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COMMENTS OF GENERAL ELECTRIC COMPANY ON  
PHASE 2 REPORT - REVIEW COPY  
FURTHER SITE CHARACTERIZATION AND ANALYSIS  
VOLUME 2C -  
DATA EVALUATION AND INTERPRETATION REPORT  
HUDSON RIVER PCBs REASSESSMENT RI/FS  
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Melvin B. Schweiger  
John G. Haggard  
General Electric Company  
Corporate Environmental Programs  
1 Computer Drive South  
Albany, New York 12205  
(518) 458-6646

John Connolly  
HydroQual, Inc.  
1 Lethbridge Plaza  
Mahwah, NJ 07430  
(201) 529-5151

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**COMMENTS OF THE GENERAL ELECTRIC COMPANY  
TO THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
CONCERNING THE PHASE 2 DATA EVALUATION AND INTERPRETATION  
REPORT FOR THE HUDSON RIVER PCBs SUPERFUND SITE (FEBRUARY 1997)**

**I. INTRODUCTION AND EXECUTIVE SUMMARY**

The General Electric Co. ("GE") is pleased to submit these comments to the United States Environmental Protection Agency ("EPA") on the "Phase 2 Report - Review Copy, Further Site Characterization and Analysis, Volume 2C - Data Evaluation and Interpretation Report, Hudson River PCBs Reassessment RI/FS" (February 1997) ("Report"). The Report presents EPA's analysis of the sediment and water column data collected during Phase 2 of the Remedial Investigation ("RI") of the Hudson River PCBs Superfund Site ("Site") Reassessment, as well as historical data collected by GE, the United States Geological Survey ("USGS") and others.

The Report is part of EPA's Reassessment, which seeks to determine the sources, transport and fate of PCBs in the Upper Hudson River for the purposes of remedial analysis. The Report analyzes the data collected in the RI and presents conclusions concerning the sources, transport and fate of PCBs in the Hudson River. If the Agency finds that the PCBs pose a risk that it believes would be prudent to abate, the evaluation and interpretation of the data should aid in determining where the PCBs come from, how they move through the river system, and how they leave the system. This, in turn, should form the basis for addressing the remedial questions of what will

happen to the system without further intrusion and whether any particular remedy would abate any perceived risk more quickly than natural recovery.

Fundamental to these determinations is a technically sound analysis of the data. The Report does not provide a persuasive account of the data, and GE respectfully submits that several primary conclusions of the Report are incorrect as a result of flawed, incomplete or incorrect analyses. The Report is notably unhelpful in answering the central questions that the Reassessment must address -- the questions of source, transport, fate, and remedial alternatives.

We start with the four major conclusions that the Agency drew from the data analysis and set forth the basis for our disagreement:

1. The area of the site upstream of the Thompson Island Dam represents the primary source of PCBs to the freshwater Hudson. This includes the GE Hudson Falls and Fort Edward facilities, the Remnant Deposit area and the sediments of the Thompson Island Pool. Report at E-2.

The Report describes the PCB load that passes the Thompson Island Dam ("TID") as moving in "pipeline" fashion, with little or no loss of PCBs from the water column, to the freshwater Hudson downstream of Troy. We disagree with this conclusion in two regards. First, the sediments downstream of the TID contribute significantly to the water column load as measured at Waterford. During low flow, this contribution is on the order of 33%. Second, external sources contribute to the PCB load in the freshwater Hudson, particularly downstream of Troy. The Albany core analyzed in the Report indicates that 15% to 25% of the PCB load found at Albany originated downstream

of the TID and not in the aged sediments of the river. Both facts are inconsistent with the theory of a conduit between the TIP and the freshwater Hudson. This correction is important. The remedial analysis must recognize that elimination of the PCB load at the TID will not eliminate the PCB loadings downstream of the TID.

2. The PCB load from the Thompson Island Pool has a readily identifiable homologue pattern which dominates the water column from the Thompson Island Dam to Kingston during low flow conditions (typically 10 months of the year). Report at E-3.

This conclusion suffers from two misleading omissions. First, the Report shows that approximately 36% of the total annual PCB load passing the TID occurred in the two-month high-flow period. Second, the high-flow load does not show the homologue pattern seen during low flow and clearly originates upstream of the Thompson Island Pool ("TIP").

These additions are important. The remedial analysis must recognize that eliminating the low-flow PCB load at the TID or eliminating the PCB load originating in the TIP will not eliminate 50% of the annual PCB load passing the TID. Only if conditions during the sampling period are unrepresentative of present conditions will this not be the case. The Report suggests, without factual demonstration from the data, that loading above the TIP has been substantially reduced since the sampling period. To conduct a remedial analysis with confidence, one must know whether that is in fact the case. This determination cannot be made until the effects of the remedial work GE has conducted can be fully evaluated.

3. The PCB load from the Thompson Island Pool originates from the sediments within the Thompson Island Pool. Report at E-4.

This conclusion is too vague to be useful in the remedial context. The Report postulates that the TIP load originates in highly dechlorinated sediments deposited before 1984 or in undechlorinated sediments more recently deposited. In order to know which of these distinct sediment classes might be a candidate for remedial action, one needs to know which class contributes the PCBs to the TIP load. This is important because each class supports distinct remedies. The Report is of no help on this issue.

More fundamentally, there is no evidence to support the conclusion that the TIP load originates from PCBs in highly dechlorinated, highly concentrated sediments. No realistic mechanism exists to resuspend these PCBs from the sediments into the water column, and the congener pattern of these sediments does not match the pattern of the TIP load.

GE believes that the increase in PCB load across the TIP originates partially from the surficial sediments of the TIP (particularly from PCBs deposited from upstream of Rogers Island in the recent past) and partially from the PCB load that passes Rogers Island undetected and only later detected up at the TID after reprocessing through the surface sediments. This limits the contribution from the sediments to amounts congruent with mechanisms that transfer PCBs from sediments to the water column; provides a more persuasive match to the congener pattern at the TID; and takes into account the major releases to the river following the 1991 collapse of the Allen Mill.

The source of the PCB load at the TID is of central importance to the remedial analysis. If current and recent releases from upstream of Rogers island are the source of the load at the TID, the remedial analysis must focus on sources upstream of Rogers Island. If the source of the load at the TID is PCBs deposited in the sediments of the TIP several years ago, the remedial analysis is likely to focus on the sediments of the TIP.

4. Sediment inventories will not be naturally "remediated" via dechlorination. The extent of dechlorination is limited, resulting in probably less than a 10 percent mass loss from the original concentrations.

This conclusion focuses on the wrong issue, mass. Dechlorination reduces the potential toxicity and bioaccumulation of the affected PCBs. Dechlorination will reduce the carcinogenicity of the PCBs; it can reduce the toxic equivalency of the PCBs by more than 90%; and it will reduce the bioaccumulation of the PCBs between 4 and 35 fold. Because of these effects, dechlorination makes a very substantial contribution to remediation and must be considered in the food-web modeling and risk assessment. Finally, the major conclusions fail to address sedimentation that buries PCBs and effectively removes them from the food chain and is an important remedial process in the dynamics of the river.

The arrangement of the Report's conclusions makes it difficult to grasp clearly EPA's view of PCB sources, transport and fate in the Upper Hudson. We attempt here to array what we believe are the Report's central positions in an order that reflects sequential movement in the river:

1. During periods of low flow, PCBs enter the TIP from above Rogers Island and are stored in the TIP, despite the fact that this stored PCB load averages approximately one-third of those PCBs that pass the TID during low flow.
2. During low flow, PCBs from relatively undechlorinated, aged surface sediments (which do not include PCBs entering the TIP in the immediate past) or PCBs from dechlorinated and highly concentrated sediments deposited before 1984 are the source of the PCBs passing the TID.
3. During low flow, the PCBs that pass the TID dominate the freshwater Hudson to Kingston.
4. During high flow, PCBs originating upstream of Rogers Island pass through the TIP and dominate the freshwater Hudson to Kingston.
5. Approximately 36% of the annual PCB load passes the TID during high-flow events. The Report suggests that this load may now be substantially reduced as a result of source-control remediation projects at GE's plant sites.

