux to surface water. To apply the equation. physical characteristics for the sediment are assumed to the average from 0–5 cm sections within the Thompson Island Pool (Reach 8) in the 1991 GE sediment data (O'Brien & Gere, 1993a), as shown in Table 2-3.

Table 2-3. Physical Characteristics Assumed for TIP Surface Sediments

θ (unitless)	0.386
f_{OC} (unitless)	0.01788
m_{DOC} (mg/L)	33.68

Figure 2-6 shows the congener pattern for sediment concentrations driving a pore water source, as computed from the gain in concentration at TIP-18C in summer 1997, and compares this pattern to the pattern found in the 0–2 cm layer in Phase 2 Cores 18–20 and unweathered Aroclor 1242.

The computed sediment concentration pattern appears to be quite different from that seen in the 0–2 cm layer of Phase 2 cores 18–20 (and the difference is greater when compared to the 0–5 cm layer of 1991 GE cores from the Thompson Island Pool). While there are some similarities in pattern, BZ#52 and BZ#28 appear to be elevated in the water column relative to the derived sediment pattern, while BZ#1 through BZ#10 are depressed. The relative importance of these congeners, which tend to have lower partition coefficients and a greater concentration in the water phase relative to sediment phase, is lowered by the fact that large sediment concentrations of congeners above BZ#28 are required to account for the water column gain by a purely pore water mechanism.

As noted above, during summer 1997 there is little difference in congener pattern (despite absolute differences in concentration) between observations at TID-West, TIP-18C, and the gain at TIP-18C relative to Rogers Island. As a result, the derived sediment concentration is similar regardless of which measurement is used as a basis for the analysis (Figure 2-7).

In sum, the available evidence contained in congener patterns does not appear to support a theory of pore water flux (either diffusion or advection) as the sole source of PCB load gain in the TIP–unless the congener pattern is strongly shifted in the water column by some unspecified mechanism. Clearly, pore water constitutes part of the source of PCBs to the TIP, but apparently not the only source. It also does not appear that unweathered Aroclor 1242 makes up the missing part of the source.

2.3.2 Alternative: Mixed Pore Water and Bulk Sediment Loading

During a typical summer period there appears to be insufficient shear stress at the sediment-water interface to scour significant quantities of PCB-contaminated sediment. Lack of significant erosion of pool sediments during summer is also consistent with observed solids concentrations. Nonetheless, the congener pattern observed in the water column is consistent with a source partially composed of PCBs on bulk sediment, rather than PCBs partitioned from sediment into pore water.

An alternative mechanism to hydrodynamic scour for introducing PCBs on sediments into the water column would be through localized disturbances which result in temporary introduction

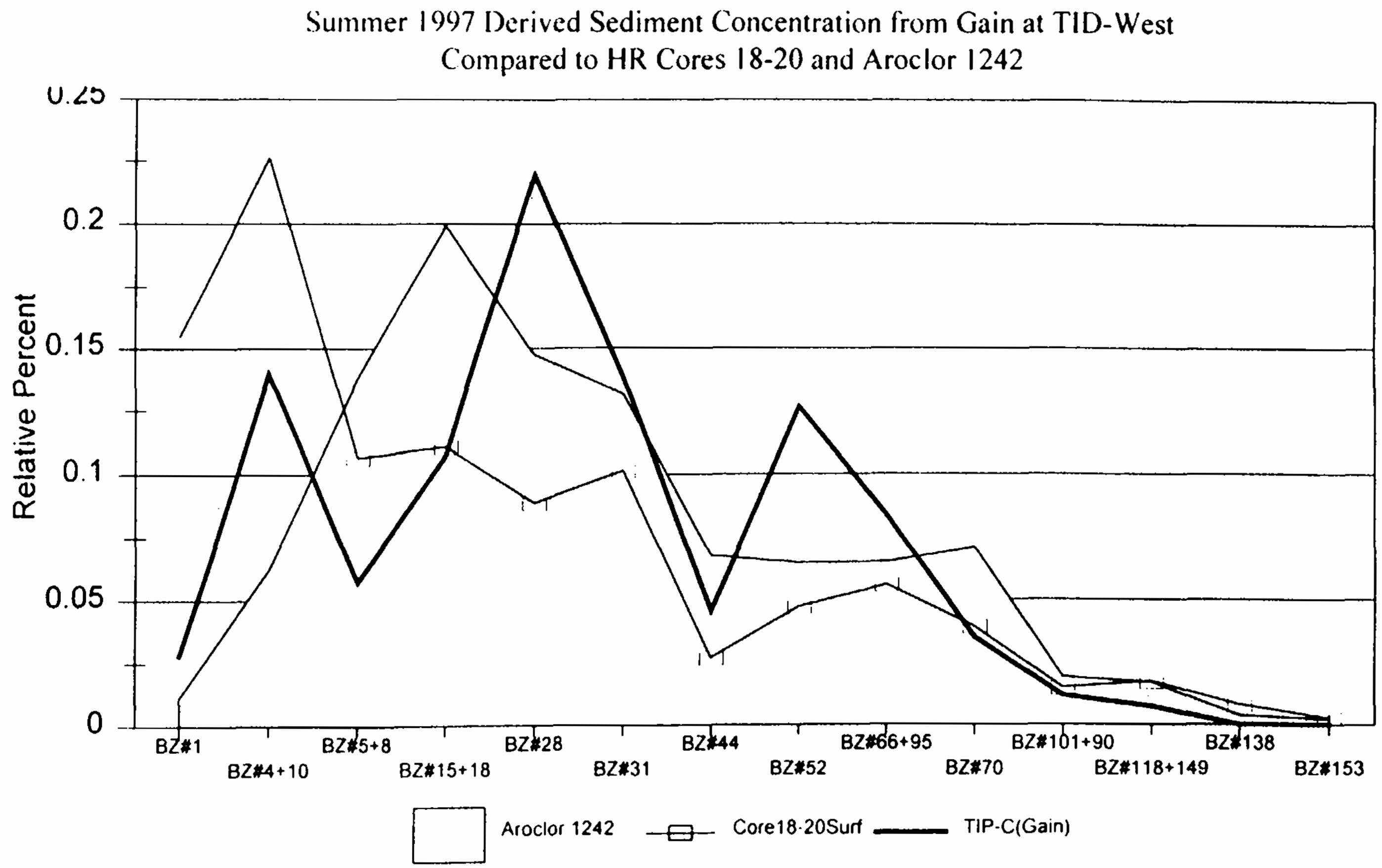

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Figure 2-6. Sediment Congener Pattern Derived from Summer 1997 Gain at TIP-18C Attributed to Pore Water Flux

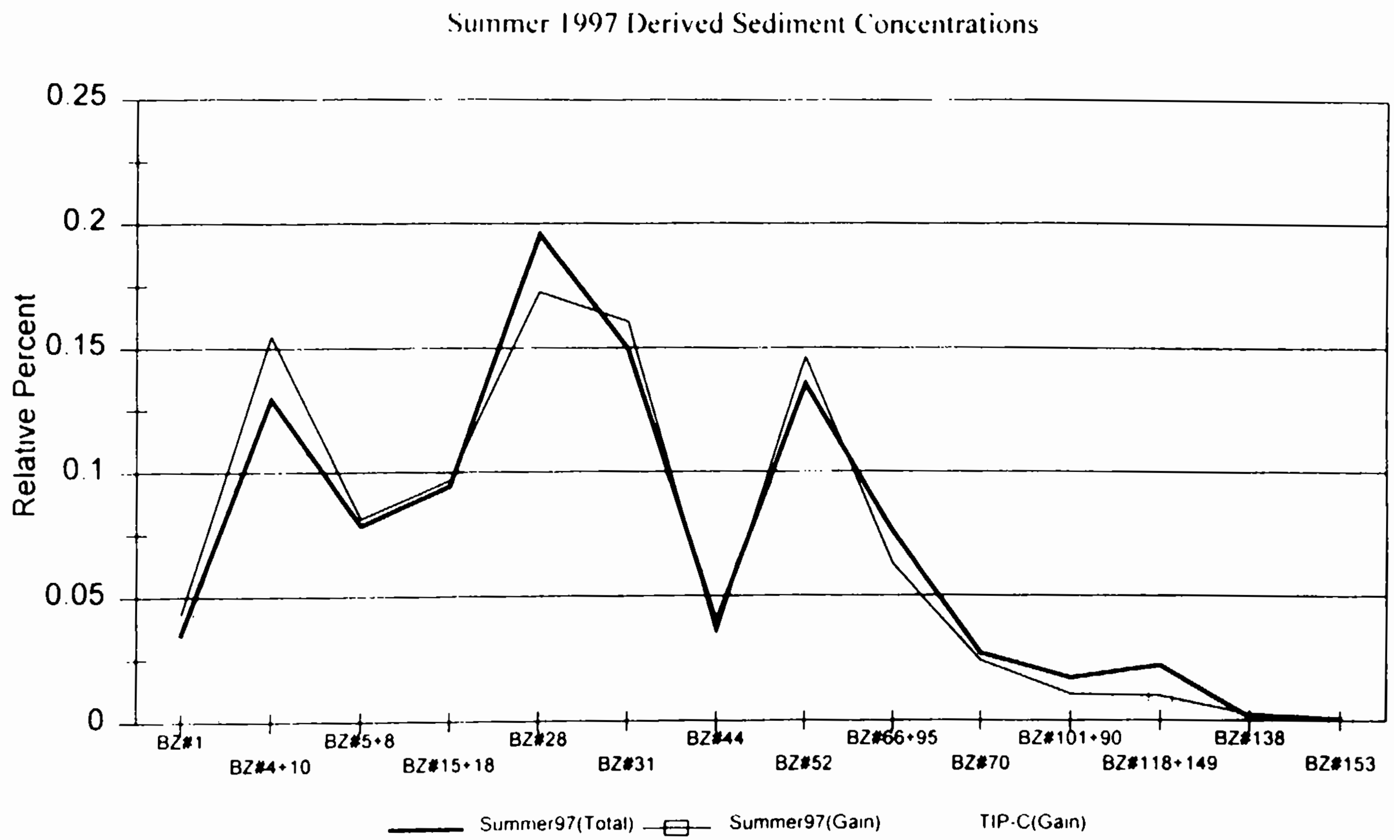

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Figure 2-7. Sediment Relative Concentrations Required to Support Observed Water Column Concentrations via Pore Water Flux

of contaminated sediment into the water column, followed by equilibration and exchange of PCBs between sediment and the water column. This sediment may either settle out locally, or replace influent solids to the TIP, such that there is little net increase in solids load. Localized, non-hydrodynamic scour disturbances which may introduce sediment into the water column from either cohesive or non-cohesive sediment areas during summer low flow periods include: bioturbation by benthic organisms, bioturbation by demersal fish, mechanical scour by propwash in shallow areas, mechanical scour by boats and floating debris in shallow/near shore areas, and uprooting of macrophytes by flow, wind, or biological action.

To test the reasonableness of this theory experiments were performed to see if the observed sediment concentrations could be reproduced by a weighted combination of surface sediment and surface sediment pore water concentrations. Direct combination—which would be consistent with net solids loading from TIP sediments to the water column, coupled with pore water exchange—does not yield a close fit to the observed congener pattern. However, a very close fit can be obtained under an assumption of sediment resuspension, exchange with the water column, and settling.

To provide a gross representation of the fractionation that occurs during the exchange process it is simply assumed that, within the water column, sediment-sorbed PCBs re-equilibrate to reproduce the average water column phase distribution shown in Table 3-8 of the DEIR (USEPA, 1997), following which the POC fraction settles back out while the dissolved and DOC fractions remain in the water column. This fractionation would result in 91% of resuspended BZ#4 remaining in the water column, but only 22% of BZ#118.

Using these assumptions, water column concentrations at TID-West can be fairly closely predicted as a mixture of pore water and water column exchange with suspended sediment, using average 0–5 cm concentrations in the TIP for sediment and pore water from the GE 1991 data (Figure 2-8). In contrast, pore water alone provides a much poorer fit. Very similar results are obtained by fitting a mixture to the estimated gain at TIP-18C in ng/L (Figure 2-9). In the case of TID-West, the best fit coefficient on pore water concentration (ng/L) is 0.0034 and that on sediment concentration (μg/kg) is 0.0058; for gain evaluated at TIP-18C the coefficient on pore water concentration is 0.0011 and that on sediment concentration is 0.0038.

In sum, observation of congener patterns in the TIP load gain suggests that this load is driven by a mix of pore water flux (advection plus dispersion) and direct exchange of sediment with the water column.

2.3.3 Influence of Advection and Dispersion on Pore Water Concentration

As has been noted above, concentrations in both surface sediment pore water and the TIP load source are enhanced in the lightest congeners (BZ#1, BZ#4+10) relative to unweathered Aroclor 1242. At first this appears somewhat surprising, as anaerobic dechlorination is not expected to be significant in the surface sediment layer, and diffusion alone is not likely to be responsible for the enhancement. The enhancement can, however, be inferred to represent differential transport in ground water seepage, and thus supports the idea that seepage loading may be significant. Different PCB congeners have partition coefficients that differ by orders of magnitude, and this affects the speed with which they are transported to the sediment water interface. Because the dechlorination end-products are among the congeners with the lowest partition coefficients, they are transported

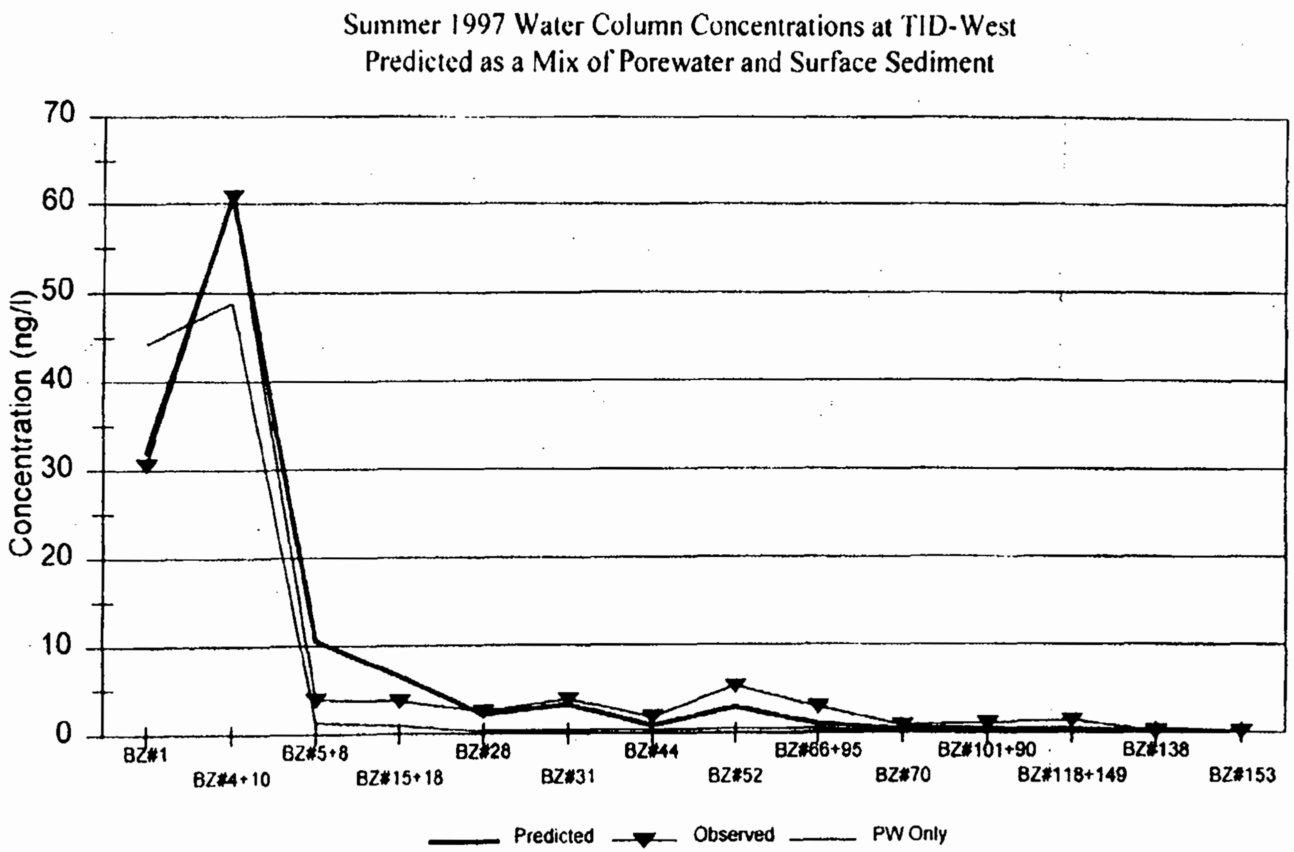

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Figure 2-8. Concentrations at TID-West Predicted as a Mixture of Pore Water and Sediment Exchange

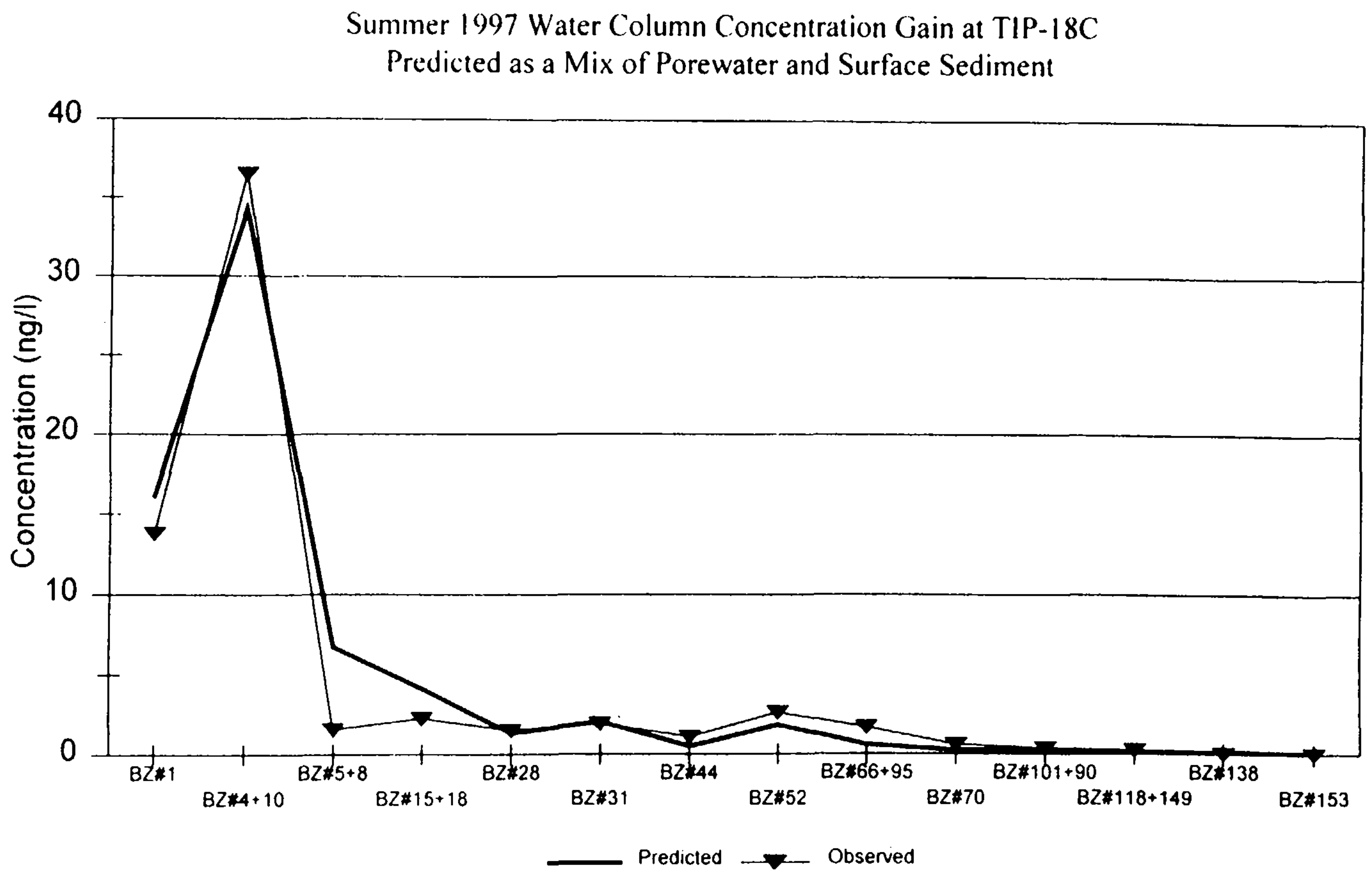

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Figure 2-9. Concentration Gain at TIP-18C Predicted as a Mixture of Pore Water and Sediment Exchange

more quickly to the surface. Thus, the observation of an increase in the molar percent of these congeners is a natural consequence of the process of flux out of the sediments.

Under ultimate equilibrium conditions with an unlimited buried sediment source, partitioning would not affect the relative concentration of congeners at the sediment water interface. However, the time to concentration breakthrough at the surface from even a small depth (*e.g.*, 1 foot) in undisturbed sediments could well be on the order of hundreds of years or more, given the partition coefficients observed, while concentration breakthroughs of the lightest congeners will be much quicker. Since most of the contaminated sediments in the Thompson Island Pool have been in place for 25 years or less, it is reasonable to expect an enhanced flux of the dechlorination end-product congeners into the water column.

This can be seen via some simple numerical experiments with a one-dimensional advection-dispersion ground water transport model. Consider the case where a substantial deposit of highly-contaminated sediment was laid down following the removal of the Fort Edward dam, then covered by a layer of less-contaminated sediment. Atop this there may be a layer of transient muck which controls interfacial transport; however, for simplicity of the example we will consider only transport within the in-place sediment and ignore the process of transport across the sediment-water interface.

For the example, consider that there is a "substantial" mass of contaminants at depth, which provides a constant-concentration boundary at 10 cm depth, defined as x=0 (in this depth range, the solution is not sensitive to the choice of the constant-concentration boundary depth). Initially, the same concentration is assumed to apply from 10 to 3 cm depth, while the overlaying surficial 3 cm is assumed to have an initial concentration one-tenth that in the layer below. Ignoring processes directly at the sediment-water interface and examining only transport within the sediment to *near* this level, the initial conditions are:

$$c(x,t=0) = \begin{pmatrix} C_1 & 0 \le x < 7 \\ C_2 & 7 \le x \end{pmatrix} \qquad \begin{matrix} (3-10cm) \\ (0-3cm) \end{matrix}$$

$$C_1 = 10 * C_2$$

while the boundary condition is:

$$c(x=0,t) = C_1$$

The solution to the one-dimensional advection-dispersion equation under these conditions (van Genuchten and Alves, 1982, simplified version of solution #A5.) is:

$$c(x,t) = C_2 + (C_1 - C_2)\ \frac{1}{2}\ erfc\left[\frac{R(x-x_1) - vt}{2\sqrt{DRt}}\right] + \frac{1}{2}\exp(vx/D)\ erfc\left[\frac{R(x+x_1) + vt}{2\sqrt{DRt}}\right]$$

where

- $erfc$ is the complementary error function,
- v is the interstitial or pore-water velocity,
- t is time,
- D is the dispersion coefficient, assumed to be 10^{-6} cm^2/s, and
- R is the retardation coefficient, or rate of movement of water relative to rate of movement of the pollutant.

The retardation coefficient, R, is defined as

$$R = 1 + \rho\ k/\theta$$

where

ρ	is the matrix dry bulk density,
k	is the distribution coefficient, equal to $K_{OC} \cdot f_{OC}$, and
Θ	is the volumetric moisture content.

Given a typical TIP organic carbon fraction in the sediments of 0.0179, matrix bulk density of 1.35 g/cm^3 and porosity of 38.6 %, predicted retardation coefficients for PCB congeners in Hudson sediments are approximately 6% of the K_{OC} coefficient.

For the purposes of the example, consider a case in which there is seepage advection through the sediments at an interstitial velocity of 3 m/yr. Figure 2-10 shows the predicted concentrations (as a fraction of the concentration in the more contaminated buried sediments) near the sediment-water interface after 25 years. Under these conditions, congeners with a log(K_{OC}) greater than about 4.8 essentially show no influence of the more contaminated sediments below, and reflect the initial concentration in the surface layer (specified to be 1/10 of C_1). However, for log(K_{OC}) equal to 4.6, the surface concentration is expected to be 54% of C_1, or five times the concentration present in the initial surface concentration. In other words, over a 25 year time frame the less strongly sorbing congeners may be mobilized from more contaminated sediments at depth, while more strongly sorbing congeners will not.

As shown in Table 2-2, BZ#1 and BZ#4+10 have estimated values of log K_{OC} less than 4.8, while other congeners tested have values greater than 5.7. This indicates that there is indeed a good probability that seepage transport/retardation processes in the sediment can account for an enrichment of BZ#1 and BZ#4+10 relative to other congeners in the spectrum.

A second point of interest in this analysis is that for most congeners the time to concentration breakthrough may be very long for undisturbed sediments buried at even a small depth. Where more contaminated sediments are buried and subject to an advective flux, but are not disturbed by erosion, this implies that the flux into the water column may still be rising, with breakthrough of many congeners into the surface layer not yet achieved. For instance, for the situation described above with a burial depth of 3 cm and an seepage velocity of 3 m/yr, surface concentrations of a congener with a log (K_{OC}) of 5.6 would take 240 years to reach 50% of the buried sediment concentration, while a log (K_{OC}) of 6 would require 600 years. For advection from buried sediments we might thus expect to see a continued *increase* in loading to the water column over time. Further, concentrations observed in the flux from the sediment should spike upwards in order of increasing partition coefficients.

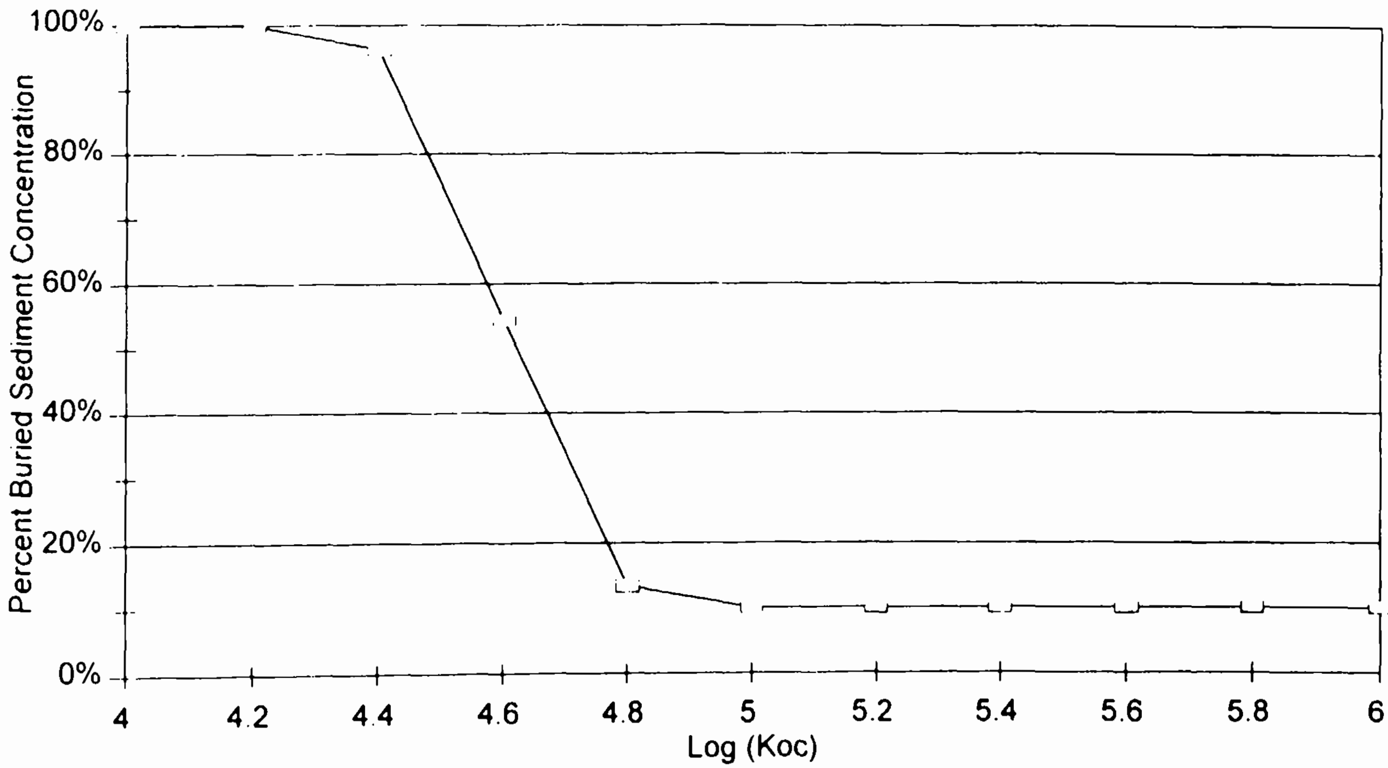

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Figure 2-10. Influence of K_{oc} on Advective Transport from Buried Sediment (3 cm Depth) to Surface Sediment after 25 Years

3. Uniform Areal Flux of PCBs

> *PCB levels in the water column increase in a near linear fashion as water passes through the TIP, indicating a nearly uniform areal flux from sediments within the TIP.* (QEA, 1998, p. 1)

PCBs appear to be loaded to the water column throughout the TIP. In other words, there are no hidden major sources apart from the contaminated sediments known to be present in the Pool. This is an expected result, as hot spot sediments are also distributed throughout the TIP.

QEA's presentation of a "near linear" flux of PCBs from sediments throughout the TIP seems intended to downplay the importance of hot spots, with a contention that equal rates of flux occur from the entire TIP sediment area. The primary evidence cited for this theory consists of four time-of-travel studies conducted under approximately 4,500–5,100 cfs flow conditions in September 1996 and June 1997, which consisted of vertically composited sampling along three-point lateral transects every 0.25 to 0.5 miles between Rogers Island and the TID. Within the TIP, however, there are so many hot spots that the argument that all sediments contribute equally is unconvincing.

Part of QEA's argument is based on an observation that organic carbon normalized PCB concentrations in surface sediment are similar in hot spot and non hot spot areas. This is contended to result in equal pore water flux; however, as discussed in Section 5.1, this argument is invalid unless the correlation between organic carbon content and sediment type (as shown, for instance, by porosity) is also taken into account.

What the time-of-travel survey results do show is that, during low flow conditions, the highest water column PCB concentrations tend to be associated with low-velocity, nearshore areas. This finding is also consistent with the bias study results comparing near shore station TID-West to center channel observations at TIP-18C (Section 1). Elevated concentrations in near shore low-velocity areas are consistent with a pore water flux loading mechanism, which would result in higher concentrations where dilution flow is lowest. These low flow areas are, however, precisely the areas where sediment deposition and accumulation of PCBs is expected. QEA points specifically to high concentrations observed in the backwater on the east shore opposite Snook Kill. This area is, however, coincident with NYSDEC hot spot 8, and serves only to show that hot spots can generate high concentrations.

For the 1996 time of travel studies there was at least one hot spot area between all consecutive sampling locations except for stations 5 and 6, just below Rogers Island. The average of the three lateral samples declined between these stations. For the 1997 time of travel studies the only pair of sampling stations which did not encompass a hot spot were stations 15 and 15A. A small increase in average PCB concentration occurred between these stations due to an increase in center channel concentrations. No increase was seen in nearshore concentrations between these stations.

In sum, the time-of-travel results suggest that PCBs accumulate to the water column at a fairly steady rate across the TIP, with a net increase of 0.4 to 0.6 kg/d during average flow rates of 4,500–5,100 cfs present during the time of travel surveys (QEA, 1998, p. 45). Given higher loads with spring flows, this would appear to be consistent with an annual average load gain of 0.79 kg/d.

as stated in Section 1. Observations of a fairly steady rate of PCB gain do not necessarily negate the importance of the hot spots as sources of PCB load.

4. Relative Contribution of Sediments below Thompson Island Dam

> *Sediments downstream of the Thompson Island Dam (TID) contribute PCBs to the water column in a manner consistent with the TIP sediments (i.e., transfer from surface sediment pore water), increasing the water column loading by approximately 50% between TID and Schuylerville.* (QEA, 1998, p. 1)

The DEIR (USEPA, 1997) suggested that the TIP was the primary instream source of PCB load in the Hudson, and that, under low flow conditions, this load was greater than that derived from sediment between Thompson Island Dam and Waterford. QEA (p. 55) states there is "an approximately linear increase in PCB loadings with river mile" between Fort Edward and Schuylerville, and "low flow loading estimates developed from USEPA water column transect data produce a spatial pattern of PCB loading that is inconsistent with spatial patterns of sediment PCB levels and our understanding of sediment-water interactions." (This latter conclusion is referenced to USEPA, 1997, Figure 4-28, which is not directly relevant; Table 3-16 is more appropriate.)

If there is indeed a sampling bias associated with observations by EPA and GE at near-shore stations near the Thompson Island Dam (see Section 1), then relative load contributions from the TIP and downstream segments need to be re-evaluated. The QEA (1998) conclusions regarding relative loading, are, however, based on very limited data which are insufficient to reach final conclusions, as no regular monitoring has been conducted downstream of the TID in recent years. In fact, the conclusion of a "near-linear" increase with river mile (QEA Figure 4-27) is based on only four samples, one from August and three from October 1997. These limited samples from late summer and fall are not necessarily representative of either early-summer or spring high-flow loading patterns.

Although the GE/QEA data are inconclusive, the presence of a potential sampling bias in TID estimates may help in explaining some apparent anomalies in the Phase 2 data: In six of nine Phase 2 low-flow analyses (Transect 1, Transect 2, Transect 5, Flow Average 2, Flow Average 3, Flow Average 4) the load at Thompson Island Dam appeared to be greater than the load at Waterford (USEPA, 1997, Table 3-16). This might be explained by dilution by and settling of clean sediment; however, presence of a sampling bias at Thompson Island Dam may provide a more intuitive and parsimonious answer. The corrections to the river flow estimates noted for Chapter 3 of the DEIR (See Book 1 of this responsiveness summary) also effect this issue.

For the Phase 2, 1993 low flow observations as reported in the DEIR, the mean load at Rogers Island was 0.49 kg/d, while mean loads at Thompson Island Dam and Waterford were both 1.16 kg/d. This represents a load gain of 0.67 kg/d between Rogers Island and TID. However, the load at Waterford is believed to be overestimated due to overly high flow estimates. (See corrections to Chapter 3 in book 1 of this responsiveness summary). The actual load at Waterford is expected to be roughly 40 percent lower at low flow conditions, (*i.e.*, 0.70 kg/day) yielding a net loss relative to the TID. If it is assumed that a sampling bias correction factor (Section 1) of 0.8 is appropriate for Thompson Island Dam load estimates, the Phase 2 load at the TID would be decreased to 0.93 kg/d, and the adjusted gain within the TIP would be 0.44 kg/d (about 0.07 kg per mile per day), while the loss between the TID and Waterford would be 0.23 kg/d (or about 25 percent of the TID load). Thus, TID sediments would appear to contribute significant amounts of PCBs to the water column while downstream reaches lose PCBs from the water column, implying little if any net contribution from the downstram sediments, even after the maximum likely correction for potential sample bias at the TID station. In fact, QEA's analysis of the time of travel surveys (QEA, 1998, p. 45) suggests that TIP sediments contribute between 0.4 and 0.6 kg/d PCBs during flow conditions around 5,000 cfs, nearly identical to the corrected value given above.

Of course, downstream hot spots are expected to contribute PCB loads to the water column to some degree, and by a mechanism similar to that found in TIP sediments. This flux is not necessarily via pore water only, as described above in Section 2.3.2. The difference in per-mile loading rates above and below the TID reflects the lower areal coverage of hot spots, on average, in reaches below the TID. Focus thus far has been on the TID sediments because these are a more concentrated source for which more data are available. It is suspected that it will be possible to model PCB fluxes from sediment both in the TIP and in downstream hot spot areas without the necessity of invoking any "anomalous" special mechanism to explain the TIP load.

5. Hot Spot versus non-Hot Spot Sources

> *[S]urface sediments within all areas of the river contribute PCBs to the water column, not simply PCBs residing in "hot spot" areas. Comparison of dry weight sediment PCB concentrations, either at depth or at the sediment surface, gives a false impression of the relative importance of various sediments within the river. The surface sediment pore water PCB concentrations, and, hence, the diffusive sediment PCB flux is controlled by PCB concentrations associated with the organic carbon component of the sediments. As these average organic carbon normalized PCB concentrations are similar within "hot spot" and non-"hot spot" areas, these areas contribute similarly to the water column PCB load.* (QEA, 1998, pp. 1-2)

QEA implicitly sets up the hypothesis that known mechanisms of flux from "old" hot spot sediments in the TIP (considered to be hydrodynamic erosion, diffusion, and pore water advection) are not sufficient to account for the "anomalous" TIP load. Therefore, additional mechanisms are needed to provide a newer, enhanced PCB load to surficial sediments in the TIP. Three additional mechanisms are postulated:

1. PCB DNAPL loading in bedload along the sediment-water interface
2. Pulse loading of PCBs due to periodic flooding of the Baker Falls plunge pool
3. Transport of oil-soaked sediment into the TIP at the time of the Allen Mill collapse.

As an implied result of these "additional mechanisms", QEA claims that organic-carbon normalized PCB surface sediment concentrations are similar across the TIP, and that these active sediment concentrations are disconnected from buried hot spots.

5.1 Surface Sediment Concentrations in the TIP

QEA (1998, Table 4-6) presents information showing that mean PCB concentration in surface sediments, *when normalized to organic carbon concentration*, is similar in the hot spot and non-hot spot areas, and is similar for fine and coarse sediment. They then state (p. 48): "The flux of PCBs from surface sediments to the water column depends on the organic carbon normalized PCB concentration, the sediment-water exchange coefficient, and the PCB partition coefficient as described using Equations A-10 to A-15 (Appendix A). Regions of the river with equal surface sediment organic carbon normalized PCB concentrations and composition contribute equally to the water column PCB load."

This argument is flawed. Suppose PCB concentrations on organic carbon are everywhere the same, but location A has a high weight percent of organic carbon, while location B has almost no organic carbon. Obviously, location A has a much greater mass of PCBs per volume of sediment and is likely to contribute more PCB load to the water column, even if similar pore water concentrations are calculated for each location under equilibrium conditions. What QEA's argument primarily reflects is that hot spot areas are "hot" because they have more fine-grained sediment with high organic carbon concentrations.

QEA's argument is invalid for any source mechanisms that involve bulk sediment movement (scour, bioturbation, etc.), and only partly valid for consideration of a purely pore water source from sediments. It is true that equilibrium partitioning assumptions imply that the observed apparent pore water concentration, $C_{PW,a}$, (including both dissolved and colloidally-sorbed PCBs) should be proportional to the organic-carbon normalized PCB concentration, but this is not the only factor. Rearranging Equation 3-29 (USEPA, 1997) yields

$$C_{PW,a} = \left(\frac{C_P}{f_{OC}}\right)\frac{\theta(1 + m_{DOC}K_{DOC})}{K_{OC}}$$

where C_P is the particulate concentration,
θ is the saturated porosity,
m_{DOC} is the mass of DOC per volume of pore water,
K_{DOC} is the partition coefficient to dissolved organic carbon, and
K_{OC} is the partition coefficient to sediment organic carbon.

Inspection of this equation shows that the apparent pore water concentration depends not just on the organic-carbon normalized sediment concentration but also on θ and m_{DOC}. As both porosity and the concentration of dissolved organic carbon tend to increase in fine-grained, organic sediments, the pore water concentration should also be higher in hot spot areas.

Analysis of the 1991 GE data from the 0-5 cm layer in the TIP reveals wide ranges in TOC concentration (from 4,961 to 69,474 ppm) and in porosity (from 16 to 70 percent). With a few exceptions, TOC concentration increases with porosity (Figure 5-1). This correlation indicates that inferences of pore water source strength cannot be based on organic carbon normalized PCB concentrations alone.

In Phase 2 results (USEPA, 1997, p. 4-20) it was noted that "locations with...finer-grained sediments have consistently higher median and mean PCB levels." The 1984 NYSDEC data also show a strong relationship between sediment texture class and total PCB concentration, with the highest concentrations in the finest grained sediments. Table 5-1 shows the averages of NYSDEC top core section and grab sample results for the near-surface layer. These results show a clear increase in average PCB concentration for sediments with finer texture and higher organic content.

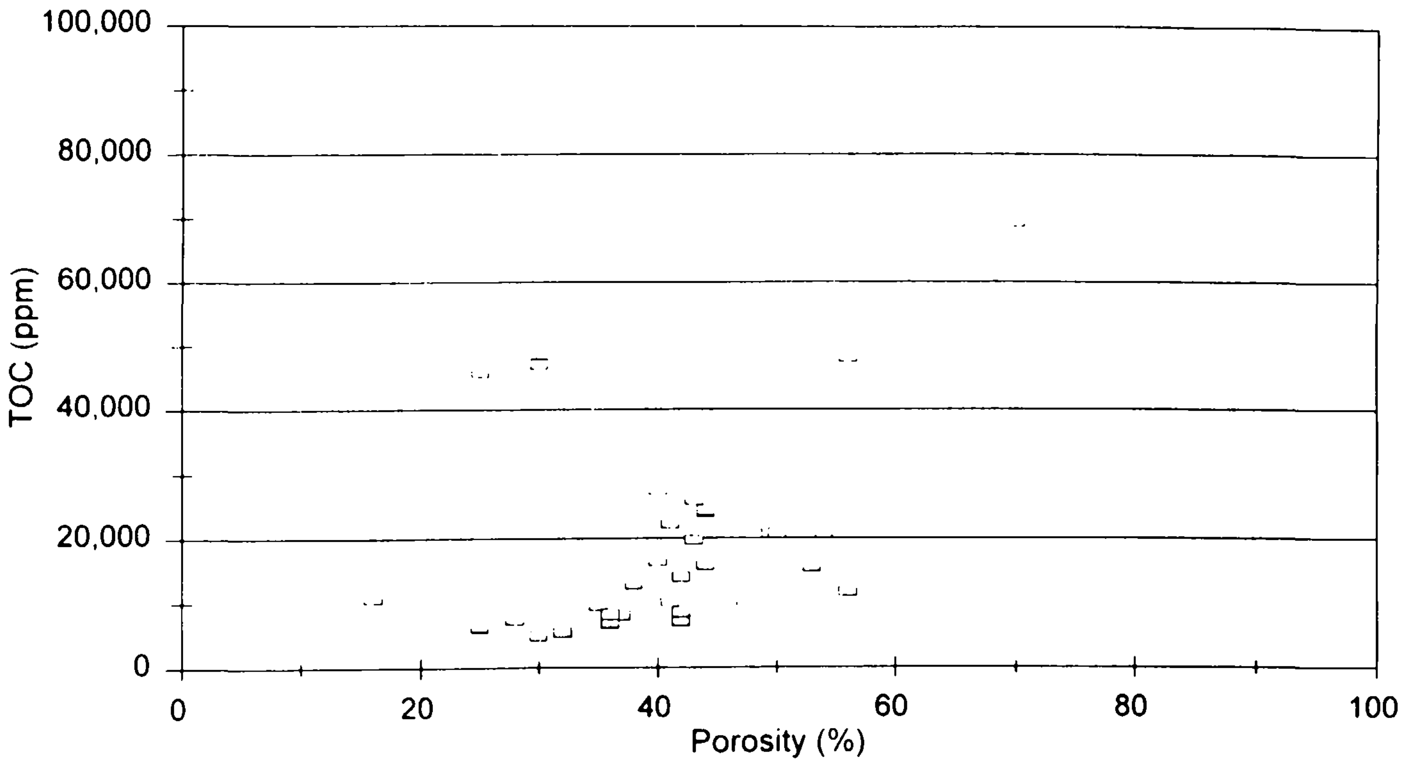

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Figure 5-1. Correlation of TOC Concentration and Porosity in TIP Surface Sediments

Results are similar for sample medians, except in the case of sediments classified as clay. A portion of these samples are believed to include intact, uncontaminated glacial clays. In any case, it appears clear that it is inappropriate to compare sediment concentrations as a source of pore water flux unless both organic carbon fraction and porosity are taken into account.