Apart from the points made in the analysis of the Report's major conclusions, this is not a plausible account of the behavior of PCBs in the river for the following reasons:

- \* The Report offers no persuasive account or explanation of the fate of the PCBs entering the TIP from above Rogers Island during low flow.
- \* The Report ignores established mechanisms of deposition and volatilization in describing the fate of PCBs below the TID.
- \* The Report treats similar reaches of the river in a dissimilar fashion. For instance, the report claims that sediment conditions immediately above the TID significantly contribute PCBs into the water column but similar sediment conditions below the TID do not.
- \* The Report assumes that the conditions observed in 1993 are representative of long-term conditions in the river and ignores the atypical impacts of the large loading of PCBs to the river in the 18 months following the collapse of the Allen Mill in September 1991.

In these comments, we offer our own account of the behavior of PCBs in the Upper Hudson, based on our analysis of the data.

Our account makes the following improvements on the one provided in the Report:

- \* It incorporates plausible mechanisms for the movement of PCBs through the river.
- \* It treats portions of the river with similar conditions in a similar manner.

- \* It recognizes the major known changes in PCB loading to the river over time.
- \* It addresses all the major processes, including sedimentation, at work in the river.
- \* It uses a more comprehensive array of data to test and constrain our evaluation of the data and the conclusions derived therefrom.

These comments focus on testing the analyses and conclusions in the Report against these benchmarks, and emphasize the importance to remedial analysis of the issues raised herein.

It is apparent that the most significant unresolved matter is the source of the PCB load at the TID at low flow which cannot be accounted for by PCBs measured at Rogers Island and PCBs expected to be diffused from the aged sediments of the TIP. GE has been and is engaged in the data collection and evaluation essential to reaching a sound answer as to the source of the unaccounted-for load. It is likely that undechlorinated Aroclor 1242 from the Allen Mill collapse and the bedrock seeps near the GE Hudson Falls plant site has entered the TIP undetected, particularly during higher flow events, and has been deposited in the Pool, contributing substantially to the unaccounted-for PCB load at the TID. This interpretation takes account of the large-scale Allen Mill release, addresses the fate of the PCBs measured at Rogers Island, avoids implausible mechanisms for PCB mobilization within the TIP and is supported by a variety of lines of additional evidence, such as the match with the congener fingerprint of the PCBs at the TID and the congener fingerprint of PCBs found in TIP fish.

Downstream of the TIP it is also important to recognize the effects of deposition and volatilization as well as external sources. While the size of the PCB load may not be substantially altered between the TID and Troy, PCBs are lost and other PCBs added to the load from sediments. In addition, the significant contribution of external sources, particularly in the tidal Hudson, must be recognized, a point we have emphasized with the Agency in the past.

The importance of the high-flow load to remedial analysis must also be recognized and addressed. The high-flow load described in the Report underscores the importance of determining the magnitude and duration of PCB releases upstream of the TIP now and over the past several years. Yet the Report is unable to address this significant issue due to lack of data. To answer the question, GE has been engaged in collecting and analyzing data following the major remedial projects at its plants.

In order to complete a technically defensible remedial analysis, EPA must develop a consistent and physically plausible explanation of the data and then test that explanation against a calibrated and validated model to ensure that the true sources of PCBs to fish, wildlife and humans are identified. The explanation of the data needs to take into account all the processes at work in the river that are relevant to remedial analyses. Where questions central to remedial analyses cannot be answered with the data presently at hand, additional data must be obtained to resolve the issues so that we can have full confidence in the conclusions reached on the basis of data interpretation and evaluation.

**II. NEITHER DIFFUSION OF PCBs FROM AGED SURFACE SEDIMENTS NOR RESUSPENSION OF HIGHLY DECHLORINATED, HIGHLY CONCENTRATED PCBs CAN ACCOUNT FOR THE PCBs THAT PASS THE THOMPSON ISLAND DAM AT LOW FLOWS.**

The Report concludes that the PCBs passing the TID at low flow are a major source of PCBs to the freshwater Hudson. Consequently, determining the source of these PCBs is essential to the remedial analysis of the Reassessment.

The Report concludes that the sediments in the TIP provide most, if not all, of the PCBs passing over the TID during low flow. The Report, however, does not specify what sediments are believed to be the source of these PCBs. Whether PCBs are derived from surface sediments (0-1 cm), near surface sediments (0-8 cm), deep sediments, hot spots or other areas is critical to understanding the ultimate source of PCBs to the water column in the TIP and downstream of the TID. The Report hypothesizes two possible sediment sources: (1) porewater diffusion of relatively undechlorinated PCBs at low concentrations in the surface sediments or (2) resuspension of extensively dechlorinated PCBs deposited before 1984. Neither source can account for all the PCBs at the TID for at least three reasons. First, there is an insufficient mass of PCBs in the aged surface sediment to account for the increased PCB load measured across the TIP. Second, there is no erosive mechanism to resuspend a sufficient quantity of dechlorinated aged sediments to provide the increased load across the TIP and, if such erosion had occurred, sediment bed elevations would be very different from what has been measured. Finally, the congener pattern of the extensively dechlorinated sediments does not match the pattern of the TID load.

A more careful analysis shows that there is a load passing the TID at low flow which cannot be accounted for by the loads measured at Rogers Island and diffusion from surface sediments in the TIP. This unaccounted-for load is similar to undechlorinated Aroclor 1242 and is probably related to PCB loadings from the vicinity of GE's Hudson Falls plant. The identification of and explanation for this unaccounted-for load is perhaps the most fundamental difference between GE's and EPA's view of what is happening in the TIP.

- A. Diffusion of PCBs from surface sediments deposited in the Thompson Island Pool before 1991 cannot account for the increase in PCB load across the Thompson Island Pool.

One of the Report's hypothesized sources for the increase in PCB load across the TIP is the diffusion of PCBs from porewater in aged surface sediments to the overlying water column. This process can account for only a portion of the load of PCBs measured at the TID. A simple mass balance calculation demonstrates that if porewater diffusion were providing all the PCBs apparently coming from the TIP (the net increase in PCBs between Rogers Island and the TID), the reservoir of PCBs in surface sediments (as measured in 1984) would be nearly depleted by now. The high resolution cores, however, do not reflect any significant depletion of PCBs from these sediments.

In this mass balance calculation, we assume that the net increase in PCBs between Rogers Island and the TID (the increased load across the TIP) comes from PCBs in the surface sediments of the TIP. This calculation uses measured annual paired loadings from Rogers Island and the TID

from 1993 to 1996 using corrected GE data (see Appendix A)<sup>1</sup> and employs a conservative measure of the active surface layer (0-8 cm). Our analyses indicate that the active surface layer is 0-5 cm. The mass of PCBs in the surface sediments was estimated using the results of the Report's analysis of the 1984 sediment data. The depletion of surface sediment PCB homologues was based on the following calculation:

$$\text{Year in which the surface sediment reservoir is depleted} = \frac{\text{Inventory}}{\text{Flux rate}} + 1984 \quad (1)$$

The surface sediment inventory was computed as follows:

$$\text{Surface sediment inventory} = \frac{c_{ss}}{w_s} \cdot D \cdot A \cdot 10^{-6} \quad (2)$$

in which:

$c_{ss}$  = surface sediment PCB homologue concentration

$w_s$  = average specific weight for sediments in the Upper Hudson = 0.77 g/cm<sup>3</sup> (Report at 4-30);

D = depth of the surface layer = 8 cm

A = area of TIP = 2,000,000 m<sup>2</sup> (Report, Table 4-7)

The results of this mass balance calculation are presented in Table 1 and show that, by now, all monochloro and dichlorobiphenyls would have been depleted from the surface sediments. This

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<sup>1</sup> We have not used the period from 1991-1993 in light of the unusually high loadings to the River during this period resulting from the releases from the Allen Mill.

is particularly significant since current water column measurements show a continuing source of mainly mono- and dichlorobiphenyls from the TIP, the same congeners that would have been depleted without continued loading from the upstream source. The significant reserves of PCBs remaining in the surface sediments of the TIP in 1991<sup>2</sup> and in the samples collected by EPA indicate that PCBs fluxed from the surface sediments must comprise a relatively minor component of the total increase in PCB load across the TIP in the 1990s.