Table 5-1. Surface PCB Concentrations in NYSDEC 1984 Data Compared to Texture Class

Texture Class	Interpretation	Average Total PCBs (mg/kg)	Median Total PCBs (mg/kg)	Median Specific Weight (g/cc)	Sample Count
FS-GRV	Fine sand and gravel	14.7	9.1	0.9	7
CS-WC	Coarse sand, wood chips	16.9	10.7	1.1	9
GRAVEL	Gravel	19.8	14.1	--	127
CS-SND	Coarse sand	25.0	13.8	1.25	22
GR-WC	Gravel, wood chips	29.9	29.3	--	19
FS-WC	Fine sand, wood chips	47.3	25.7	0.9	79
CLAY	Clay	54.9	6.7	1.0	10
FN-SND	Fine Sand	80.8	31.1	0.8	290
MUCK	Muck	121.1	103.8	0.5	14

It should be noted that it is reasonable to expect a smoothing out of surface concentrations relative to buried hot spot concentrations. However, such a general smoothing of surface sediment concentrations does not indicate that the surface PCB inventory is unconnected to buried hot spots. PCBs introduced into the water column by erosion or other disturbance of bulk sediment would be subject to local-scale settling, spreading concentrations. Some settling may also occur of PCBs loaded to the water column via pore water advection, following partitioning to solids in the water column, while lateral interflow could also "smear" the pore water signal.

5.2 PCB DNAPL Loading

Another theory advanced by QEA/HydroQual is that transport of PCBs from the Bakers Falls area into the Thompson Island Pool may proceed through bedload movement of droplets of dense non-aqueous phase liquids (DNAPL). Because they are denser than water, droplets of pure-product PCBs would sink and remain near the bottom (if there was insufficient vertical mixing), and so might move past the Fort Edward/Rt. 197 sampling station without detection. PCB DNAPL loading could contribute a fresh supply of unweathered Aroclor 1242 to the surface sediment layer in the Thompson Island Pool, and offer an alternative to in-place sediments as the source for TIP PCB load.

If such a phenomenon did exist, it would imply that load estimates obtained from concentration measurements at the Rt. 197 station at the head of the Thompson Island Pool are biased low— resulting in a further diminishment of the importance of load generated from in-place Thompson Island Pool sediments. It is well established from GE field observations that PCB DNAPL seeps occur in the area of the Bakers Falls plunge pool. What is not established is whether any significant amounts of PCB transport past Fort Edward occur as bedload DNAPL.

The main objection to such a theory is that no observational evidence has been collected to support the transport of PCB DNAPL droplets into the Thompson Island Pool. In addition, the following should be noted:

- Average surface sediment concentrations in 1991 and 1992, as well as the pattern of a derived sediment which would account for the TID load via pore water flux, show a significant elevation in concentration of monochlorobiphenyls and dichlorobiphenyls relative to Aroclor 1242 which is consistent with a source driven by weathered PCBs, and not consistent with significant replenishment of surface PCB concentrations by PCB DNAPL.

- 1992 core samples did not provide any evidence of accumulation of unweathered Aroclor 1242 in depositional areas of the Thompson Island Pool. They do suggest accumulation of additional PCBs (Section 5.4), but only after significant fractionation in the water column.

- Energetic hydrodynamics at and below the plunge pool suggest that any PCB droplets which moved out of the pool would likely be broken up and mixed throughout the water column, although no quantitative analysis has been performed. A water column cross section obtained by O'Brien and Gere for GE in 1997 confirms the general homogeneity of the water column. (QEA, 1998).

- The condition in which PCB DNAPL is most likely to be swept out of the plunge pool is during spring high flows; however, comparison of load estimates at Rt. 197 and TID-West suggests that the PCB load during high flows is likely transported through the TIP with little mass loss. (It is assumed likely that the apparent high bias associated with TID-West samples would not apply during energetic high flow conditions.)

HydroQual (1997c) conducted a study from September 18–20, 1996 with fluorescent resin particles (of approximately the same density as Aroclor 1242) to investigate the possibility of transport of DNAPL droplets. The resin particles were released in slurry form into the fish bypass line at AHDC's hydroelectric plant, and recovery monitored by passive filtration at a station at Fort Edward 300 feet upstream of the north end of Rogers Island (river mile 194.9), at the Rt. 197 bridge at Rogers Island (river mile 194.2), and 500 feet upstream of the Thompson Island Dam (river mile 188.8). Samples were collected at three depths and analyzed for resin particles as well as PCBs. Released particle size ranged from 19 to 380 μm. The experiment suffered from a number of methodological and analytical problems which resulted in difficulties in completing the resin particle mass balance. It was estimated, however, that 28% of the particle mass (primarily in the size range greater than 190 μm) was retained upstream of Fort Edward, 18% was retained between Fort Edward and Rogers Island, and 44% was retained within the Thompson Island Pool, with only 1% of particle mass (entirely in the 19–38μm size class) detected at the Thompson Island Dam station (this estimate does not, however, account for delayed transport of particles which may have been retarded in eddies and backwaters beyond the three days of the experiment).

The estimates of particle retention should be used with extreme caution, as they appear to be subject to considerable uncertainty. Of particular concern is the possibility that much of the mass of smaller particle size classes (< 114 µm) may have passed through the *in situ* filtration devices. This would result in an over estimate of the percent of particles retained in each reach.

HydroQual's study is somewhat informative as to the trapping patterns of rigid fluorescent resin particles, but may not tell us much about the transport of PCB droplets. In contrast to the resin, PCB droplets are liquid and may (1) deform and break into smaller particles, (2) gradually dissolve into the water column, (3) sorb to organic sediment particles (whereas the resin particles may tend to form hydrostatic bonds with clay particles), and (4) infiltrate into bottom sediment (if of sufficient mass). Perhaps the most notable result of the experiment is that it failed to show preferential bedload transport of the resin particles.

In their report, HydroQual (1997c, Figure 38) makes much of the fact that, in observations of 18 September 1996 at the Fort Edward station (upstream of Rogers Island), the bulk of PCB mass in the water column was detected near the sediment interface. This was due to high TSS concentrations near the sediment interface on this date, probably representing localized scour. The same condition does not seem to be found downstream at Rogers Island on 18 September, and the vertical distribution of PCB concentrations showed no clear trend in observations taken on September 19 and September 20, 1996 at the two stations, while the flourescent particle mass (HydroQual 1997c, Figure 20) shows little or no vertical trend on all three dates.

In sum, there is no evidence to suggest that DNAPL bedload transport past Rt. 197 is a significant component of the annual PCB mass balance above Thompson Island Dam. It is clear that releases of pure-product Aroclor 1242 at Bakers Falls represent much of the PCB concentration observed at Rt. 197; however, no evidence has been presented which indicates that the Rt. 197 observations are biased low. Consistent with this conclusion, QEA (1998, p. 39) states: "it is unclear whether this mechanisms [PCB DNAPL loadings] has been contributing to the anomalous loading observed from the TIP during the 1990s.

5.3 Flood Pulse Loading of PCBs

PCB DNAPL seeps to the Bakers Falls plunge pool have clearly contributed to the PCB load entering the TIP, although it is not at all clear they have had a significant impact on surface sediment concentrations within the TIP.

GE investigated two different mechanisms of pulse transport of DNAPL out of the plunge pool: spring high flow loading and short-term pules during hydropower operations. The experiments were conducted during 1997, which is a period in which the loading upstream of Rt. 197 appears to have been minimal, apparently due to control of seeps in the plunge pool, so the results may not be very informative as to loading mechanisms during the early 1990's.

High flow sampling was conducted during the spring event of April 6–9, 1997 (O'Brien & Gere, 1998), during which maximum flow at Fort Edward was approximately 19,400 cfs. No significant elevation of PCB concentrations was found in bedload sediments at Rogers Island, and QEA (1998, p.41) concludes: "Based upon the high flow data collected in 1997, flow event driven water column and sediment bed load PCB transport do not appear to be significant mechanisms for continued pulse loadings of PCB from the plant site and into the TIP."

GE also conducted monitoring to assess shorter period loading of PCBs from the plunge pool associated with fluctuations in flow through the AHDC hydroelectric facility, which cause periodic "flushing" of the plunge pool (O'Brien & Gere, 1997). Surprisingly, they found that flushing of the plunge pool resulted in elevation of concentrations in the plunge pool, probably due to collection of small DNAPL seeps in the bedrock outcrop of the falls, rather than removal of mass downstream. QEA (1998, p. 44) concludes that "periodic inundations of Bakers Falls provides relatively insignificant PCB loads into the TIP."

Taken together, these findings suggest that PCB DNAPL from the Bakers Falls plunge pool is transported downstream primarily through either dissolution and/or emulsification of very small droplets into the water column. Enhanced transport during spring high flows may then be associated with increased velocity and turbulence of DNAPL resident in the plunge pool, increasing the rate of interfacial PCB transfer and suspension of small droplets. One interesting possibility is suspension of small, non-settling-size droplets which tend to become associated with or coat particulate matter in the water column. This might help explain why PCB congener partition coefficients observed at Fort Edward during the Phase 2 sampling effort appear to be out of equilibrium toward the particulate phase during transects 2 through 5 (USEPA, 1997, Figure 3-10), with the apparent disequilibrium not evident during the winter low flow (transect 1) and late summer low flow conditions (transect 6).

If Bakers Falls PCBs are transported into the TIP primarily mixed into the water column this has two important implications: (1) the Rt. 197 sampling station is likely to be approximately unbiased, and (2) PCBs from the Bakers Falls area are likely to have re-contaminated surface sediment within the TIP only to the extent allowed by general settling of water column particulate matter. Potential contributions of Bakers Falls PCBs to surface PCB concentrations in the TIP are discussed further in Section 5.4.

5.4 Mass Loading of Contaminated Sediment Following the Allen Mill Collapse

QEA (1998, p. 36) also suggests the possibility that the Allen Mill collapse resulted in the bulk movement of highly contaminated sediment into the TIP, although little further discussion is provided. Thus far, no evidence seems to be available to support this theory, such as discovery of surface deposits in the TIP with an elevated concentration closely resembling Aroclor 1242. Instead, it appears likely that any contaminated sedimented mobilized from the Allen Mill collapse was transported into the TIP more gradually as part of the general water column PCB transport process.

Monthly PCB loads estimated at the Rt. 197 station are shown in Figure 5-2, based on calculations using a monthly averaging estimator (Dolan *et al.*, 1981), which has been demonstrated by Preston *et al.* (1989) to provide relatively accurate estimates of load for samples obtained on a fixed time schedule. Superimposed on the bars showing monthly load estimates is a 12-point moving average line, which indicates long term trends. The loads first spike upwards in September 1991, following the failure of the gate structure in the Allen Mill. Intermittent high loads continued

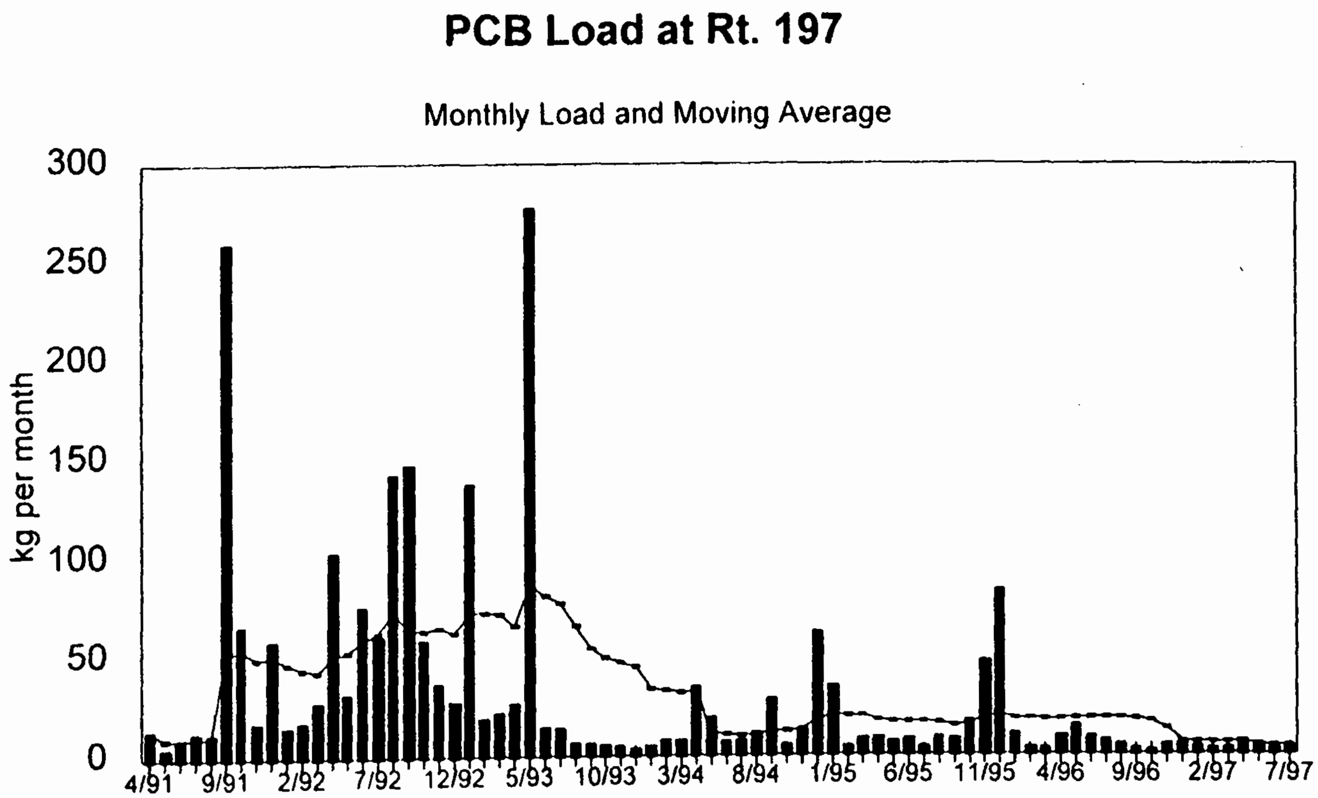

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Figure 5-2. PCB Load at Rt. 197 (Rogers Island); Monthly Load from GE Data using an Averaging Estimator, with 12-point Moving Average

through the spring of 1993, when flow through two of the three water ways in the mill was stopped. Removal of contaminated material from the mill continued through fall of 1995, but average loads (on an annual basis) remained relatively stable through 1994–1996. In September 1996 an apparatus was installed to collect PCB DNAPL seepage at the base of Bakers Falls, while in January 1997 a ground water production well was installed to hydraulically limit PCB seepage. (QEA, 1998, p. 7 discusses hydraulic control of the DNAPL source in general, but no detailed information on this effort has been provided.) Since these latest remedial actions, PCB loading above Rt. 197 appears to have remained low.

From Figure 5-2, it appears that the bulk of PCB mobilization from the Bakers Falls area occurred between September 1991 and May 1993. Did this loading result in additions to the surface PCB inventory in the TIP? If so, evidence should be seen in the surface layers of the Phase 2 High Resolution Cores, collected in depositional areas of the Thompson Island Pool in the fall of 1992.

These cores were cut in two centimeter slices, and comparison of the 0–2 cm layer with the 2–4 cm layer should help reveal the effects of 1991–1992 loading from the Bakers Falls source. Comparisons on the basis of total PCBs and Aroclor 1242 equivalents contained in the Phase 2 data base (USEPA, 1997) are similar. As the Bakers Falls source was unweathered Aroclor 1242, results in terms of Aroclor 1242 equivalents are presented in Table 5-2. Five cores taken within the TIP are included in this table, as well as one core taken a few miles below the TID, above Lock #5. All six cores were collected in October or November of 1992.

Table 5-2. Comparison of 0–2 cm and 2–4 cm Aroclor 1242 Equivalent Concentrations in Fall 1992 High Resolution Cores in the Thompson Island Pool

Core	River Mile	Location	Aroclor 1242 (µg/kg) 0–2 cm	Aroclor 1242 (µg/kg) 2-4 cm	% Increase, Surface Layer
HR-018	185.8	Above Lock #5	8,886	5,752	54%
HR-019	188.5	Thompson Island Dam	23,922	30,904	-22%
HR-020	191.2	Thompson Island Pool	26,046	20,652	26%
HR-023	189.3	Thompson Island Pool	2,952	1,141	159%
HR-025	194.2	Rogers Island West	6,149	8,717	-29%
HR-026	194.1	Rogers Island East	97,529	113,419	-14%

Three out of six core tops show an elevation in PCB concentrations relative to the 2–4 cm layer. The results in the two Rogers Island cores may suggest that the Bakers Falls load passed Rogers Island predominantly in the water column, rather than as bed load. Three out of four of the other stations showed an increase. Results are difficult to interpret, however, because of the highly varying basis of comparison in 2–4 cm slices. In cores 18, 20, and 23 surface concentrations are greater than 2–4 cm concentrations, but then increase again over depth from 4 cm to the PCB maximum, which is between 12 and 30 cm in depth. The occurrence of a minimum in the 2–4 cm layer in these cores suggests that surface-layer PCB concentrations had been increased by recent upstream loadings past Rogers Island. Ability to replicate these temporal changes should be a key test of the PCB fate and transport model.

6. Summary

In this review, a number of major flaws have been found in the GE/QEA analysis. GE's criticism of the DEIR's finding that a significant PCB load originates from TI Pool sediments is based primarily on the assumption that there is a high degree of sampling bias at the TI Dam-West station over the period from 1991 to 1997. However, the analyses conducted in this report show that the degree of sampling bias is less than implied by GE/QEA and that the findings of the DEIR regarding PCB loads are still valid after the correction for the analytical bias in the GE data. In addition, the GE/QEA analysis depends on a sediment transport model for the TI Pool which assumes that all areas of contaminated material are being buried, a condition which is highly unlikely in a river setting such as this one. Finally, GE/QEA assumes that there is an oil-phase-based transfer of PCBs to the TI Pool, despite the absence of evidence for it. While the GE/QEA analysis does provide some insights into the Upper Hudson River system, the conclusions presented in the report are frequently overstated and not supported by the data. USEPA's review of the GE/QEA report is summarized in the Executive Summary at the front of this document.

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Thompson Island Pool Sediment PCB Sources

Prepared for General Electric Co.
Albany, New York

MARCH 1998

FINAL REPORT

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FINAL REPORT

GENhud 131

THOMPSON ISLAND POOL SEDIMENT PCB SOURCES

Prepared for:

General Electric Company
Corporate Environmental Programs
Albany, New York

Prepared by:

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March 19, 1998

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SECTION 1
INTRODUCTION

Since 1990, the U.S. Environmental Protection Agency (USEPA) has been performing a reevaluation of the 1984 Superfund no-action decision for the PCB-containing sediments within the upper Hudson River. One principal objective of the reassessment is to determine the relative importance of the varied sources contributing to water column PCB loadings. This report provides a quantitative analysis of water column PCB sources within the TIP based on the extensive historical database of water and sediment PCBs generated by the state and federal governments and the more recent data sets generated by the General Electric Company (GE).

As a result of this work the following major conclusions can be drawn:

- During the 1990s, the amount of PCBs leaving the TIP was significantly overestimated due to a sampling bias at the routine sampling station located at the downstream limit of the TIP;

- The composition of water column PCBs attributed to the TIP sediments indicates that relatively undechlorinated PCBs are the principal source and that surface sediment pore water is the principal point of origin;

- PCB levels in the water column increase in a near linear fashion as water passes through the TIP, indicating a nearly uniform areal flux from sediments within the TIP; and

- Sediments downstream of the Thompson Island Dam (TID) contribute PCBs to the water column in a manner consistent with the TIP sediments (i.e., transfer from surface sediment pore water), increasing the water column loading by approximately 50% between TID and Schuylerville.

The analyses presented in this report demonstrate that surface sediments within all areas of the river contribute PCBs to the water column, not simply PCBs residing in "hot spot" areas. Comparison of dry weight sediment PCB concentrations, either at depth or at the sediment surface, gives a false impression of the relative importance of various sediments within the river. The surface sediment pore water PCB concentrations and, hence, the diffusive sediment PCB flux is controlled by PCB concentrations associated with the organic carbon component of the sediments. As these average organic carbon normalized PCB concentrations are similar within "hot spot" and non-"hot spot" areas, these areas contribute similarly to the water column PCB load. This finding has important implications for the development and evaluation of remedial strategies for the river.

The conclusions of this report are in many cases inconsistent with those reached by the USEPA in the Data Evaluation and Interpretation Report (USEPA, 1997). The differences are primarily due to the results of additional data collection since the release of the USEPA report and the application of a rigorous, quantitative PCB fate and transport modeling effort sponsored by GE. USEPA is in the process of developing a similar model.

This report has been prepared by Quantitative Environmental Analysis, LLC. (QEA) on the behalf of the GE to document the results of numerous field research, data analysis, and modeling efforts investigating the origin, fate, and transport of PCBs within the upper Hudson River. Section 2 provides a historical background of the Hudson River PCB problem and describes significant events that have impacted the observed temporal changes in water column PCB loadings. Section 3 describes the basic physical and chemical processes affecting PCBs in aquatic environments and their incorporation into a state-of-the-science PCB fate and transport model. Section 4 presents the results of field research, data analysis, and modeling studies conducted on the river over the last several years that are the basis for the conclusions presented above. Section 5 presents the summary, conclusions, and recommendations drawn from the analysis presented.

SECTION 2
BACKGROUND

2.1 History

Over an approximate 30 year period, ending in 1977, two GE capacitor manufacturing facilities in Fort Edward and Hudson Falls, New York discharged PCB-containing wastewaters into the upper Hudson River. Much of the PCBs accumulated in sediments upstream of the former Fort Edward Dam located approximately 2 miles downstream of the Hudson Falls capacitor plant (Figure 2-1). Removal of this dam in 1973 by the owner (Niagara Mohawk Power Corporation) and subsequent high flow events resulted in the movement of large quantities of PCB-containing sediments downstream. Some of these sediments deposited further downstream in pools formed by dams along the Champlain Canal, which is coincident with the Hudson River channel (USEPA, 1984).

In the late-1970s, the New York State Department of Environmental Conservation (NYSDEC) undertook a number of studies to determine the concentration and distribution of PCBs in the water column, sediments, and biota of the upper Hudson River. As a result, they identified sediment "hot spot" areas defined as regions of the river containing sediments with PCB concentrations exceeding 50 parts per million (ppm). Forty of these "hot spots" were identified in the 40 mile stretch of the upper Hudson River between Fort Edward and Troy, N.Y. Twenty "hot spots" were located in the TIP, a six mile section of the river formed by the TID, which is the first dam downstream of the former Fort Edward Dam. In the early 1980's, the NYDEC proposed that the sediments from the TIP "hot spots" be removed and placed in a landfill in Ft. Edward, New York. Due to community opposition, the NYSDEC was unable to proceed with the project.

In 1984, the USEPA placed the upper Hudson River on the Superfund National Priorities List and issued a Record of Decision (ROD). The ROD determined that the approximately 60 acres of shoreline PCB deposits upstream of the former Fort Edward Dam, formed when the pool elevation dropped approximately 20 feet due to the removal of the dam, were to be capped in-place to minimize direct contact with the exposed PCB-containing sediments. For the PCB-containing sediments within the TIP and downstream, an interim no-action decision was reached for a number of reasons, including: 1) declining PCB levels in water and fish as a result of source control measures on the plant sites and natural attenuation processes in the river, and 2) the unproven status of contaminated sediment removal technology (USEPA, 1984).

After the 1984 ROD, GE entered into agreements with the Federal government to implement the remnant deposits capping program. This was carried out between 1988 and 1991 (JL Engineering, 1992). In addition , GE implemented a water column monitoring program beginning in 1989 (Harza, 1990) to monitor the construction activities on the remnant deposits and to demonstrate that the remedy was functioning as intended[1]. The NYSDEC continued to pursue a TIP "hot spot" dredging and landfill program, and in 1987 began the process of siting a local landfill, which ended in 1989.

In 1990, the USEPA reopened the 1984 no-action decision on the PCB-containing sediments of the upper Hudson River and initiated a reassessment remedial investigation and feasibility study (RRI/FS). Although GE was only one of two named potentially responsible parties (PRPs; the other being Niagara Mohawk Power Corp.), the USEPA decided to complete the RRI/FS using government contractors and funds. The complexity of the technical issues associated with assessing the origin, fate, and transport of PCBs in the system has delayed the original schedule of the RRI/FS, which is now scheduled for completion sometime after the year 2000.

[1]This program and later variants provided much of the water column PCB data presented in this report.

Although GE was not permitted to perform the RRI/FS for the USEPA, the company collected relevant scientific data that would enable: 1) a better understanding of PCB dynamics within the system, and 2) the development of a state-of-the-science PCB fate and transport model. The data collection program started in earnest during the spring of 1991 (O'Brien & Gere, 1993a, 1993b). A key component of the program was the routine (at least weekly) monitoring of water column PCB concentrations at a number of stations in the upper Hudson River, including (Figure 2-1):

- Route 27 Bridge in Hudson Falls (background station),
- Route 197 Bridge in Fort Edward (downstream of the plant sites and remnants deposits and upstream of the TIP), and
- the TID (downstream of the TIP).

This monitoring has continued and now provides a valuable data set to evaluate the temporal trends in water column PCBs in the upper Hudson River.

2.2 Hudson Falls and Allen Mill Remediation

During the routine monitoring performed by GE, a significant increase in water column PCB loading was detected after mid-September 1991. This loading originated upstream of the Fort Edward and downstream of the Route 27 Bridge stations (Figure 2-1). Within a weeks time, PCB levels within the river increased from less than 100 ng L^{-1} to approximately 4000 ng L^{-1} (O'Brien & Gere, 1993a). After significant investigation, the source of the increased water column PCB loading was attributed to the collapse of a wooden gate structure within an abandoned paper mill (Allen Mill) located adjacent to the Hudson Falls capacitor plant on Bakers Falls (O'Brien & Gere, 1994a; Figure 2-1, inset). The gate had kept water from flowing through a tunnel cut into bedrock below the mill, presumably since the mill's closure in the early 1900s. The tunnel contained oil phase PCBs that migrated there via subsurface bedrock fractures.

In January 1993, with the cooperation of the Bakers Falls Hydroelectric Dam owner and the NYSDEC, the water flow through the mill was largely controlled. By Spring 1993, two of the three water ways within the mill were isolated from the river and planning for the removal of PCB containing material from within the Allen Mill commenced. Removal continued until the fall of 1995. Approximately 45 tons of PCBs were contained in the 3,430 tons of sediment removed from the Allen Mill (O'Brien & Gere, 1996a).

As part of the investigation and clean-up of the Allen Mill, dense non-aqueous phase liquid (DNAPL) seeps of PCBs were discovered within the exposed bedrock of the falls. In 1994, during the construction of the new dam at Bakers Falls, PCB DNAPL seeps were observed in the portion of the falls adjacent to the Hudson Falls plant site. A number of actions have been taken to contain and control these PCB seeps including grouting of bedrock fractures, manual collection of PCB oils, when accessible, and the operation and installation of pumping wells to hydraulically control the seeps. The release of PCB DNAPL through these bedrock seeps has declined in response to mitigation efforts, but has not ceased. While efforts are made to collect the material, uncollected oils are released into the river when the falls are inundated during elevated river flow events. Sediments and debris from the vicinity of the original wastewater outfall located immediately upstream of the dam and the area where the seeps are concentrated are being removed in an additional effort to control the seeps. This removal is scheduled for completion during the Summer of 1998.

In September 1996, divers discovered an additional area of PCB DNAPL seepage at the base of the Bakers Falls adjacent to the eastern shore in an area referred to as the plunge pool. A subaquatic collection system was installed to arrest the flow of the PCBs into the river. This seep produced approximately 0.5 pounds per day of PCBs. In January 1997, a ground water production well was installed on the shoreline upgradient from this seep in an effort to hydraulically control

PCB discharges from the seep. This well produces significant quantities of PCB DNAPL and appears to have controlled discharges from the seep as PCB DNAPL has not been observed in the subaquatic collection system since the installation of the on-shore recovery well.

In addition to the activities to control riverbed PCB seeps and PCB movement from the Allen Mill, GE has conducted an intensive investigation and remedial program at the Hudson Falls plant site. DNAPL PCBs have been discovered in the fractured bedrock below the site. To date, over 3,000 gallons of oil have been removed from the subsurface. A series of 26 ground water pumping wells have been installed to create a hydraulic barrier between the site and the river, not only to collect PCB-containing ground water but also PCB-oil (GE, 1997). The effectiveness of this system in reducing PCB flux from the site to the river is being monitored by measuring PCB levels in the river, and through an assessment of the hydraulic capture zone created by the groundwater pumping system.

2.3 Upper Hudson River Water Column PCB Sources

Numerous upper Hudson River water column PCB sources have been identified and quantified using water column PCB data collected from four primary monitoring locations: the Route 27 Bridge, the Route 197 Bridge at Fort Edward, the western abutment at TID, and the Route 29 Bridge at Schuylerville (located approximately six miles downstream of the TIP).

2.3.1 Upstream of the plant sites

The background station at the Route 27 Bridge typically yields water column PCB concentrations of less than the method detection limit of 11 ng/l (ppt). While there are known PCB sources upstream of this sampling station, most notably Niagara Mohawk Power Corporation's

Queensbury site, they do not appear to be significant sources of PCBs to the water column of the upper Hudson River. Water column PCBs at the Route 27 Bridge station are likely present at quantities between 1 and 11 ppt (USEPA, 1997).

2.3.2 Plant sites, Allen Mill, and remnant deposits

Potential external PCB sources between the Route 27 Bridge and the Route 197 Bridge in Fort Edward (Figure 2-1) include: the Hudson Falls capacitor site, the Allen Mill, the remnant deposits (including the site adjacent to the former Fort Edward Plant outfall area referred to as the 004 site) and the Fort Edward capacitor manufacturing site. The steep river bed grade in this reach of the river produces flow velocities that inhibit sediment deposition. Therefore, there are only limited areas of sediment accumulation in this portion of the river, and water column PCB loadings observed at the Fort Edward station generally reflect the activity of the external sources. This activity is illustrated in Figure 2-2 which presents the results of water column PCB measurements made at the Fort Edward station since the 1970s. Additionally, Figure 2-3 shows the PCB loading observed at this station during three spring high events in the 1990s. The following observations can be made from these data:

- PCBs have been present in samples collected from this station since the late-1970s,
- PCB levels declined between the late 1970s and late 1980s,
- PCB levels increased dramatically in September 1991 as a result of inputs from the Allen Mill,
- Remediation of Allen Mill and efforts to control PCB releases to the Hudson River reduced the large PCB loading observed during the 1991-1993 period, and
- PCB levels during the annual high flow period have declined in response to source control measures implemented at the mill and plant site.

These data indicate that a non-sediment PCB source has been active for many years. Even before the failure of the Allen Mill gate, a base load of PCB was entering the river, presumably from fractures in bedrock near the Hudson Falls site. Only recently has this base load of PCB been controlled. Although plant site sources still exist, it appears that remedial measures at the Hudson Falls plant site have reduced water column PCBs in this segment of the river to levels below those observed in the late-1980s. The current flux from the site is still being evaluated. Finally, these data indicate that the Allen Mill event, while transitory, represents the largest external PCB loading event, both in duration and magnitude, seen in this section of the river since the late-1970s.

2.3.3 Contaminated sediment deposits

The contaminated sediments within the upper Hudson River represent a source of PCBs to the water column. Within a given reach of the river, this source can be estimated as the difference in the product of PCB concentrations and flow between an upstream and downstream station[2]. Figure 2-4 presents PCB loading between either Ft. Edward and Schuylerville (12 mile length of the river) or between Ft. Edward and TID (6 mile length of river). for the period 1980 to 1997. The earlier data (1980 to 1991) depicts loading over the longer reach (12 miles) and the later data (1991-1997) depicts loading over the TIP region only. Figure 2-5 presents the loading from the TIP alone between 1993-1997. These data indicate that:

•Through the 1980s, PCB loading from the contaminated sediments decreased from approximately 1 pound per day to approximately 0.25 pounds per day (although significant year-to-year variation is apparent);

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[2]This ignores any losses from the water column due to settling or volatilization which have been judged to be minor at low to moderate river flows.

•An increase in PCB loading, from approximately 0.25 pound per day to between 1 and 2 pounds per day occurred between 1989 and the early 1990s;

•The loading exhibits a seasonal pattern with the highest loading observed following the annual spring high flow period and the lowest loading observed in the winter;

•The PCB loading through the 1990s has not showed significant declines although the data contains significant year-to-year variations; and

•The lowest PCB loading since 1993 was observed in 1995, a year in which Spring flows were significantly lower than in other recent years.

While the decrease in PCB loading through the 1980s is consistent with natural recovery of the system through the burial of contaminated surface sediments with clean material, the cause of the apparent increase in loadings observed from this region of the river in 1991 is unclear. Several changes, both in the river monitoring program and the activity of external PCB sources occurred during this period. First, a monitoring station was added at the TID to assess PCB loadings directly from the TIP. Second, the PCB analysis scheme was changed from an Aroclor-based scheme that failed to detect the lowest chlorinated congeners to one that quantified the full spectrum of PCB congeners. Finally, over an approximately 18 month period beginning in 1991, the river experienced the largest external PCB loading since the late 1970s. Each of these changes may have exerted some influence on the observed PCB loadings from the TIP in the 1990s.

Estimates of PCB flux from TIP sediments, based on surface sediment conditions measured in the summer of 1991, cannot account for the PCB loadings observed from the TIP (HydroQual, 1995a)[3]. Possible causes for this apparent increase in PCB loading were presented in earlier reports and formed the basis for the data collection programs undertaken over the last few years (HydroQual,

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[3]The TIP anomaly is defined as the excess PCB loading observed from the TIP since approximately 1992 that can not be accounted for by known PCB fate processes given the known PCB concentration of surficial sediments (HydroQual, 1995a).

et al., 1997a, 1997b, O'Brien & Gere 1997a, 1997b). The results of this work will be discussed in Section 4 of this report.

2.4 USEPA's Analysis of Water Column PCB Data

In association with the on-going RRI/FS of Hudson River PCBs, the USEPA issued a report in February 1997 that documented their interpretation of water column and sediment data collected in 1992 and 1993 (USEPA, 1997). The USEPA concluded that PCBs passing the TID during low flow conditions[4] were the major source of PCBs to the freshwater Hudson. Additionally, the USEPA contended that sediments within "hot spot" areas of the TIP contribute the majority of PCBs passing the TID during low flow periods.

The USEPA's interpretation of the data did not recognize that the loading observed from the TIP could not be explained via known PCB fate and transport mechanisms given the level of PCBs within surface sediments (the TIP anomaly; GE, 1997). Moreover, the agency did not fully consider the temporal correspondence between the appearance of the excess loading, the upstream PCB loadings from the plant site areas, and the change in sampling and analytical methods. Based upon a qualitative assessment of the data, the agency offered three possible mechanisms for transfer of PCBs from the sediment to the water column:

1) sediment pore water diffusion of relatively undechlorinated PCBs partitioned from the particulate to the pore water phase,

2) groundwater-induced advective flux of sediment pore water PCBs within the TIP, and

3) resuspension of sediments contaminated with extensively dechlorinated PCBs deposited prior to 1984.

[4]Less than 10,000 cfs at the USGS Fort Edward gauging station.

The USEPA did not conduct a quantitative mass balance evaluation to test these hypothesized mechanisms, but simply offered them as possible explanations for the observed loading from the TIP (USEPA, 1997). They deferred rigorous analysis of these mechanisms to the PCB fate and transport modeling phases of the project (USEPA, 1997).

The apparent impact of recent plant site loadings on PCB dynamics in the river, and the uncertainties expressed by the USEPA over mechanisms controlling such dynamics, underscores the need to develop a quantitative understanding of PCB origin, fate, and transport in the Hudson River system. It is only after such understanding is achieved that a technically defensible analysis of remedial alternatives for PCBs in Hudson River sediments can be developed. Recognizing this need, GE has conducted an extensive field research program and data analysis effort to identify and quantify the principal sources of PCBs in the system and the mechanisms controlling PCB fate and transport. Of particular concern was the anomalous PCB loading observed from the TIP.

SECTION 3
QUANTITATIVE MODELING OF TIP SEDIMENT-WATER INTERACTIONS

To allow objective, quantitative evaluation of potential remedial measures in the Hudson River, GE has sponsored the development of state-of-the-science PCB fate, transport, and bioaccumulation models. This section describes the developmental state of these models, how well the model comports to existing data , and how model applications aided in the identification of the source of the PCB loading referred to as the TIP Anomaly.

3.1 Modeling Framework

A series of models have been developed to forecast changes in water column, sediment, and biota PCB levels in the upper Hudson River. Given initial sediment PCB concentrations and a time series of daily flows, total suspended solid (TSS), and PCB concentrations in the river at Fort Edward and each of the major tributaries, these models predict a time series of PCB concentrations in the water column, sediment, and biota. Four models are used: hydrodynamic, sediment transport, PCB fate, and PCB bioaccumulation (Figure 3-1). Sediment-water interactions of the TIP are driven by processes described in the hydrodynamic, sediment transport, and PCB fate models. Therefore, these models are the principal focus of this modeling discussion.

Hydrodynamics refers to the movement of water through the river and the friction or shear stress that this movement causes at the interface between the water and the sediment bed. A hydrodynamic model computes the velocity and depth of the river, as well as the shear stress at the sediment-water interface, in response to upstream flows and flows entering the river from tributaries. Sediment transport includes the movement of suspended and settled solids within the river and the settling and resuspension of solids that occurs at the sediment-water interface as a result of the shear caused by the moving water. A sediment transport model computes the concentration of solids in the water column and the rate at which sediment accumulates in the bed. PCB fate includes the transport of PCBs dissolved in the water or sorbed to solids, transfer between the dissolved and sorbed phases, transfer between the water and atmosphere, and degradation that occurs chemically or biochemically. A PCB fate model computes the concentrations of PCBs in the water column and sediment in general accordance with the equations presented in Appendix A.

The models are equations developed from the basic principles of conservation of mass, energy and momentum from laboratory and field studies of individual phenomena (§ A.1). The equations are general and can be applied to any river system. The application of the equations to a specific system such as the upper Hudson River involves the determination of appropriate values for each of the parameters in the equations. Site-specific data are the basis for assigning values, either directly or by the process of model calibration. Each of the models was calibrated and validated using a data record that extends from 1976 to the present. The extensive database that is available makes the Hudson River uniquely suited for the application of these models.

Two hydrodynamic models have been developed and calibrated and validated in order to provide the necessary hydrodynamic input for the sediment transport and PCB fate models. A two-dimensional, vertically-integrated hydrodynamic model is needed to define the distribution of shear stresses at the sediment-water interface that controls sediment transport. By contrast, a one-dimensional hydrodynamic model is sufficient to define the average transport of PCBs within the water column. The one-dimensional model is also more computationally efficient and was therefore used to drive long-term PCB fate simulations.

The sediment transport model uses the results of laboratory and field studies to describe the resuspension and deposition processes of cohesive and non-cohesive sediments. The model described here does not consider the resuspension of non-cohesive sediments. This process is included in ongoing modeling work. Results of the sediment transport model in the form of resuspension and deposition fluxes are used directly by the PCB fate model.

The PCB fate model includes mechanistic descriptions of the transport, transfer and reaction processes occurring in the river as described in § A.1 and presented in Figure 3-1. PCBs are assumed to partition between dissolved and particulate phases, with partitioning assumed to be rapid, such that equilibrium conditions are generally well approximated. The dissolved phase is composed of freely dissolved PCBs and PCBs sorbed to dissolved and colloidal organic matter. Freely dissolved PCBs are transferred from the water column to the atmosphere by volatilization across the air-water interface. Particulate-phase PCBs settle from the water column to the sediment bed, and are resuspended from the sediment bed into the water column. Dissolved PCBs are exchanged between the water column and sediment bed in accordance with the laws of diffusion, that is, from a region of higher concentration to one of lesser concentration, with the rate of transfer controlled by a mass transfer coefficient.

3.2 Model Calibration

3.2.1 Hydrodynamics

Applying the one- and two-dimensional hydrodynamic models to the upper Hudson River requires that the river be divided into discrete segments or grid elements. The eight dams on the river make it necessary to construct a separate grid system for each reach. The eight distinct hydrodynamic models, one for each reach, are linked together by running the system from Reach 8 (TIP) downstream to Reach 1. The downstream output of one reach provides the inlet boundary condition information for the adjacent downstream reach. The two-dimensional grid for the TIP is shown in Figure 3-2. While the two-dimensional model utilizes a variable, curvilinear grid, the one-dimensional model uses a constant grid spacing of 762 m (2,500 ft). Both models extend from Rogers Island at Fort Edward to the Troy Dam.

The hydrodynamic models were calibrated and validated using two sets of data. The first data set consists of water surface elevations measured at two locations in Reaches 1 to 7 and three locations in Reach 8 on November 28 and 29, 1990 (O'Brien & Gere, 1991). The mean flow rate at Fort Edward during this period was 7,860 cfs, with a maximum variation of less than 2 percent. One measurement was taken at the dam and the other was measured at an upstream location. Model calibration in each reach was conducted by fixing the dam stage height to the measured value and then adjusting model parameters until good agreement was achieved between the predicted and measured stage heights at the upstream location. In the one-dimensional model, Manning's coefficient (n) was the adjustable parameter; in the initial two-dimensional model the horizontal eddy viscosity (A_H) was the calibration variable and bottom friction coefficient (c_f) was assumed to have a constant value of 0.0025 in all reaches. The results of the calibration exercise demonstrated that, for a given flow rate, water surface elevation can be predicted with average errors of 8 and 1 percent for the one- and two-dimensional models, respectively. The two-dimensional model has been recalibrated using a variable friction coefficient related to sediment type.

Both models were validated using a second set of data consisting of stage height measurements collected in the TIP during the May 1983 flood. This flood had a peak flow at Fort Edward of 34,100 cfs, which corresponds to a recurrence interval of approximately 10 years. The stage heights were measured by NYSDOT personnel at staff gages 118 and 119 on the Hudson River/Champlain Canal. These staff gages approximately correspond to river stage heights at river miles 190.0 and 193.7. Values of the calibration parameters (i.e., n and A_H) were not changed during the model validation, the results of which are shown on Figures 3-3 and 3-4 for the one-dimensional and two-dimensional models, respectively.

3.2.2 Sediment transport

The sediment transport model used the same grid as the two-dimensional hydrodynamic model to describe the upper Hudson River. The particle size distribution of suspended solids was approximated as two particle size classes in the model. Class 1 represents cohesive sediments (i.e., clays and silts with particle diameters of less than 62 µm) while Class 2 is composed of coarser, non-cohesive sediments, primarily fine sands with diameters between 62 and 250 µm. The deposition rate of the Class 1 particles was a function of shear stress and particle concentration. The deposition rate of the Class 2 particles was the product of particle concentration and an assumed settling velocity. Erosion potential parameters were determined from upper Hudson River data on the relationship between mass of resuspended sediment per unit of surface area and applied shear stress (HydroQual, 1995b).

The sediment transport model was calibrated using suspended solids data from the April 1982 flood. This flood had a peak flow rate of 27,700 cfs at Fort Edward, which corresponds to a return period of three to four years. The settling velocity of Class 2 sediments was set at 24 mm s^{-1}, which corresponds to a particle diameter of 200 µm, and the tributary sediment loads were assumed to be composed of 35 percent Class 1 and 65 percent Class 2 sediments. Comparisons of predicted and observed TSS at Schuylerville, Stillwater, and Waterford for the April 1982 flood are presented in Figure 3-5. Predicted TSS concentrations at Schuylerville and Stillwater are in close agreement with measured values. However, the model under predicts TSS concentrations at Waterford during the peak of the flood. This under prediction is likely due to an underestimation of solids loading from the Hoosic River. More recent calibrations of the sediment transport model using new tributary solids loading data confirm this assessment of the preliminary model calibration presented in Figure 3-5.

The calibrated sediment transport model was used to generate a relationship between the mass of sediment resuspended and flow rate for each of the eight reaches from Fort Edward to the Troy Dam. These relationships were then used in the PCB fate model to determine erosion rate in each model segment for a specified flow rate. In a similar manner, a relationship between the effective settling velocity and flow rate was developed from results of the sediment transport model.

3.2.3 PCB fate

The one-dimensional hydrodynamic model grid was used to model PCB fate. Daily values for river flow and water depth for the period from 1977 to 1996 were obtained from the hydrodynamic model. Rates of resuspension and deposition were obtained from the sediment transport model.

The sorption partition coefficient was determined from an analysis of dissolved and particulate PCB measurements taken by the USEPA as part of the Phase 2 field data collection program (USEPA, 1997). A 20°C value of 40,000 L kg^{-1} dry sediment was used in the model. This value corresponds to an organic carbon normalized partition coefficient (K_{oc}) of $10^{5.4}$ L kg^{-1} organic carbon.

Dissolved organic carbon in sediment pore water was included as a competitive sorptive phase. The partition coefficient for DOC was fixed at 10 percent of K_{oc}, based on an analysis of 1991 field data (O'Brien & Gere, 1993b).

The volatilization rate constant was calculated from two film theory using a Henry's Law constant of $3x10^{-4}$ atm-m^3 mol^{-1}, a liquid film mass transfer coefficient calculated using the

O'Connor-Dobbins reaeration equation and a gas film mass transfer coefficient fixed at 100 m day^{-1} (Equation A-8).

The vertical diffusion of PCBs between the pore waters of adjacent sediment segments was modeled using a diffusion coefficient of 1 cm^2 day^{-1}. A temperature dependent mass transfer coefficient with a value at 20°C of 2 cm day^{1} was used to model the exchange of PCBs between the pore water and the water column (Equation A-15).

Two external sources of PCBs were considered in the model. First, PCBs entering from upstream prior to 1991 were estimated from a correlation of PCB concentration with flow at Fort Edward based upon USGS data. Daily flows assigned at the upstream boundary were used to evaluate the associated PCB concentration, except on days when data were available; then the actual measured values were used. The correlation was modified over time to reflect the decrease in upstream PCB levels. From 1991 through 1996, the monitoring data at Fort Edward were used directly to define the upstream boundary concentration (Figure 2-2).

The second external PCB source was an empirically defined, exponentially decreasing load that was added to the TIP in the period between 1977 and 1983. The source of these PCBs has not been determined, but may have been related to leaching from dredge spoils deposited along the shoreline or a consequence of dredging activities.

Model calibration results for the March 1977 through September 1996 period are shown in Figures 3-6 through 3-9. Figure 3-6 compares temporal profiles of calculated and observed surface sediment (0-5 cm) PCB concentrations in TIP and downstream in the vicinity of Schuylerville, Stillwater, and Waterford. The declines in concentration between 1977 and 1991 that are predicted by the model are in general agreement with the observed declines. The model predicts a slightly greater decline in the TIP than the data (68% versus 60%). The model also underestimates the average concentration measured in 1984. This underestimation may be due to a sampling bias because the 1984 sampling program targeted areas of higher concentration. The methods used to average the data are currently under review to determine if alternate averaging methods should be employed.

Figure 3-7 compares the annual PCB load passing Waterford that has been estimated from the USGS PCB data with that computed by the model. The model picks up the overall trend in the data, as well as the year-to-year variations due to variations in river flow and associated resuspension.

Since the calibration of this model, an analytical bias has been identified in the water column PCB data appearing in Figure 3-7 (Tetra-Tech, 1997; HydroQual, 1998). This bias is associated with the analytical methods employed by the USGS. A preliminary analysis of the survey's laboratory records suggests that the historical water column data are biased low as the technique does not account for the entire compliment of mono- and dichlorinated PCBs within the samples (HydroQual, 1998). Preliminary estimates suggest the bias ranges from 10 - 40 percent and depends on the relative proportion of mono- and dichlorinated PCBs in the samples. Since, mono- and dichlorinated PCBs account for a significant portion of the total water column PCB loading occurring across the TIP, additional efforts are underway to more fully characterize this bias, and possibly correct a portion of the USGS database. Considering these limitations of the data, the absolute water column concentrations predicted by the model are of less importance than the model predicted change in water column levels over the 15 year monitoring period. The model accurately predicts the factor of five decline in measured water column PCB levels between 1976 and 1991.

From 1991 to 1996, the data for calibration are largely restricted to the results of weekly monitoring of the water column at TID; although limited data are available from Schuylerville[5]. The comparison of the model to these data is less favorable than to the historical USGS water column data, even considering the bias in the USGS data. Figure 3-8 compares computed and observed water column PCB levels at Schuylerville for the period from 1989 through 1991. The model and data closely correspond in 1989, but the model underpredicts the observed levels in 1991. The comparison at TID for 1993 through 1996 demonstrates a consistent low bias by the model (Figure 3-9). The computed concentrations at TID are 300 to 500 percent lower than those measured. In contrast, the preliminary analysis of the bias in the USGS data appears to be less than 50 percent. Therefore, it is unlikely that the differences observed between model predictions and monitoring data can be solely attributed to the bias in the USGS data.

This difference between model projections and observed data was unexpected given the favorable comparison of model predictions to the data from 1977 to 1991, even considering the potential bias in the USGS data. Efforts to alter the model calibration to achieve water column levels consistent with the TID data were unsuccessful. No combination of reasonable rates of sediment-water interaction were able to reproduce both the long-term trends in sediment PCB levels and the TID water column PCB levels.

3.2.4 Summary of preliminary PCB fate and transport modeling

State-of-the-science hydrodynamic, sediment transport, and chemical fate models were developed to describe the PCB dynamics within the Hudson River system and to provide a means

[5] Limited additional data collected by GE in 1991 and 1992 and the USEPA in 1993 are available for stations located downstream of the TID.

of predicting PCB concentrations in the different media into the future. The favorable comparison of the model predictions to observed field data between the late 1970s and 1991 indicated that the models provided a consistent and accurate assessment of the mechanisms controlling PCB fate in the system over this period. The degradation of the model calibration to water column data collected after 1991 suggested that the models did not accurately account for the varied sources and processes affecting PCB dynamics within the TIP region of the river. Another PCB source(s), loading mechanism(s), or data inadequacy(s), not accurately represented by the models, was controlling PCB loading observed from the TIP region of the river.

A number of hypotheses were developed to explain these observations and were tested through a rigorous analysis of existing field data and the development and execution of a field research program (HydroQual, 1996, 1997a, 1997b, O'Brien & Gere, 1995, 1997b). These efforts are describe in Section 4.

SECTION 4
EVALUATION OF ALTERNATIVE HYPOTHESES FOR ANOMALOUS PCB LOADING WITHIN TIP

During 1996 and 1997, GE conducted an extensive field research program and data analysis effort to evaluate different hypotheses for the anomalous PCB loading observed within the TIP. As described in Section 3, known and understood PCB fate and transport mechanisms could not account for the entire loading observed from the TIP region of the river. An alternative PCB source, loading mechanism, or data inadequacy was required to account for this anomalous loading. The hypotheses considered to explain the loading anomaly fell into three general categories:

- additional mechanism of PCB exchange between sediments and water column,
- additional PCB sources, and
- erroneous estimates of PCB flux due to biased sampling.

The USEPA advanced the hypothesis of alternative mechanisms for PCB exchange between sediments and the water column in their Data Evaluation and Interpretation Report (DEIR; USEPA, 1997) and Preliminary Model Calibration Report (PMCR; USEPA, 1996) developed as part of their ongoing RRI/FS. In the DEIR, the USEPA hypothesized that either groundwater induced advective flux or resuspension of dechlorinated sediments in addition to diffusive flux mechanisms may account for the loading observed at TID. During preliminary model calibration, the USEPA invoked all of these mechanisms to transport PCBs from surface sediments into the overlying water column to account for the TID loading. Data analysis conducted by GE and documented in formal comments on these reports does not support these mechanisms as possible explanations for the observed anomalous loading (GE, 1997). GE undertook a field research program designed to evaluate the plausibility that these mechanisms can contribute significantly to the observed loading from the TIP.

The hypothesis that additional PCB sources may have been introduced into the TIP and were responsible for the anomalous loading was considered in light of recent PCB DNAPL loadings to the river. DNAPL PCBs within fractured bedrock underlying the GE Hudson Falls Plant site (O'Brien & Gere, 1996a) is believed to have migrated through bed rock fractures and accumulated in waterways within the 150 year old Allen Mill (O'Brien & Gere, 1994a). Collapse of a wooden gate structure within the mill is believed to have resulted in the transport of PCB DNAPL into the Hudson River during September 1991 and until flow through the waterways was controlled in January 1993 (O'Brien & Gere, 1994a). Although these sources were controlled by remedial measures (O'Brien & Gere, 1996a), PCB DNAPL from the plant site continued to enter the river directly through fractures in the river bed until remedial measures on the plant site mitigated these sources. The temporal correspondence of the mill loadings and the increase in PCB loadings from the TIP suggested the mill loadings as the causative factor. For this hypothesis to be true, PCBs must have passed the Fort Edward sampling station (Figure 2-1) undetected and then been deposited within the pool. This could occur if PCBs enter the river between sampling events or are transported as part of the bed load passing under sampling devices. PCB DNAPL transport was evaluated in a field research program sponsored by GE (HydroQual, 1997c).

The hypothesis that biased sampling may have resulted in erroneous estimates of PCB flux into or out of the TIP was considered as a possible cause of the TIP anomaly. For this hypothesis to be true, PCBs must have either; 1) entered the headwaters of the TIP undetected by the routine water column monitoring program and, following transport through the TIP, been detected within samples collected at the sampling station downstream of the TIP at TID, or 2) been unrepresentatively elevated within samples collected from the shore-based station located at TID. Data from limited sampling conducted during the early 1990s from the eastern and western shore areas at TID were in general agreement, supporting the representativeness of the western shore-based sampling location (O'Brien and Gere, 1996c). This hypothesis was further tested during extensive field efforts conducted in 1996 and 1997 and appears to be the principal cause of the anomalous loadings.

The results of specific field research programs and data analysis efforts evaluating these different hypotheses for the observed anomaly are presented below.

4.1 Additional Mechanism of PCB Exchange Between Sediments and Water Column

The hypothesis that additional mechanisms of PCB exchange between the sediments and the overlying water column were responsible for the anomalous loading was evaluated through an intensive data evaluation effort as well as field research. The effect of long-term elevated PCB flux from the sediments either as a result of surface sediment erosion or ground water advection, was assessed within a mass balance framework. The results of these analyses were presented in comments to the USEPA on their DEIR (GE, 1997). Additionally, in-field groundwater advection measurements were made and the resulting groundwater velocities were compared to those required to sustain the anomalous loading as presented in the USEPA PMCR (1996). Moreover, low flow water column TSS measurements were made through the TIP to assess the possibility that sediment resuspension may be contributing to the observed loading under low flow conditions. Finally, quantitative sediment transport modeling, based on state-of-the-science cohesive sediment transport theory, was conducted to estimate low-flow sediment resuspension and test the plausibility that this mechanism is contributing to the TIP anomaly.

4.1.1 Effect of long-term high flux on sediment PCB inventory

A mass balance calculation was performed to test the hypothesis that the anomalous PCB loading could be attributed to surface sediment PCB transport processes, either surface sediment resuspension or ground water advection. In this calculation, the net increase in PCBs between Rogers Island and the TID was assumed to originate from PCBs in the surface sediments of the TIP, defined conservatively as 0-8 cm. No vertical mixing was assumed between surface sediments and deeper sediments. The inventory or mass of PCB homologs within the surface sediments ($M_{j,ss}$) was estimated using the results of USEPA's reanalysis of the 1984 sediment data (USEPA, 1997) as follows:

$$M_{j,ss} = C_{j,ss}\, \rho_{ss}\, z_{ss}\, A_{tip} \tag{4-1}$$

where:

- $C_{j,ss}$ is the average concentration of PCB homolog j within the surficial sediments (0-8 cm) as calculated from 1984 data ($M\ M^{-1}$),
- ρ_{ss} is the density of surface sediments ($M\ L^{-3}$),
- z_{ss} is the depth of the surface layer (L), and
- A_{tip} is the surface area of the TIP (L^2).

The surface sediment area of the TIP ($2.0\text{x}10^6\ m^2$) and the density of surface sediments ($0.77\ g\ cm^{-3}$) were developed from information provided by the USEPA (USEPA, 1997). Annual total loadings of PCB homologs (j) across the TIP ($W_{tip,j}$) were calculated using measured annual paired loadings from Rogers Island and the TID from 1993 to 1996 (O'Brien & Gere, 1994b, 1995, 1996b, 1997c) in accordance with the following expression:

$$W_{tip,j} = \frac{\sum_{i=1}^{n} Q_{fe,i} * (C_{tid,i,j} - C_{ri,i,j})}{n} x\ 365 \quad (4\text{-}2)$$

where:

- $Q_{fe,i}$ is the daily average flow at the USGS Fort Edward gauging station for day i ($L^3\ T^{-1}$),
- $C_{tid,i,j}$ is the concentration of PCB homolog j on day i at the TID station ($M\ L^{-3}$),
- $C_{ri,i,j}$ is the concentration of PCB homolog j on day i at the Rogers Island station ($M\ L^{-3}$), and
- n is the number of paired samples collected at the Rogers Island and TID stations for the year in question.

The calculated average annual total PCB loadings across the TIP, calculated as the sum of homolog loadings, are presented in Table 4-1. The average annual load ranged from a low of 84 kg yr^{-1} in 1995 to a high of 407 kg yr^{-1} in 1996. The four year average loading is 248 kg yr^{-1}.

Table 4-1. Average Annual Total PCB Loading Across TIP from 1993 to 1996.

Year	No. of Paired Samples	Average PCB Load (kg yr^{-1})
1993	49	202
1994	34	297
1995	45	84
1996	57	407
Average	**46**	**248**

The depletion of 1984 surface sediment PCBs was estimated simply by dividing the estimated 1984 surface sediment mass of PCB homologs by the annual flux rate as calculated above using paired Rogers Island and TID data and projecting into the future. The year in which the surface sediments would become depleted of homolog j (Yr_j) was calculated as follows:

$$Yr_j = \frac{M_{j,ss}}{W_{j,tip}} + 1984 \tag{4-3}$$

The results are presented in Table 4-2 below[6].

[6]This calculation is conservative since historical flux rates were likely greater than those measured in the 1990s because the higher surface sediment PCB concentrations in the 1980s would have resulted in higher flux rates than those observed in the 1990s.

Table 4-2. Surface Sediment PCB Inventory Depletion Under Average 1993-1996 TIP PCB loadings.

Homolog	Mass of PCBs in TIP Surface Sediments in 1984[1] (MT)	Load from TIP (MT yr^{-1})	Year in Which Surface Sediment Reservoir Depleted
Mono	0.58	0.055	1995
Di	1.40	0.117	1996
Tri	1.00	0.062	2000
Tetra	0.41	0.016	2009
Penta	0.13	0.002	2040
Total	**3.52**	**0.25**	-

1) The mass of PCB homologs was calculated by multiplying the average PCB homolog distribution of the 1994 low resolution cores (USEPA, 1995) and the estimates of TIP PCB mass obtained by statistical analysis of the 1984 NYSDEC data (USEPA, 1997).

This mass balance calculation indicates that, if surface sediments of the TIP were the sole source of PCBs contributing to the apparent loading increase observed over the TIP, then the mono, di, and tri homologs present within the surficial sediments in 1984 would be entirely depleted by the year 2000. This is particularly significant since the current water column measurements show a continuing source of mono- and dichlorinated PCBs from the TIP. Moreover, sediment sampling by both GE in 1991 (O'Brien & Gere, 1993b) and the USEPA in 1992 (USEPA, 1997) and 1994 (USEPA, 1995) indicate that significant reserves of PCB remain within the surface sediments of the TIP. Therefore, on a mass balance basis, the PCB loadings observed from the TIP between 1993 and 1996 cannot be representative of long-term surface sediment-water exchange processes. Another source of PCBs, possibly related to upstream sources, or data inadequacies as discussed below must be contributing to the observed loading from the TIP in the 1990s.

4.1.2 Measurement of ground water seepage rates

Direct field measurements of ground water seepage rates provided data with which to evaluate the hypothesis that ground water advection may be responsible for the anomalous PCB load detected in the TIP. This effort was prompted by the USEPA's invocation of a groundwater mechanism in the PMCR to account for the anomalous PCB loadings (USEPA, 1996). The mechanism of groundwater advection of PCBs from the sediments to the water column is described in detail in Appendix A, and a complete description of the groundwater investigation is documented elsewhere (HSI GeoTrans, 1997).

Direct measurement of groundwater seepage has been widely employed as a means of assessing the hydraulic and chemical interactions between groundwater and surface water, and to examine spatial and temporal patterns of groundwater seepage (Lee, 1977; Lee and Cherry, 1978; and Woessner and Sullivan, 1984; Gallagher et al., 1996). The seepage meters employed to monitor groundwater seepage within the Hudson River were modeled after the original design by Lee (1977), with modifications to reduce the potential for measurement biases that have been documented in the literature (e.g., Belanger and Montgomery, 1992, Shaw and Prepas, 1989). Seepage meters consisted of a cylindrical stainless steel vessel equipped with two ¼ inch Teflon bulkhead fittings, a Teflon air sampling bag equipped with a release valve, and ¼ inch Teflon tubing (HydroQual, 1997b; Figure 4-1). Two seepage meters were deployed at each of the six locations depicted in Figure 4-2. Measurements were taken at multiple sites within the TIP and one downstream site to allow delineation of spatial trends in groundwater seepage rates. Multiple seepage rate measurements were conducted over approximately a one month period between late May and late June 1997. This period was immediately after the annual spring high flows and snow melt, when hydraulic gradients between the groundwater system and the river were expected to be at their greatest.

The seepage meter study produced pronounced temporal and spatial patterns in groundwater seepage (HSI GeoTrans , 1997). Average seepage rates declined over the monitoring period from a high of 0.18 L m^2 hr^{-1} in late May to a low of -0.03 L m^2 hr^{-1} in mid June (Figure 4-3). A decreasing temporal trend occurred in measurements collected within the headwaters of the TIP at Site S1 (Figure 4-2). This observation is consistent with the reduction in hydraulic gradient observed in piezometers installed adjacent to the seepage meters (HSI GeoTrans, 1997) and that expected in response to seasonal changes in surface water and groundwater elevations.

Within the TIP, ground water seepage increased with distance upstream of the TID (Figure 4-4). This is expected since the hydraulic gradients near the TID would be affected by the artificial increase in surface water elevation produced by the dam. Seepage measurements were generally positive (flux of groundwater into the Hudson River) at sites S1 through S3 (Figure 4-4) located 3-5 miles upstream of the TID (Figure 4-2). In contrast, groundwater flow was consistently negative at site S5 (Figure 4-4) located just one mile upstream of the TID (Figure 4-2).

The groundwater seepage investigation produced temporal and spatial patterns in groundwater seepage that were consistent with both independent measurements of hydraulic gradients between the surface water and groundwater systems and our understanding of the Hudson River system. Piezometers installed adjacent to the seepage meters generally yielded hydraulic gradients indicative of water movement in the same direction measured within the seepage meters (HSI GeoTrans, 1997). Moreover, spatial and temporal patterns in groundwater seepage were consistent with those expected in response to both seasonal changes in surface water and groundwater elevation and the artificially elevated surface water condition at the downstream limit of the TIP as a consequence of the TID. However, the ground water seepage rates were, on average, approximately an order of magnitude lower than the value assumed during preliminary calibration of the USEPA PCB fate and transport model (1.3 L m^{-2} hr^{-1}; USEPA, 1996; Figures 4-3 and 4-4).

Ground water induced PCB flux from the sediments to the water column of the TIP were estimated as the product of groundwater seepage flow developed from the ground water seepage measurements and estimates of sediment pore water PCB concentrations in accordance with Equation A-19. The total groundwater flow was estimated as the product of the average volumetric seepage flux and the total area of the TIP. The mean surficial sediment pore water PCB concentration was calculated from the 0-5 cm section of sediment cores collected in 1991 based upon equilibrium partitioning concepts described in Equations A-13 and A-14. The organic carbon-based PCB partition coefficient was calculated using USEPA water column partitioning data (USEPA, 1997) and corrected for temperature using temperature correction functions (GE, 1997). The pore water dissolved organic carbon concentration was calculated as the mean surficial sediment (0-5 cm) TIP dissolved organic carbon measurements from the 1991 sediment survey (O'Brien & Gere, 1993b), and the equilibrium constant describing partitioning between freely dissolved PCBs and PCBs adsorbed to dissolved organic carbon was assumed equal to 0.1 K_{oc}.

Applying the parameter values in Table 4-3 to Equations A-13, A-14 and A-19 yielded groundwater induced PCB flux measurements of approximately 30 g day^{-1}. Assuming these seepage measurements represent an average seepage flux for the entire year, groundwater induced PCB loading contributes an estimated 11 kg yr^{-1} of PCBs to the water column. This represents approximately 4% of the average PCB loading observed from the TIP between 1993 and 1996 (Table 4-2). These estimates are conservatively high due to the assumption that the spring 1997 measurements are representative of groundwater flux for the entire year, even though they were collected during a period in which the hydraulic gradient between surface water and ground water was expected to be at its greatest. Based on these measurements and calculations, groundwater induced PCB flux cannot account for the anomalous loading observed from the TIP.

Table 4-3. Parameters Used to Calculate Groundwater Induced Advection of PCBs from Surface Sediments to the Water Column.

Parameter	Description	Value (units)
K_{oc}	organic carbon-based PCB partition coefficient	$10^{5.4}$ (L kg^{-1})
K_{doc}	dissolved organic carbon PCB partition coefficient	$10^{4.4}$ (L kg^{-1})
C_s/f_{oc}	organic carbon normalized surficial sediment (0-5 cm) PCB concentration	2110 (mg kg oc^{-1})
m_{doc}	pore water dissolved organic carbon concentration	33.7 (mg L^{-1})
q_{avg}	average measured ground water seepage rates	0.04 (L m^{-2} hr^{-1})
A_{tip}	area of the TIP	2.0 x 10^6 (m^2)

4.1.3 Estimates of low to moderate flow sediment bed resuspension

The hypothesis that low to moderate flow sediment resuspension may be contributing to the observed PCB loading from the TIP was assessed using the calibrated hydrodynamic and sediment transport model described in Section 3. The approach included the following:

- calculation of the total mass of sediment resuspended at different flow rates as the sum of the mass of sediment eroded from the different hydrodynamic/sediment transport model grid elements, and

- calculation of PCB resuspension at different flow rates as the product of the mass of sediment resuspended and surficial sediment PCB concentrations calculated as the area-weighted average of the 0-5 cm sections collected in 1991 (21.8 mg/kg; O'Brien & Gere, 1993b).

Additionally, field measurements of TSS through the TIP during the elevated loading period were collected and analyzed to test the predictions of the sediment transport model.

At flow rates less than 10,000 cfs, sediment, and consequently PCB, resuspension is minimal (Table 4-4 and Figure 4-5). At the average annual river flow rate of approximately 5,000 cfs at Fort Edward, the estimated mass of sediment erosion is approximately 6 kg[7]. Using the average 0-5 cm PCB data collected in 1991 (O'Brien & Gere, 1993b), this corresponds to an estimated PCB erosion of only 0.12 grams. It is only after river flow rates approach 10,000 cfs that sediment bed erosion significantly contributes to water column PCB loading. This is consistent with our understanding of sediment erosion processes, which predict no resuspension at bottom shear stresses less than the critical shear stress as described in § A.2.2.

The critical shear stress established for the cohesive sediments of the TIP is 1 dyne cm^{-2} (HydroQual, 1995b). The lack of significant bed erosion at flows less than 10,000 cfs indicates that there are only limited areas within the TIP where shear stresses exceed 1 dyne cm^{-2} at these flows. This is reflected in the data presented in Table 4-4. At 5000 cfs, less than 0.5% of the cohesive sediment bed area within the TIP is subject to sheer stresses greater than 1 dyne cm^{-2}. This increases to approximately 1% at flows of 10,000 to 20,000 cfs (Table 4-4). Moreover, negligible resuspension from the non-cohesive sediment bed occurs at flow rates below 10,000 cfs; the non-cohesive bed is not mobilized and fine sands cannot be resuspended because of bed armoring effects caused by coarse sands and gravels.

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[7]Sediment bed erosion is not represented as a rate ($M\ T^{-1}$) since erosion occurs instantaneously (see Appendix A).

Table 4-4. Estimates of TIP Sediment and PCB Erosion as a Function of River Flow.

River Flow[1] (cfs)	Cohesive Bed Eroded[2] (%)	Mass of Sediment Eroded[3] (kg)	Mass of PCBs Eroded[4] (g)
2500	.05	1.09e-03	2.37e-05
5000	.32	5.92e+00	1.29e-01
6000	.75	1.64e+02	3.57e+00
7000	.80	1.78e+02	3.88e+00
8000	.84	3.25e+02	7.08e+00
9000	.87	4.92e+02	1.07e+01
10000	.89	1.32e+03	2.88e+01
15000	.95	1.32e+04	2.88e+02
20000	.96	5.61e+04	1.22e+03

1) Flow at the headwaters of the TIP at Fort Edward, N.Y.
2) Percent of TIP sediment surface area subject to erosion under different river flows as calculated using the hydrodynamic and sediment transport model described in Section 3.
3) Mass of sediment eroded under the different flow conditions as calculated using the hydrodynamic and sediment transport model described in Section 3.
4) Estimates of PCB erosion calculated by multiplying the mass of sediment eroded by the 1991 area-weighted mean surface sediment (0-5 cm) PCB concentration within the TIP (21.8 mg/kg; O'Brien & Gere, 1993b).

The lack of significant sediment bed erosion at low to moderate river flows was also observed in field studies conducted on the river in 1996 and 1997 (O'Brien & Gere, 1998). Time of travel surveys, consisting of sampling at stations located along lateral transects established every 0.25 to 0.5 miles between Rogers Island and TID (Figure 4-6), yielded TSS concentrations that were generally less than 5 mg L^{-1} and did not produce patterns indicative of sediment bed erosion (Figure 4-7). During these studies, water column samples were collected from upstream to downstream so as to correspond with the flow of river water as it traversed the TIP and should have detected regions of the river subject to erosive conditions at the sampled flows.

The hypothesis that low flow sediment resuspension is contributing to the TIP anomaly can not be supported by sediment fate and transport theory or field data. The application of state-of-the-science hydrodynamic and sediment transport models predicts insignificant sediment bed erosion under the low to moderate flow conditions under which the TIP anomaly has been observed. Field measurements of TSS support these predictions. Therefore, the USEPA hypothesized mechanism of low-flow sediment resuspension cannot explain the TIP anomaly.

4.2 Additional PCB Sources

The second general hypothesis to explain the anomalous TIP PCB loading considers the possibility that additional PCB DNAPL loadings from the Allen Mill and Hudson Falls Plant site are entering or have entered the TIP without being detected at the Rogers Island sampling stations. Potential DNAPL loading mechanisms include:

- preferential transport of PCB laden sediments and PCB DNAPL along the sediment-water interface,

- pulse loading of PCBs associated with the periodic flooding of the Bakers Falls plunge pool as a result of the operation of the Adirondack Hydro Development Corporation's (AHDC) turbines or during elevated flow events, and

- transport of oil-soaked sediment into the TIP at the time of the Allen Mill collapse.

These hypothesized PCB sources were the subject of an extensive field research program sponsored by GE in 1996 and 1997.

4.2.1 Simulation of PCB oil transport

The hypothesis that PCB DNAPL loadings may be transported from the plant site areas into the TIP was examined in a field research program that simulated the fate of PCB DNAPL in the river. The program included the direct discharge of a conservative tracer with properties similar to PCB DNAPL into the river near Hudson Falls and tracking of the tracer downstream. The details of this study have been documented elsewhere (HydroQual, 1997c). In summary, the study included:

- injection of 20 pounds of fluorescent particles (Figure 4-8) with a density similar to that of Aroclor 1242 into the river from the AHDC Hydroelectric Plant,

- collection of daily composites of water column and bed load particle samples in specially designed sampling devices (Figure 4-9) at or near routine water column monitoring stations for three days following fluorescent particle injection,

- analysis of water column and bed load particle samples for fluorescent resin particle concentration,

- calculation of the total mass of fluorescent particles passing each station over the three day period by scaling up the mass of particles trapped within the sampling devices to reflect the entire river cross section, and

- development of fluorescent particle mass balances to evaluate particle transport and, by inference, the transport of PCB DNAPL within the Hudson River.

The results of the three day fluorescent particle mass balance appear in Figure 4-10. Of the 9.1 kg of particles injected into the river near the Hudson Falls Plant site (RM 196.9), an estimated 73% (6.6 kg) was transported downstream to the Fort Edward station (RM 194.4). These calculations suggest that an estimated 27% (2.5 kg) of the fluorescent particle mass released into the river was retained between the particle injection point and the Fort Edward station. This pattern of particle retention continued downstream, as approximately 18% of that injected (1.6 kg) was retained within the river between the Fort Edward and Rogers Island sampling stations. Over the three day study, only an estimated 2% (0.1 kg) of the particles were transported downstream of the Thompson Island station (Figure 4-10). These data indicate that 98% of the particles injected in the river near the Hudson Falls plant site were retained in the river upstream of Thomson Island.

Fluorescent particles retained upstream of the Fort Edward station consisted predominantly of the smallest particle size class (19-38 μm) and the two size classes greater than 190 μm (Figure 4-11c). This distribution was calculated as the difference between the mass of particles injected (Figure 4-11a) and the mass of particles passing the Fort Edward station (Figure 4-11b), on a size class basis. The apparent retention of the smaller particles between the injection point and the Fort Edward station may be the combined result of: 1) under sampling of smaller particles by the 100 μm mesh of the *in situ* filtration devices and, 2) loss of particles near the injection point. The larger particles retained upstream of the Fort Edward station likely settled within the river near the injection point as they were never detected downstream.

Several inferences with regard to the transport and fate of PCB DNAPL within the Hudson River may be drawn from the fluorescent particle data. First, PCB DNAPL droplets in excess of 190 μm will likely be sequestered near the discharge point where they would be subject to dissolution. Mobilization of these droplets downstream may be limited at flows less than the 7000 cfs observed during this study, but may occur under higher flow conditions. Such temporary storage is demonstrated by the presence of fluorescent particles in sediment bed load samples collected during the spring high flow event of April 1997 (HydroQual, 1997c). Second, PCB DNAPL existing in the river over the particle size range tested (19-380 μm) would be deposited upstream of the TID. That is, little, if any DNAPL would be transported downstream of the TIP. Once within these sediments, DNAPL would be subject to other fate determining processes such as dissolution, diffusion, advection, and partitioning onto sediment solids.

The PCB DNAPL transport study provides a unique data set from which to infer the fate of PCB DNAPL loadings within the Hudson River system. The fluorescent particles employed during this study possessed a density similar to that of PCB DNAPL oils found on the Hudson Falls plant site and a particle size distribution believed to be representative of DNAPL oil droplets within the river (HydroQual, 1997c). As such, the behavior of these particles was considered to represent PCB DNAPL fate and transport in the system. Several conclusions regarding PCB DNAPL were drawn from the results of this study:

- PCB DNAPL with droplet sizes greater that approximately 200 μm entering the river under low river flow conditions will be sequestered near the point of entry into the system,
- PCB DNAPL sequestered in the river may be mobilized during high flow events, possibly as part of the sediment bed load, and
- PCB DNAPL transported into the TIP will be deposited within the surface sediments of the TIP.

The results of the PCB DNAPL study generally support the hypothesis that PCB DNAPL loadings from the Hudson Falls plant site (§1.2) may have contaminated the surface sediments of the TIP. This may have been occurring throughout the 1980s. However, it is unclear whether this mechanism has been contributing to the anomalous loading observed from the TIP during the 1990s.

4.2.2 High flow water column and sediment bed loading

The results of the DNAPL study suggest that PCBs may be transported from the vicinity of the Hudson Falls plant site and into the TIP as a pulse loading within the water column or within the sediment bed load during periods of high flow. To evaluate this hypothesis, high flow water column and sediment bed load sampling was conducted on the Hudson River during the spring high flow period of 1997 (O'Brien & Gere, 1998). The approach included:

- water column sampling and analysis for PCBs and TSS from the Fort Edward and TID stations along the rising and falling limb of the spring high flow event hydrograph between April 6 and 9, 1997, and

- sediment bed load sampling and analysis for PCBs within the east and west channel of Rogers Island (Figure 2-1) during the high flow event using a specially designed bed load sampling device (Figure 4-12).

Water column samples were collected as vertically integrated composite samples consisting of discrete samples collected from three depths in the east and west channels of Rogers Island at Fort Edward and as discrete grab samples collected in a stainless steel vessel at TID.

During the 1997 spring high flow period, instantaneous flows at the Fort Edward gauging station increased from approximately 9,000 cfs on April 6 to a maximum flow rate of approximately 19,400 cfs on April 8, 1997 (Figure 4-13a). These flows produced only modest increases in TSS levels (Figure 4-13b), as TSS concentrations never exceeded 12 mg/L, indicating that the event did not produce bottom sheer stresses capable of causing significant sediment resuspension. Water column total PCB concentrations also remained low during the high flow event, ranging between 10 and 30 ng/L (Figure 4-13c). At peak flow, water column concentrations represent a PCB loading of 1.3 kg/day at the Fort Edward station (Figure 4-13d).

The PCB loadings observed during the 1997 high flow period represent a significant reduction in high flow event driven PCB transport in the system compared to similar events sampled in 1992 and 1993 immediately following external PCB loadings to the system (Figure 2-3). The 1992 and 1993 spring flood events produced maximum PCB loadings of approximately 50 lbs/day and approached the loadings observed in the late 1970s. These observations indicate:

• high flow events were an important mechanism transporting PCBs downstream from the plant site regions of the river and into the TIP during the early 1990s, and

• remedial measures conducted on the plant site (§1.2) appear to have mitigated PCB discharges to the river and significantly reduced high flow PCB transport in 1997 (Figure 2-3).

Flow event-driven transport of sediments and associated PCBs along the sediment-water interface (sediment bed loading) does not appear to be a significant mechanism by which PCBs are transported into the TIP. Particulate phase PCB concentrations of sediment bed load samples collected from both the east and west channel of Rogers Island contained less than 15 mg/kg PCBs (Figure 4-14), and two of the three samples collected contained less than 5 mg/kg PCBs. These concentrations are significantly lower than the water column particulate phase PCB concentrations measured at Fort Edward by the USEPA in 1993 and the average surface sediment (0-5 cm) PCB concentrations measured in 1991. These data indicate that sediment bed loading in 1997 was not a significant contributor to the PCB loading into the TIP.

Based upon the high flow data collected in 1997, flow event driven water column and sediment bed load PCB transport do not appear to be significant mechanisms for continued pulse loadings of PCB from the plant site regions and into the TIP. However, the high flow events in the early 1990s did mobilize significant PCB loads into the system. These loadings may have contributed to PCB DNAPL transport into the TIP as the results of the DNAPL transport study (§

4.2.1) indicate that PCB oils transported downstream of the plant site would be deposited in the TIP. This mechanism may have contributed to the elevated TIP loadings observed following the Allen Mill loading event by elevating surface sediment PCB concentrations. Additionally, PCB loading via this mechanism may have contributed to TIP surface sediment PCB contamination prior to the mill event. However, the results of the 1997 high flow study indicate that remedial measures conducted on the Hudson Falls plant site and the Allen Mill have mitigated these sources to the river and greatly reduced the transport of PCB into the TIP. Hence, to the extent that flow event driven pulsed loadings contributed to the TIP load in the early 1990s, their effect should be greatly diminished in the future.

4.2.3 Pulse loadings during periodic flooding of Bakers Falls plunge pool

Pulse loadings during periodic flooding of the Bakers Falls plunge pool as a result of the operation of the AHDC hydroelectric facility is another possible source of PCBs to the TIP. The trash rack assemblies that protect the turbines from debris transported through the intake raceway require cleaning every few days. During this process, flow through the facility ceases and the racks are pneumatically cleaned of debris, which is carried by water flow through a bypass structure along the western shore of Bakers Falls and into the plunge pool. Due to the reduced flow through the hydroelectric facility, the surface water elevation of the pool upstream of Bakers Falls increases and spills over the dam. This inundates the falls and provides additional waters for flushing of PCBs downstream.

The periodic flooding of Bakers Falls was considered as a possible source of PCBs to the TIP due to the PCB DNAPL seeps located within fractures in the bed rock outcroppings of the falls and within the plunge pool. A specific monitoring program was designed to assess the relative contribution of this PCB source to the TIP loading anomaly (O'Brien & Gere, 1997a).

The approach used to monitor the impact of hydrofacility operation on PCB transport in the system included (O'Brien & Gere, 1997a):

- release of rhodamine WT dye into the plunge pool prior to trash rack washing activities at the hydroelectric facility,
- monitoring of the dye front and collection of samples representing water flushed from the pool at three locations: the plunge pool, Fort Edward, and the TID, and
- analysis of collected samples for PCBs and TSS.

Three hydrofacility operation monitoring events were conducted; one in September 1996 and two in June 1997.

The periodic flushing of Baker Falls appears to have a significant effect on the PCB concentrations found within the plunge pool (Figure 4-15). During two of the three sampling events, PCB concentrations within the plunge pool increased substantially from near the method detection limit of 11 ng/l before inundation of the falls to approximately 400 ng/l (June 9, 1997) and 130 ng/l (June 23, 1997) after falls inundation. These data suggest that PCB DNAPL that accumulates on the bedrock outcrops of the falls, is transported into the plunge pool as water flows over the falls. The magnitude of the release from the falls is difficult to assess from the plunge pool data due to uncertainties over flow characteristics of the pool. Therefore, the impact of the loading from the falls was assessed by examining the transport of these PCBs downstream at the Fort Edward station.

Periodic loading of PCBs as a result of hydroelectric facility operations had little effect on PCB loadings into the TIP. Although water column PCB concentrations at the Fort Edward station increased in response to the loadings from the plunge pool, these increases were relatively small (Figure 4-15). Moreover, there was no evidence of any correlation between the PCB levels observed within the plunge pool and those observed at Fort Edward. The largest increase in PCB concentrations in the plunge pool was observed during the June 9, 1997 sampling event. In contrast, PCB concentrations from the Fort Edward station on this date increased only slightly. Therefore, the total mass of PCB transported downstream as a result of this loading mechanism is not sufficient to appreciably increase PCB loading observed at the Fort Edward station.

Data collected in association with the hydrofacility operations monitoring indicate that periodic inundation of Bakers Falls provides relatively insignificant PCB loads into the TIP. Hence, this mechanism is not likely responsible for anomalous loadings from the TIP.

4.2.4 Localized PCB source areas within TIP

PCB DNAPL loadings from the Hudson Falls plant site area and the Allen Mill during the early 1990s (§ 2.2) may have contaminated surface sediments within localized regions of the TIP. This hypothesis was generally supported by the PCB DNAPL study which indicated that oil phase PCBs entering the river within the vicinity of the Hudson Falls plant site would be transported downstream and deposited in the TIP (§4.2.1). To assess the importance of this potential cause of the TIP anomaly, time-of-travel surveys were conducted through the TIP. These surveys were designed to monitor a single mass of water as it traveled through the pool. In this way, localized areas potentially contributing a disproportionate quantity of PCBs to the water column load could be detected.

Detailed information regarding the methods employed for the TIP time-of-travel studies is provided elsewhere (O'Brien & Gere, 1998). In summary, the surveys consisted of sampling along lateral transects established every 0.25 to 0.5 miles between Rogers Island and TID, with sampling stations at three positions across each transect: east shore, west shore, and center channel (Figure 4-

6). Transects were sampled from upstream to downstream so as to correspond with the flow of river water. Stations along each transect were sampled simultaneously. Time-of-travel between each transect was estimated from flow information retrieved from the USGS gauging station located in Fort Edward (1996) and by monitoring a pulse of dye injected into the river (1997). A total of four time of travel surveys were conducted: two in September 1996 and two in June 1997. Samples from each station consisted of vertically stratified composite samples collected from three depths and were analyzed for PCBs and TSS.

The four TIP time of travel surveys exhibited similar spatial trends in total PCB concentration within the center channel (Figures 4-16 and 4-17). PCB concentrations were generally at or near the method detection limit of 11 ng/L at the Rogers Island sampling station and increased gradually to approximately 30 ng/l over the first 2 miles of the TIP, to river mile 193. Over the four mile section of the TIP between river mile 193 and 189, center channel PCB concentrations increase by approximately 40 to 60 ng/L. At average flows of approximately 4,000 cubic feet per second (cfs) observed during the surveys, this increase represents a mass loading rate of 0.4 - 0.6 kg day^{-1}. These mass loading rates represent sediment areal flux rates of approximately 0.3 to 0.4 mg m^{-2} day^{-1} across this region of the TIP. This mass loading rate is generally consistent with the load expected from observed 1991 surface sediment PCB concentrations. It does not appear that any additional load, other than that attributed to surface sediments, is required to achieve the observed water column PCB concentrations between river miles 193 and 189.