- B. Resuspension of highly dechlorinated, highly concentrated PCBs from the Thompson Island Pool sediments is implausible and cannot account for the increase in PCB load across the Thompson Island Pool.

EPA's other hypothesis -- that highly dechlorinated PCBs at concentrations greater than 120 ppm and deposited prior to 1984 are the source of the increased PCB load across the TIP -- is also implausible. The mass of PCBs in these sediments is insufficient to maintain the increased load of PCBs across the TIP during low flow, and there is insufficient erosion in the TIP to expose and resuspend such sediments. In any event, the composition of PCBs in these sediments does not match the TIP load on a congener basis.

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<sup>2</sup> HydroQual has calculated that the average PCB concentration in surface sediments (0-5 cm) of the TIP was about 30 ppm in 1984 and 20 ppm in 1991.

1. Resuspension of dechlorinated PCBs is inconsistent with the Thompson Island Pool bathymetry.

The Report's hypothesis that "dechlorinated" sediments may be the source of the increased load across the TIP relies on the mechanism of "resuspension" to place these PCBs into the water column. As resuspension is a surface sediment process, this hypothesis requires that the PCBs originate from areas with surface sediments containing PCBs in sufficient concentrations to match the homologue pattern of PCBs found at the TID. The Report concluded that these PCB concentrations had to be greater than 120 ppm. Simple mass balance calculations, however, show that the increased load could only have been provided by erosion to depths of over 75 cm on average. Such erosion is implausible and unreasonable. Had it occurred, it would have resulted in changes in sediment bed elevation levels between 1984 and 1991 that are not seen in measured levels.

To evaluate whether the resuspension of PCBs from these deposits is plausible, we made an estimate of the surface area in the TIP containing PCB concentrations exceeding a conservative value of 100 ppm ( $A_{100}$ ). The kriging analysis of the NYSDEC 1984 data presented in the Report provides an estimate of approximately 69,000 m<sup>2</sup> (Figure 1) of river bottom in the TIP where such deposits occur. The average vertical profile of PCBs within these areas was constructed using results from the 1984 NYSDEC cores (Figure 2). The average TIP loading increase over the 1993 and 1996 period would require an estimated loading from the sediments of 254 kg/yr since 1984 ( $W_{pcb}$ ) (Table 2).

The following equation provides a calculation of total sediment mass scoured from these areas on an annual basis:

$$W_{sed} = \frac{W_{pcb}}{C_{100}} \quad (3)$$

where  $W_{sed}$  is the mass of sediment loading required on a yearly basis and  $C_{100}$  is the actual average surficial sediment PCB concentrations in areas with concentrations greater than 100 ppm. The depth of scour required to achieve these PCB loading estimates can then be calculated as follows:

$$D_t = \frac{W_{sed}}{\rho_s A_{100}} \quad (4)$$

where  $D_t$  is the depth of scour in year t (cm) and  $\rho_s$  is the bulk density of the sediment ( $g/cm^3$ ). Both  $C_{100}$  and  $\rho_s$  vary as simulated scour removes surface sediments and exposed sediments of varying PCB concentration and bulk density.

Figure 3 presents the depth of scour required on an annual basis to achieve the concentrations necessary to maintain the TID load. As can be seen, approximately 75 cm of sediments within these areas would have to have been eroded between 1984 and 1993 to provide the increased load across the TIP. EPA's analysis of its geophysical data indicates that such massive scour has not occurred. Indeed, these data indicate that the aged dechlorinated sediments are largely intact (report at 4-91).

2. Resuspension of dechlorinated PCBs is inconsistent with the minimal resuspension of PCBs in the Thompson Island Pool at low flows.

The Report's hypothesis that highly dechlorinated surface sediments are the source of the increased load across the TIP is implausible because it requires significant erosion of these sediments during low flow, when such erosion is known not to occur.

Laboratory and field studies on the resuspension properties of cohesive sediments from the TIP show that a critical shear stress exists below which erosion does not occur (HydroQual, 1995). Similarly, resuspension of non-cohesive sediments will begin once the bottom shear stress exceeds a certain critical value, which is typically greater than the cohesive critical shear stress (van Rijn, 1984). Bed armoring processes, in both cohesive and non-cohesive bed areas, will also limit the amount of sediment eroded at a particular flow rate (Karim and Holly, 1986; Rahuel et al., 1989; Ziegler and Connolly, 1995). The result of these well-established sediment processes and observed measurements is that sediment resuspension under low flow conditions is very limited, and once the flow rate is below a particular value, no resuspension occurs.

Sediment transport studies in various riverine systems have shown that the concept of no or negligible erosion of the sediment bed during low flow conditions is valid. An effective method for quantitatively evaluating resuspension and deposition processes in a river is to use a calibrated and validated sediment transport model to predict solids fluxes across the sediment-water interface under various flow conditions. A sediment transport model of the TIP has been developed, calibrated and validated by HydroQual for GE. This model has also been successfully used by EPA in

contaminated sediment studies of the Fox River in Wisconsin (Gailani et al., 1991), Saginaw River in Michigan (Cardenas et al., 1995) and Buffalo River in New York (Gailani et al., 1996), in addition to other riverine applications by HydroQual (Ziegler and Nisbet, 1994, 1995). These past studies have shown that this model, if properly calibrated, can simulate sediment transport processes with sufficient accuracy to use it as a diagnostic tool to study resuspension and deposition fluxes in the Upper Hudson River under low flow conditions.

The sediment transport model was thus used to predict resuspension and deposition fluxes in the TIP under low flow conditions. Model simulations show that negligible gross resuspension of the cohesive sediment bed occurs for flow rates less than 5,000 cfs (Figure 4). To further investigate resuspension and deposition dynamics during low flow conditions, a simulation was performed for a constant flow rate of 3,200 cfs at Rogers Island. This flow rate corresponds to the mean value at Fort Edward during the EPA sampling periods in May and June of 1993. The data from this period were the primary basis for the low-flow resuspension hypothesis proposed in the Report. Model results show that net deposition, with only a minimal amount of resuspension, occurs in the TIP at this flow rate. The gross resuspension flux in the TIP is about 1,000 times smaller than the gross deposition flux, and the sediment that is eroded comes from a thin, surficial layer (approximately 10  $\mu\text{m}$  thick) that is composed of loosely-consolidated, recently-deposited sediment (Figure 4). These results, combined with the observed resuspension properties of sediments, demonstrates the implausibility of the Report's hypothesis that relatively high gross deposition and resuspension rates, producing a small net change in water column solids load, caused the observed changes in PCB loading through the TIP during the 1993 low-flow periods.

3. The congener fingerprint of the PCBs at the Thompson Island Dam shows that dechlorinated PCBs are not the source; rather the source is likely relatively unaltered Aroclor 1242.

The Report relies on homologue fingerprinting, combined with its two "dechlorination" indices, to identify pre-1984 sediments as a possible source of the increased load of PCBs across the TIP. There are two significant problems with the Report's analysis. First, while a crude composition match of PCB TIP load to dechlorinated, aged sediments on a homologue basis can be made, a much better match can be made on a congener basis or with the relatively undechlorinated PCBs in surface sediments. Second, the Report relies on a simplistic "geochemical" analysis that purports to show that all PCBs within the freshwater portion of the Hudson River can be derived from a mixture of fresh and biologically dechlorinated Aroclor 1242. This analysis fails to recognize that partitioning can also account for changes in PCB composition observed in the river, leading to a better understanding of the PCBs seen at the TID.

For the first point, we have examined the similarity between the congener composition of the total water transect samples and the sediment samples that represent potential sources to the water. The TIP high-resolution core slices with more than 100 ppm of PCB were used to represent the more highly contaminated and dechlorinated sediments of the TIP. The surface slices of the TIP high-resolution cores were used to represent the surface layer. The percent weight of each congener in each total water column sample at TID was plotted against its average percent weight in the dechlorinated sediments (Figure 5) and against its average percent weight in the surface sediments (Figure 6). In these figures all congeners that were not detected were placed on the axes. In both

cases, there is a positive relationship between water and sediment. However, the scatter about the relationships is much greater for the dechlorinated sediments. That is, the congener composition of the water column is more similar to relatively undechlorinated surface sediments than to more contaminated dechlorinated sediments. Accordingly, contrary to the Report's hypothesis, the TID load cannot originate from the more contaminated, dechlorinated TIP sediments.

To the second concern, when partitioning between solid and dissolved phases is incorporated into the analysis, as can be seen from a graphical analysis, the dechlorination indices ("indices") used in the Report indicate that particulate and dissolved PCBs sampled at the TID originate from different mixes of sources, and both include significant contributions of relatively unaltered Aroclor 1242.

Index values for sediment samples, dissolved and particulate water column samples, and Aroclor standards are plotted in Figure 7, similar to the index plots provided in the Report. The index values of the particulate PCBs sampled at Rogers Island and at the TID (filled squares and circles on Figure 7) center on Aroclor 1242 (large open square symbol at the position (0.14,0.00)), demonstrating that the source of these PCBs is unaltered or very slightly altered Aroclor 1242.

Partitioning of PCBs between the solid and the dissolved phases can alter the composition of PCBs and therefore the values of the indices. To demonstrate this, the original Aroclors (large open square symbols) and the dissolved material that would result from partitioning from original Aroclor sorbed to particulate material (large open triangles) are plotted on Figure 7. The

composition of dissolved partitioned material was computed using partition coefficients derived from data set forth in the Report. Computed dissolved partitioned Aroclor samples are always to the right and above the original Aroclors. In addition, the dissolved partitioned Aroclor 1242 and 1016 samples lie close to the scatter of sediment samples, demonstrating that in the Upper Hudson, simple partitioning can result in dissolved water column samples with index values similar to dechlorinated sediments. That is, when the indices employed in the Report are applied to water samples, they do not necessarily characterize dechlorination.

Computed dissolved PCBs partitioned from dechlorinated sediments also appear within the scatter of the sediment data, to the right of the sediment source. For example, the large inverted triangles represent the average aged surface sediment concentration in the TIP computed from the 1991 GE data (0-5 cm depth; filled: sediment, open: computed dissolved partitioned material). A comparison of the positions of computed partitioned Aroclor 1242 and 1991 TIP surface sediments suggests that the degree of dechlorination of the source material for dissolved PCB samples can be characterized from the position of a dissolved sample on this plot. However, in contrast to the method used in the Report, the measured dissolved samples must be compared with the computed positions from fresh and dechlorinated particulates.

The dissolved PCBs sampled at Rogers Island are located within the scatter of the sediment data, slightly to the right of their respective particulate samples. In general, the Rogers Island samples do not lie as far right as partitioned Aroclor 1242 and lie slightly below dissolved partitioned Aroclor 1254. This suggests that dissolved material at Rogers Island may be a

combination of partitioned Aroclors 1242 and 1254 and that this material does not originate from dechlorinated sediment.

The dissolved PCBs sampled at the TID are also located within the scatter of the sediment data, between the computed dissolved materials partitioned from the 1991 surface sediment data and from Aroclor 1242. Thus, dissolved PCBs at TID are not likely to originate entirely from dechlorinated sediments; they are more likely to originate from a combination of sources that on average is less dechlorinated than the partially altered 1991 surface sediments. As a result, unaltered or very slightly altered Aroclor 1242 must be an important contributor to dissolved PCBs at the TID, a fact that the Report does not recognize.

**III. THE PCB LOAD AT HIGH FLOW ACCOUNTS FOR MORE THAN ONE THIRD OF THE ANNUAL LOAD OF PCBs THAT PASS THE THOMPSON ISLAND DAM AREA. THIS LOAD ORIGINATES NEAR GE'S HUDSON FALLS PLANT SITE.**

- A. There is no dispute that discharges from the vicinity of the Hudson Falls site contributed at least half of the annual PCB load to the Thompson Island Dam and downstream areas in the form of undechlorinated Aroclor 1242.

The Report's analysis of water column PCB monitoring data collected during the 1993 spring high flow event showed that an estimated 250 kg of PCBs originating upstream of the Roger's Island monitoring station were transported through the system. This represents approximately 36 percent of the total PCBs which passed TID for the entire year and all the TID load at high flow. This PCB load differs from the loading from the TIP in that it is largely in the particulate matter phase and exhibits a PCB congener distribution of non-dechlorinated Aroclor 1242, similar to that observed within the Allen Mill and entering the river from bedrock fractures.

More specifically, the spring high flow event data collected by the EPA demonstrate that a major portion of the total PCB loadings to the system originate from the Hudson Falls plant site area and occur over a very short time frame. Such time variable PCB loading from Hudson Falls is further supported by the observation that the flow weighted average PCB loading from upstream of Roger's Island was approximately 50% of that measured during a transect monitoring event collected under similar flow conditions. The Report attributes this difference to the variable loading dynamics associated with the GE Hudson Falls source. That is, short term PCB loadings captured by the transect sampling were not present in the flow-averaged event samples. Moreover, as the transect 4 data were collected after the river reached an initial peak of approximately 20,000 cfs (Figure 8),

we believe that the EPA data underestimates the actual loading from the Hudson Falls Plant site area. This is because we believe that PCBs are mobilized at lower flows along the rising limb of the spring event hydrograph than that sampled.

Although the EPA water column data suggest that the spring high flow event loading passes through the system, the EPA high resolution sediment cores show recent deposition of non-dechlorinated Aroclor 1242 similar in composition to that mobilized during the spring high flow event. These observations are consistent with current understanding of sediment depositional processes: sediments are generally deposited during elevated flow events. This is significant because it suggests a link between the Hudson Falls Plant Site area loadings and surface sediment PCB levels, which control the sediment water column interaction and biota PCB exposure levels.

- B. GE has undertaken extensive remedial work at the Hudson Falls site but the extent of the source reduction and control is presently unknown.

In September 1991, elevated river water levels of PCBs were detected by GE upstream of the TIP. Intense subsequent investigations localized the source area to the eastern shoreline near river mile 196.8, in the vicinity of the GE Hudson Falls plant site. The results of these investigations revealed the presence of active seeps of Dense Non-Aqueous Phase Liquids (DNAPL) along the eastern cliff face and the rock face of the eastern raceway within the Allen Mill. In addition, free phase PCB oil (Aroclor 1242) and oil contaminated sediments (up to 70,000 ppm) were found within the Mill and the tailrace tunnel.

A number of different remedial measures have been implemented to mitigate the seepage of PCBs from the vicinity of the plant site to the River: 1) DNAPL seepage from the rock face of the eastern raceway is now routinely captured; 2) hydraulic control of conduits through the Mill was achieved in 1993; 3) a slurry wall was constructed within the eastern raceway in 1994 to reduce seeps from this region; 4) removal of DNAPL and oil-contaminated sediments from the Allen Mill containing 50 tons of PCBs was completed in 1995; 5) DNAPL-recovery wells have been installed in the vicinity of the plant site that have recovered more than 8000L of DNAPL to date; and 6) barrier wells utilizing hydraulic control to further reduce DNAPL transport through subsurface fractures are being installed. These remedial efforts have reduced the PCB loading of undechlorinated Aroclor 1242 to the Hudson River, but it is not yet possible to determine the degree of control that has been achieved or to predict how much PCB is still likely to enter the River.