The TIP survey results indicate elevated PCB concentrations in waters along the eastern and western shoreline. These occasional high values do not necessarily indicate the presence of an area of elevated PCB flux from the sediments. Rather, they appear to be the result of lateral variations in river flow. For example, pronounced increases in water column PCB concentrations along the eastern shore across from the Snook Kill (Figure 4-18; Transect 12) can be attributed to a change in hydrodynamics in this region of the river. The elevated concentrations occur downstream of a group of small islands that impede river flow along the eastern shore (Figure 4-6). Field measurements of flow velocities in this region of the river indicate the high concentrations were measured in backwater areas (O'Brien & Gere, 1998). Under these conditions, surface sediments at the same PCB concentration as upstream areas and exhibiting the same areal PCB flux would produce higher water column PCB concentrations. This phenomenon was observed along several of the near shore areas (Figure 4-18).

To illustrate the backwater effect, consider a section of the river having a sediment area A_s (L^2). Water flows into and out of this section of the river at a rate of Q (L^3 T^{-1}). Assume water flowing in does not contain PCBs and the only water column source is diffusion from contaminated sediments (J_s: M L^{-2} T^{-1}). At steady state, the PCB concentration in water leaving this area (C_{out} :M L^{-3}) can be calculated as:

$$C_{out} = \frac{J_s A_s}{Q} \qquad \text{4-4}$$

Given a uniform areal PCB flux rate of 0.4 mg m^{-2} day^{-1} and a sediment area of 100,000 m^2 (the approximate area of the eastern river channel between transects 10 and 12), the PCB concentration in water traveling over this sediment would increase in inverse proportion to the river flow rate, as shown in Table 4-5.

Table 4-5. Relationship between river flow rate and PCB concentration considering a constant sediment flux rate.

Flow Rate (cfs)	C_{out} (ng/L)
10	1635
50	327
100	164
500	33
1000	16

To further demonstrate the importance of river hydrodynamics in determining spatial patterns of water column PCB concentrations, the two-dimensional hydrodynamic model described in Section 3 was used to estimate river flow velocities within the TIP. These results are presented in Figure 4-19 for a total river flow rate of 4380 cfs[8]. The model predicts the greatest river flow velocities within the center channel, with lower velocities along the shorelines, a pattern consistent with the field measurements described above. The impact of spatially varying flow velocities on observed water column PCB concentrations was simulated by:

•applying a spatially uniform flux of a conservative substance from the sediments to the water column,

•calculating water column concentrations for each of the model grid elements, and

•normalizing water column concentrations to the average concentration passing TID[9].

[8]The average flows for the TIP time-of-travel surveys.

[9]In this way the influence of hydrodynamics on the predicted water column concentrations can be observed independent of the actual flux used in the calculation.

The results of these calculations appear in Figure 4-19 and demonstrate that given a uniform sediment flux rate, water column concentrations are dependant on river hydrodynamics. The largest concentrations occur in regions with the slowest flow velocities. This simplified representation of a uniform sediment source underscores the importance of understanding small-scale differences in river hydrodynamics when interpreting the spatial patterns in water column PCB loading observed during the time of travel surveys.

In addition to river hydrodynamics, spatial patterns in water column PCB concentrations depend upon spatial variations in sediment PCB flux. The flux of PCBs from surface sediments to the water column depends on the organic carbon normalized PCB concentration, the sediment-water exchange coefficient, and the PCB partition coefficient as described using Equations A-10 to A-15 (Appendix A). Regions of the river with equal surface sediment organic carbon normalized PCB concentrations and composition contribute equally to the water column PCB load. Data gathered by the NYSDEC in 1984 indicate that mean organic carbon normalized PCB concentrations are similar inside and outside the sediment "hot spot" areas (Table 4-6; Figure 4-20)[10]. Moreover, organic carbon normalized PCB concentrations were similar for both coarse grained and fine grained sediments collected in 1991 from the TIP (Table 4.6). Therefore, coarse grained and fine grained sediment areas and "hot spot" and non-"hot spot" areas are expected to have similar sediment pore water PCB concentrations and, through the process of sediment diffusion, similar areal PCB fluxes. Such conditions would produce the pattern of gradually increasing water column PCB concentrations observed within the center channel during the time-of-travel surveys conducted in 1996 and 1997 (Figures 4-16 and 4-17). Thus, the differences in water column PCB concentration between the center channel and the near-shore zones are not evidence that "hot-spots" dominate the PCB flux.

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[10]In this analysis, 1984 organic carbon concentrations were estimated as 40% of the reported volatile solids concentration.

In fact, the sediment data suggest that the non-"hot spot" areas dominate because they constitute the vast majority of the river bottom. Localized variations in river hydrodynamics are the likely cause of the concentration variations observed during the time-of-travel surveys.

Table 4-6. TIP Organic Carbon Normalized Surface Sediment PCB Concentrations: 1) Both Inside and Outside NYSDEC "Hot Spots" in 1984 (0-2.5 In.), and 2) for Coarse Grained and Fine Grained Sediments Collected in 1991 (0-5 cm).

Sediment Survey	Location/ Sediment Type	# Observations	Mean PCB Concentration (mg/kg oc)	Std. Deviation (mg/kg oc)
1984 NYSDEC	Inside "Hot Spots"[1]	155	2045	2069
	Outside "Hot Spots"	177	2030	1827
1991 GE	Coarse Sediments	16	2941	1824
	Fine Sediments	41	2185	2265

1) These statistics excludes one sample collected in 1984 which contained 331,000 mg PCB/kg oc.

The TIP time-of-travel surveys did not reveal any localized regions of elevated surface sediment PCBs within the pool that are disproportionately contributing to the water column PCB load. Elevated water column PCB concentrations along several of the near shore areas have been, at least partially, attributed to localized changes in the hydrodynamics. PCB loadings characterized using center channel data uninfluenced by localized hydrodynamics depict an approximately uniform increase in PCB mass loading that is consistent with surface sediment exchange processes and the 1991 surface sediment PCB concentrations. These observations are discussed further in §4.3 below.

4.3 Erroneous Estimates of PCB Flux Due to Biased Sampling

The hypothesis that biased sampling may have resulted in erroneous estimates of PCB flux into or out of the TIP was considered as a possible cause of the TIP anomaly. Biased low estimates of PCBs transported into and/or biased high estimates of PCB transported out of the pool could have produced the anomaly. Initial assessments of the routine monitoring stations located along the Route 197 Bridge in Fort Edward and the western wing wall of the TID suggested that samples collected from these stations provided reasonably representative estimates of PCB loading into and out of the TIP, respectively (O'Brien & Gere, 1993a; HydroQual, 1995a). Nonetheless, this hypothesis was further tested during extensive field efforts conducted in 1995, 1996, and 1997.

4.3.1 Route 197 Bridge in Fort Edward

The approach for assessing the representativeness of the Fort Edward monitoring station involved the simultaneous collection of water column samples from the routine monitoring station and at stations across a transect perpendicular to river flow located approximately 0.5 miles upstream (Figure 4-21). The transect was located in a region of the river characterized by shallow, vertically well mixed, and swift moving waters to minimize the potential for vertical stratification of water column PCBs due to particle size sorting or sediment bed loading. Nonetheless, samples were collected from two depths: near the air-water interface (0-3 inches of water column) and the sediment-water interface (3-6 inches from the sediment bed; O'Brien & Gere, 1996c). Samples along the transect were collected as temporal composites with equal volume aliquots collected every hour over a six hour period. Samples were collected from the routine monitoring station on the same day as the transect samples as an equal volume composite of samples collected at three depths from both the east and west channel of Rogers Island (O'Brien & Gere, 1996c). Sampling was performed twice during the fall of 1995 (September 17 and October 3, 1995).

The routine monitoring station located at the Fort Edward station provides reasonably representative data for assessing the PCB loading into the TIP. Results of the transect study indicate that PCB concentrations of samples collected from the routine monitoring station agree well with samples collected across the transect located 0.5 miles upstream (Figure 4-22). PCB concentrations in transect samples were generally within 25% of the concentrations found in samples collected from the routine station. Furthermore, the transect monitoring indicates that PCBs within this reach of the river, and under the flow conditions sampled, are both vertically and laterally mixed (Figure 4-22). There was no significant difference between PCB concentrations within the shallow or deep samples collected at the transect stations nor any significant trend in PCB concentration across the river (Figure 4-22).

These data indicate that routine monitoring at the Fort Edward station provides reasonable data upon which to base estimates of PCB loading into the TIP. Therefore, it is not likely that biased sampling at the Fort Edward station contributed to the TIP anomaly.

4.3.2 Thompson Island Dam

The approach for assessing the representativeness of the TID monitoring station involved the simultaneous collection of water column samples from the center channel of the river at a location approximately 1000 feet upstream of the dam and from the routine station at the western wing wall of the dam. The results of the time-of-travel surveys indicated that samples from this center channel station accurately represent average PCB concentrations within this section of the river and are uninfluenced by localized changes in hydrodynamics that may bias samples collected along the shoreline (§4.2.4). Additional sampling was conducted from the eastern wing wall of the dam and from stations located immediately downstream of the dam within the western and eastern channels of the river at Thompson Island (Figure 4-23). Sampling and analysis methods generally followed the protocols described within the sampling and analysis plans (O'Brien & Gere, 1997a, 1997b). Generally, where water column depth permitted, samples consisted of vertically integrated composites made up of discrete aliquots collected from three depth intervals (0.2, 0.5 and 0.8 times the total depth) using a stainless steel Kemmerer Bottle sampler. Where water depth restricted the use of the Kemmerer Bottle, grab samples were collected using a stainless steel beaker. Several of the sampling rounds also consisted of temporal composites consisting of discrete aliquots collected over a several hour period and composited. Finally, the sampling occurred from upstream to downstream with the timing corresponding to the estimated time-of-travel of a parcel of water between the stations. Water column samples were analyzed for PCBs and TSS.

The TID monitoring program found that the routine shoreline sampling station at TID-west (Figure 4-23) consistently yielded PCB concentrations in excess of those observed from the center channel station. Fifteen pairs of samples were collected from the center channel of the river and TID-west between September 1996 and November 1997. In all pairs, the samples from the TID-west station contained higher PCB concentrations (Table 4-7 and Figure 4-24). The difference between the samples ranged from 3 to 167 ng/L representing between a 6 and 163% increase (Table 4-7 and Figure 4-24). The increase observed between the two stations does not appear to be the result of resuspension of contaminated sediments since there does not appear to be any significant bias in TSS concentrations between the two stations (Figure 4-25).

Table 4-7. Paired Center Channel and TID-west Total PCB Concentrations

Date	Center Channel ($ng\ L^{-1}$)	TID-west ($ng\ L^{-1}$)	Difference ($ng\ L^{-1}$)	% Difference[1]
18Sep96	54	142	88	163
25Sep96	50	53	3	6
29Oct96	50	102	52	104
4Jun97	84	113	29	35
17Jun97	105	272	167	159
30Jun97	175	271	96	55
14Jul97	92	190	98	107
28Jul97	67	116	49	73
13Aug97	50	90	40	80
9Sep97a	64	107	43	67
9Sep97b	70	90	20	29
10Sep97	52	94	42	81
01Oct97	65	72	7	11
10Oct97	74	82	8	11
16Oct97	83	87	4	5
Mean	76	125	50	66
Std. Dev.	32	67	46	52

[1] Percent difference calculated (TID-west - center channel)/center channel * 100.

The difference in PCB levels between the two stations suggested that either: 1) one or both sampling stations were biased and unrepresentative of average PCB concentration in water passing the TID, or 2) the sediments between the center channel station located approximately 1000 feet upstream of the dam and the dam were contributing, on average, approximately half the total PCB load observed over the entire TIP (Table 4-7). A second phase of the monitoring program was conducted to evaluate this.

Phase 2 of the TID monitoring program involved the collection of water column samples from numerous locations both upstream and downstream of the TID during four sampling events in August and September, 1997. As with the other sampling events, samples from the TID-west station contained higher PCB concentrations than those collected upstream at the center channel station (Figure 4-26). The center channel samples produced PCB concentrations consistent with the generalized PCB loading pattern observed throughout the TIP as observed during the time-of-travel surveys (§4.2.4). Similarly, water column samples collected downstream of the dam in both the western and eastern channels were consistent with center channel samples collected upstream of the dam, and were significantly lower than concentrations along the shoreline at the dam. PCBs in samples downstream of the dam within the western and eastern channels were, on average, 34% lower than in samples collected from the dam. These data clearly indicate that the routine samples collected from the TID-west station are not representative of average concentrations passing the TID.

Water column monitoring conducted by the USEPA from the western shoreline upstream of the TID likely contains a bias similar to that of the TID-west station. On October 1, 10, and 16, 1997 water column samples were collected from a western shoreline station upstream of the TID from a location close to that sampled by the USEPA during their water column transect and flow averaged sampling studies. These samples produced PCB concentrations significantly higher than those collected from the more representative center channel stations upstream and downstream of the dam (Figure 4-26). These data provide strong evidence that the TIP PCB flux estimates developed by the USEPA are based upon biased data.

Water column monitoring downstream of TID at Fort Miller[11] and Schuylerville, NY provides further evidence that the routine TID-west station and the USEPA TID station produces biased high PCB concentrations. Samples from the Fort Miller and Schuylerville stations contained PCB concentrations consistent with both the measurements at the stations downstream of the TID and our understanding of PCB dynamics in the river (Figure 4-27). The sediments within river reaches between TID and Fort Miller, and Fort Miller and Schuylerville contain PCBs at levels that should produce water column PCB loadings through sediment-water exchange mechanisms under low flow conditions (O'Brien & Gere, 1993b). The monitoring conducted since August 13, 1997 between Fort Edward and Schuylerville produces an approximately linear increase in PCB loadings with river mile (0.1 lb mi^{-1} day^{-1} ; Figure 4-27), indicating that the sediments of the TIP are contributing no more PCBs than adjacent reaches downstream.

In contrast, low flow loading estimates developed from USEPA water column transect data produce a spatial pattern of PCB loading that is inconsistent with the spatial patterns of sediment PCB levels and our understanding of sediment-water interactions (USEPA, 1997; Figure 4-28). Samples collected by the USEPA during August 1993 produced a spatial pattern of PCB loading that suggested the loading from the TIP was elevated compared to adjacent reaches of the river, as the calculated loading at the TID exceeded that measured at the Schuylerville station (Figure 4-28). This is inconsistent with spatial patterns of PCB loading observed during the same season in 1997 using data from stations considered to be free of sampling bias (Figure 4-28). This analysis provides further evidence that the loading estimates developed by the USEPA and presented in the DEIR (USEPA, 1997) overestimate PCB loading from the TIP.

[11]The Fort Miller sampling station is located approximately two miles downstream of the TID.

4.3.3 Possible mechanism for the observed bias at TID-west

The observed bias at TID-west may be the result of incomplete lateral mixing. The region immediately upstream of the TID along the east and west shorelines consist of emergent aquatic vegetation beds that may be hydraulically isolated from the main stream of the river. PCB concentrations in these waters are likely elevated in comparison to PCBs in the center channel samples as the diffusive flux from sediments is integrated into a smaller volume of water. Shear forces along the boundaries of these water masses may promote the transport of waters containing higher PCB concentrations within a thin band along the shorelines. This thin band of water may be what is sampled from the shoreline locations at the TID and what was sampled by the USEPA during its transect and flow averaged sampling studies of 1993 (USEPA, 1997). This hypothesis is supported by two-dimensional hydrodynamic model estimates of river flow velocities (described in §3.2.1) which identify a region of river flow immediately upstream of the TID that is lower than that in the main channel of the river. Additionally, application of a spatially uniform flux of a conservative substance from the sediments to the water column (§4.2.4), produces normalized concentrations at the TID west station that are in excess of that observed across the face of the dam (Figure 4-29). These data demonstrate that river hydrodynamics play an important role in the representativeness of the samples collected from the TID-west station. Nonetheless, it is apparent that the routine sampling station located at the western wing wall of the TID produces PCB concentrations that are not representative of the average PCB concentration across the TID.

4.3.4 Composition of the sediment PCB source

The composition of the summer low-flow (June - August 1997) average TIP load was calculated as the difference in water column derived PCB congener peak loading across the TIP using unbiased data collected from Fort Edward and the vicinity of the TID. The source of this loading was assessed by calculating the required composition of a surface sediment source, assuming equilibrium partitioning between sediments and pore waters and a diffusive mass transport mechanism. Specifically, the approach included:

1) Calculation of TIP water column PCB peak (based on a DB-1 capillary column) loadings from paired Fort Edward (C_{fe}) and unbiased TID water column PCB data (C_{tid}) in accordance with the following equation:

$$W_{wc} = Q_{fe}(C_{tid} - C_{fe}) \qquad 4\text{-}5$$

where:

Q_{fe} is Fort Edward flow ($L^3 T^{-1}$), and

2)Calculation of the sediment-phase PCB composition assuming the load calculated using Equation 4-5 originates from surface sediments and is transported to the water column via diffusional processes. This load was calculated by substituting W_{wc} for W_d in Equation A-15 (Appendix A), solving for C_s on a DB-1 peak basis, and calculating the congener peak and homolog distributions. The parameters used in the calculation are summarized in Table 4-8.

Table 4-8. Parameters Used in the Calculation of Surface Sediment PCB Source Signature.

Parameter	Description	Value	Units	Source
K_f	Sediment-water Exchange Coefficient	2	cm day^{-1}	GE Model Calibration
A_s	Surface Sediment Area	$2x10^6$	m^2	GE Hudson River GIS
m_{doc}	Pore Water DOC	33.7	mg L^{-1}	GE 1991 Sediment Survey
K_{oc}	Temperature Corrected Partition Coefficient	Varies w/ Temp. and Congener Peak	L kg^{-1}	USEPA Phase 2 Data as calculated in GE (1997)
f_{oc}	Fraction Organic Carbon	1.82	%	GE 1991 Sediment Survey
K_{doc}	DOC Partition Coefficient	0.1 K_{oc}	L kg^{-1}	—

The homolog distribution of the summer low flow TIP load appears in Figure 4-30a. On average, the homolog distribution of the TIP load consists of approximately 55% mono- and dichlorinated PCBs (Figure 4-30a). Back calculating the particulate-phase PCB concentration of surface sediments yields the average homolog distribution in Figure 4-30b. This PCB source best matches the surface sediment PCB composition as represented by the 0-2 cm sections of the USEPA high resolution cores collected from the TIP in 1992 (Figure 4-31a). In contrast, the source of the TIP load does not appear to match the composition of PCBs found at depths greater than 8 cm (Figure 4-31b). This analysis indicates that the source of the TIP PCB load is surface sediments as expressed through a diffusive flux mechanism.

4.4 New Paradigm for Sediment-Water PCB Exchange in the TIP

The discovery that a sampling bias at the TID-west station was responsible for the anomalously high PCB loading estimates from the TIP sets up a new paradigm for sediment-water interactions in the upper Hudson River: PCB loading patterns within the river are consistent both with conventional sediment-water exchange mechanisms and PCB concentrations and compositions found within the surface sediments. In response to loadings emanating from sediments throughout the upper Hudson River, primarily by way of diffusion, water column PCB concentrations increase approximately linearly with distance downstream. The observations of elevated loadings from the TIP following the release of PCBs from the plant site areas appear primarily to be the result of biased high PCB levels in samples collected from the TID-west station. This discovery now allows calculations of PCB fate and transport in the river to proceed without invoking extraneous PCB sources or unsupported sediment-water exchange mechanisms to account for the observed loadings.

The discovery of the sampling bias at the TID-west station invalidates conclusions drawn by the USEPA regarding TIP sediment loadings. In the DEIR, the USEPA concluded that the measured TIP load originated from the TIP sediments (USEPA, 1997). Based upon the unbiased sampling conducted since the fall of 1997, it appears that a significant portion of this loading was due to the sampling bias. The USEPA also stated that PCB transport downstream of the TIP was conservative, with little or no change in water column PCB loads with distance downstream. This pattern was produced by the biased high PCB data collected at the TID station. Unbiased data collected since the fall of 1997, produces a gradual increase in water column PCB loading between Fort Edward and Schuylerville as water flows over downstream PCB deposits (Figure 4-27).

SECTION 5
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary

A state-of-the-science model of PCB fate and transport has been configured to represent the upper Hudson River system and calibrated using extensive field data from the study area. The ability of the model to represent the short-term and long-term changes in water column and sediment PCB levels over the period from 1977 to 1991 indicates that the model provides a reliable, quantitative representation of the significant mechanisms in the upper Hudson River that affect the fate and transport of PCBs. However, comparison of the model to water column monitoring data from the TID for the period from 1991 to 1996 suggested that the model underestimated the increase in PCB levels between Rogers Island and the TID. Efforts to alter the model calibration to achieve water column levels consistent with the TID data were unsuccessful. This failing of the model led to the formation of hypotheses regarding additional PCB sources and biased sampling.

5.2 Conclusions

An extensive field sampling program and data analysis effort designed to address the various hypotheses regarding TIP PCB loading sources revealed five major conclusions:

1. <u>The water column concentrations measured at the TID overestimated the average PCB concentration in water passing this location</u>. The shoreline sampling location is influenced by a quiescent backwater immediately upstream that tended to result in higher PCB concentrations than the cross-sectional average concentration. Unbiased data collected in the main channel upstream and downstream of the TID indicate that cross-sectional average concentrations are approximately 1.5

times lower than those measured at the shoreline stations. The unbiased data indicate that sediments within the TIP contribute between a 0.5 and 1 lb/d of PCBs to the water column.

2. PCB levels increase in a linear fashion as water passes through the TIP, indicating a nearly uniform areal flux from sediments within the pool. The spatial patterns in water column PCB loading indicate that the diffusive flux of PCBs from sediments is similar across the TIP. This is due to the similarity of surface sediment organic carbon-normalized PCB concentrations that produce spatially invariant areal PCB flux.

3. The composition of the TIP PCB load is consistent with the surface sediment PCB composition considering equilibrium partitioning and sediment pore water exchange processes. During the summer low flow period, the composition of the TIP load closely resembles that which would result from equilibrium partitioning and pore water exchange with the surface sediments of the TIP. The composition is inconsistent with pore water exchange with sediments containing extensively dechlorinated PCBs such as those buried within the hot spot regions of the river.

4. Water column PCB loadings increase as water travels downstream of the TIP. The spatial patterns in water column PCB loading developed from unbiased data are consistent with known and understood sediment-water exchange mechanisms and surface sediment PCB concentrations. The conclusions drawn by the USEPA regarding the origin and fate of the TIP sediment source are not supported by the unbiased data. The biased data overestimate the magnitude and importance of the TIP sediment source.

5. While a significant portion of the TIP anomaly can be explained by sampling bias at the TID station, it is still possible that the Allen Mill event increased PCB levels in surface sediments within the TIP. Care must be taken when calibrating the long term fate and transport models to even

the unbiased data currently being collected as they may be affected by elevated surface sediment concentrations resulting from the mill loadings. Calibration to the corrected USGS data may provide a means to determine if the Allen Mill event did increase the surface sediment concentrations within the TIP. This would allow more accurate estimates of the sediment to water mass transfer coefficient and yield more reliable estimates of future water column PCB concentrations.

6. Based on observations of DNAPL in the river bed at Bakers Falls, the extent of DNAPL presence at the Hudson Falls site, and the results of the DNAPL transport study, it is possible that PCB DNAPL from the plant entered the river throughout the 1980s and was deposited in surface sediments of the TIP. Since this mechanism and PCB loading is not represented in the PCB fate and transport models, the models may not accurately describe what is occurring in the river. For example, surface sediment mixing, sediment water exchange, and PCB partitioning may be sensitive to an underestimation of surface sediment loading. However, the 1997 high flow data indicate that remedial activities at the site have successfully controlled the movement of DNAPL from the plant site into the river. This suggests that recovery rates may be accelerated over those observed in the late 1980s. The on-going water column monitoring program will provide data from which to evaluate the recovery rate of the river. Moreover, as it has been seven years since the last extensive survey, additional sediment sampling within the TIP may yield important information on the impact of the Allen Mill event and subsequent recovery on surface sediment PCB concentrations.

5.3 Recommendations

1. The analytical bias in PCB concentrations reported by the USGS for monitoring stations south of Ft. Edward during the mid to late 1980's should be assessed and corrected before the data are used in model calibration. If this data set is not corrected, the impact of the Allen Mill PCB

loadings on surface sediment PCB concentrations within TIP may be indeterminable, resulting in considerable uncertainty in model projections.

2. Model calibration needs to be based on at least 1 year of data from the unbiased sampling station located immediately downstream of TID. GE began collecting this data as well as data from Schuylerville last September. This is necessary given the strong seasonal variability in the PCB loading from the TIP observed in the existing data set.

3. Consideration should be given to performing additional sampling and analysis for PCBs in TIP sediments. Extensive surveys were conducted in 1977, 1984, and 1991. Given the uncertainty over the impact of the Allen Mill event on surface sediment PCB concentrations and the amount of time that has transpired since the last survey, this data would be useful in model calibration and increasing the reliability of the projections.

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FIGURES

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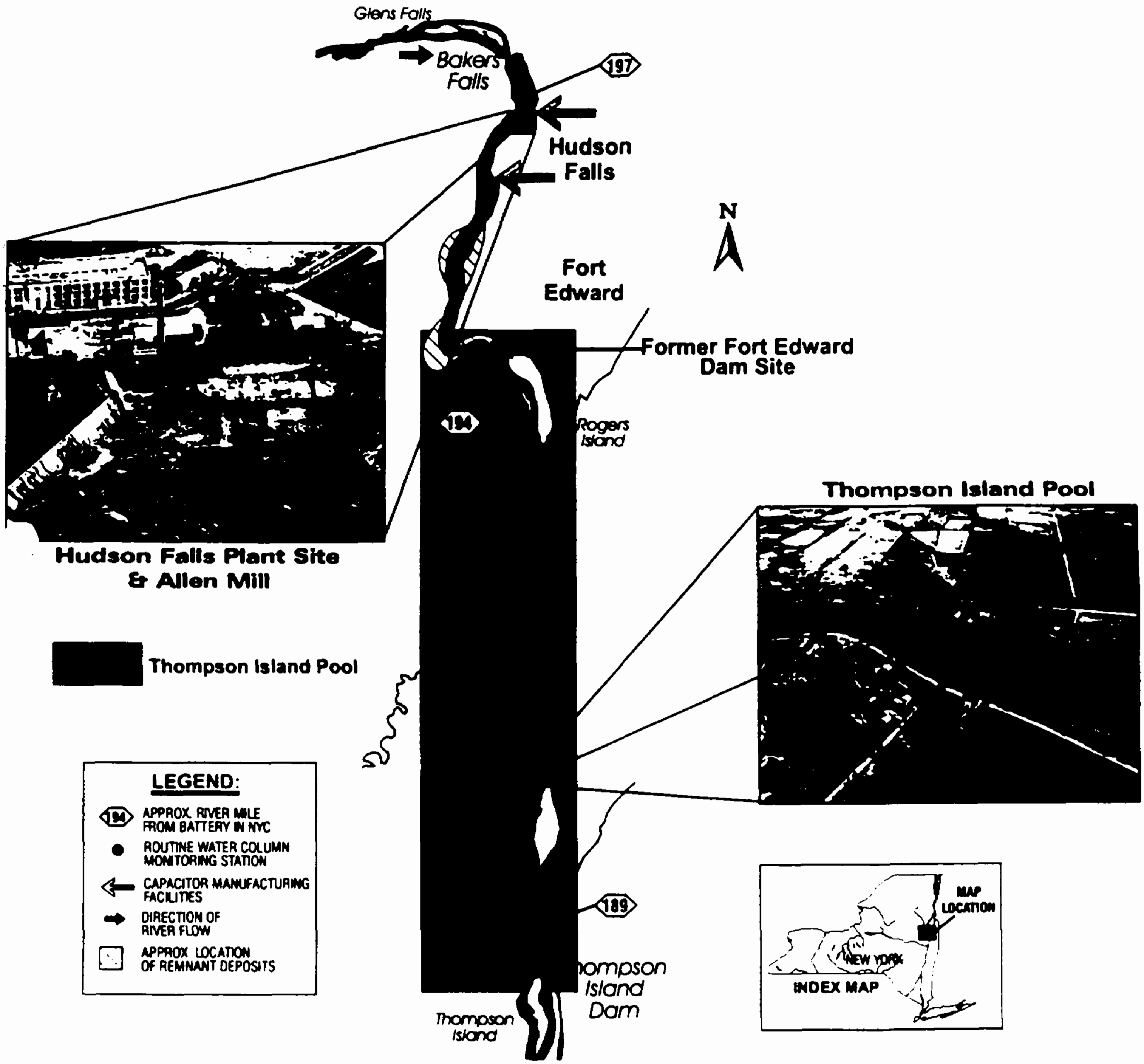


Figure 2-1.
Map of Hudson River from Glens Falls to Thompson Island Dam.

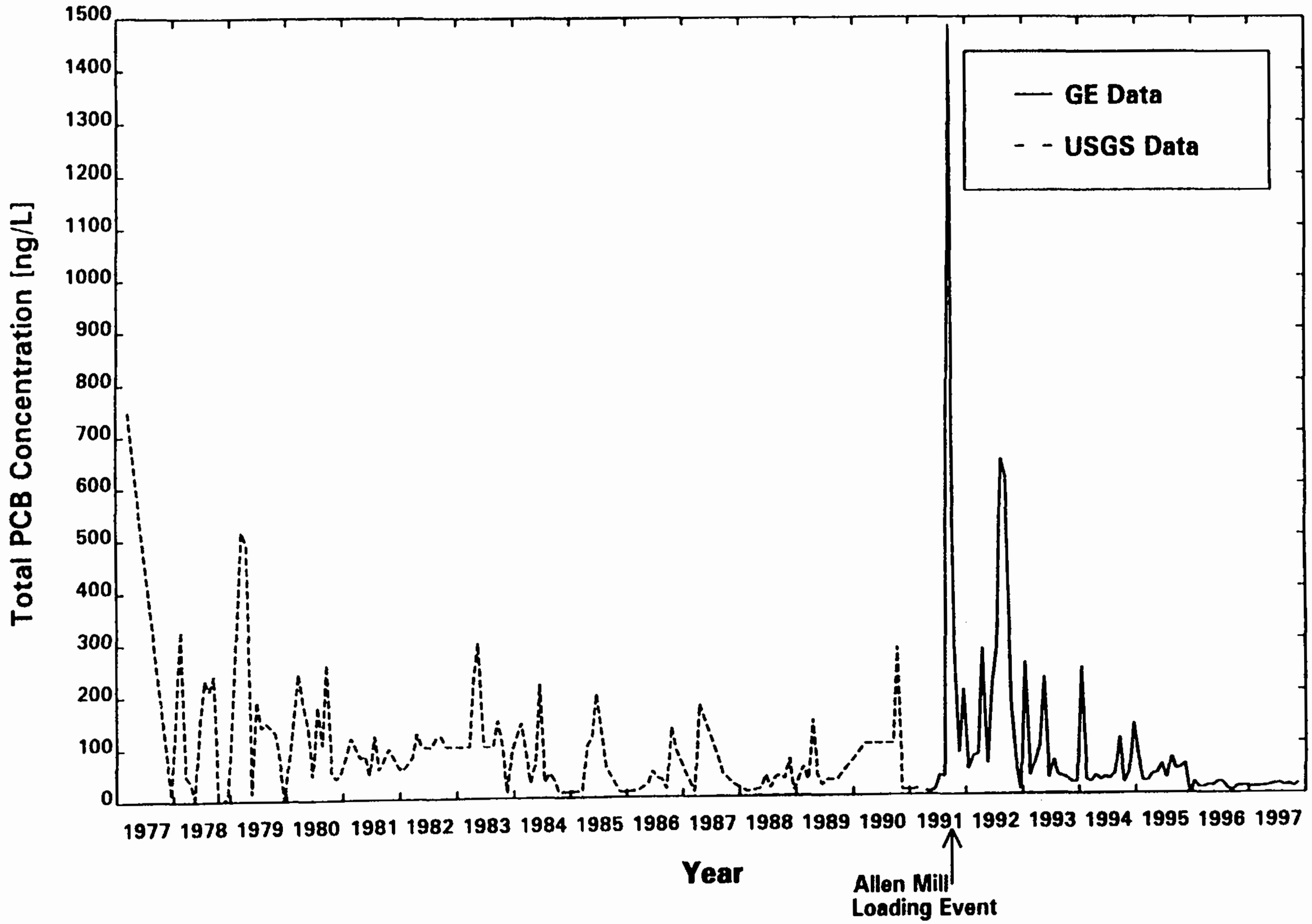


Figure 2-2.
Temporal Trend in Water Column PCB Concentrations at Fort Edward.

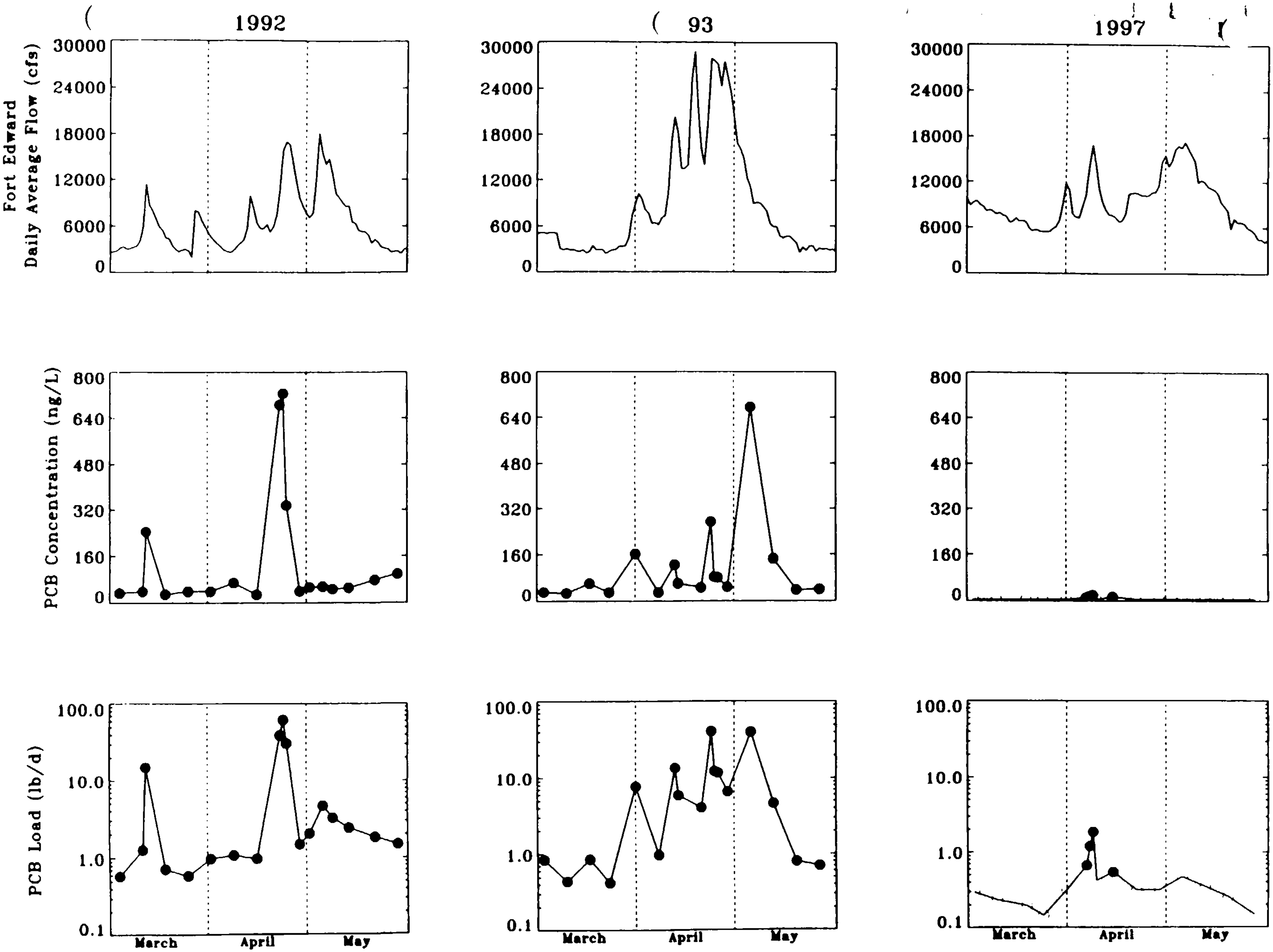


Figure 2-3.
Water Column PCB Loading at Fort Edward during Spring High Flow Events.
Note: Daily averages plotted. Non-detect PCBs plotted as open symbols at ½ MDL.

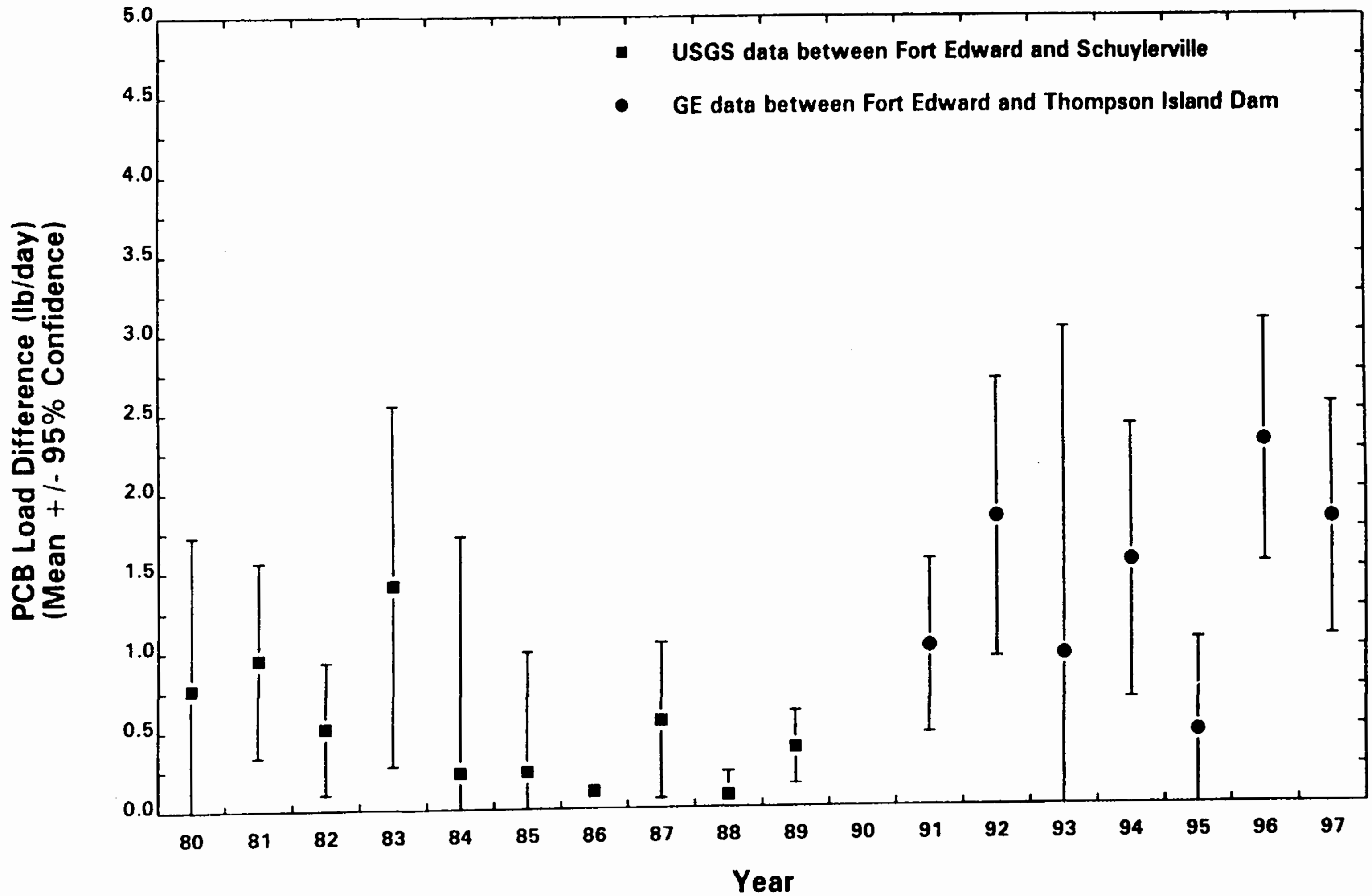


Figure 2-4.
Temporal Trends in Mean Annual Low Flow Water Column PCB Loading from Thompson Island Pool (1980-1997).
Note: Data for flow < 10,000 cfs at Fort Edward plotted; High loads from 9/91 to 12/91 are excluded.

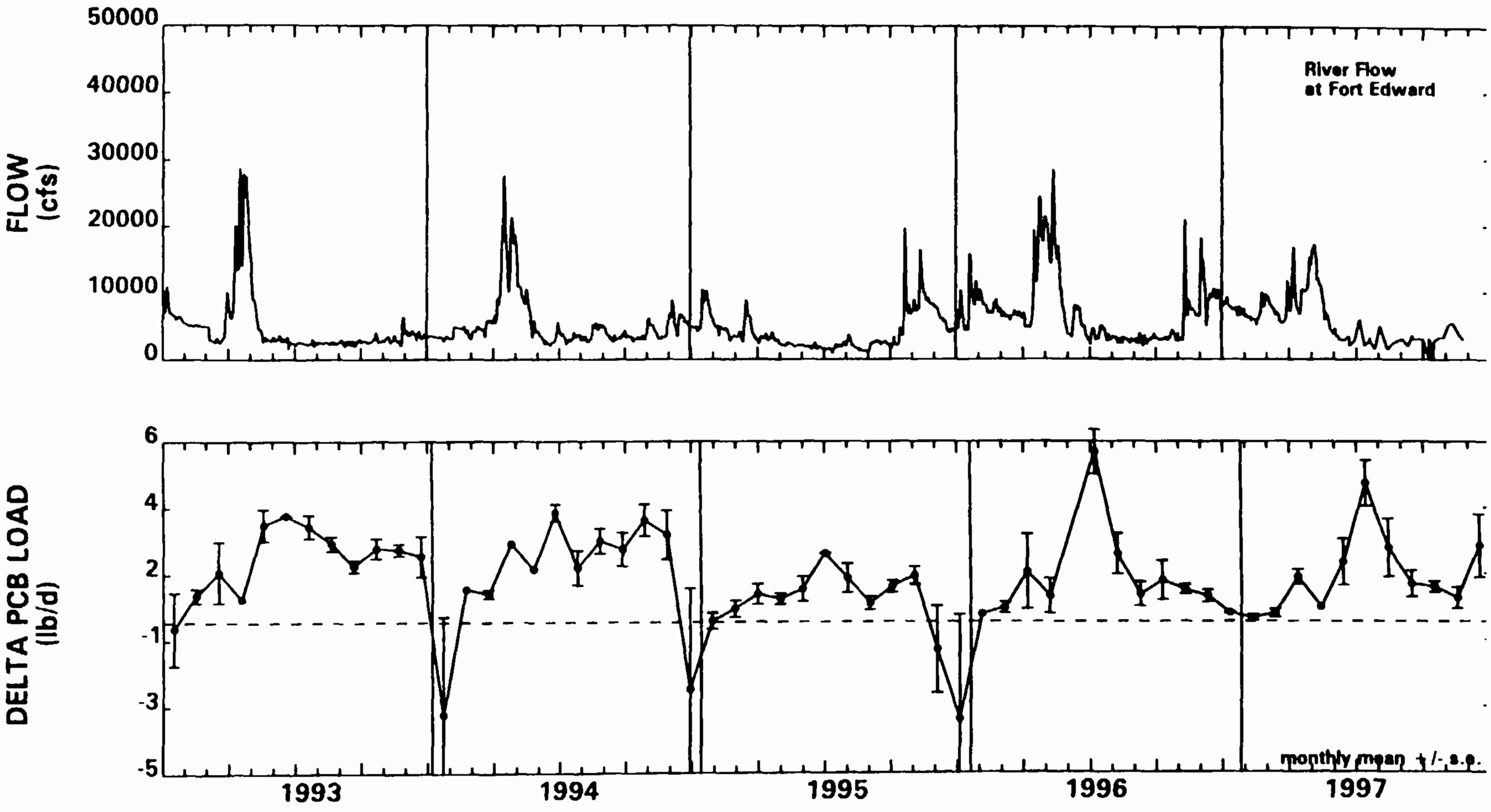


Figure 2-5.
Temporal Trends in Mean Monthly Low Flow Water Column PCB Loading from Thompson Island Pool (1993-1997).
Note. Data for flow < 10,000 cfs at Fort Edward plotted

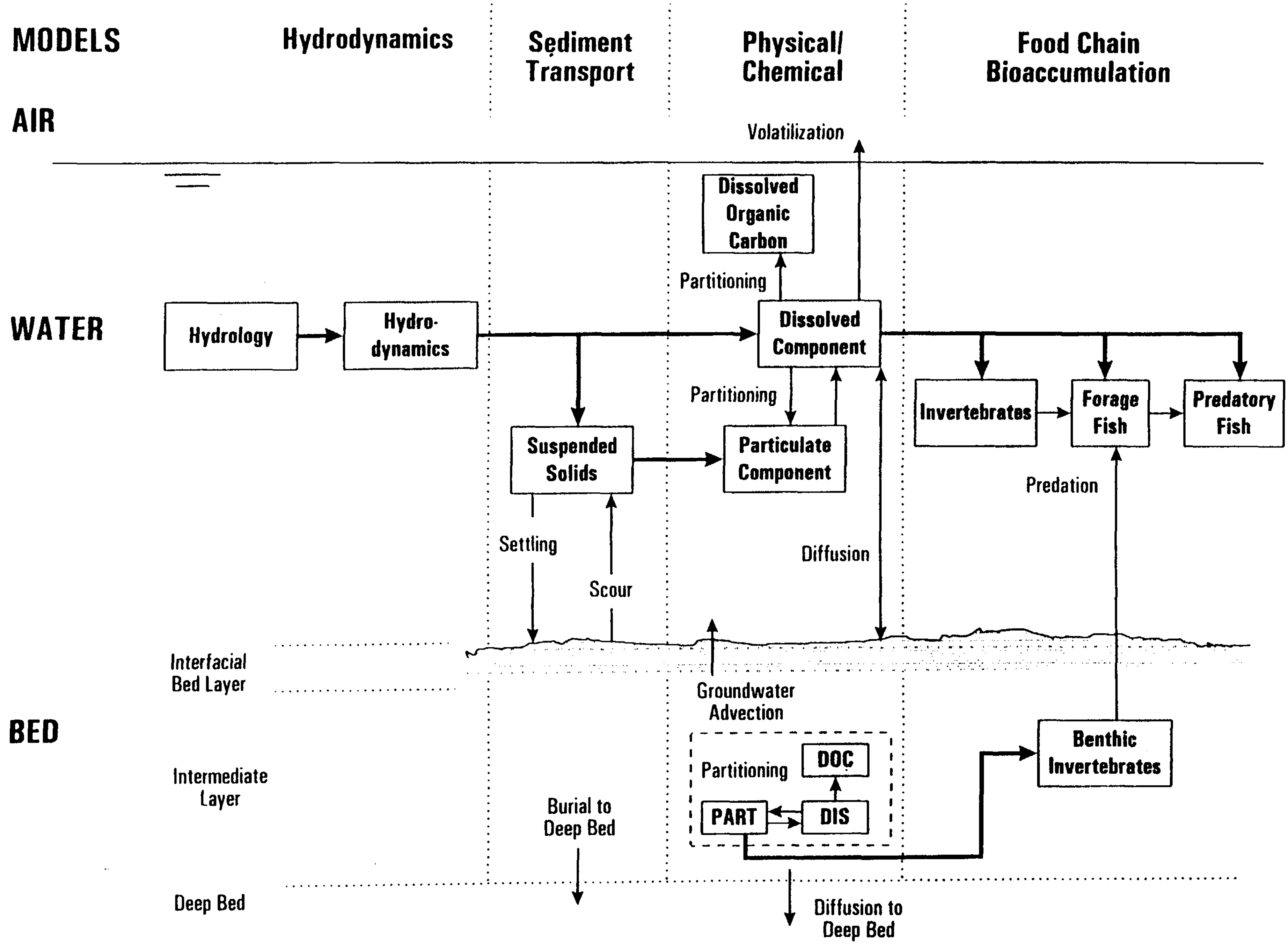


Figure 3-1.
Models, State Variables, and Kinetic Processes for PCB Dynamics.

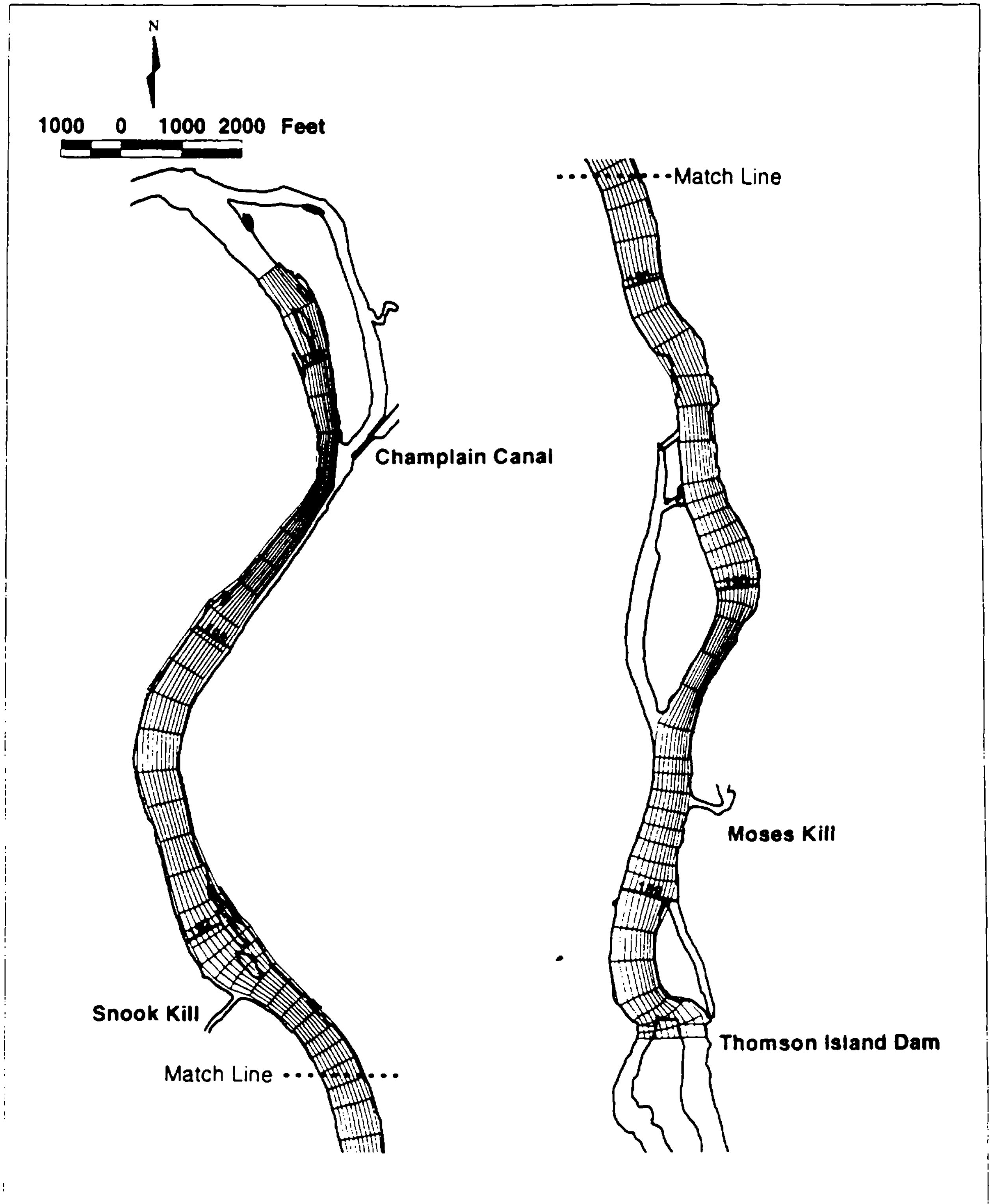


Figure 3-2.
Sediment Transport Model Grid for Thompson Island Pool.

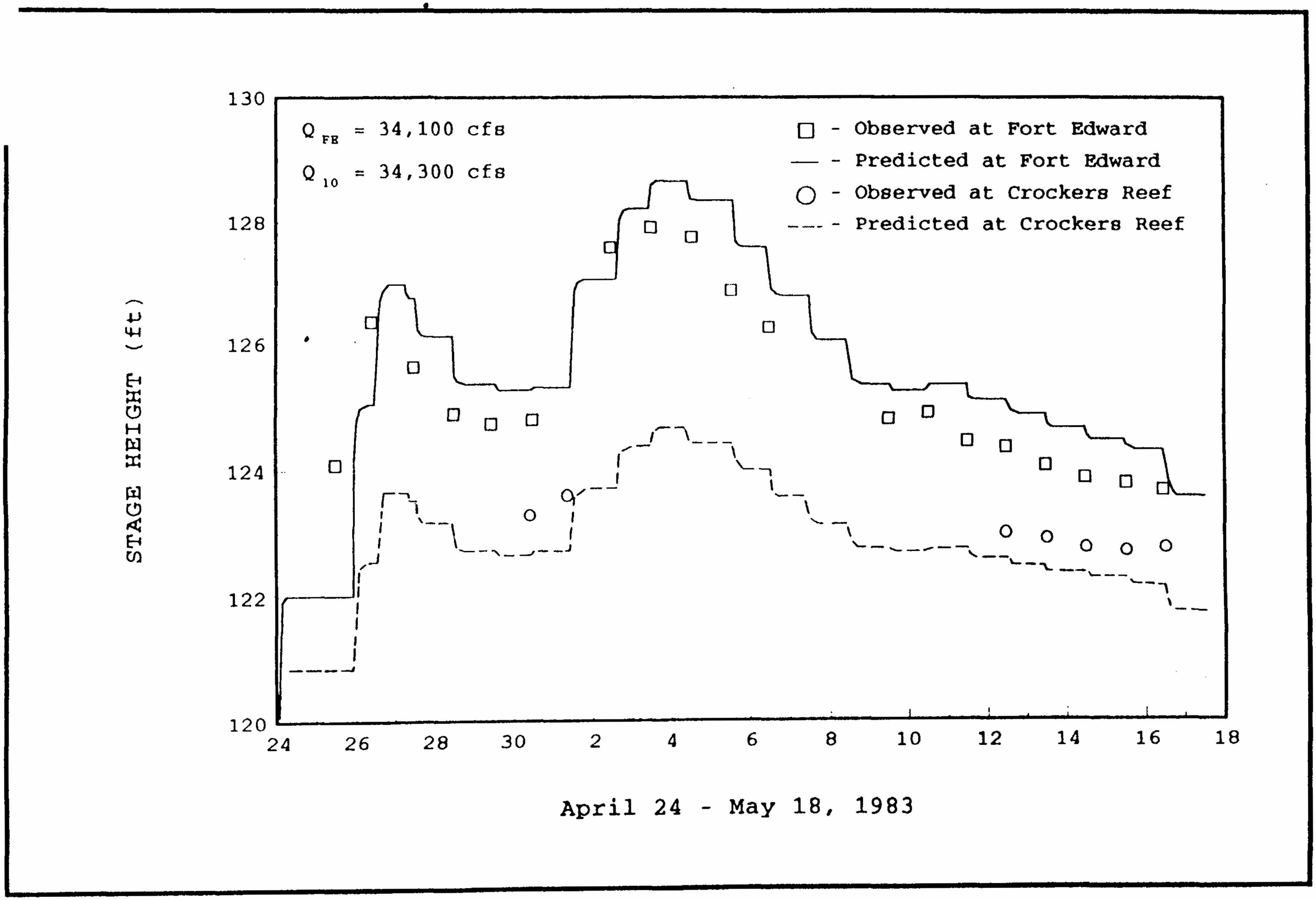


Figure 3-3.
1-D Hydrodynamic Model Predictions and Data: Stage Height During 1983 Flood.

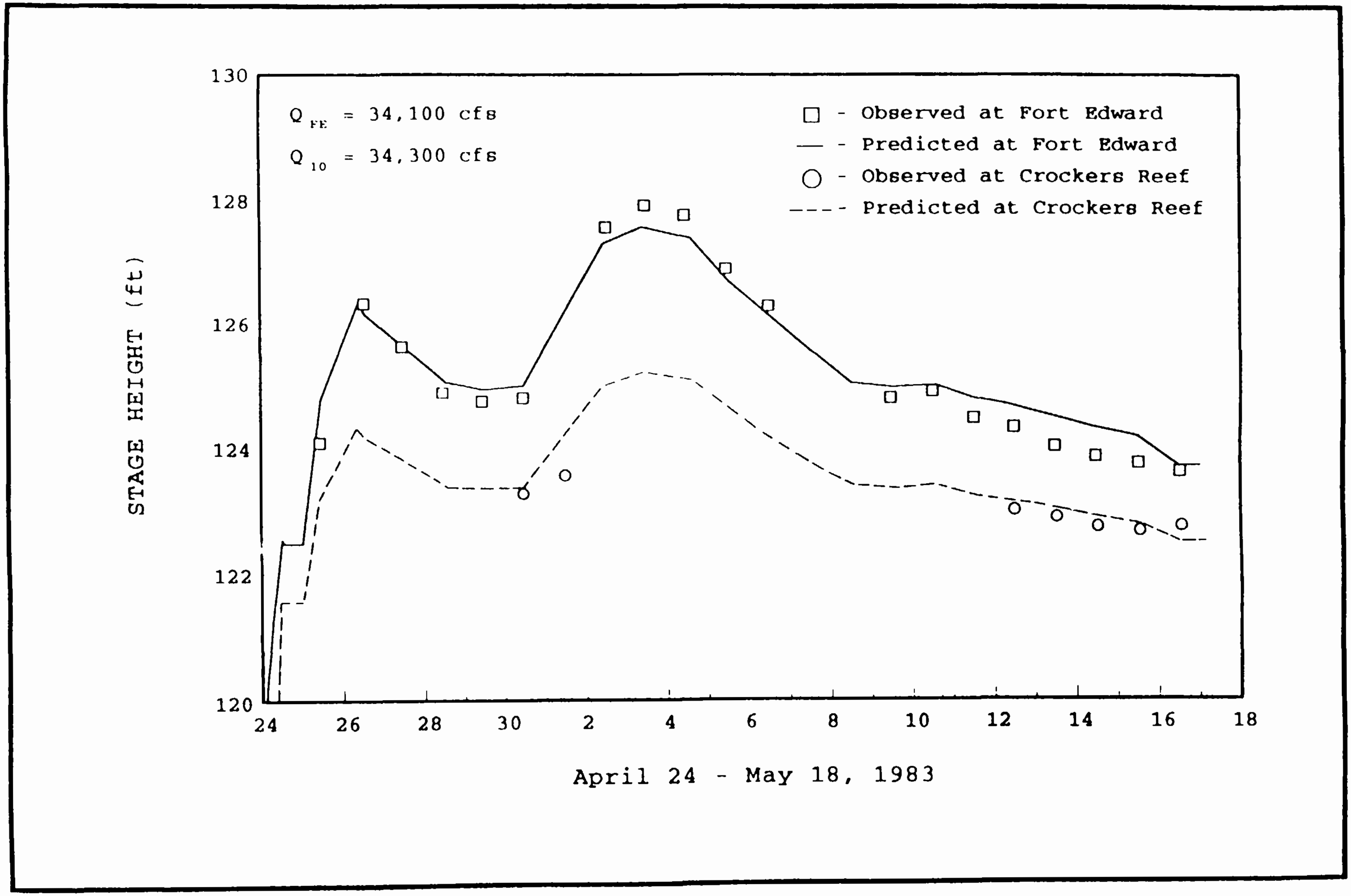


Figure 3-4.
2-D Hydrodynamic Model Predictions and Data: Stage Height During 1983 Flood.

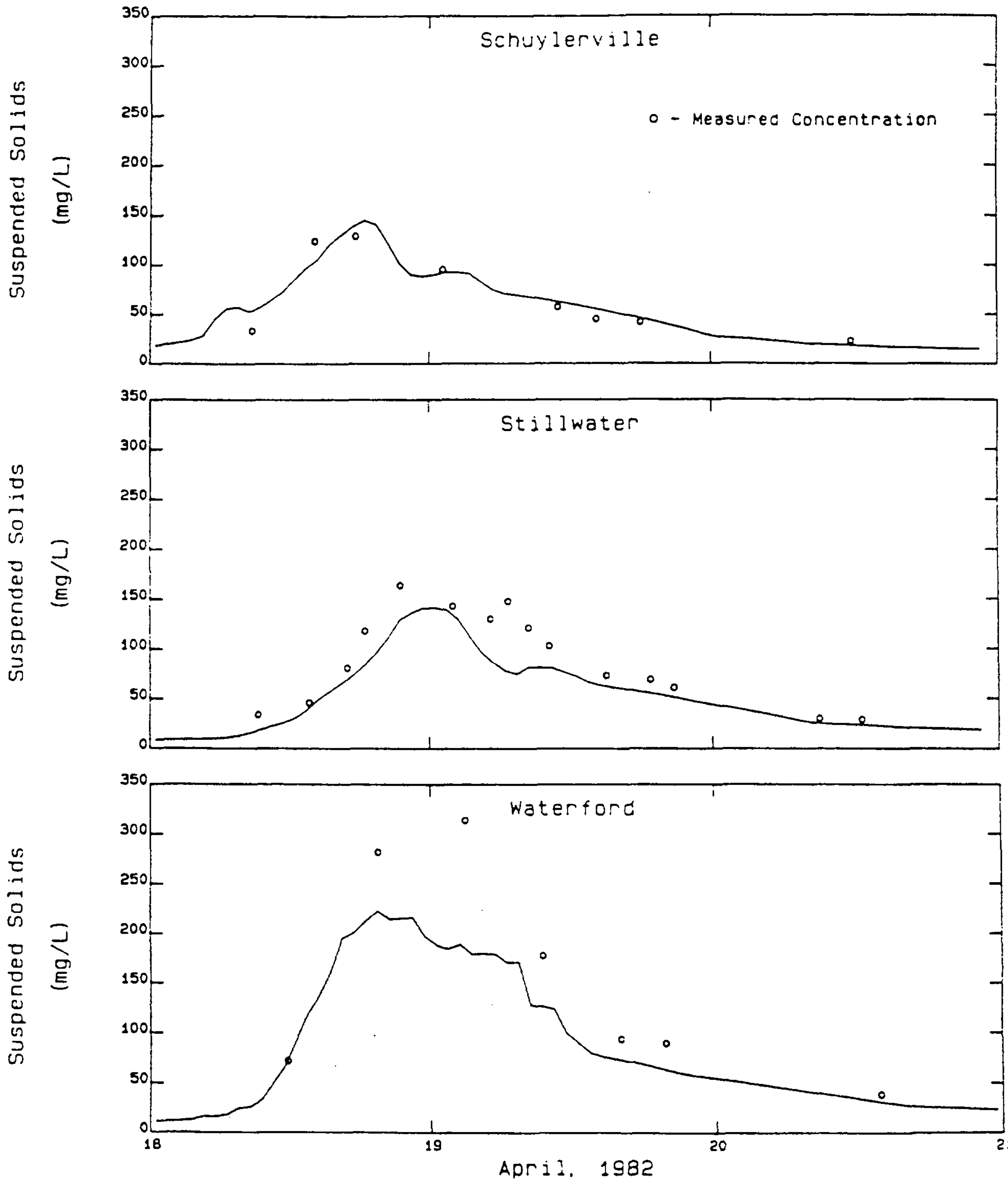


Figure 3-5.
Model-Predicted and Observed TSS Concentrations at Schuylerville, Stillwater, and Waterford.

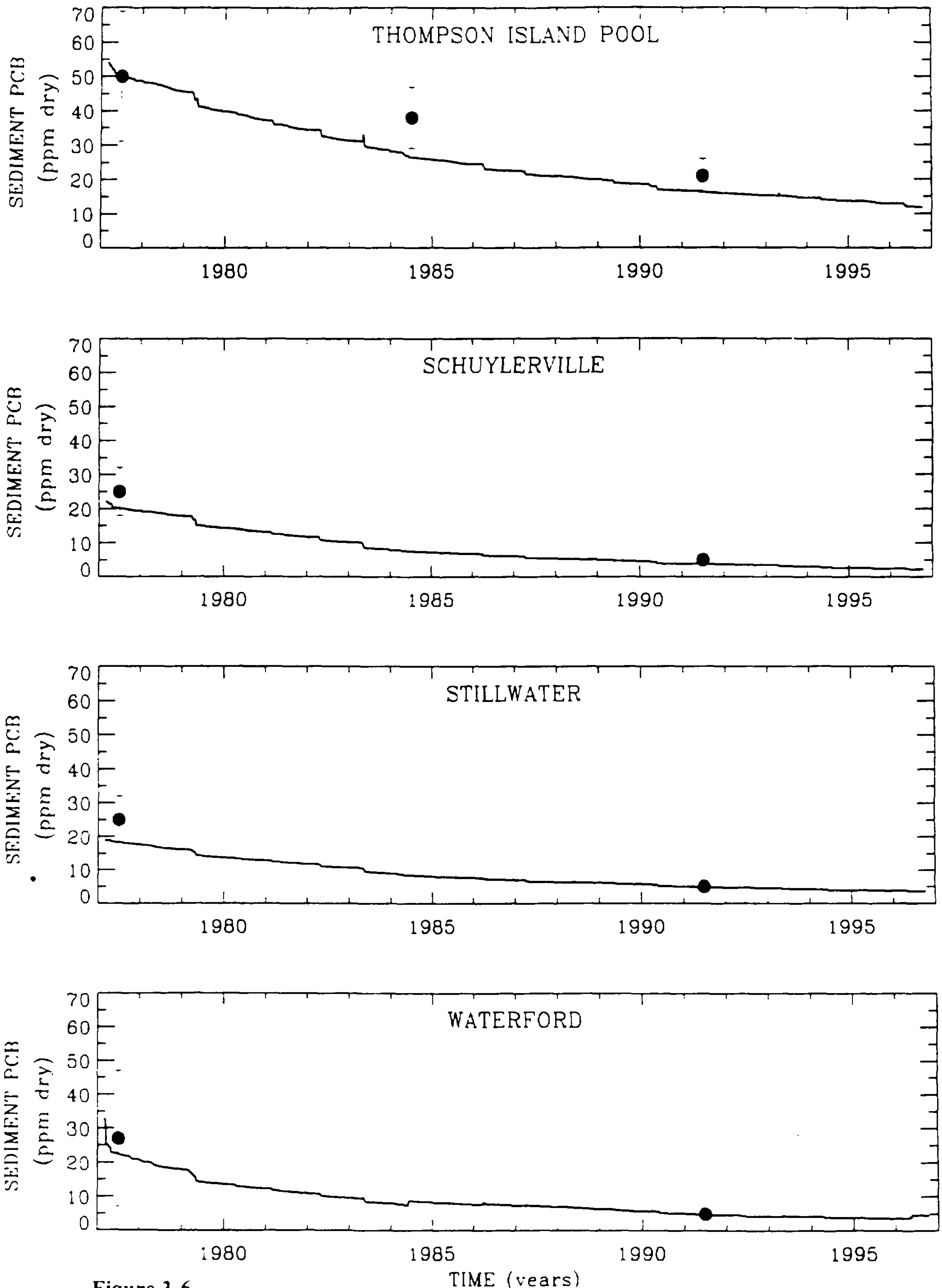


Figure 3-6.
Comparison of Computed and Observed Surface (0-5 cm) Sediment PCB Levels in Four Areas of the Upper Hudson River.

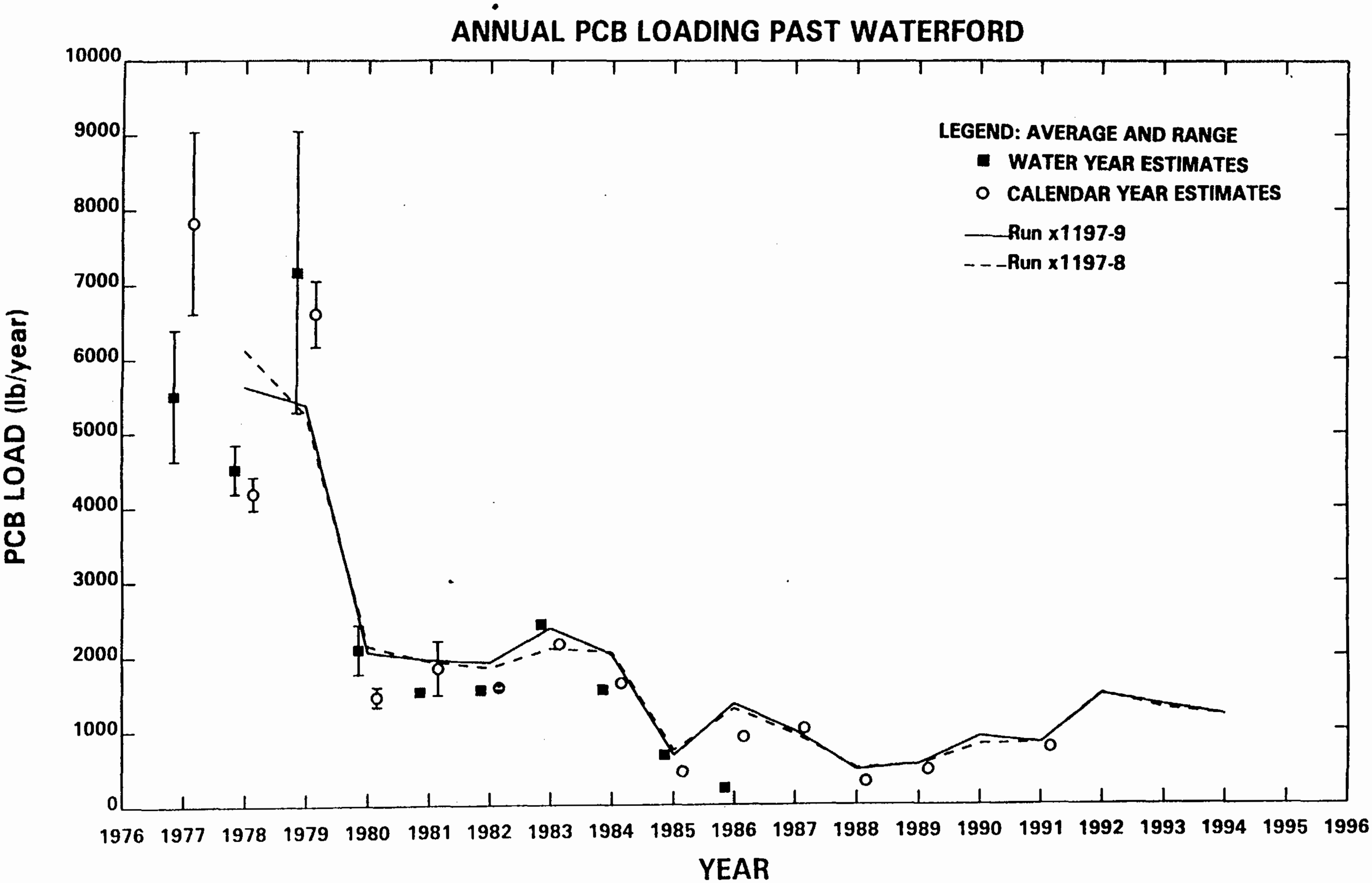


Figure 3-7.
Comparison of Estimates of the Annual PCB Load Passing Waterford, NY Computed from the USGS Data (symbols) and from the Daily Model Results (lines).

Schuylerville

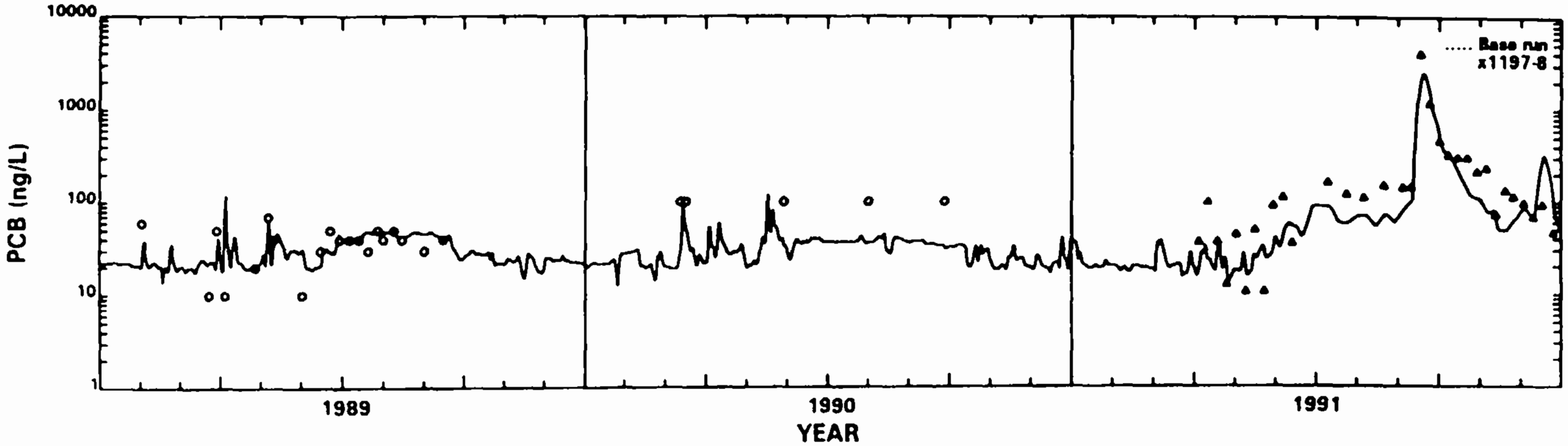


Figure 3-8.
Comparison of Computed and Observed Water Column PCB Levels at Schuylerville for the Years 1989 - 1991.

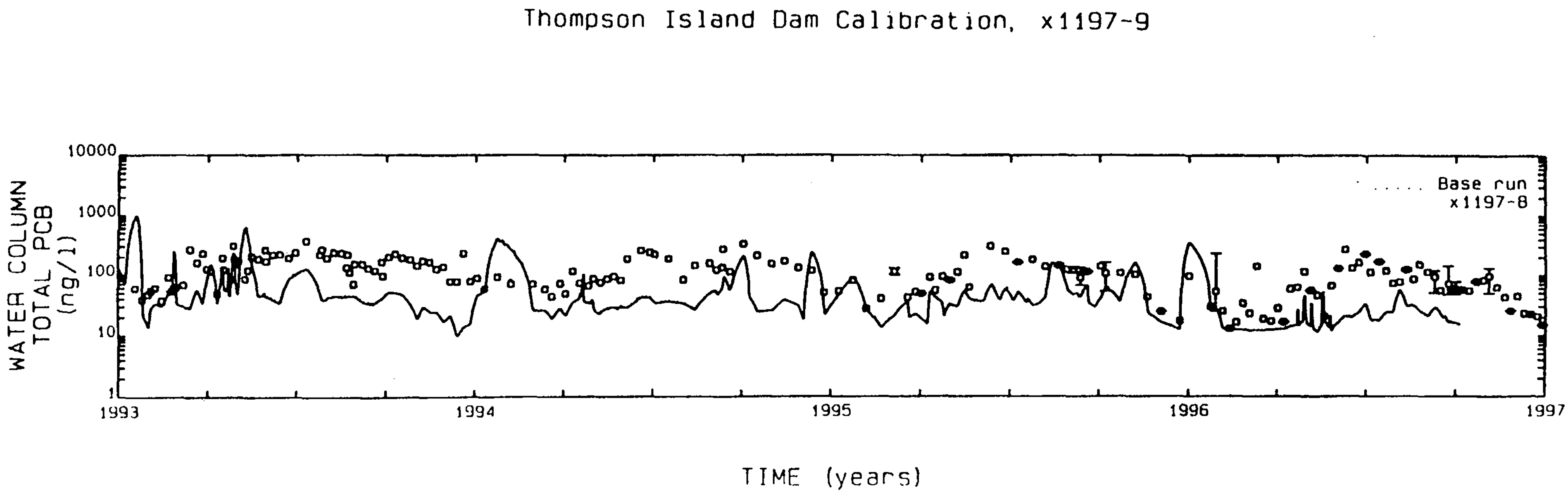


Figure 3-9.
Comparison of Computed and Observed Water Column PCB Levels at Thompson Island Dam for the Years 1993 - 1996.

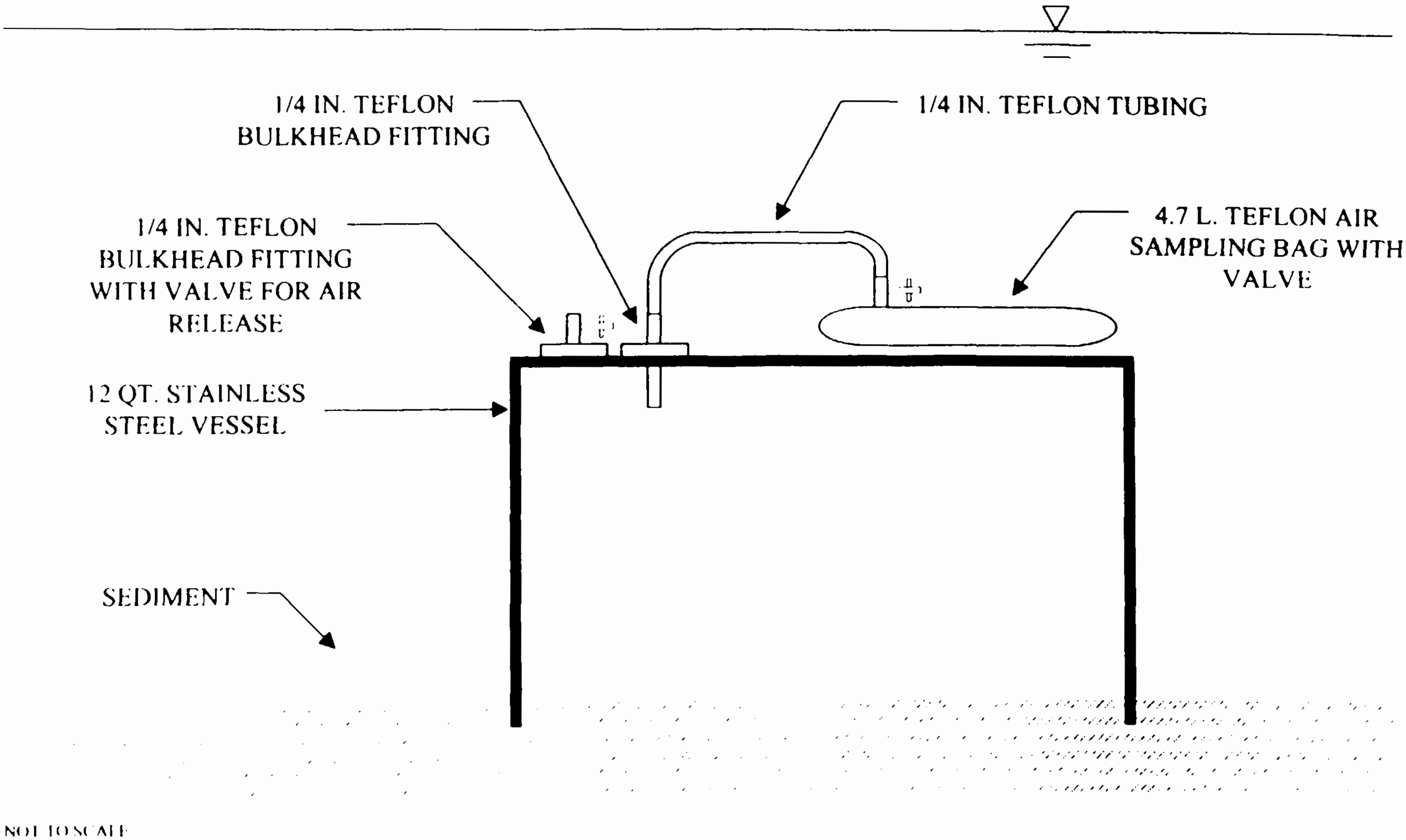


Figure 4-1.
Schematic of Groundwater Seepage Meter.

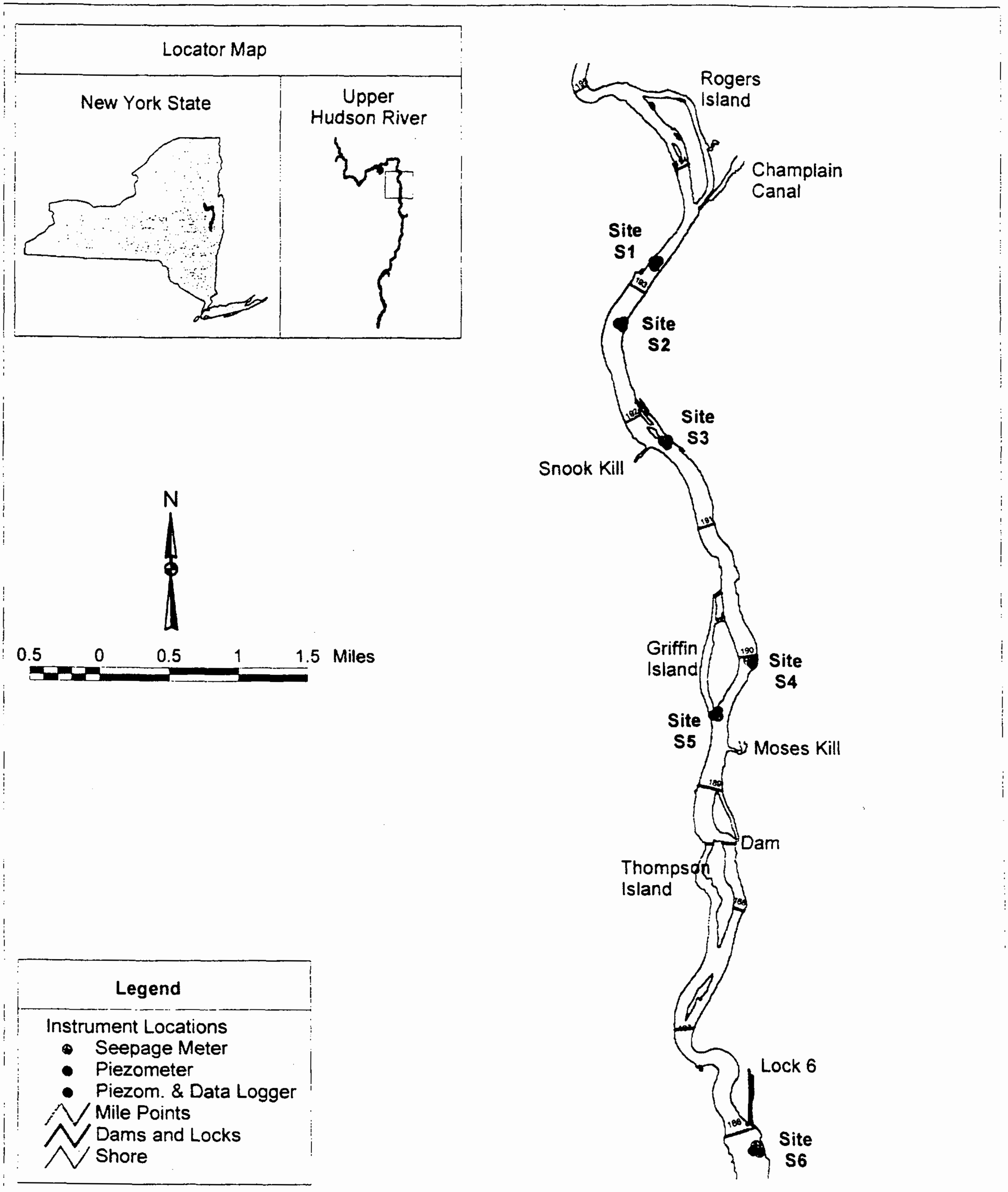


Figure 4-2.
Locations of Spring 1997 Groundwater Seepage Monitoring Stations.

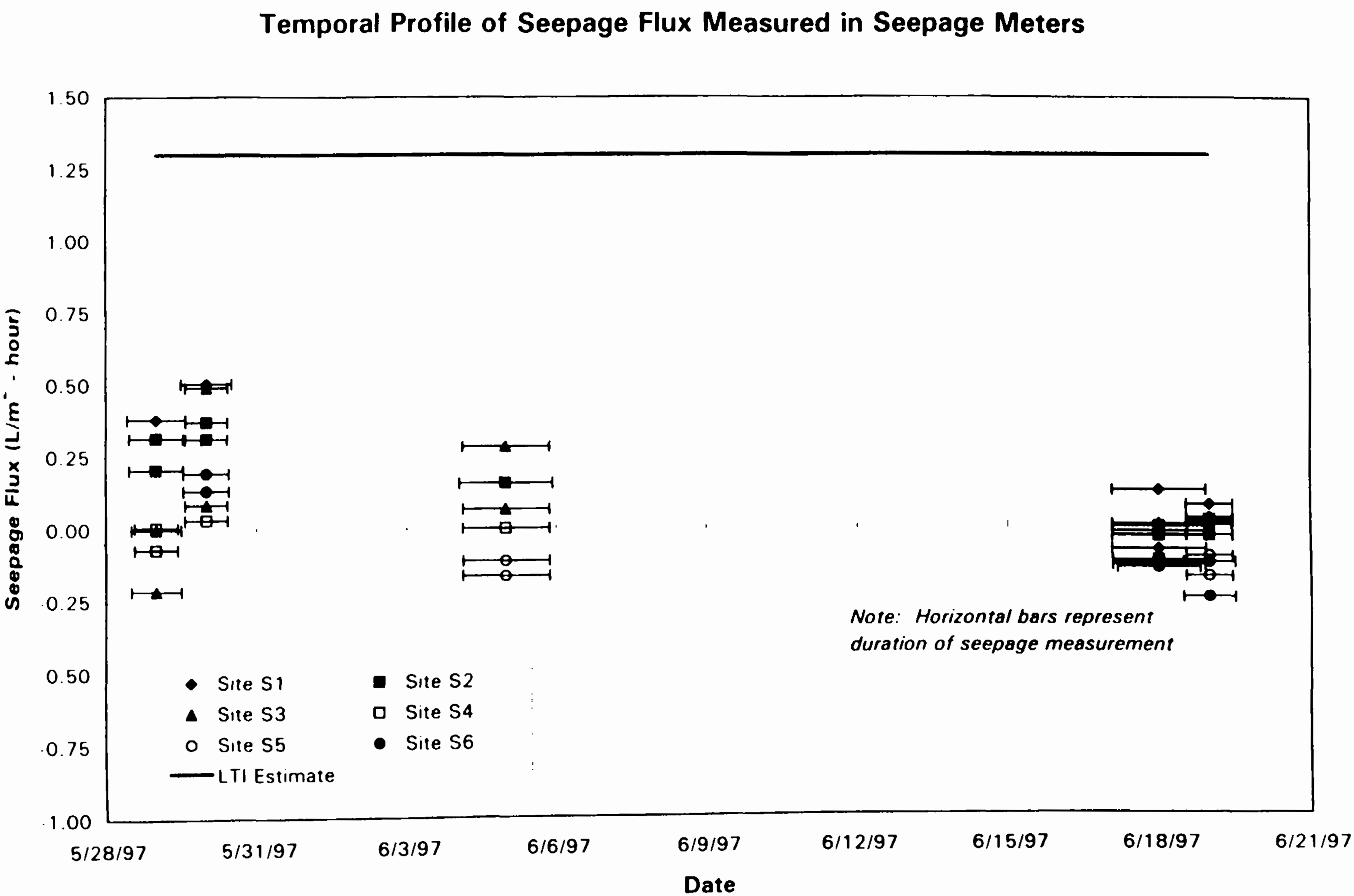


Figure 4-3.
Temporal Trends in Measured Groundwater Seepage into Thompson Island Pool.