**IV. DURING BOTH HIGH AND LOW FLOW, A SUBSTANTIAL PORTION OF THE PCBs PASSING THE THOMPSON ISLAND DAM ORIGINATES FROM NEAR THE HUDSON FALLS PLANT SITE.**

The Report demonstrates that during the Phase 2 sampling period, Aroclor 1242 recently entering the river from the area of the Hudson Falls plant site makes up almost all of the PCB load at the TIP during high flow and that high flow loads make up more than one third of the annual PCB load at the TIP. The data show that this Hudson Falls source also contributes a substantial portion of the PCB load at the TIP during low flows. First, some PCBs are measured at Rogers Island entering the TIP during low flow. Next, mass balance shows that a PCB load passes the TID during low flow that cannot be accounted for by the sum of the load entering the TIP and the load attributed to diffusion from the aged sediments of the TIP as they were prior to 1991. Next, the PCB congener fingerprint of this unaccounted-for load indicates that its likely source is undechlorinated Aroclor 1242. The PCB fingerprint of the fish in the TIP corroborates this, also indicating an undechlorinated Aroclor 1242 source. The fluctuation from year to year of the unaccounted-for load at the TID since 1992 clearly suggests a close connection between the releases from the Hudson Falls site area and the magnitude of the unaccounted-for load. Monitoring results at Rogers Island do not reflect a PCB load congruent with identifying the Hudson Falls sources as the origin of the unaccounted-for load; but EPA's 1993 data, 1992 GE data, and a comparison of load behavior in 1995 and 1996 all indicate that unaltered fresh PCBs are flushed into the TIP as flows rise at Hudson Falls. Such time-variable flows are likely to pass Rogers Island undetected by a weekly sampling program. GE is presently collecting data to evaluate this proposition.

A. At low flow, there is a PCB load at the Thompson Island Dam that is unaccounted for by the sum of the measured load entering the Thompson Island Pool and the load that would be diffused from aged Thompson Island Pool sediments.

1. Calculation of unaccounted-for load by mass balance.

The data show a PCB load at the TID that is not accounted for by the sum of the measured PCB load entering the TIP and the load that would be diffused from the aged sediments. The existence and magnitude of the unaccounted-for load at the TID can be determined by subtracting from the water column PCB load at the TID (1) the load attributable to sediment porewater diffusion and (2) the water column load of PCBs entering the TIP at Rogers Island. The diffusive fluxes of PCB congeners from the surface sediment were calculated using GE's 1991 surficial sediment PCB data and EPA's equilibrium partitioning concepts, including the use of temperature-corrected partitioning coefficients. The water column PCB load increase across the TIP was calculated by subtracting water column PCB loads at Rogers Island from those at the TID using paired Rogers Island and TID water column samples from the corrected GE database (Appendix A) for 1991-1996 and daily average USGS flow measurements.

The following mass flux equation calculates the diffusive flux of individual PCB congeners from TIP sediment porewater to the water column:

$$J_s = K_f A_s (C_d' - C_{wc}) \quad (5)$$

where  $J_s$  is the diffusive mass flux of individual PCB congeners (kg/day),  $K_f$  is the sediment/water exchange coefficient (m/day),  $A_s$  is the sediment surface area of the TIP ( $m^2$ ),  $C_d'$  is the mean

surficial sediment porewater PCB concentration ( $\text{kg/m}^3$ ) calculated from the 0-5 cm section of sediment cores collected in 1991, and  $C_{wc}$  is the water column PCB concentration ( $\text{kg/m}^3$ ).

Total dissolved porewater PCB concentrations ( $C_d'$ ) contain two components: freely dissolved PCBs ( $C_d$ ) and that adsorbed onto dissolved organic carbon ( $C_{doc}$ ):

$$C_d' = C_d + C_{doc} \quad (6)$$

Freely dissolved PCBs are in equilibrium with PCBs sorbed to sediment organic carbon. This relationship is described by:

$$C_d = \frac{C_s}{f_{oc} K_{oc}} \quad (7)$$

where  $C_s$  and  $f_{oc}$  are the mean surficial sediment (0-5 cm) PCB concentration ( $\text{mg/kg}$ ) and fraction organic carbon calculated from the 1991 sediment survey data, respectively,  $K_{oc}$  is the organic carbon-based PCB partition coefficient ( $\text{L/kg}$ ) calculated using EPA water column partitioning data and corrected for temperature using temperature correction functions appearing in Appendix A.  $C_{doc}$  is in equilibrium with  $C_d$  and can be calculated as:

$$C_{doc} = C_d m_{doc} K_{doc} \quad (8)$$

where  $m_{doc}$  is the porewater dissolved organic carbon concentration ( $\text{mg/L}$ ) calculated as the mean surficial sediment (0-5 cm) TIP dissolved organic carbon measurements from the 1991 sediment survey, and  $K_{doc}$  ( $\text{L/Kg}$ ) is the equilibrium constant describing partitioning between freely dissolved

PCBs and PCBs adsorbed to dissolved organic carbon, which was assumed equal to 0.1  $K_{oc}$ .

Substituting Equation 7 and 8 into Equation 6 yields the following expression for porewater PCB concentrations:

$$C_d = (1 + m_{doc} K_{doc}) \frac{C_s}{f_{oc} K_{oc}} \quad (9)$$

Using Equations 5 and 9, the sediment diffusive flux equation becomes:

$$J_s = K_f A_s \left[ \left( (1 + m_{doc} K_{doc}) \frac{C_s}{f_{oc} K_{oc}} \right) - C_{wc} \right] \quad (10)$$

Equation 10 allows calculation of sediment diffusive flux of PCB congeners from known sediment PCB congener concentrations using principles of equilibrium partitioning.

The sediment water exchange coefficient ( $K_f$ ) can be estimated by substituting the water column PCB congener flux estimates for the summer low flow period of 1991 into Equation 10 and adjusting  $K_f$  to minimize the sum of differences in individual PCB congener loading estimates. Negative PCB congener loadings due to detection limits for the higher PCB congeners in water column samples are disregarded (Figure 9; panel d).

Based upon 1991 sediment PCB measurements including PCB congener concentrations, the sediments of the TIP can contribute through diffusive mechanisms an estimated 200 to 300 g/day of PCBs to the water column for 1991 to 1996 (panel b; Figures 10 through 15)<sup>3</sup>. The PCB congener distribution of this load is shifted toward the lighter end of the congener spectrum due to the relatively low  $K_{oc}$  values for the lightly chlorinated PCBs.

When the actual PCB load increase across the TIP is calculated for periods after 1991, more PCB is present than can be explained by the diffusion calculation. The water column PCB congener load increase across the TIP ( $J_{wc}$ ) can be calculated for the summer low flow periods (June -August) of 1991-1996 using the following expression:

$$J_{wc} = Q_{ri}(C_{tid} - C_{ri}) \quad (11)$$

where  $Q_{ri}$  is the daily average flow recorded at the Rogers Island monitoring station on the day of sampling, and  $C_{tid}$  and  $C_{ri}$  are the individual corrected PCB congener concentrations (Appendix A) at the TID and Rogers Island monitoring stations, respectively.

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<sup>3</sup> Sediment diffusion load varies due to differences in mean summer surface water temperatures and their effect on  $K_{oc}$ .

The unaccounted-for load at the TID ( $J_u$ ) can be calculated on a PCB congener basis by subtracting the estimated diffusive flux of PCBs ( $J_s$ ) from the difference in water column PCB loadings between the TID and Rogers Island as follows:

$$J_u = J_{wc} - J_s \quad (12)$$

The results of this calculation for the summer low-flow period (June-August) of 1991 to 1996 are presented on a homologue basis in Figures 10 through 35 (Panel c). The 1992 unaccounted-for PCB load was 559 g/day. This is twice the surface sediment diffusive flux calculated using the 1991 surface sediment PCB data. This increased to approximately 1000 g/day in 1993 and 1994 and declined in 1995 to less than 250 g/day. In 1996 the unaccounted-for PCB load was approximately 1200 g/day.

- B. The fingerprint of the unaccounted-for load at the Thompson Island Dam indicates the likely source is undechlorinated Aroclor 1242.

The composition of this unaccounted for load indicates its probable source. On a homologue basis, this unaccounted-for load was dominated by dichlorobiphenyls and generally resembled the homologue mass loadings attributable to diffusion from surface sediments (Figures 10 through 15; panel c). Assuming the unaccounted for PCB load is derived exclusively from a surficial sediment diffusional process, one may calculate the expected mean surface sediment and porewater PCB composition which would produce this load by diffusion.

The sediment phase PCB homologue distributions required to produce the unaccounted for PCB load were calculated on a yearly basis for the summer low flow period (June-August) for 1992 through 1996 and monthly for 1996. These results are summarized in Tables 3 and 4 and presented as PCB homologue distributions in Figures 10 through 15, panel d.