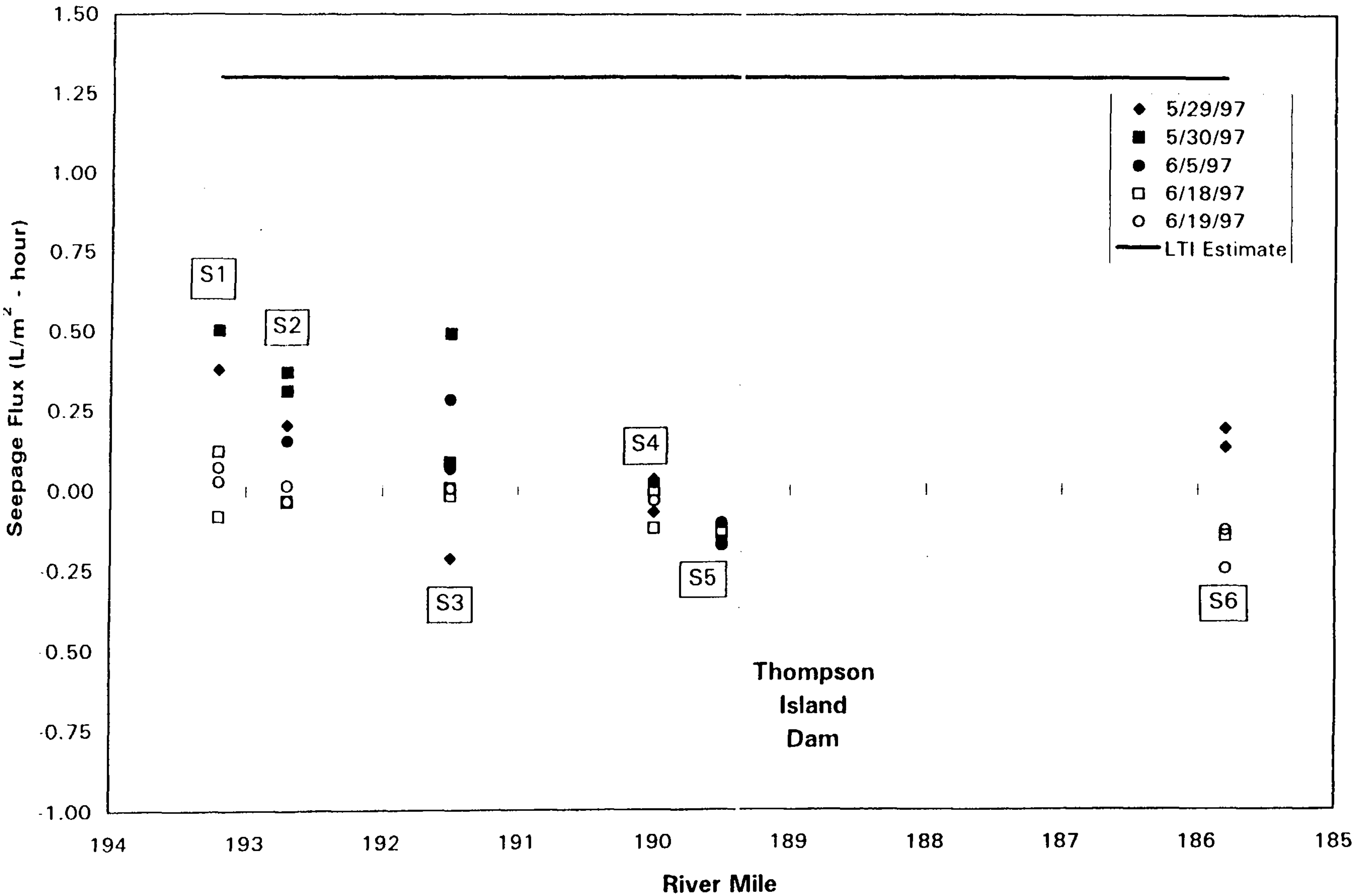
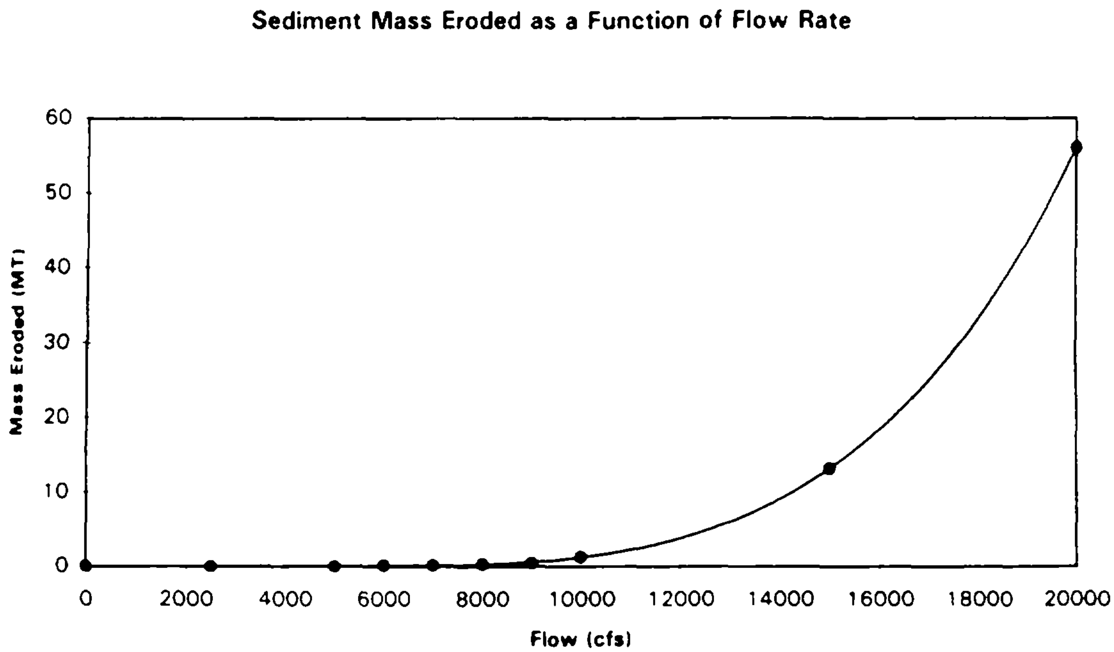


Figure 4-4.
Spatial Trends in Measured Groundwater Seepage into Thompson Island Pool.



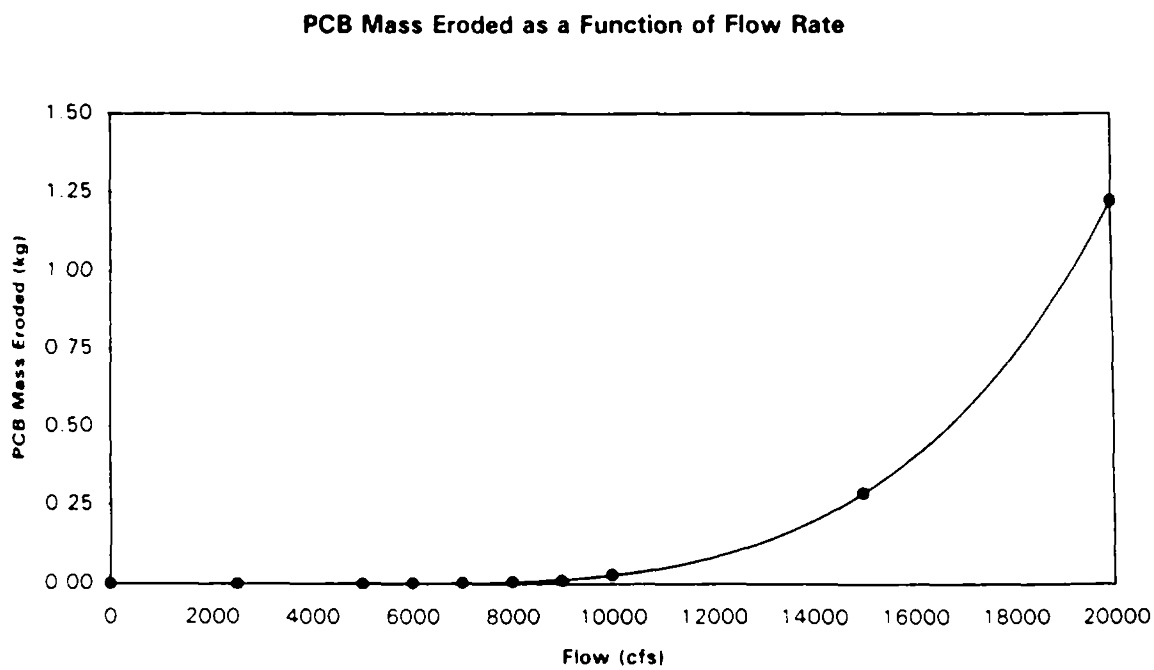
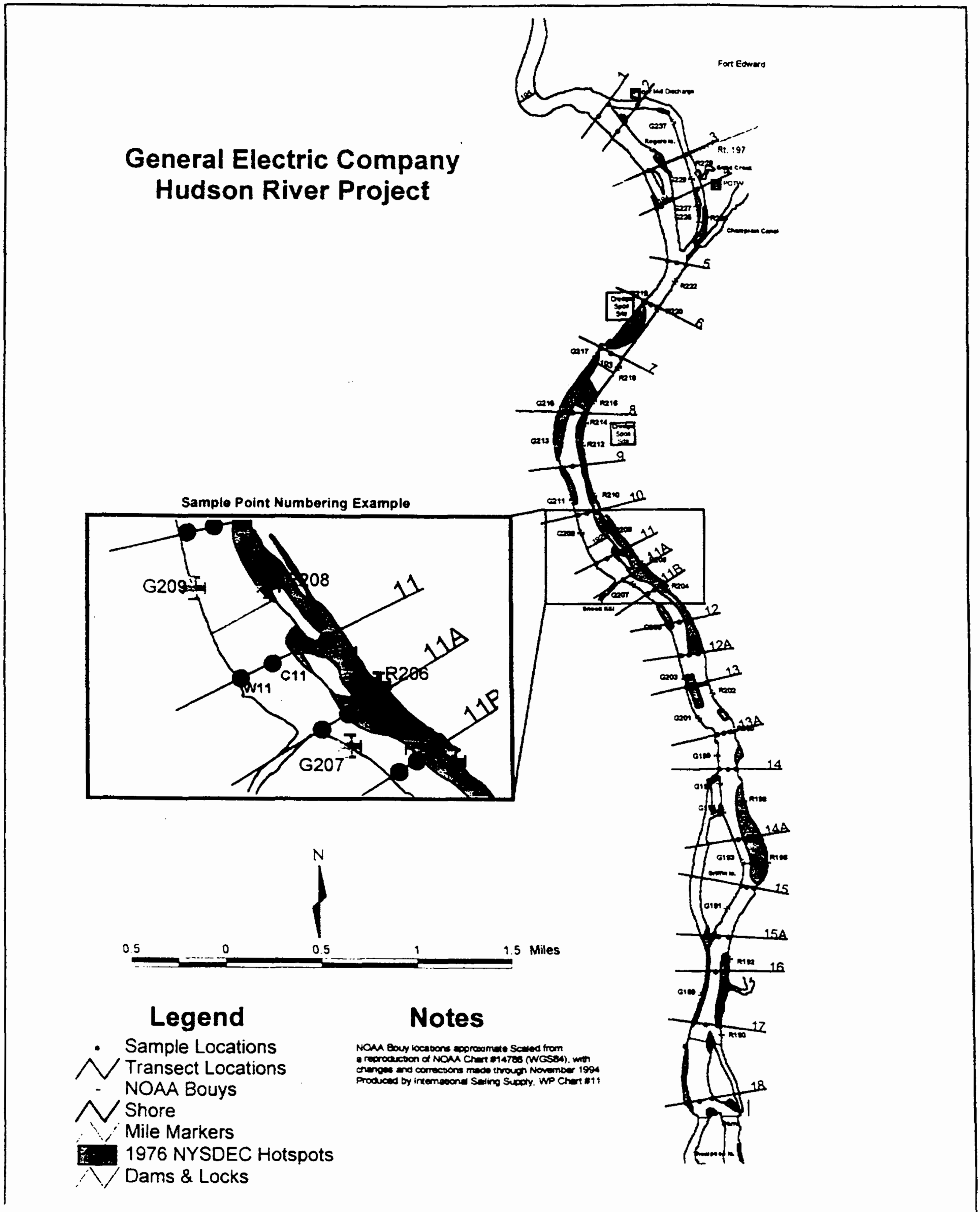


Figure 4-5.
Model-Predicted Sediment Bed Resuspension as a Function of Flow Rate.



10.0698

Figure 4-6.
Sampling Locations for Thompson Island Pool Time of Travel Surveys.

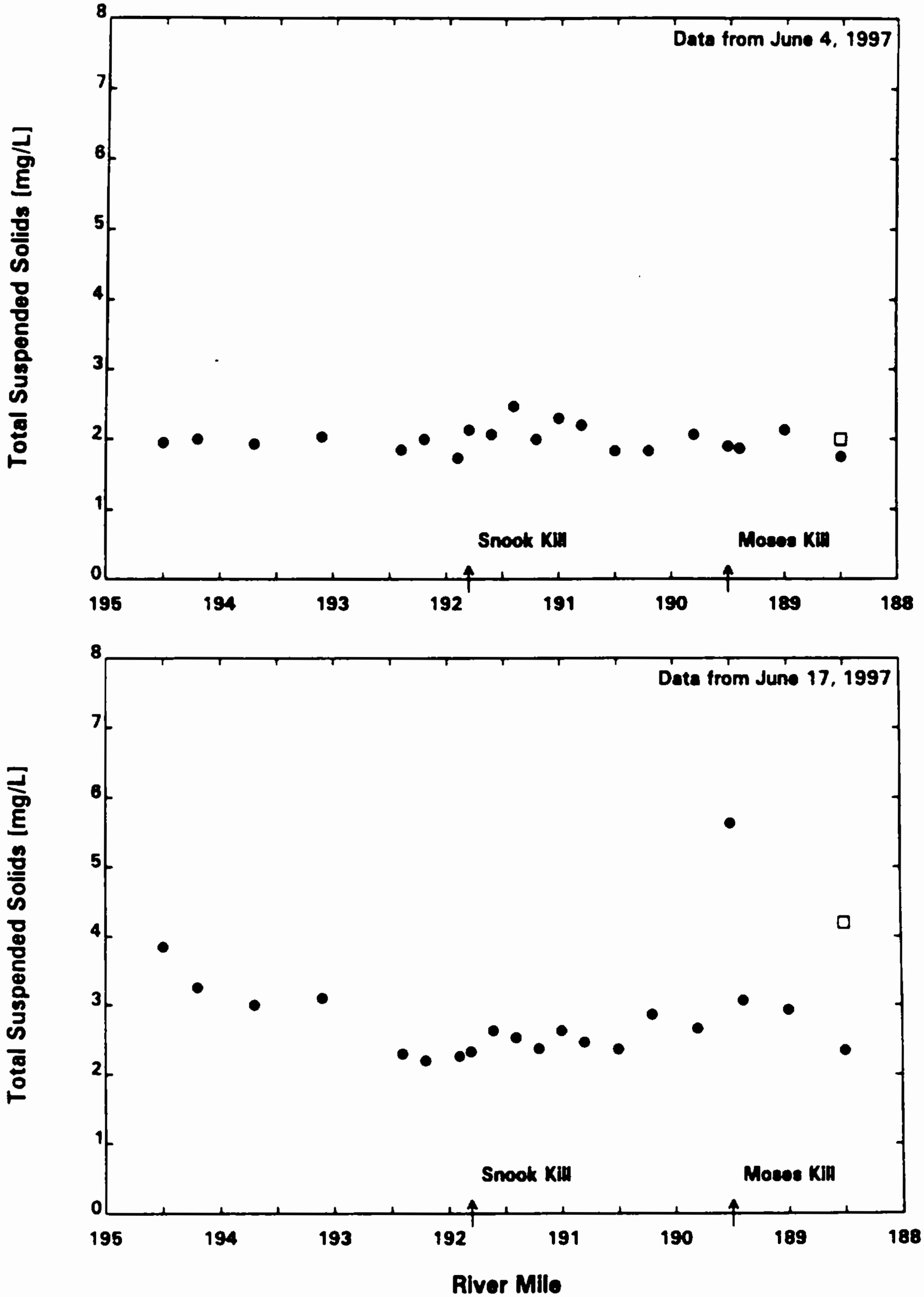


Figure 4-7.

Spatial Profile of TSS Concentrations for 1997 Time of Travel Surveys.

Note: Lateral averages plotted. open squares represent PCRDMP samples at west wingwall of TID

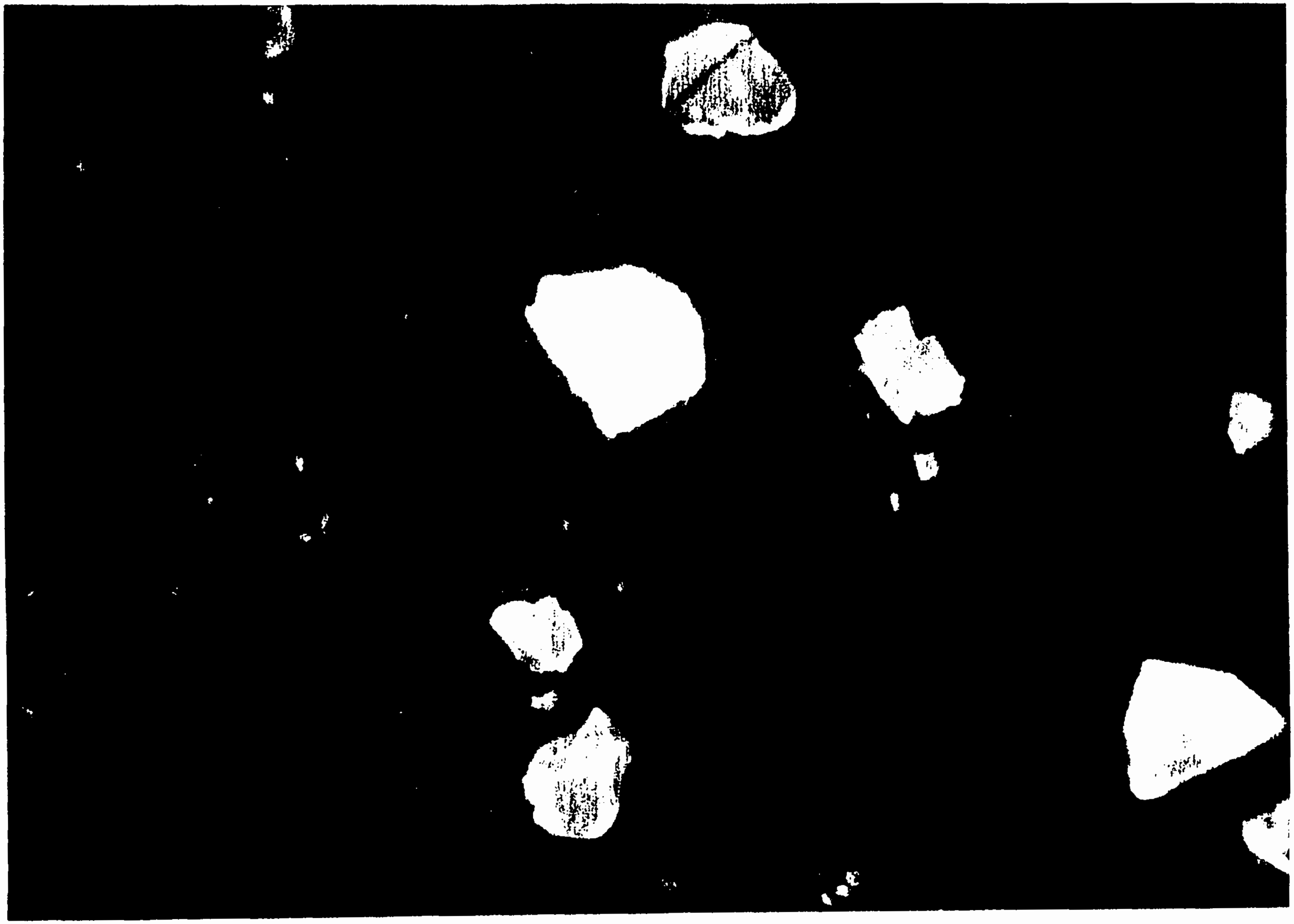


Figure 4-8.
Epifluorescent Photograph of Fluorescent Particles within Natural Sediment at Approximately 100x Magnification.

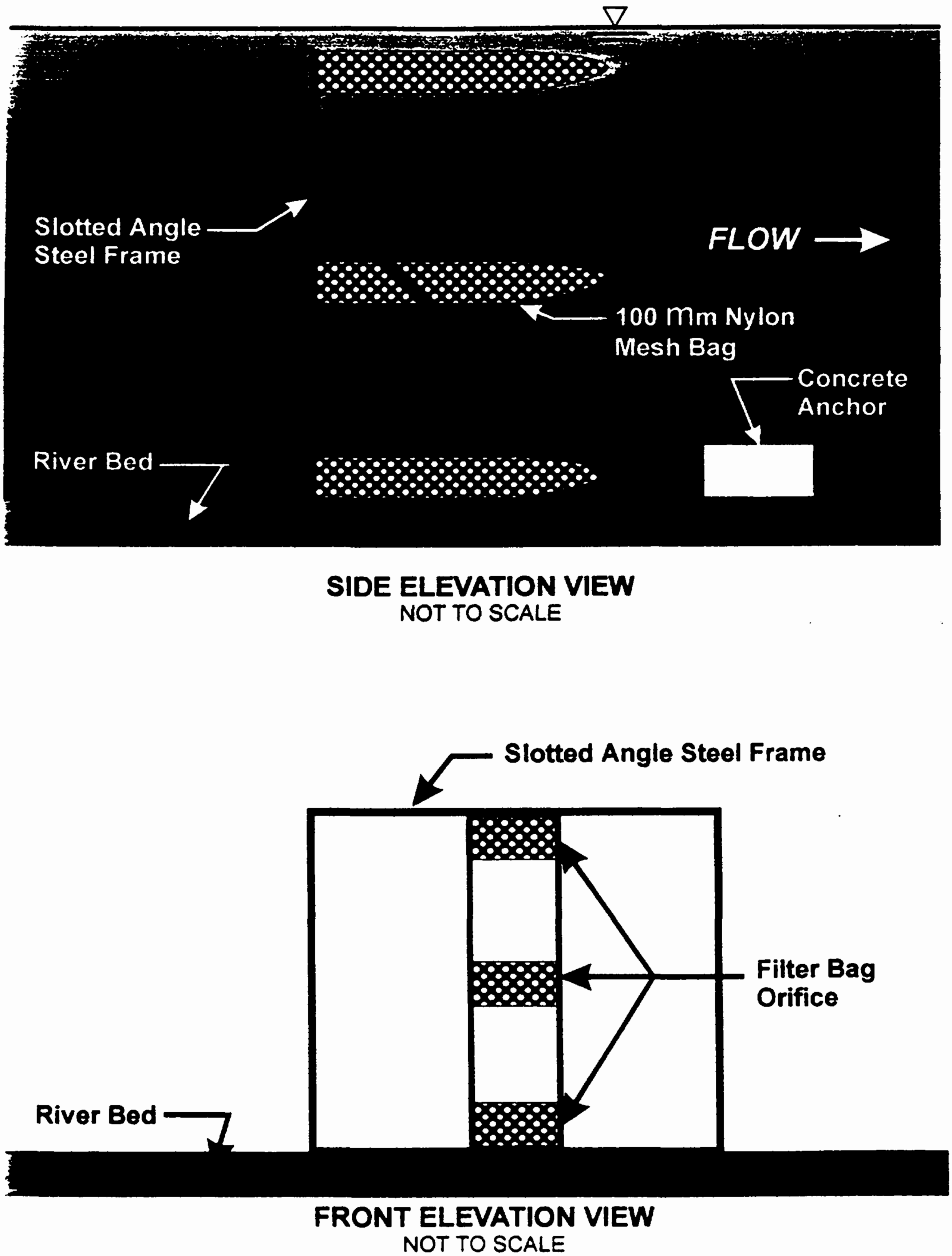


Figure 4-9.
Schematic of *In-Situ* Particle Filtration Device.

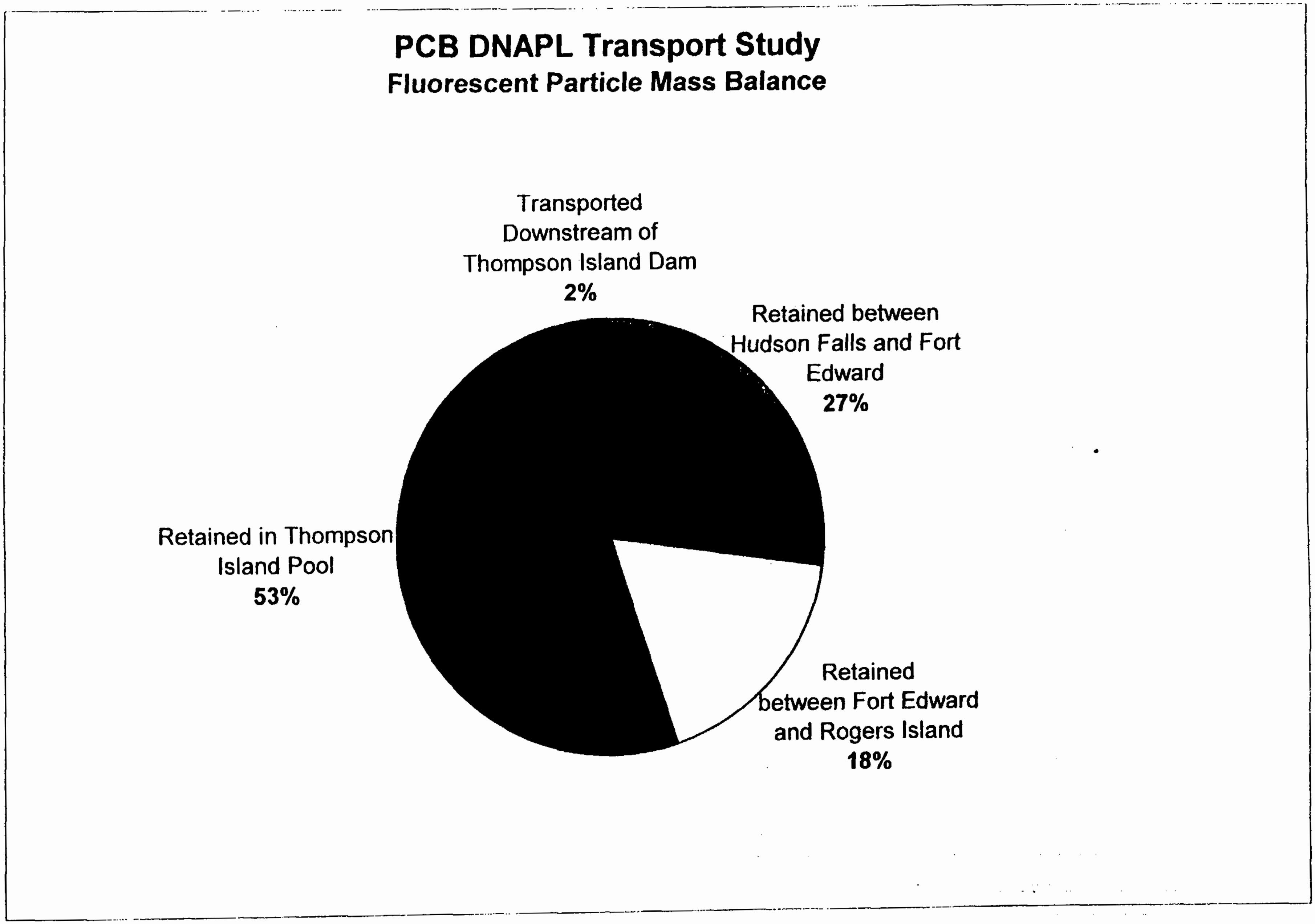


Figure 4-10.
Fluorescent Particle Mass Balance for PCB DNAPL Transport Study.

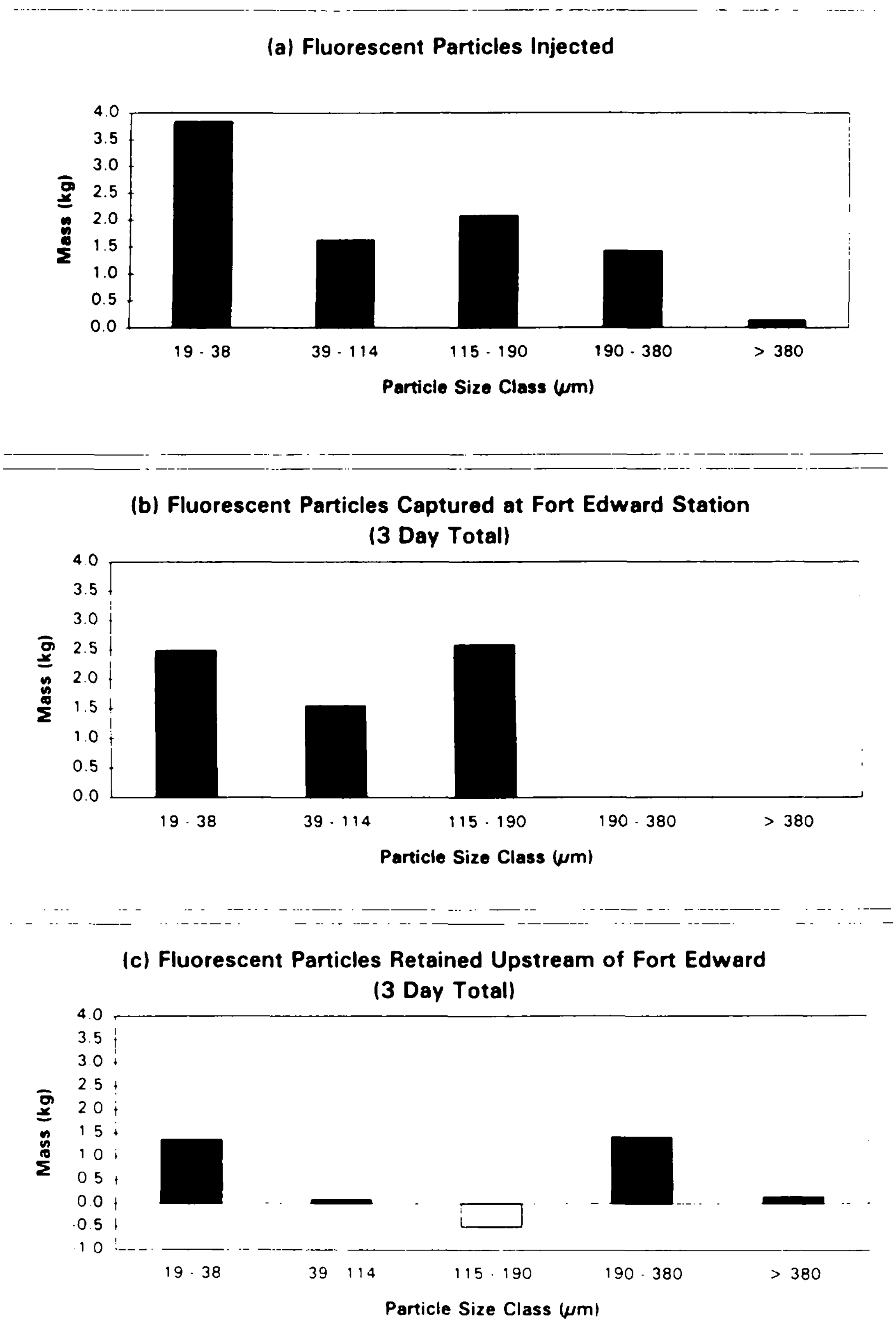


Figure 4-11.
Fluorescent Particle Size Distribution for PCB DNAPL Transport Study.

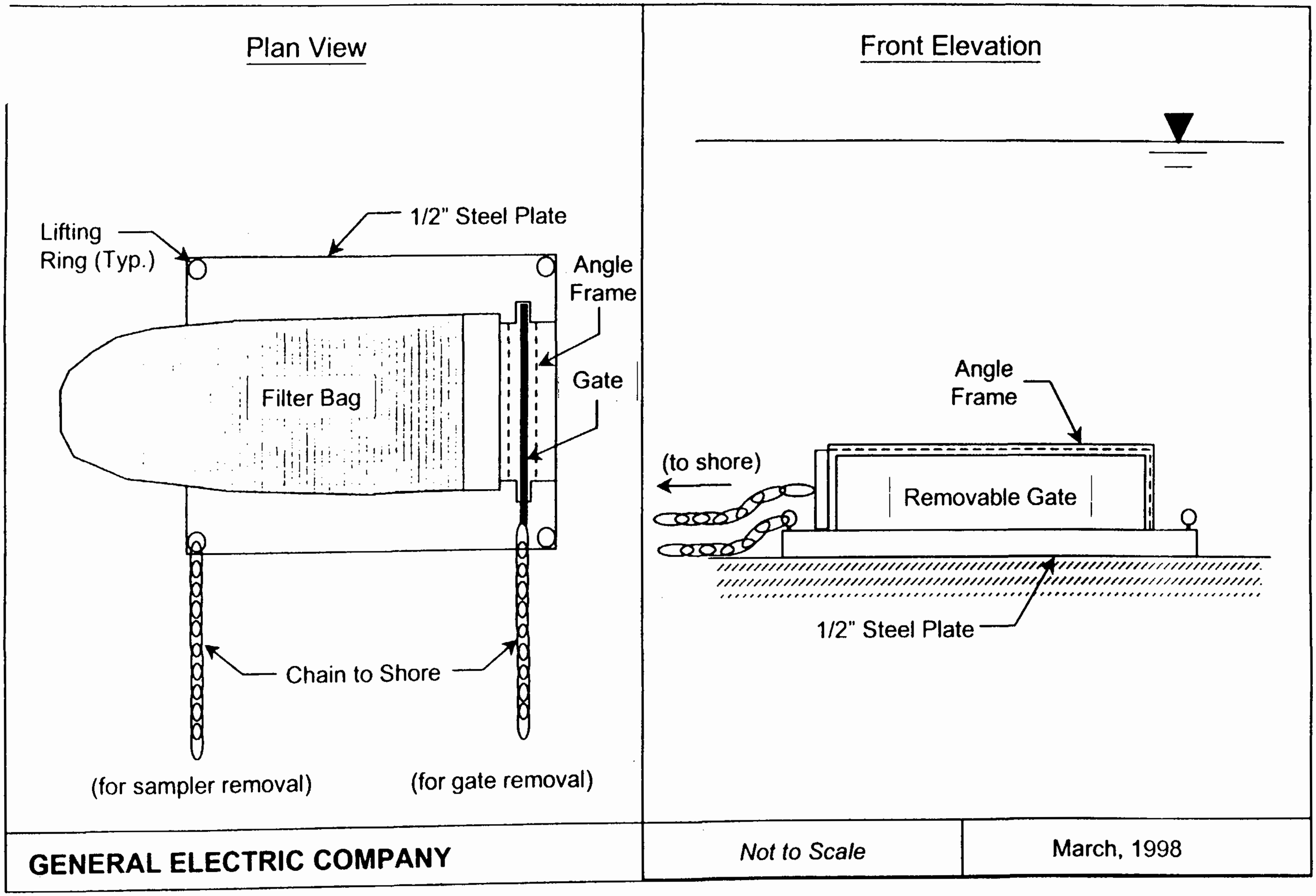


Figure 4-12.
Schematic of Passive Bed Load Sampling Device.

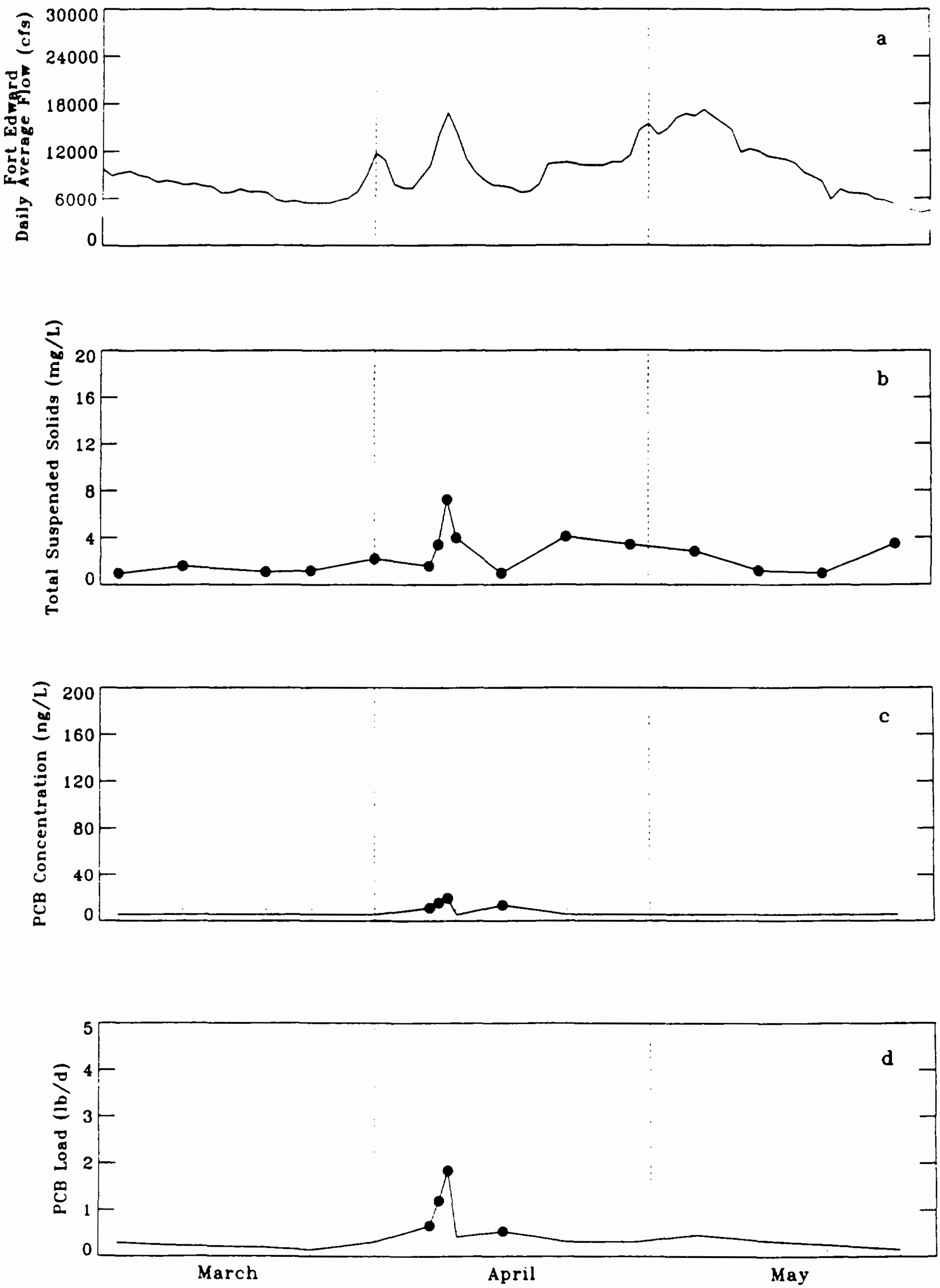


Figure 4-13.

Temporal Trends in TSS and PCB Concentration and Loading During the 1997 Spring High Flow Period.

Note: Daily averages plotted. Non-detect PCBs plotted as open symbols at ½ MDL

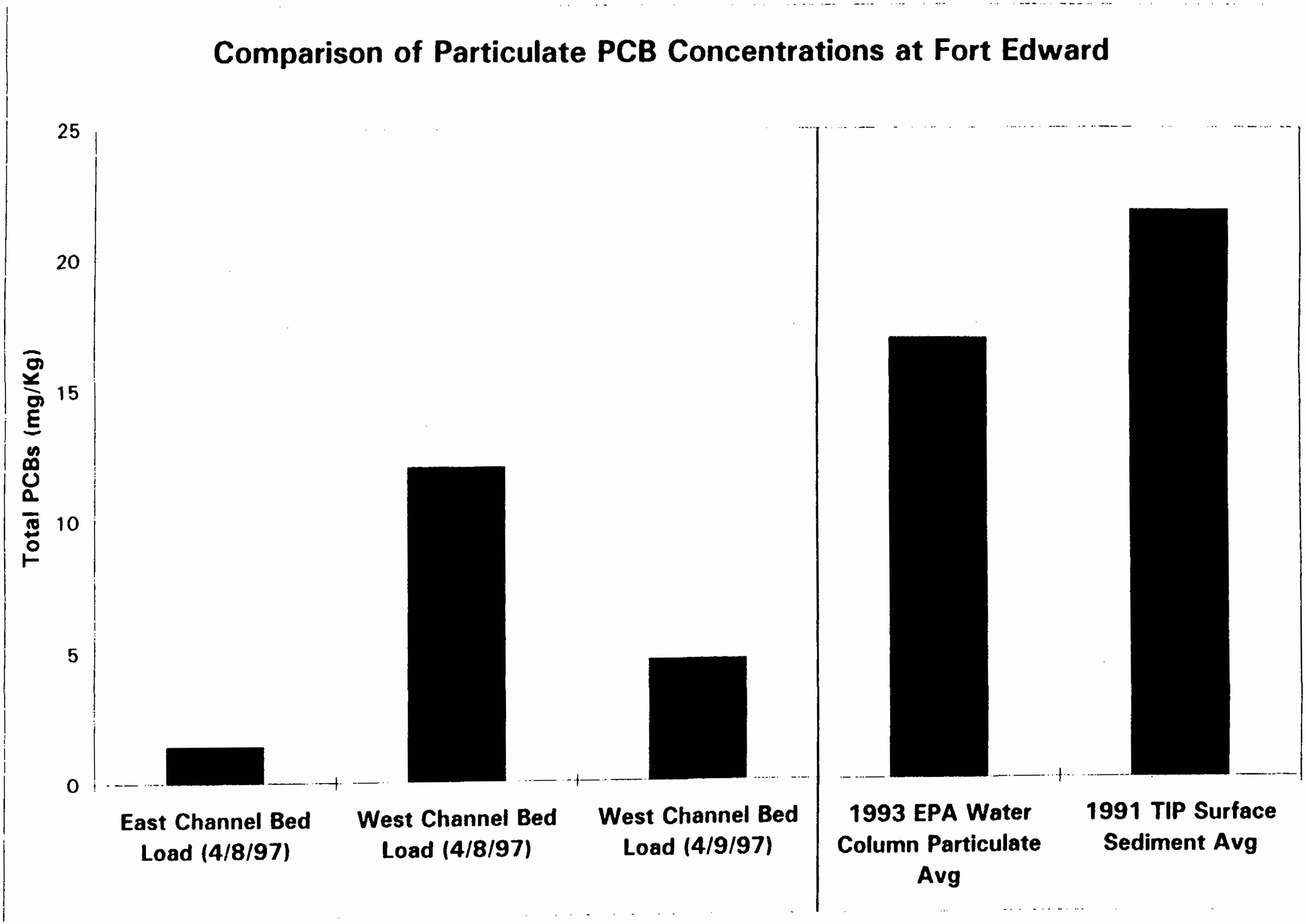
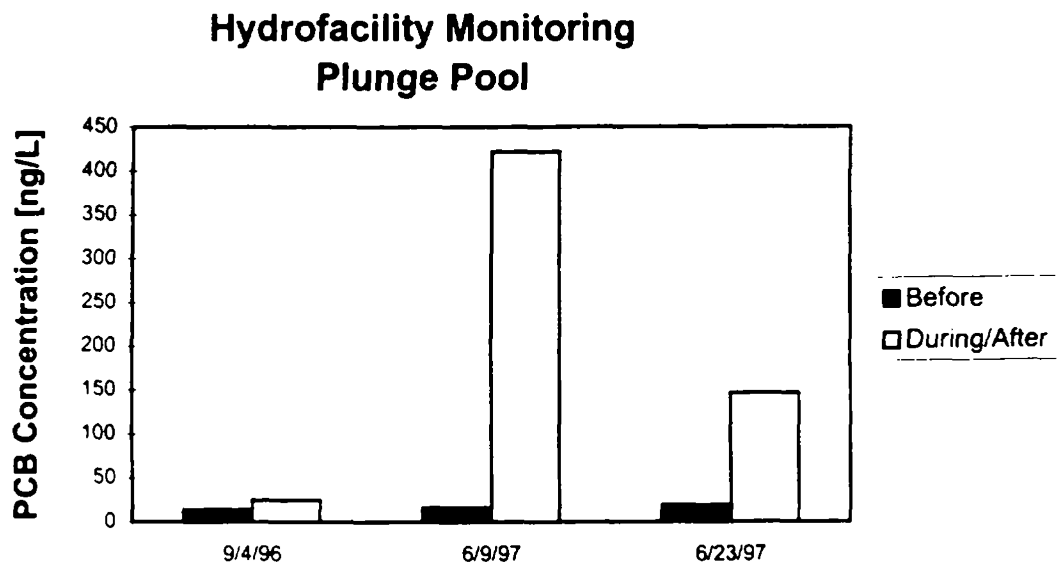
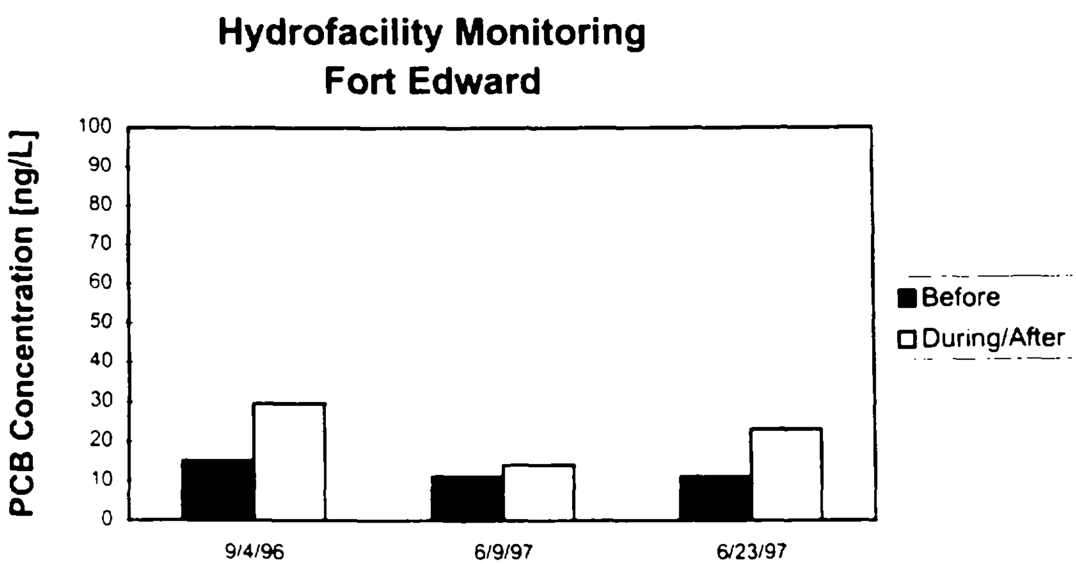


Figure 4-14.
Particulate PCB Concentrations for the Fort Edward Station.



* Non-Detects Plotted at Detection Limit



* Non-Detects Plotted at Detection Limit

Figure 4-15.
Water Column PCB Concentrations at Bakers Falls Plunge pool and Fort Edward from Hydrofacility Monitoring Program.

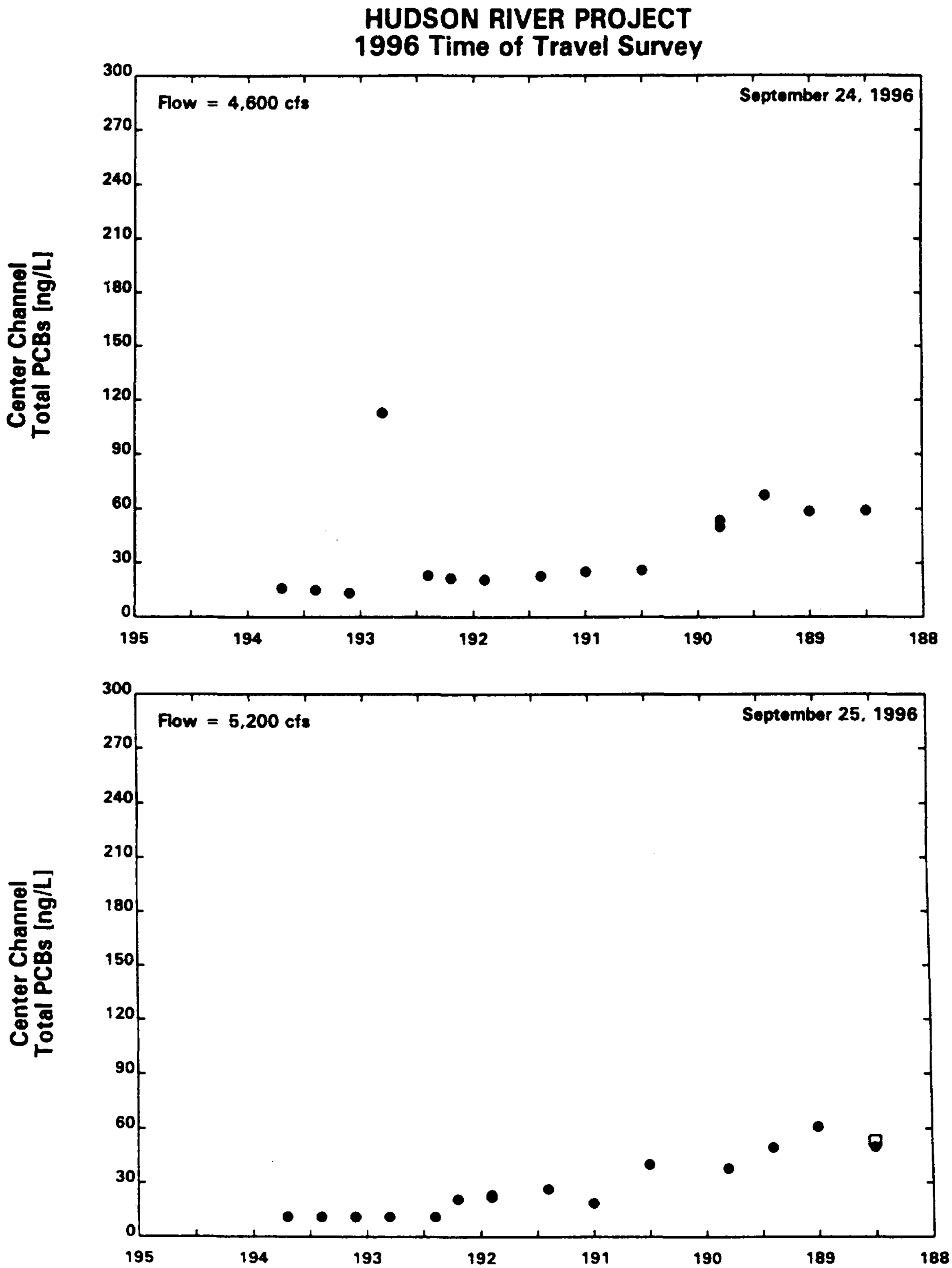


Figure 4-16.

Center Channel PCB Concentrations from the 1996 Time of Travel Surveys.

Note: Open square represents PCBDMP sample at west wingwall of TID

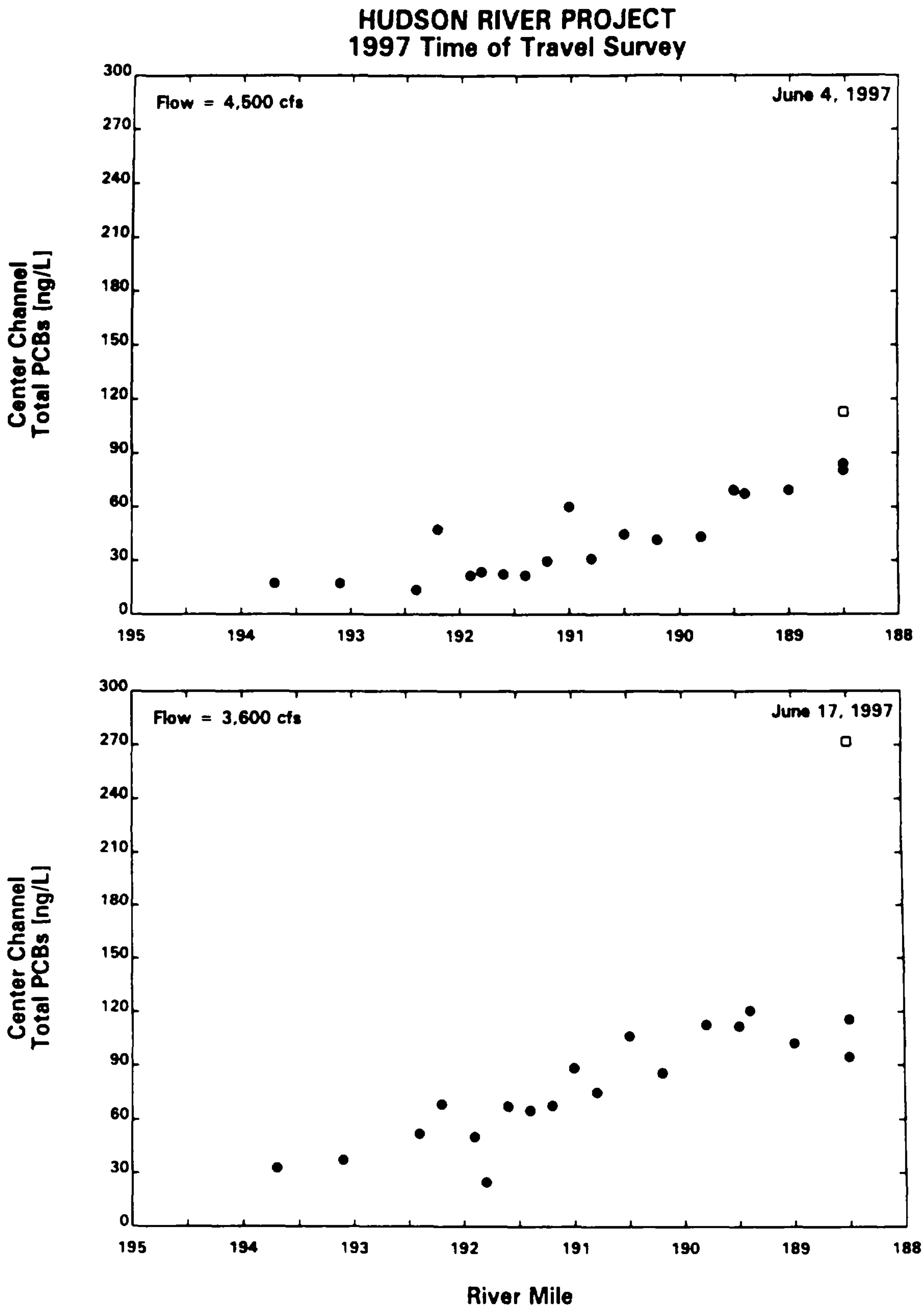


Figure 4-17.
Center Channel PCB Concentrations from the 1997 Time of Travel Surveys.
Note: Open squares represent PCRDMP samples at west wingwall of TID

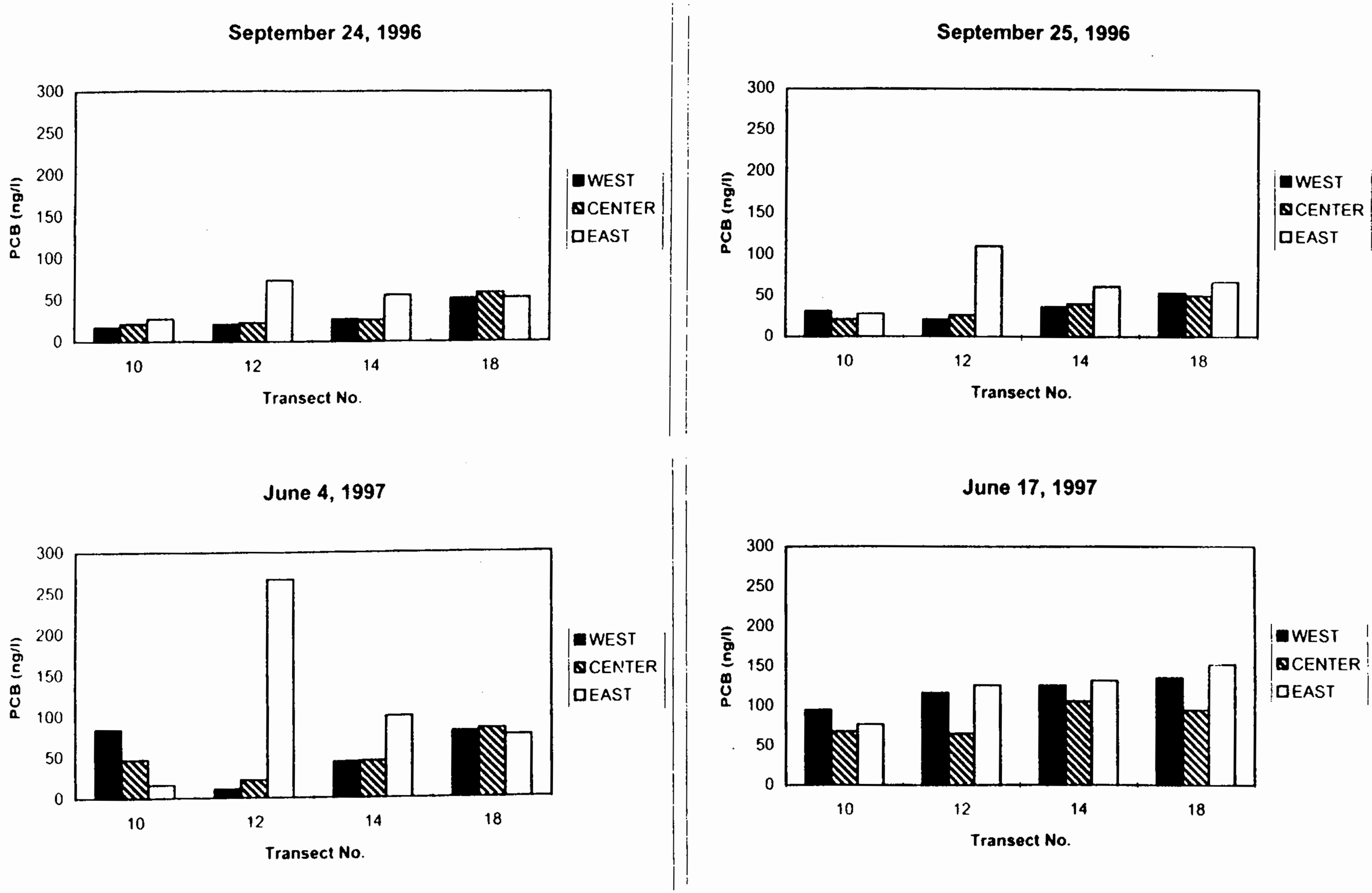


Figure 4-18.
Comparison of West, Center, and East Channel PCB Concentrations at Select Transects from the 1996 and 1997 Time of Travel Surveys.

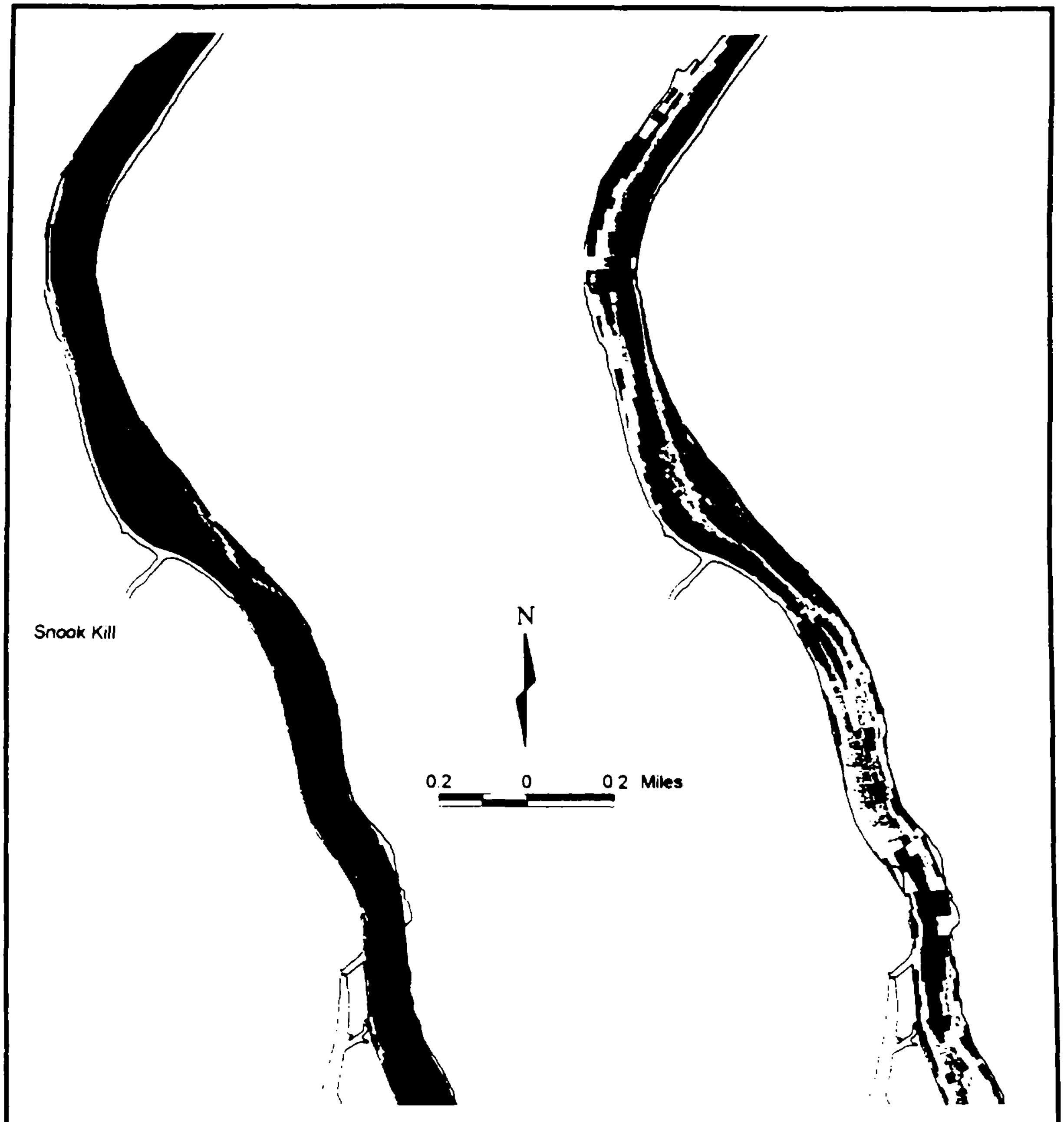


Figure 4-19.
Flow Velocity and Normalized Conservative Sediment Tracer Concentration Predictions for the Snook Kill Vicinity of TIP.

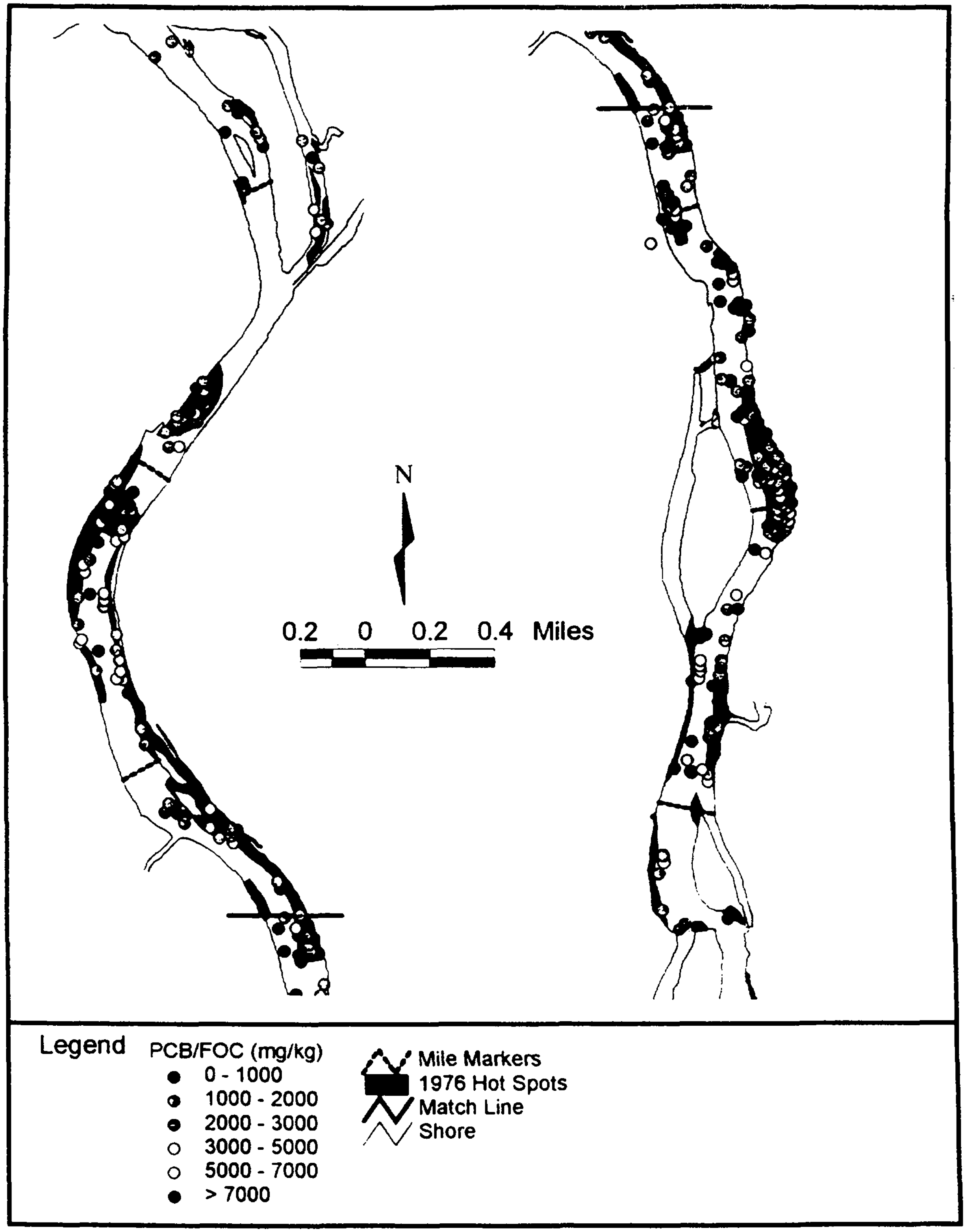


Figure 4-20.
1984 Organic Carbon Normalized Surface Sediment PCB (0-2.5 in.) Concentration within the TIP.

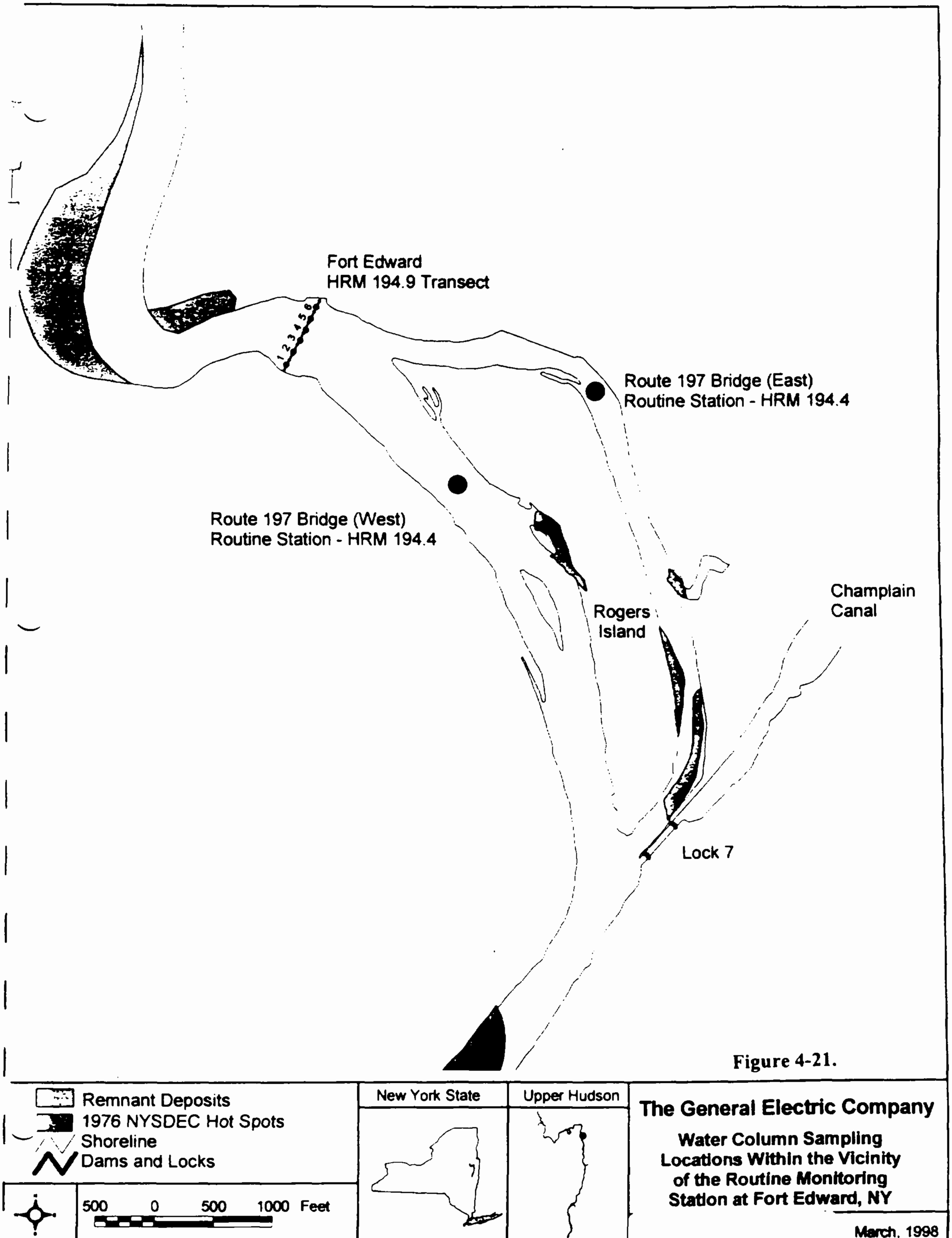


Figure 4-21.

10.0713

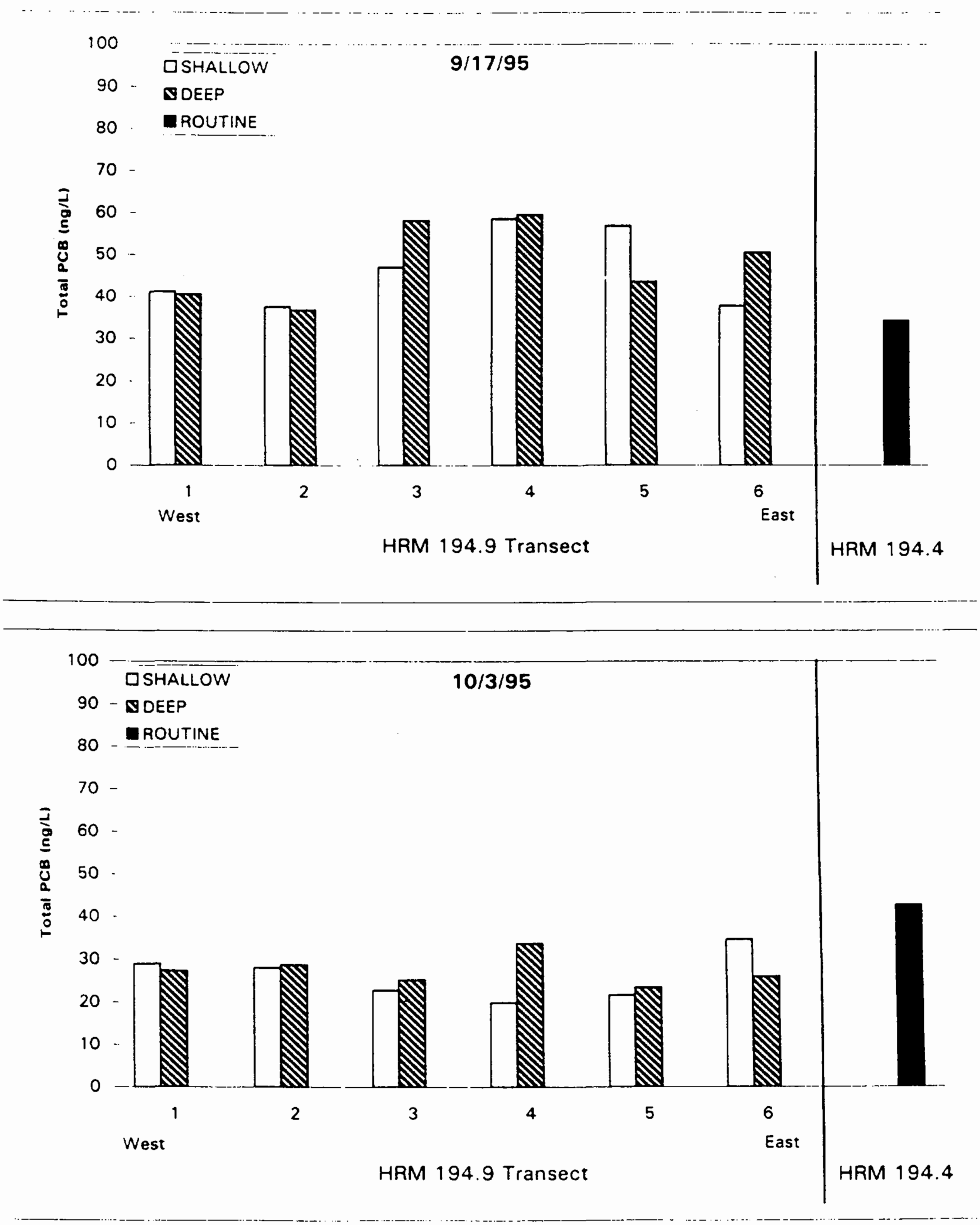


Figure 4-22.
Water Column PCB Concentrations Within the Vicinity of Fort Edward from the 1995 River Monitoring Test.

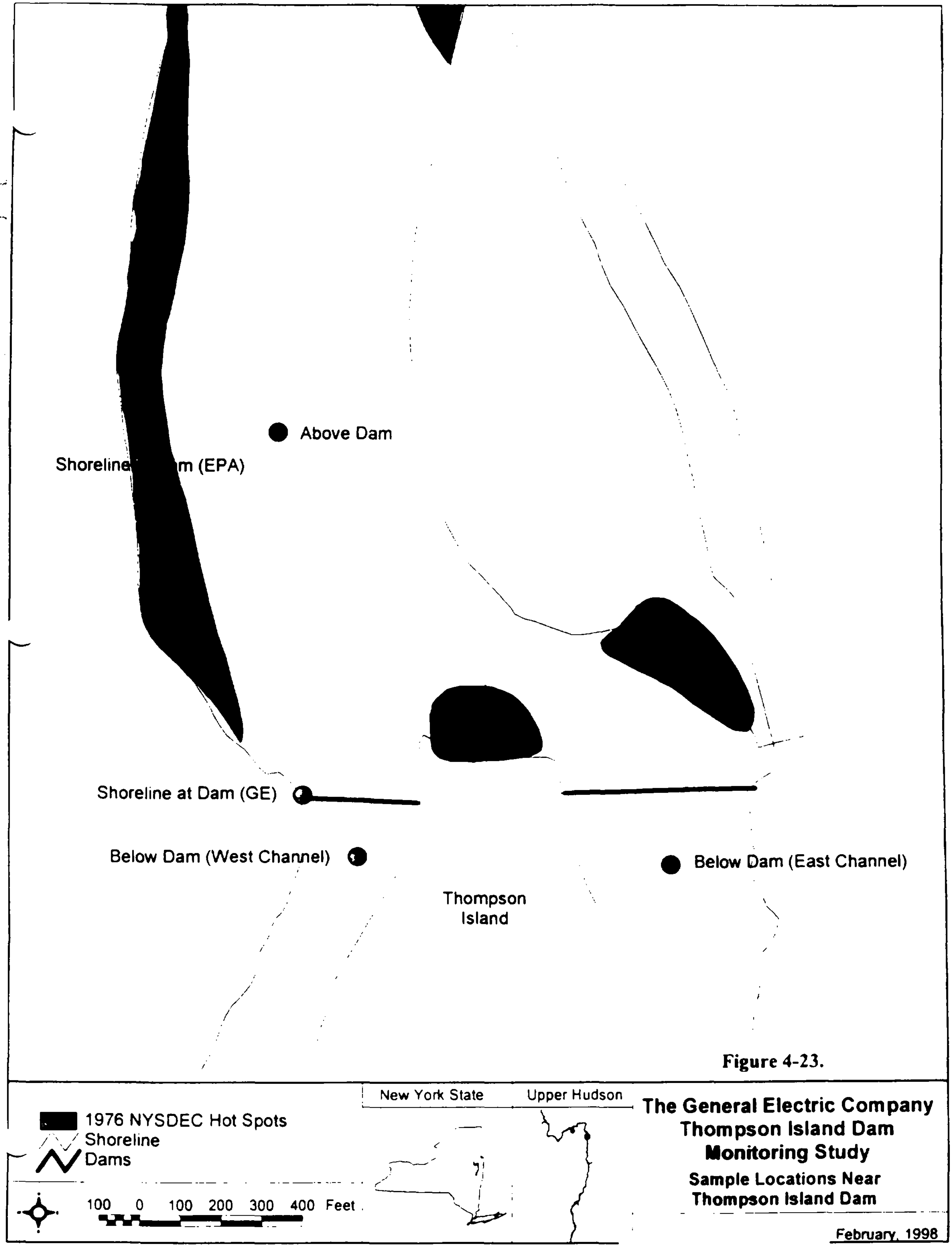

Above Dam
Shoreline m (EPA)
Shoreline at Dam (GE)
Below Dam (West Channel)
Below Dam (East Channel)
Thompson
Island
1976 NYSDEC Hot Spots
Shoreline
Dams
100 0 100 200 300 400 Feet
New York State
Upper Hudson
The General Electric Company
Thompson Island Dam
Monitoring Study
Sample Locations Near
Thompson Island Dam
February, 1998

Figure 4-23.

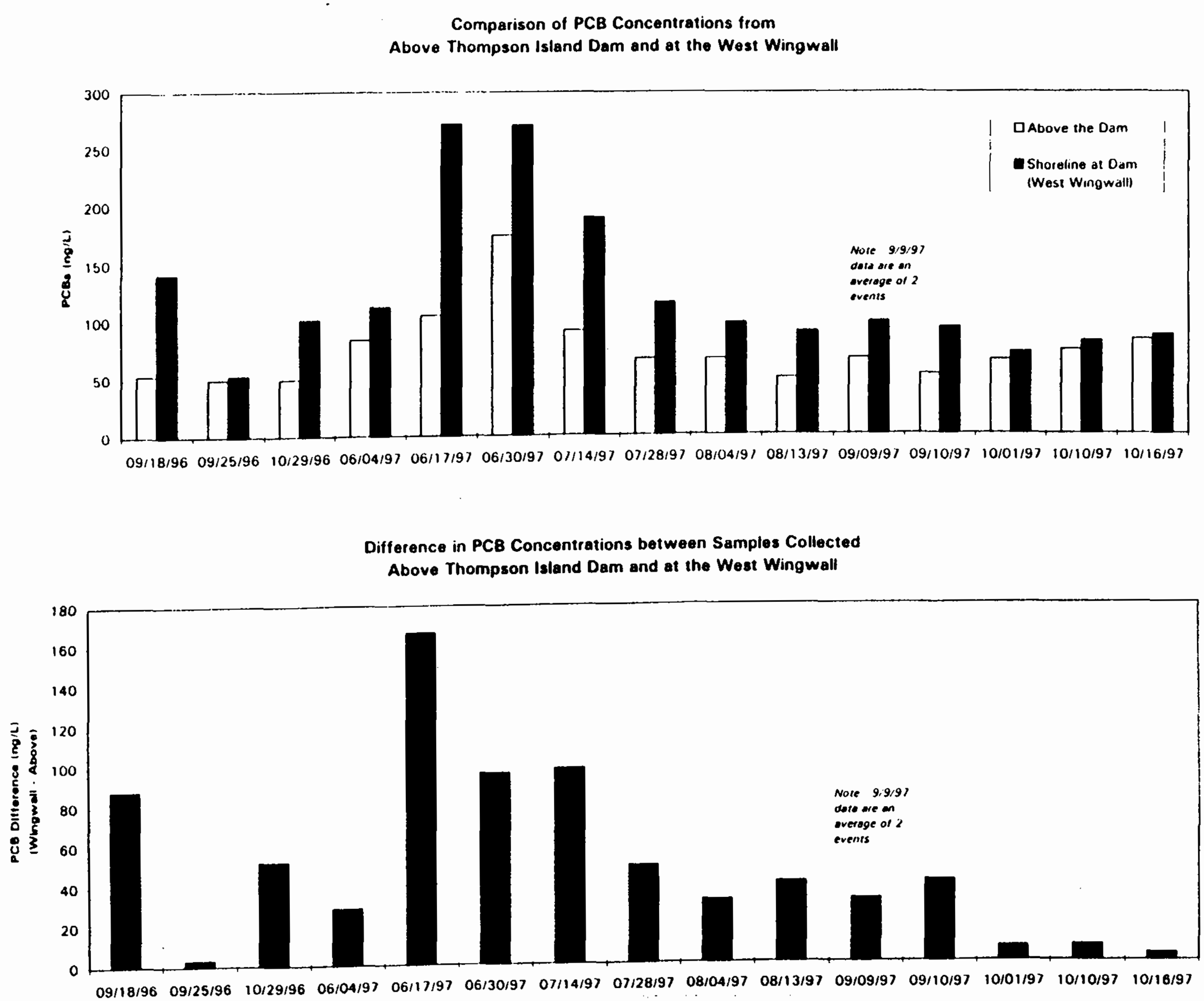


Figure 4-24.
Comparison of PCB Concentrations Upstream of Thompson Island Dam and at the West Wingwall.