As can be seen in these Tables and Figures, the homologue composition of the unaccounted-for load closely resembles Aroclor 1242. The congener composition of the unaccounted-for load is markedly similar to surface sediment PCB congener distributions (Figure 16) and deviates considerably from deep dechlorinated sediments on the TIP (Figure 17). These data indicate that the unaccounted-for load from the TIP originates from an undechlorinated Aroclor 1242 source.

- C. The PCB fingerprint in the TIP fish is consistent with PCBs recently entering the river above the Thompson Island Pool.

Analysis of PCBs in fish supports the conclusion that the source of the unaccounted-for load at the TID is relatively undechlorinated PCBs, and the homologue and congener composition of the fish provides a way to identify PCB sources to the food web.

Two analyses were performed to test whether fish body burdens are representative of PCBs originating in sediments containing dechlorinated or relatively undechlorinated PCBs. First, using the GE bioaccumulation model, the relationship between the homologue composition in fish and the homologue compositions of surface sediments and the water column can be explored. One may assume that varying degrees of dechlorination in exposure sources result in differing homologue

distributions in the fish. These compositions can be computed and compared with the observed composition in TIP fish in order to characterize the likely composition of the exposure sources. Second, congener-based fingerprinting indices can be used to assess the similarity in PCB composition between surface sediments and fish.

The total PCB bioaccumulation model developed by HydroQual was modified to compute bioaccumulation on a homologue-specific basis. Table 5 identifies the sources of the parameter values for individual homologues. To characterize the homologue composition of the exposure sources, several model simulations were performed using exposure concentrations and distributions derived from TIP data. Table 6 identifies the basis for the derivation of the exposure values.

Figures 18 through 21 computed and observed homologue distributions in fish. Model results for pumpkinseed were compared with pumpkinseed data collected in the TIP after 1989. Model results for largemouth bass were compared with largemouth and smallmouth bass data collected in the TIP after 1989 using fish greater than 400 g. The dashed lines represent the spread of the mean of the data +/- two standard errors.

The data best match pumpkinseed homologue distributions computed using the surface slice of the high-resolution cores and the measured water column distribution (Figure 18). The largemouth bass distributions computed using either surface slices, 0-2 cm (Figure 18) or the 0-5 cm layer (Figure 19) best reproduce the observed distributions. As the degree of dechlorination in the exposure sources increases, the model results diverge from the measured homologue distributions

(Figures 18 through 21). Thus, the PCB composition of the fish is most consistent with a relatively unaltered source.

Several indices of dechlorination have been developed (Appendix C). These are ratios between the proportions of individual congeners in a sample. The numerator is the proportion of a congener that is dechlorinated and the denominator is the proportion of a congener that is left relatively unmodified by dechlorination. For each ratio, congeners within the same homologue group are used, so that partitioning and bioaccumulation differences are minimized. The degree to which these ratios indicate dechlorination can be tested by comparing their values to other indices of dechlorination in sediments; for example, the number of chlorines per biphenyl. They are found to be indicators of dechlorination in sediments. The ratios can be used in a diagnostic fashion to compare samples collected from sediment, water and fish.

These ratios decline as dechlorination proceeds. For example, four of these ratios are plotted against the number of chlorines per biphenyl (Cl/BP) using high-resolution core sediments from the Upper Hudson (Figure 22). The dashed lines indicate values of the ratios and Cl/BP for Aroclor 1242. The ratios in the sediments approach the Aroclor 1242 value in samples in which Cl/BP approaches the Aroclor 1242 value. In addition, values of the ratio decline in dechlorinated sediments.

Figure 23 presents the values of these four ratios in fish collected from the TIP by NOAA in 1993. Comparison of the fish ratios with the sediment ratios in Figure 22 indicates that slightly

altered Aroclor 1242 is the source of PCBs to these fish. Similar results are obtained with fish caught in earlier years.

- D. The behavior of the unaccounted-for load is consistent with the Allen Mill collapse and seeps from the bedrock.

Having established that the source of the unaccounted-for PCB load at the TID appears to be relatively undechlorinated Aroclor 1242, possible sources for these PCBs must be explored. The releases of DNAPL PCB oil from the Allen Mill and/or the bedrock seeps near GE's Hudson Falls facility are the likely sources and the temporal parallels between the behavior of the unaccounted-for PCB load and the sources near Hudson Falls suggests a close connection between the two.

The USGS and GE data sets provide a 20-year record of water column PCB data that can be used to assess long-term spatial and temporal patterns of PCB loadings in the upper Hudson River. Historical loadings from the TIP were estimated from the corrected USGS PCB data. Low flow PCB loading from the TIP was calculated as the difference in PCB loadings based on paired flow and PCB data at Schuylerville and Fort Edward during periods of flow less than 10,000 cfs at Fort Edward from 1980-1989 (Figure 24).<sup>4</sup> Loads for the period 1991-1996 were calculated using paired flow and PCB data collected as part of GE's water column monitoring program.<sup>5</sup>

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<sup>4</sup> The USGS record did not contain data from the Fort Edward or Schuylerville Station at flows less than 10,000 cfs for 1990 - 1995. Large loadings calculated for 1977 - 1979 period were excluded in this figure to highlight observed changes between the late 1980s and early 1990s.

<sup>5</sup> GE collected data in 1991 to provide preliminary estimates of the bias in the USGS methodology and to "correct" historical USGS water column PCB records (see Attachment 1).

The PCB loads from the TIP declined steadily from approximately 1.2 lbs/day during the early 1980s to an estimated 0.5 lbs/day in the late 1980s (Figure 24).<sup>6</sup> These data document the recovery of the system from the impacts of process discharges and the erosion of PCB-contaminated sediments after the removal of the Fort Edward Dam in 1973. The principal processes contributing to this recovery likely included the reduction of PCB deposition from sources within the remnant reach of the River and the deposition of clean solids from the tributaries.

Summer low flow loadings in 1991, prior to the September 1991 Allen Mill collapse, were comparable to the loadings calculated using the USGS data for late 1980s (Figure 24). In 1992, low flow PCB loadings from the TIP increased by a factor of 4 from an estimated 0.5 lbs/day in the late 1980s to approximately 2 lbs/day (Figure 24).

Thus, the unaccounted-for load from the TIP is temporally correlated with PCB releases from the Allen Mill. Considering its estimated magnitude, the Allen Mill release is likely the cause of this increased loading. PCBs discharged from the Mill were likely transported downstream and deposited within the surficial sediments of the TIP and subsequently released to the water column

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<sup>5</sup> (continued...) The GE data have been corrected for the analytical bias in quantitation of peaks 5, 8, and 14, which contain coeluting congeners BZ#4 and 10, BZ#5 and 8, and BZ#15 and 18, respectively.

<sup>6</sup> PCB levels monitored at Schuylerville were used to infer PCB levels at the TID for the periods in which data were unavailable.

as a dissolved phase loading through the processes of partitioning between sediment and oils and sediment porewater, with subsequent diffusion into the overlying water.

Under this scenario, loadings from the TIP should decline as the 1991-1993 loads are eluted from the surficial sediment porewater, buried by the deposition of clean solids, dechlorinated and transported out of the TIP. The unaccounted-for PCB load originating in the TIP declined from approximately 1.0 kg/day in 1993 to less than 0.25 kg/day in 1995 (Figure 12 through 14, panel c). This reduction suggests that the system was recovering from loadings from the Allen Mill between 1991 and 1993. The 1996 unaccounted-for PCB loadings increased from 1995 levels to approximately 1.2 kg/day. This suggests that between 1995 and 1996 additional PCBs originating upstream were deposited on surficial sediments in the TIP.

- E. The monitoring at Rogers Island appears to understate the PCB load entering the Thompson Island Pool.

It is clear that the unaccounted-for load of PCBs in the TIP resembles unaltered Aroclor 1242. The most likely source of this material is located upstream in the vicinity of Hudson Falls. However, for this source to explain this unaccounted-for loading requires that the PCB pass the monitoring station at Rogers Island undetected. Given that the PCBs from this source are dense, nonaqueous phase liquids (DNAPL) and the limited monitoring, this is likely the case.