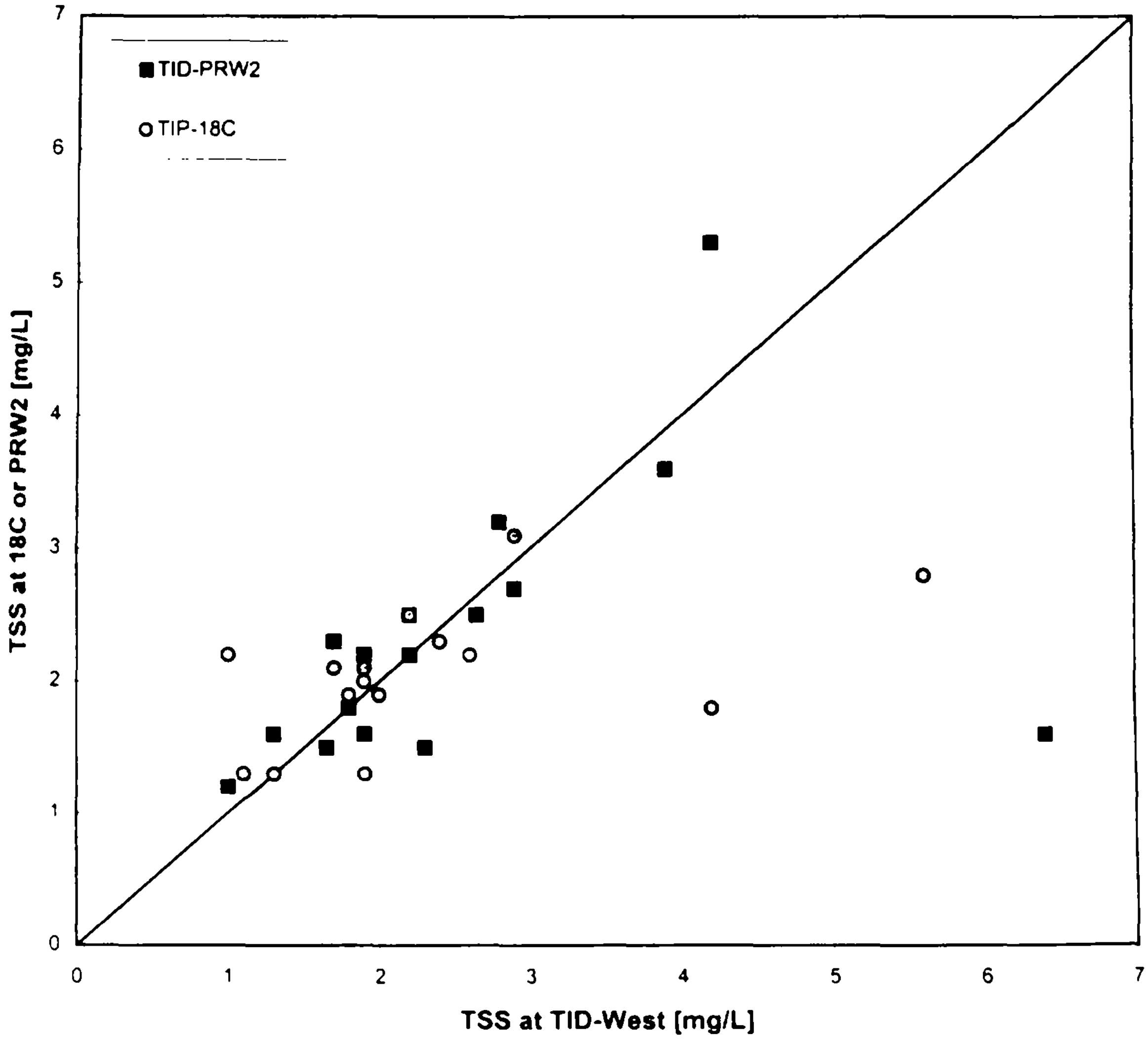


Figure 4-25.
Comparison of TSS Concentrations Upstream of Thompson Island Dam and at the West Wingwall.

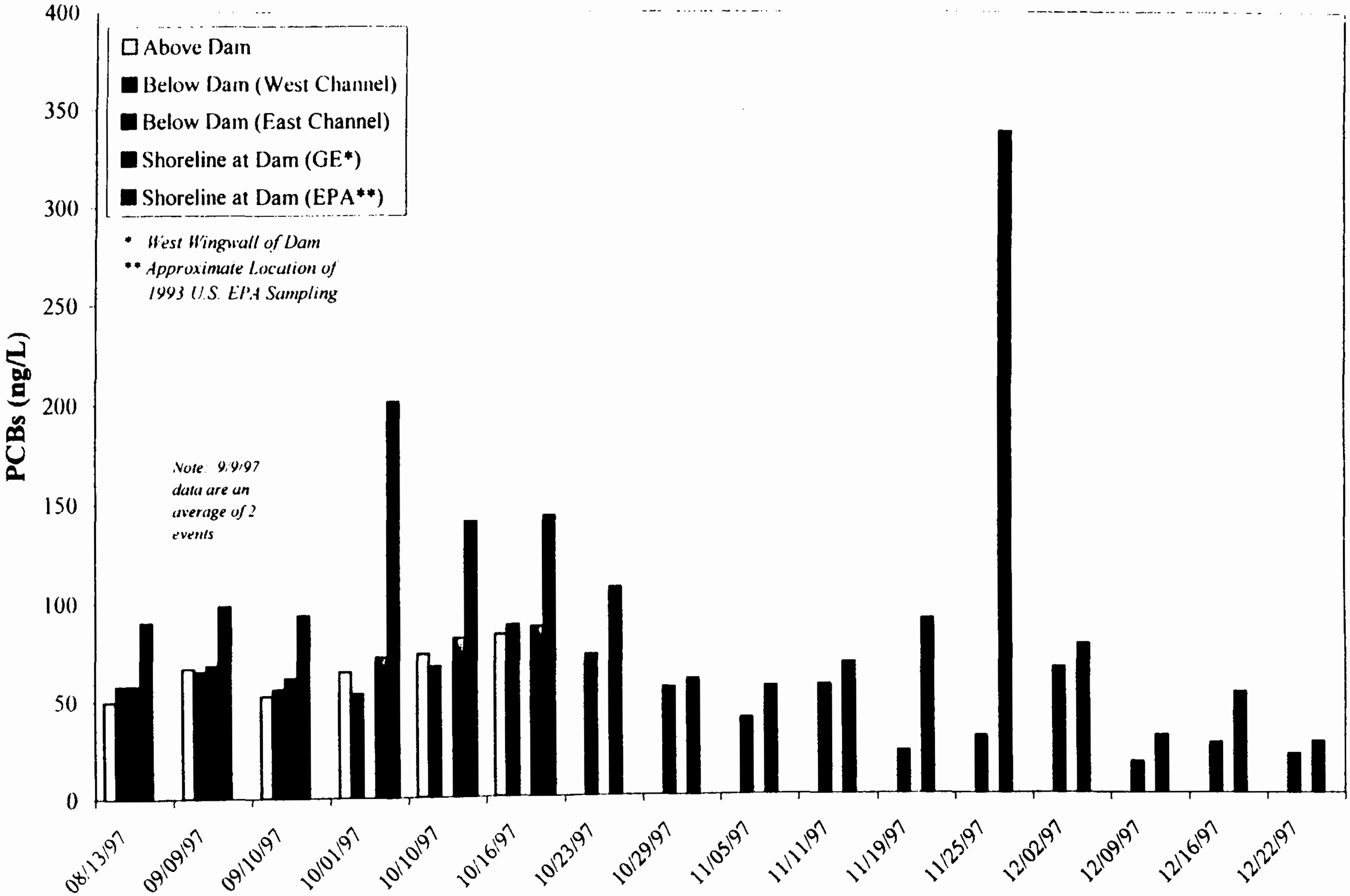


Figure 4-26.
Comparison of PCB Concentrations Within the Vicinity of Thompson Island Dam.

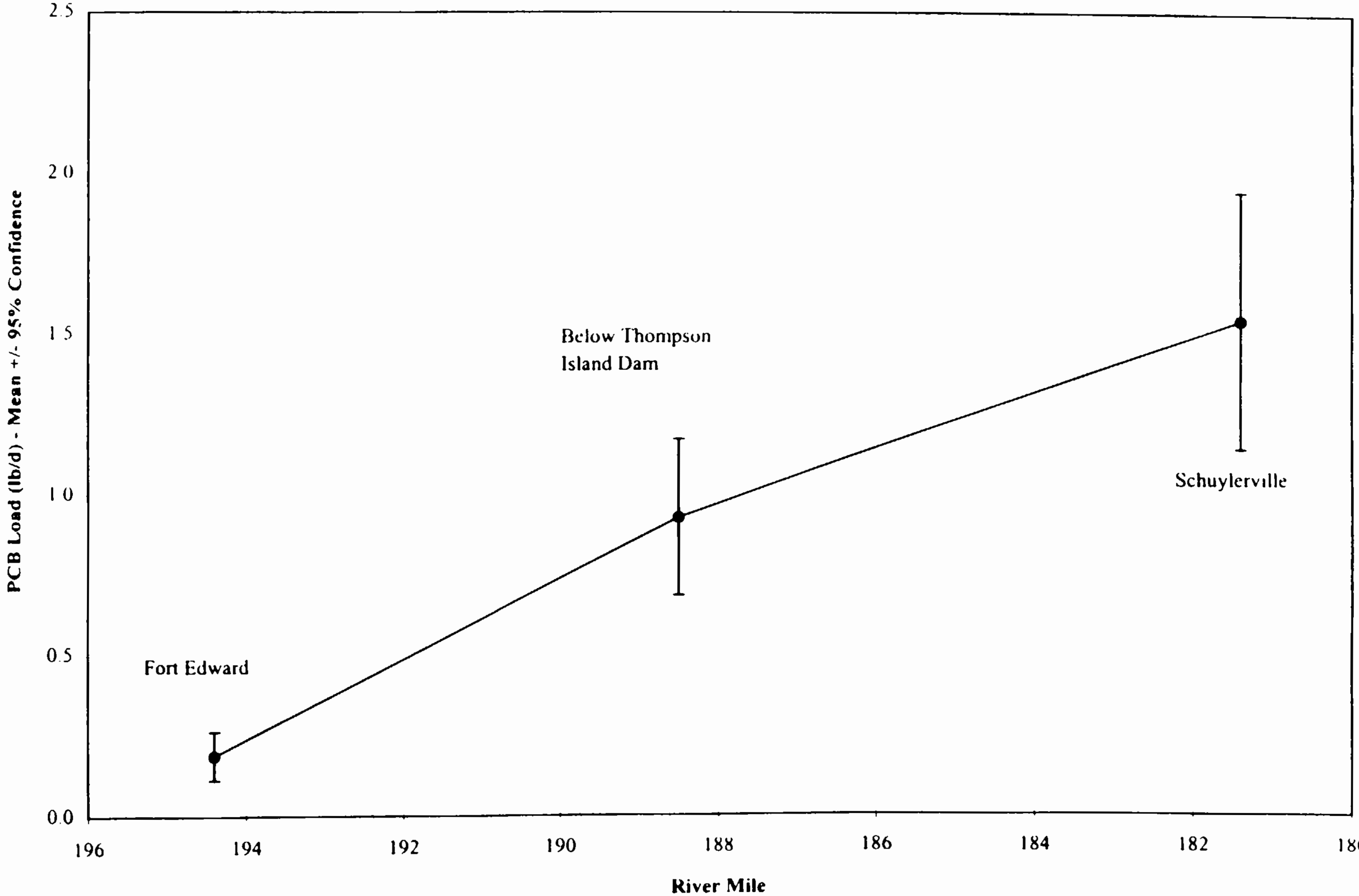


Figure 4-27.
Spatial Profile of Mean Upper Hudson River PCB Loading (Aug - Dec 1997).

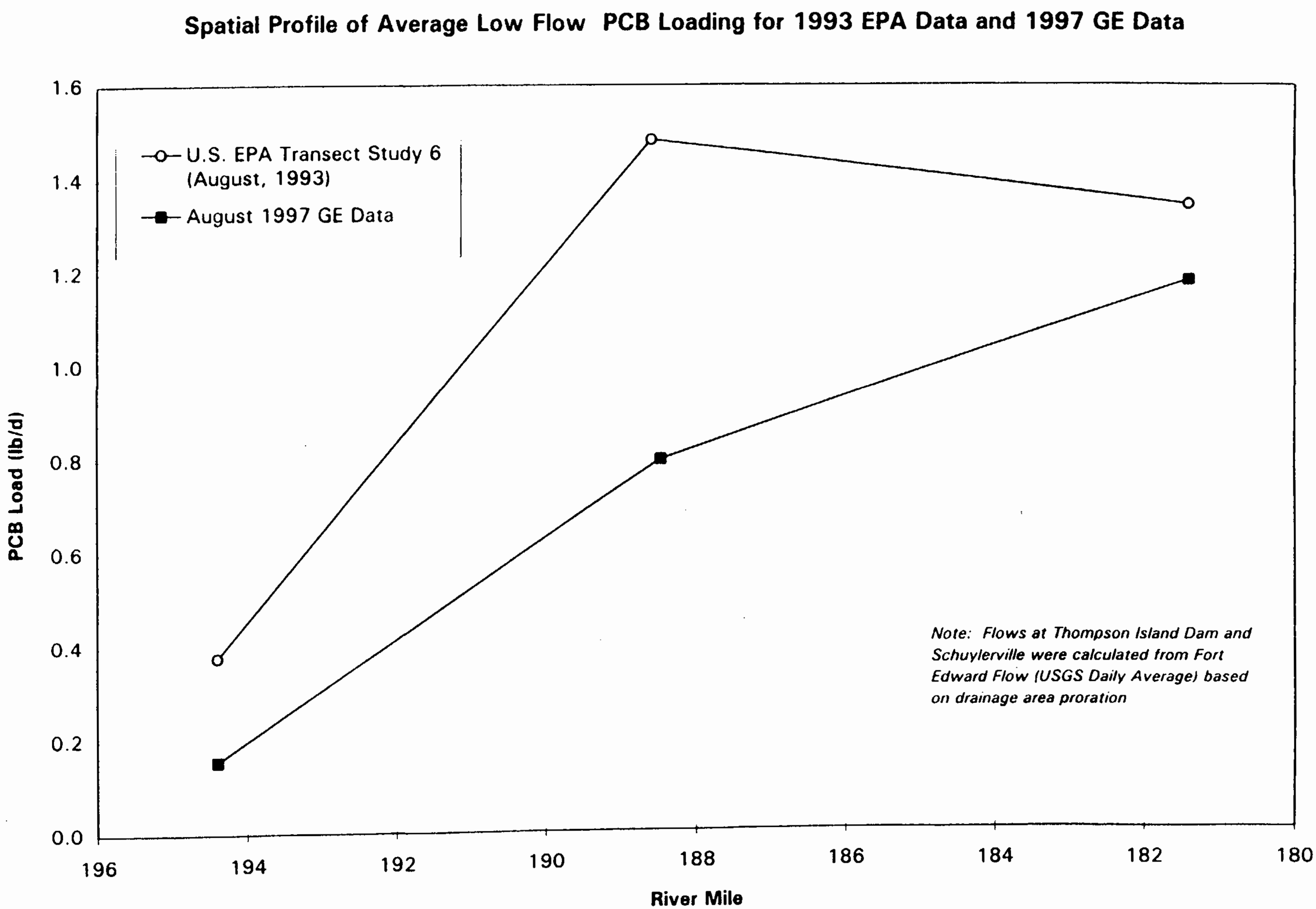
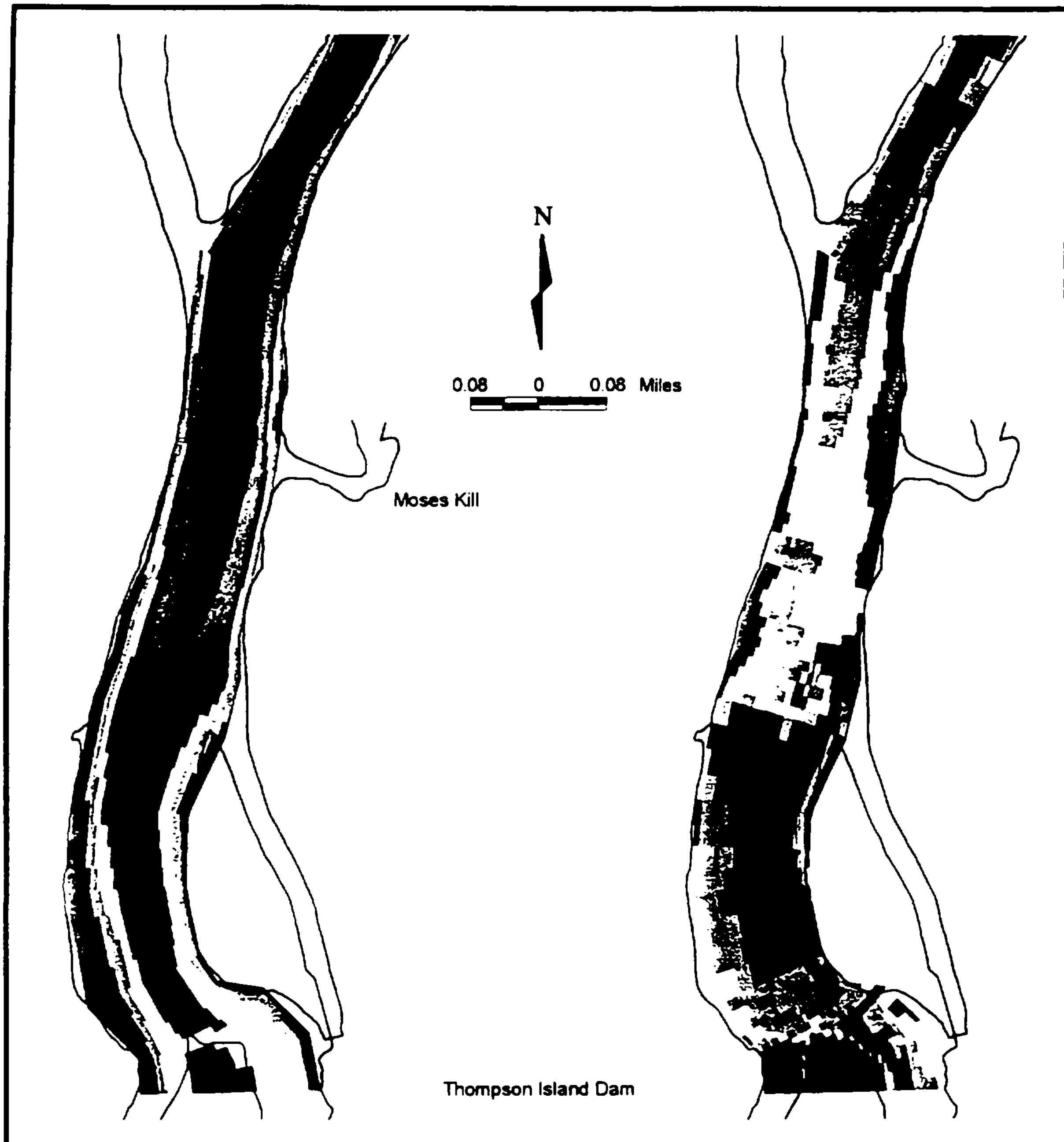
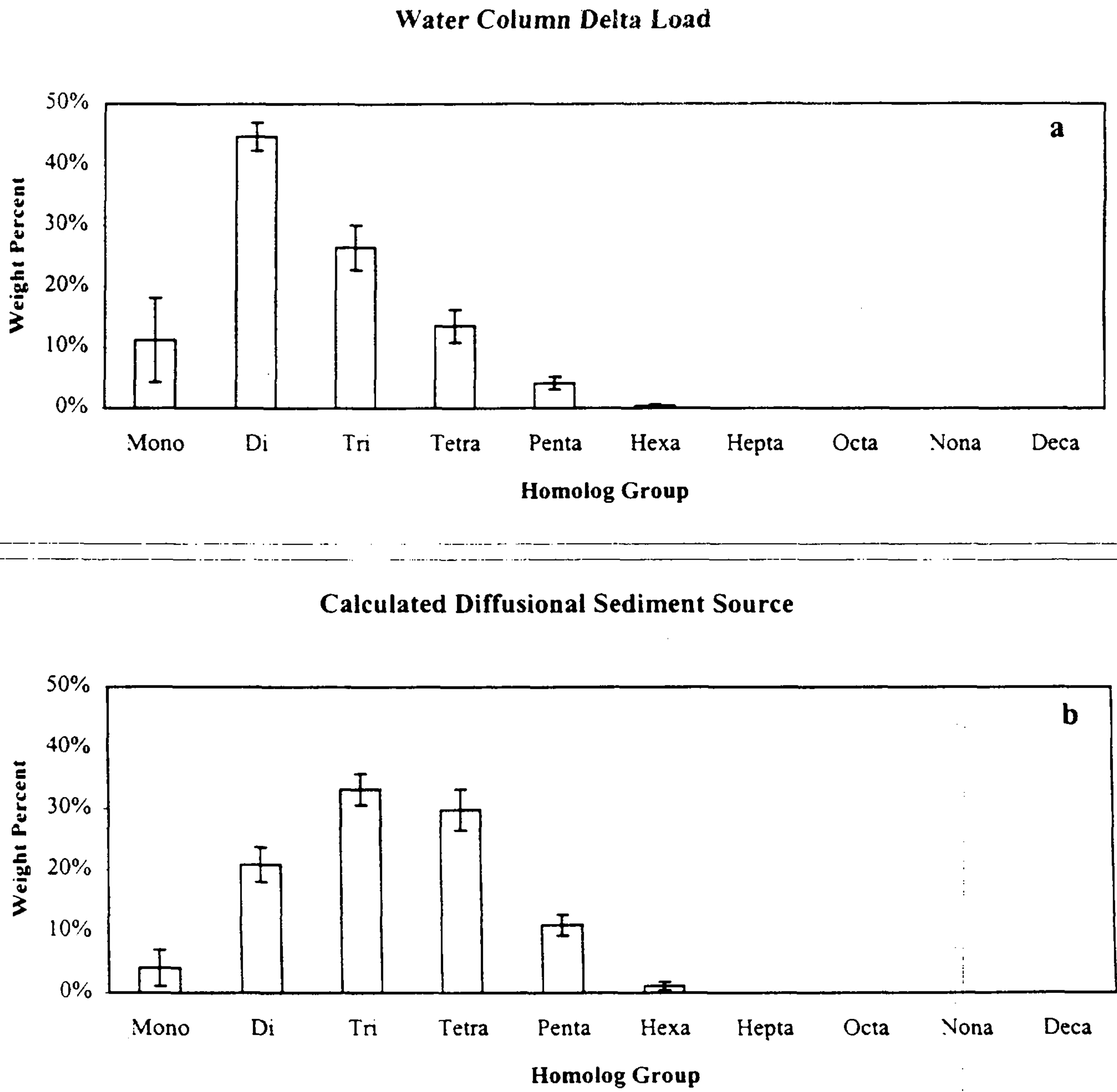


Figure 4-28.
Spatial Profile of Upper Hudson River PCB Loading During Summer Low Flow Period for EPA (August 1993) and GE Data (August 1997).



Shoreline Normalized Concentration < 0.80 0.80 - 0.85 0.85 - 0.90 0.90 - 0.95 0.95 - 1.00 > 1.00	**Figure 4-29.** Flow Velocity and Normalized Conservative Sediment Tracer Concentration Predictions for the Thompson Island Dam Vicinity of the TIP.	Shoreline Velocity (m/s) 0.00 - 0.05 0.05 - 0.10 0.10 - 0.15 0.15 - 0.20 0.20 - 0.25 > 0.25



Mean +/- 95% Confidence Interval for June to August 1997

Upstream Station:	Fort Edward
Downstream Stations:	TIP 18C and TID PRW-2

Figure 4-30.
PCB Homolog Distribution of Water Column Delta Load Across the TIP and Calculated Sediment Source Required to Produce Water Column Load by Equilibrium Partitioning.

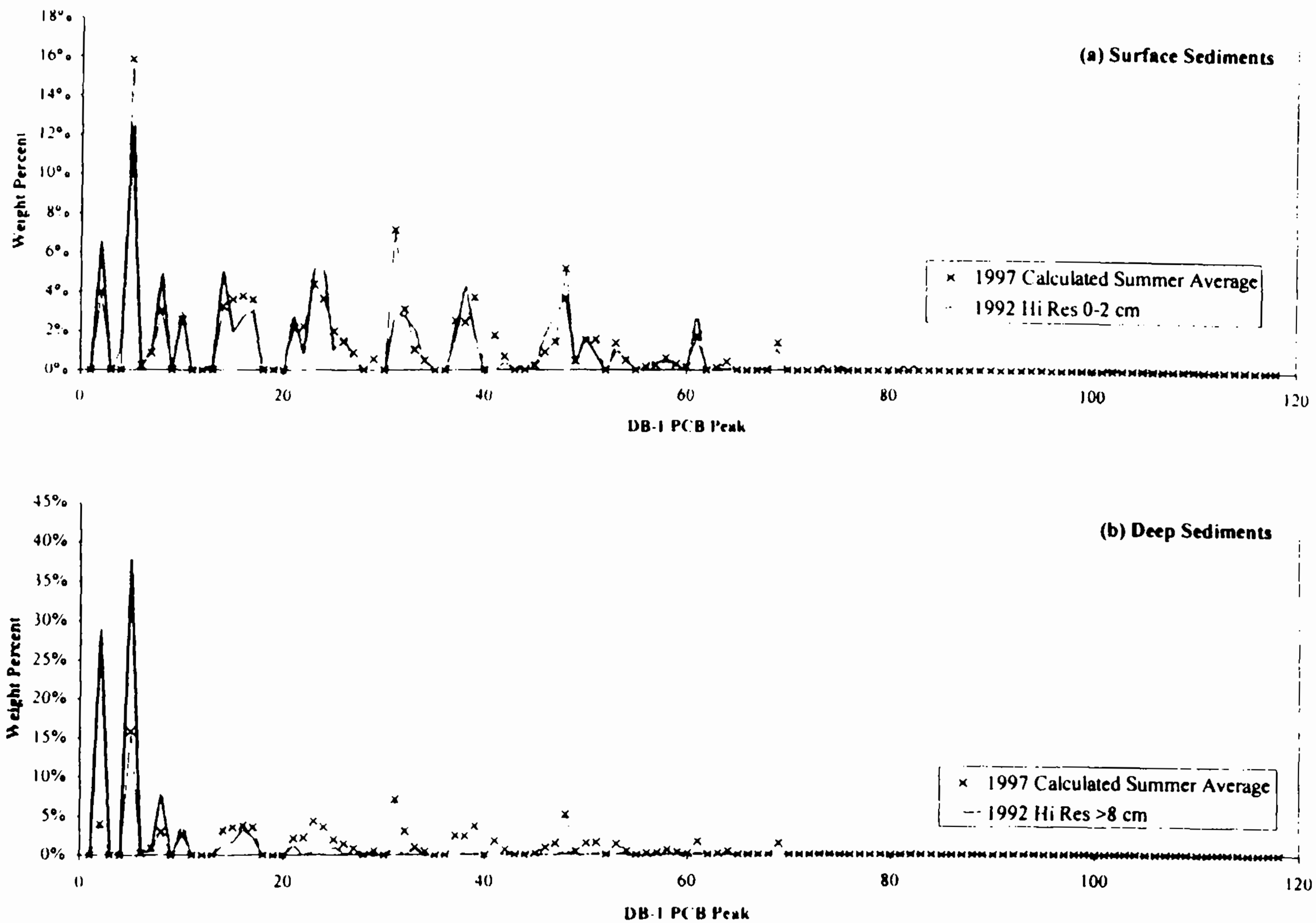


Figure 4-31.
Comparison of PCB Peak Compositions for Calculated Diffusional Sediment Source (1997 Summer Average) with Sediments from 1992 EPA High Resolution Cores Collected from TIP.

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APPENDIX A

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APPENDIX A
CONCEPTUAL MODEL OF TIP PCB DYNAMICS

A.1 PCB Mass Balance

The conceptual model of PCB dynamics in TIP is presented graphically in Figure A-1. PCBs in the water column are present in three phases: 1) freely dissolved, 2) sorbed to particulate matter, and 3) bound to dissolved organic carbon (DOC). The relative distribution among these water column PCB phases is described by equilibrium partitioning concepts. TIP water column PCB concentrations are affected by external loadings from the upstream plant site areas, loadings from sediment sources, advective transport to downstream reaches, and exchange with the atmosphere via volatilization. A brief description of these mechanisms and processes with respect to their importance in TIP PCB dynamics is described below.

A.1.1 Partitioning

Total water column PCBs are expressed as the sum of the dissolved, particulate-bound, and DOC-bound fractions. Equilibrium partitioning, with local linear sorption is used to describe the distribution among these phases. Particulate phase PCBs are bound to the organic carbon fraction of the water column suspended solids and are in equilibrium with the freely dissolved phase. The organic carbon partition coefficient is used to characterize the distribution between these two phases as follows:

$$C_p = C_d K_{oc} f_{oc} m_{ss} \qquad \text{(A-1)}$$

where:

C_p	is the water column particulate PCB concentration ($M\ L^{-3}$),
C_d	is the water column dissolved PCB concentration ($M\ L^{-3}$),
K_{oc}	is the PCB organic carbon partition coefficient ($L^3\ M^{-1}$),
f_{oc}	is the organic carbon fraction of water column particulates ($M\ M^{-1}$), and
m_{ss}	is the water column suspended solids concentration ($M\ L^{-3}$).

PCBs sorbed to water column DOC (C_{doc}; $M\ L^{-3}$) are in equilibrium with the freely dissolved phase, as described by the following equation:

$$C_{doc} = C_d K_{doc}\, m_{doc} \qquad \text{(A-2)}$$

where:

K_{doc}	is the PCB dissolved organic carbon partition coefficient ($L^3\ M^{-1}$), and
m_{doc}	is the water column dissolved organic carbon concentration ($M\ L^{-3}$).

Total TIP water column PCBs can be written in terms of the dissolved phase concentration:

$$C_{tip} = C_d \left(1 + K_{oc} f_{oc}\, m_{ss} + K_{doc}\, m_{doc} \right) \qquad \text{(A-3)}$$

where:

C_{tip}	is the total PCB concentration in the TIP water column ($M\ L^{-3}$).

A.1.2 External loadings

External PCB loadings to the TIP potentially exist anywhere water flows into the system. The magnitude of an external PCB loading depends on the flow rate and PCB concentration of the contributing source:

$$W_e = Q_e C_e \tag{A-4}$$

where:

- W_e is the external PCB loading ($M\ T^{-1}$),
- Q_e is the volumetric flow rate of the external source ($L^3\ T^{-1}$), and
- C_e is the PCB concentration of the external source ($M\ L^{-3}$).

External loadings result from sources such as tributaries, industrial discharges, and sewer outfalls.

A.1.3 Sediment sources

PCBs within the TIP sediments contribute to water column PCBs through three mechanisms: 1) bed resuspension, 2) pore water diffusion, and 3) groundwater advection. The sediment PCB load is the product of the mass flux due to each mechanism listed above and the surface area of PCB-contaminated sediments. The total loading from TIP sediment sources (W_s; $M\ T^{-1}$) is therefore the sum of the flux from these three loading mechanisms taken over the sediment area (A_s; L^2)

$$W_s = A_s \left(J_r + J_d + J_{gw} \right) \tag{A-5}$$

where:

- J_r is the sediment PCB resuspension flux ($M\ L^{-2}\ T$),
- J_d is the sediment PCB pore water diffusive flux ($M\ L^{-2}\ T$), and
- J_{gw} is the sediment PCB groundwater advective flux ($M\ L^{-2}\ T$).

The physical and chemical processes that govern the sediment PCB flux ascribed to these mechanisms are described in Section A.2.

A.1.4 Settling

PCBs are lost from the water column via settling. In this process, particulate phase PCBs settle from the water column and are deposited on surficial sediments. PCB mass loss from the water column due to settling is parameterized with the mean settling velocity:

$$Settling\ Loss = v_s\ C_p\ A_s \qquad \text{(A-6)}$$

where:

- v_s is the mean particulate settling velocity ($L\ T^{-1}$).

A.1.5 Advection

Water column PCBs within the TIP are affected by advection from the upstream to the downstream reaches as a consequence of water movement through the TIP. Advective mass transport is the product of the PCB concentration and the river discharge. Upstream loadings and downstream transport are summed to produce the net advective PCB mass transport:

$$Net\ Advection = QC_{up} - QC_{tip} \qquad \text{(A-7)}$$

where:

Q is the Hudson River discharge within TIP ($L^3\ T^{-1}$), and
C_{up} is the water column PCB concentration flowing into TIP ($M\ L^{-3}$).

In the modeling framework discussed in Section 3, the measured PCB load passing the Fort Edward station was treated as a boundary condition. This loading was calculated as the product of the flow and PCB concentration of water passing the Fort Edward station. In this manner, external PCB loadings to the river from sources upstream of the TIP including the remnant deposits, Allen Mill loadings, river bed DNAPL seeps, and sediment sources were incorporated into the modeling assessment.

A.1.6 Volatilization

Volatilization is the net mass exchange across the air-water interface and is driven by a concentration gradient between the air and water phases. Since atmospheric concentrations are considerably lower than the TIP water column concentrations, volatilization represents a PCB loss mechanism. The volatilization flux is expressed in general terms as the product of the dissolved phase PCB concentration and the volatilization mass transfer velocity. The net volatilization mass transfer is the product of the volatilization flux and the surface area of the air-water interface:

$$Volatilization\ Loss = v_v\ C_d\ A_w \qquad \text{(A-8)}$$

where:

v_v is the volatilization mass transfer velocity ($L\ T^{-1}$), and
A_w is the surface area of the air-water interface (L^2).

A.1.7 Governing equation

The governing mass balance equation to describing PCB dynamics in TIP can be expressed as: the time rate of change of PCB mass is equal to the sum of PCB sources less the sum of PCB sinks within the TIP. PCB sources include external loadings, internal sediment sources, and advection from upstream. PCB sinks include advection to downstream, settling, and volatilization. Assuming constant volume (V), the governing mass balance equation can be expressed as:

$$V \frac{\partial C_{tip}}{\partial t} = \sum C_e Q_e + A_s \left(J_r + J_d + J_{gw} \right) - v_s C_p A_s + Q C_{up} - Q C_{tip} - v_v C_d A_w \qquad \text{(A-9)}$$

where:

t is time (T), and
V is the TIP volume (L^3).

The overall mass balance equation contains concentrations in terms of total, dissolved, and particulate PCBs. Using the partitioning relationships presented in section A.1.1, the mass balance may be expressed in terms of total water column PCBs. The mass balance equation presented above is coupled with similar expressions for upstream and downstream reaches, resulting in a system of equations for the entire river reach being modeled. Furthermore, the particulate phase and sediment source terms require coupling of the water column and sediment solids and PCB mass balance equations.

A.2 Sediment PCB Source Loading Mechanisms

As discussed above, sediment loading mechanisms play an important role in TIP PCB dynamics. Sediment PCB loading mechanisms include diffusive flux, sediment resuspension, and groundwater advection.

A.2.1 Diffusive flux

Diffusion contributes PCBs to the water column due to a concentration gradient between the water column and surface sediment pore water. Diffusion is traditionally described using Fick's First Law, in which the diffusive flux is proportional to the concentration gradient:

$$J_d = -\varphi D_s \frac{\partial C}{\partial x} \qquad \text{(A-10)}$$

where:

- φ is the surface sediment porosity ($L^3 L^{-3}$),
- D_s is the diffusion coefficient ($L^2 T^{-1}$), and
- $\partial C/\partial x$ is the surface sediment pore water PCB concentration gradient ($M L^{-4}$).

The diffusion equation is simplified by expressing the concentration gradient as the difference between the pore water and water column PCB concentrations over a finite characteristic mixing depth:

$$\frac{\partial C}{\partial x} \approx \frac{C_d^{\prime} - C_{d,tip}}{\Delta x} \qquad \text{(A-11)}$$

where:

C_d' is the pore water PCB concentration ($M\ L^{-3}$);
Δx is the surface sediment mixing depth (L).

Grouping the porosity, diffusion coefficient, and mixing depth into a bulk exchange coefficient, and expressing the sediment flux in terms of mass loading, results in the following expression:

$$W_d = k_f A_s \left(C_d^{\prime} - C_{d,tip} \right) \qquad \text{(A-12)}$$

where:

W_d is the water column PCB load from sediment pore water diffusion ($M\ T^{-1}$),

and

k_f is the sediment diffusion exchange coefficient ($L\ T^{-1}$).

Equilibrium kinetics with local linear sorption is assumed to describe the partitioning between the freely dissolved pore water PCBs, and PCBs sorbed to sediment organic carbon:

$$C_d = \frac{C_s}{K_{oc} f_{oc}} \qquad \text{(A-13)}$$

where:

C_s is the dry weight surface sediment PCB concentration ($M\,M^{-1}$).

Sediment pore water PCBs are the sum of freely dissolved and DOC-bound fractions:

$$C_d' = C_d\left(1 + m_{doc}K_{doc}\right) \qquad \text{(A-14)}$$

where:

m_{doc} is the sediment pore water dissolved organic carbon concentration ($M\,L^{-3}$).

Since the sediment pore water PCB concentration is typically much larger than the water column concentration, the water column concentration can be neglected in the resulting sediment diffusive loading equation:

$$W_d = k_f A_s\left(1 + m_{doc}K_{doc}\right)\frac{C_s}{f_{oc}K_{oc}} \qquad \text{(A-15)}$$

The equation shown above states that the diffusive loading is proportional to the surface sediment concentration and surface area of PCB-containing sediments. Although surface sediment PCBs within the TIP are not spatially homogeneous, the diffusive loading equation can be used with area-weighted averages for organic carbon normalized PCB concentrations to calculate the net TIP flux.

A.2.2 Sediment resuspension

Resuspension or bed scour is the process by which surface sediments are mobilized and resuspended into the water column in response to shear forces produced by water movement over the bed. Only a finite amount of material can be resuspended from a cohesive sediment bed that is exposed to a constant bottom shear stress. This phenomenon, referred to as bed armoring, has been observed and quantified in numerous laboratory studies (Tsai and Lick, 1987; Parchure and Mehta, 1985). The amount of fine grained sediment that is resuspended (ε; M L^{-2}) at a given shear stress (τ; F L^{-2}) is given by the following empirical expression:

$$\varepsilon = \alpha \left(\frac{\tau - \tau_0}{\tau_0} \right)^m \qquad \tau \geq \tau_0 \qquad \text{(A-16)}$$

where:

- α is a system constant dependent on time since material was deposited as determined from field studies,
- τ_0 is the critical shear stress below which sediment is not subject to resuspension (F L^{-2}),

At $\tau < \tau_0$, ε is equal to zero. Equation A-16 determines the net resuspension at a given shear stress.

The flux of sediment resuspended from the TIP at a given flow rate is dependent on the spatially varying bottom shear stress ($\tau_{i,j}$) as calculated using a two-dimensional hydrodynamic model. Using estimates of ε within each of the model grid elements, the maximum total mass of PCBs resuspended at a given flow (W_r) can be calculated as follows:

$$W_r = \sum_{i=1}^{n} \varepsilon_i A_i C_i \tag{A-17}$$

where:

- ε_i is the mass of sediment eroded from hydrodynamic grid element i ($M\ L^{-2}$),
- A_i is the area of grid element i (L^2), and
- C_i is the surface sediment PCB concentration within grid element i ($M\ M^{-1}$).

This loading is distributed evenly over an assumed 1 hour resuspension period.

A.2.3 Groundwater advection

Groundwater advection occurs due to a hydraulic gradient within a porous media. One dimensional groundwater flow is described by Darcy's Law, in which the flow is related to the hydraulic gradient and the hydraulic conductivity of the media:

$$Q_{gw} = -K A_s \frac{\partial h}{\partial x} \tag{A-18}$$

where:

- Q_{gw} is the upward groundwater flow ($L^3\ T^{-1}$),
- A_s is the area perpendicular to flow (L^2),
- K is the sediment hydraulic conductivity ($L\ T^{-1}$), and
- $\partial h/\partial x$ is the vertical hydraulic gradient ($L\ L^{-1}$).

The upward flow of groundwater through surface sediments and into the TIP water column results in a net PCB loading. As groundwater travels through PCB-contaminated sediments, the interstitial pore water reaches an equilibrium with the solid-phase PCBs. Therefore, the net groundwater advective PCB loading to the TIP water column is the product of the upward groundwater flow and the surface sediment pore water PCB concentration:

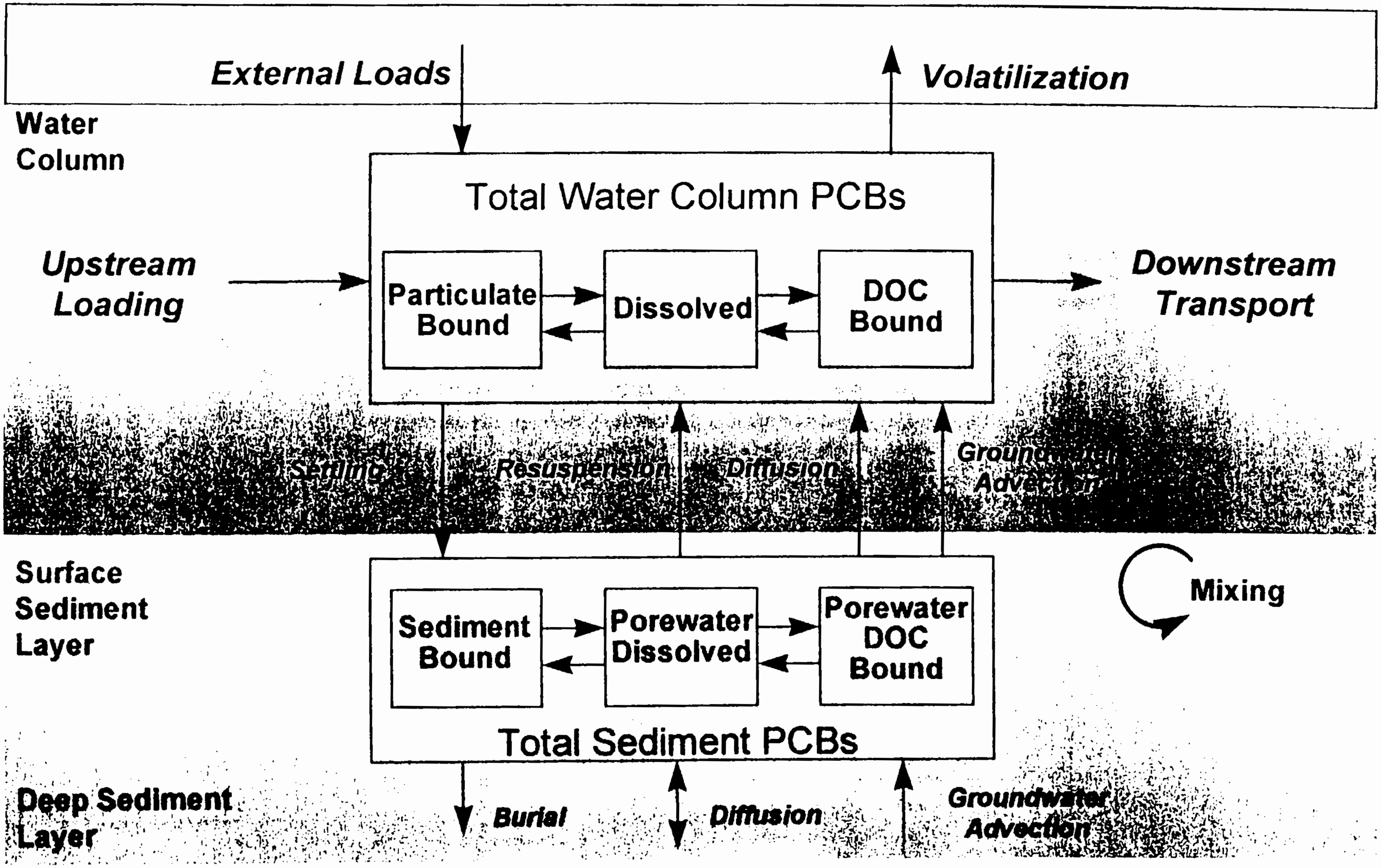
$$W_{gw} = Q_{gw} C_d^{\prime} \qquad \text{(A-19)}$$

where:

W_{gw} is the groundwater advective PCB loading to the water column ($M\ T^{-1}$).

The total internal sediment PCB loading within the TIP is the sum of the loadings from surface sediment pore water diffusion, sediment resuspension scour, and groundwater advection. Since the total sediment PCB loading varies both spatially and temporally, it is important to gain an understanding of the factors that influence the relative importance of these three loading mechanisms. These processes were considered in the quantitative modeling framework described in Section 3, and several field studies described in Section 4 were conducted to examine each loading mechanism.

Figure A-1.
Conceptual Model of PCB Dynamics in the Hudson River.



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