First, the presence of DNAPL in the vicinity of the Hudson Falls Site is well established. Numerous river bed seeps were exposed upon the dewatering of Baker's Falls when Adirondack Hydro Development Corp.'s hydroelectric facility was being constructed along the western shore of the Falls. Recent work at GE's Hudson Falls plant has shown that PCB DNAPL oils are transported through bedrock fractures and enter the Hudson River from river bed seeps adjacent to the Hudson Falls plant site. These seeps represent a significant source of PCB DNAPL to the River. At one of these seeps (Seep 13), discovered within the Baker's Falls plunge pool during an underwater inspection by divers, an estimated 16 liters (22.5 Kg) of PCB DNAPL oils were collected over a period of 3-1/2 months beginning in September 1996 (Figure 25).<sup>7</sup> Second, the weekly monitoring at Rogers Island will not detect events of limited duration that might mobilize PCBs for this region of the river, such as high flow events.

1. Flushing of DNAPL during high flow is likely to escape detection at Rogers Island.

Oil-phase loads from the Allen Mill and the bedrock seeps introduce indeterminate errors in water column monitoring designed to measure particulate and dissolved phase PCB loads. The behavior of DNAPLs within natural aquatic systems is not well understood. It is likely that DNAPL oil droplets from bedrock fractures will behave in a manner similar to particles possessing the same diameter and density and likely will settle onto the river bed during low flows. As flow velocities

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<sup>7</sup> Localized groundwater pumping efforts appear to have mitigated PCB losses through Seep 13 (Figure 25).

along the sediment/water interface increase during periods of elevated flow, the DNAPL droplets will become resuspended in the water column and will be transported downstream. Such resuspension occurs almost instantaneously at the point when critical sheer velocities are reached at the sediment bed surface. It is possible that oil discharges near the Hudson Falls Plant Site accumulate within quiescent regions of the river adjacent to the site and are mobilized during high flow events.

There is evidence for flushing of significant amounts of PCBs from the River in the EPA high flow water column transect study. PCB loading from the region upstream of the TIP during this event contributed approximately 18 Kg/day PCB, primarily in the particulate phase. This particulate phase PCB transport occurred in the absence of sediment resuspension. These data generally support the hypothesis that oil phase PCB loading may be occurring during periods of high flow. EPA monitoring did not occur on the rising limb of the event hydrograph (Figure 8) and probably missed the peak PCB load, because critical sheer velocities for oil resuspension were likely reached prior to the EPA sampling. Similar high flow data collected by GE in 1992 showed elevated PCB loadings from upstream of the TIP with little or no evidence of sediment scour (Figure 26). Finally, neither the EPA water column monitoring program nor the GE high flow monitoring program collected sediment bed load samples. Such loads are likely to represent a significant portion of PCB DNAPL transport, particularly during periods of high flow. As observed in the EPA transect data, particulate PCB loads from upstream are preferentially deposited within the TIP. This

indicates surface sediment PCB contamination mechanisms which are consistent with the increased loads following the Allen Mill collapse and DNAPL PCB seeps from the Hudson Falls area.

Seasonal patterns in the unaccounted-for PCB loading at the TID in 1996 also suggest that PCB oils collect near the Hudson Falls Plant Site and are mobilized during high flow events. Monthly calculations of the unaccounted-for TIP load for 1996 indicate that, prior to the April high flow event, PCBs within the water column could largely be derived from sediment diffusive mechanisms considering the 1991 surficial sediment PCB concentrations (Table 4). Following the spring high flow period, an unaccounted-for load was apparent, varying in magnitude from 0.6 to 2.0 Kg/day during April through August and decreasing steadily to less than 0.2 Kg/day by October (Table 4). This seasonal variability and correlation with spring high flow suggests that PCB loadings from the vicinity of the Hudson Falls plant site are associated with high flow events. This is supported by the observation that the unaccounted-for loadings in 1995, a low flow year in which spring high flows never exceeded 15,000 cfs, were considerably lower than the 1994 and 1996 unaccounted-for loads.

2. Hydro plant operation likely causes flushing from Baker's Falls plunge pool.

Another possible method for PCBs to enter the TIP from sources in the vicinity of Hudson Falls undetected is related to the operation of the newly constructed hydroelectric facility at Baker's Falls. In front of the turbine intakes this facility has trash racks which are cleaned every few days.

During the cleaning process, a water bypass structure is used which discharges significant amounts of water into the plunge pool at the base of Baker's Falls. This has been observed to transform the plunge pool from calm to turbulent.

Divers have observed PCB oils seeping into the plunge pool and accumulating on the river bed. The flushing of water into the plunge pool during the trash rack cleaning is likely to move PCBs downstream in pulses that would not be detected by the weekly monitoring at Rogers Island unless coincidentally synchronized with the trash rack cleaning. In the Fall of 1996, one round of monitoring was conducted to coincide with this cleaning and was intended to monitor the potential movement of a pulse of PCBs downstream. PCB levels at Rogers Island increased from 15 ppt to 42 ppt. Since flow conditions are generally low during the cleaning, it is likely that PCB oil would be deposited in to the pool and would only later be detected in "dissolved" form at the TID. GE is conducting additional sampling this spring and summer to determine the importance of this transport mechanism.

3. GE is working to resolve the Rogers Island measurement issue.

Preliminary results of the PCB DNAPL transport study conducted by GE in the Fall of 1996 (HydroQual, 1996) suggest that PCB DNAPL oils emanating from Hudson Falls are retained within the reach of the river between Hudson Falls to the TID. This is based on the observation that only 2 percent of the fluorescent particles (selected to represent PCB DNAPL) were transported

downstream of the TID (Figure 27). To the extent that these fluorescent particles simulated DNAPL transport, these data suggest that DNAPL originating from Hudson Falls is largely retained within the river upstream of the TID. Moreover, preliminary analysis of fluorescent particle size distribution data indicates that particles with an average diameter of approximately 100 *um* constitute the majority of the mass of particles retained within the Hudson Falls to Fort Edward reach of the river. These larger particles were not transported downstream under the flow conditions during the study (est 800-8000 cfs) suggesting that oil droplets with mean particle diameter of greater than approximately 100 *um* are retained near Hudson Falls at flows less than 8,000 cfs and are likely transported downstream during higher flow periods. Additional analysis of these data is underway, and a full report will be submitted to EPA.

Additionally, as reported to EPA, GE is undertaking an extensive data collection program focused on this potential loading mechanism. Due to the importance of the unaccounted-for TIP loading in evaluating remedial options, it is imperative that the source be determined.

**V. THE CONTRIBUTION OF PCB SOURCES DOWNSTREAM OF THOMPSON ISLAND DAM MUST BE RECOGNIZED AND QUANTIFIED**

The Report concludes that PCBs in the water column are conservatively transported downstream from the TID to the freshwater tidal Hudson with little or no loss or gain. This implies that sediments downstream of the TID or other external sources of PCBs, such as a point source or tributary, are insignificant. This is inaccurate. Consequently, the significance of the load passing the TID is overstated and the benefits of reducing that load will be overstated. A more careful analysis demonstrates that sediments in the reaches of the Upper River below the TID are important PCB sources and that the contribution of the PCBs passing the TID decreases downstream. In the freshwater portion of the lower Hudson, EPA's own analysis shows that external sources of PCBs contribute significantly to the sediment -- for instance, 25 percent at Albany.

**A. PCBs passing the TID are decreased downstream by volatilization and deposition.**

The Report contends that the PCBs passing the TID are transported downstream from Reach 7 through Reach 1 and into the Lower River with little or no loss in PCB mass: the data indicate "the occurrence of quasi-conservative transport of water column PCBs (i.e., no apparent net losses or gains) throughout the Upper Hudson to Troy" (Report at E-3), and that the PCBs "pass relatively unaltered, as through a conduit, through the length of the Upper River during winter and spring conditions" (Report at 3-87). GE agrees that the net load of PCBs in the water column does not vary markedly through these reaches of the upper Hudson River; however, we disagree that the region

above the TID sets water column PCB concentrations and loads downstream of the TID to Kingston. The Report's conclusion rests on an incomplete consideration of the physical transfer processes which affect the fate and transport of PCBs in the Upper Hudson River.

The fate and transport mechanisms relied on in the Report to explain spatial patterns in PCB loadings in the various reaches of the Upper Hudson River are inconsistent. The Report hypothesizes various mechanisms to describe PCB dynamics within the TIP during the different water column monitoring events. For example, sediment deposition, sediment resuspension, porewater diffusion, and groundwater advection are cited as possible causes of changes in PCB loading patterns across the TIP. In contrast, reaches downstream of the TID are described as a pipeline in which upstream loads are transported downstream with very little sediment/water interaction. Interpretation of the spatial and temporal patterns observed in the data should be described from a consistently applied mechanistic perspective. There is no sound explanation for why sediments within the TIP would be highly reactive while sediments downstream of TIP containing similar PCB concentrations and subjected to similar physical forces would behave differently. Moreover, the more plausible account for both the TIP and the downstream reaches is that which the Report implies downstream of the TID: aged, dechlorinated PCBs in sediments deposited several years ago make a very limited contribution to the PCBs found in the water column.

Several transport mechanisms change water column PCB loads in the Upper Hudson River, including particulate settling, volatilization, dilution due to tributary solids, and inputs from local

sediments. Deposition zones and several so-called PCB "hot spots" are found in a number of locations downstream of the TID, indicating that settling of PCB-contaminated particles occurs in this region. Volatilization of dissolved-phase PCBs will occur at all locations in the river and at all times, with the transfer rate across the air-water interface varying spatially and temporally, depending upon local conditions. Addition of tributary solids and flow will dilute water column PCB concentrations in the main stem of the Upper Hudson; however, the additional tributary solids will also reduce the PCB load due to partitioning of dissolved PCBs onto uncontaminated tributary sediments and subsequent deposition of these solids. Tributary sediment loadings to the River occur downstream of the TID (HydroQual, 1995), are significant and result in reduced PCB transport. These processes reduce water column PCB loads downstream of the TID. These losses are offset to some degree by the addition of PCBs to the water column from the sediments in Reaches 7 through 1.

The impacts of fate processes can be evaluated in the context of a mass balance model. EPA's report does not contain such an analysis. The GE model, however, has been used to examine the fate processes acting upon PCBs in the upper Hudson River: transport with the river flow; adsorption-desorption among dissolved, particulate and colloidal phases; settling and resuspension of the particulate phase; diffusion between the water column and the surface sediment and within the sediment; volatilization from the water column dissolved phase to the atmosphere; and burial of sediment-associated PCBs through sedimentation. This model has been compared to water column and sediment data over a 14-year period at locations throughout the Upper River. Based on the

model's ability to reproduce these data using well-accepted descriptions of the fate processes, it can be used to examine PCB dynamics within the system.

Figure 28 compares the three EPA estimates of loading through the Upper Hudson River for the June to August 1993 period with the model simulation for the same period. The dashed-line profile represents the conservative transport of PCBs that EPA claims exists from the TID to Troy. The model shows a 19% loss of PCBs in the downstream direction that is the net result of volatilization, net deposition of solids and sorbed PCBs, and the addition of PCBs to the water column from downstream sediments and, to a lesser degree, by downstream tributary inputs. This net loss is small enough to be within the uncertainty bounds of the data. The EPA data collection in the summer of 1993 found an approximately 20% increase in the PCB load between the TID and Waterford. This was a period during which the increase in the PCB load across the TIP reflected the impact of the Allan Mill release. Conditions downstream of the TID may also have been influenced by the same event.

Figure 29 provides further clarification of the origins and fate of the TID PCBs in the river during this period. Here, the lower limit of the shaded region represents the profile of water column PCB load without a sediment source in Reaches 1-7. PCB load in the river decreases by 45.1% between Thompson Island Dam and Waterford. This decrease is a result of the combined effects of settling (the unshaded region, 17.4%) and volatilization (the shaded region, 27.6%). Considering the results of Figures 28 and 29 together, the sediments in Reaches 7 - 1 contribute 32.3% to the

downstream load passing Waterford with upstream sources and TIP sediments contributing the remainder.

- B. In the freshwater Lower River, external sources contribute significantly to the PCB load.

The Report uses a simple dilution model (PCB/<sup>137</sup>Cs) to estimate the contribution of Upper River PCBs to PCBs in the sediments of the freshwater Lower River and to support its contention that PCBs are conservatively transported from the TID to Kingston. The methodology is flawed because it fails to account for the increasing solids yield from the drainage basin below the TID and the losses of PCBs to volatilization and deposition, as described in the previous section, and cannot explain the variability of cesium data upstream of Stillwater. EPA should have recognized these deficiencies and abandoned this approach when it could not describe the change in PCB/<sup>137</sup>Cs between the TIP and Stillwater.

The Report's PCB/<sup>137</sup>Cs model is based on an assumption of uniform distribution of cesium in sediments throughout the Hudson River. While this uniformity of cesium inputs from tributaries may be true at any given point in time (cesium levels are known to be decreasing over time), the demonstration of this spatial uniformity using data on Figure 3-63 from the Report is wrong because the cesium data upstream of Stillwater are inexplicably variable and frequently at levels much higher than downstream. This is an instance where the Report's analysis is not consistently applied throughout the river system. The dilution analysis did not work in the segment of the river upstream

of Stillwater; therefore it was only employed downstream of Stillwater, ignoring what is arguably the most important part of the River from a PCB source standpoint.

Further, the data downstream from Stillwater should not necessarily be expected to be uniform, over a fixed depth interval. This is because spatial variation in deposition rate would make the sediments in this fixed 0-2 cm layer representative of different time periods at different locations, and hence different cesium levels. Moreover, the presence of a mixed surface layer with varying mixing depths at different locations would also complicate the assignment of sediments to a known time period. These difficulties are compounded when PCB and the (PCB/<sup>137</sup>Cs) are considered, because again, the 0-2 cm layer which is assumed to represent sediment deposited between 1991 and 1992 is not necessarily representative of this period. The analysis also neglects the decrease in PCB concentrations in the water column resulting from net deposition and volatilization from the water column, processes which are partially offset by sediment sources of PCB. Accordingly, simple dilution by tributary solids cannot account for all of the decrease in downstream PCB sediment concentrations.

Significant increases in the solids load due to tributary inputs as one moves downstream also invalidate the Report's simplified dilution analysis. The sediment yield, i.e., annual sediment load per square mile of drainage area, increases by about a factor of five between Fort Edward and the Federal Dam at Troy (Phillips and Hanchar, 1996). The large sediment load from tributaries in the Upper Hudson River enhances the deposition of PCB-contaminated solids in the river and modifies

the rate of change of the PCB/cesium ratio from that which would occur by simple dilution. Both of these effects complicate the PCB/cesium analysis and undermine the Report's dilution hypothesis.

EPA used comparisons between the PCB composition in the high resolution core collected at RM 177.8 near Stillwater and cores in the lower River to imply the contribution of upper River PCBs to the PCBs in the lower River. The Agency characterizes this contribution as that of the "combined TI Dam load" (report at. 3-120), although, as discussed earlier, the load from the Upper River to the Lower River reflects contributions from sediments below the TIP as well. Using cores collected at Albany and Kingston, the Agency concludes that the importance of the Upper River PCB source has varied over time, being most important during the period between 1975 and 1981 and less important more recently. Comparison of the congener patterns in the top sections of the Albany and Stillwater cores reveals differences that were attributed to the addition of other Aroclors between Stillwater and Albany. Simple mixing of the Stillwater core composition with the PCB compositions of Aroclors 1016 and 1260 was used to imply that about 22 percent of the PCBs in the core were derived from non-Stillwater sources.

The EPA analysis of the Albany core probably underestimates the contribution of sources other than the Upper River. Any Aroclor 1242 (the most widely-used mixture) entering the river between Stillwater and Albany was attributed to the Upper River. Further, the composition of the Albany core top is biased toward the upper River because of the high loadings from the upper River that occurred in the fall of 1991 and summer of 1992. Thus, it is likely that sources other than the

upper River contribute substantially to the PCBs in the sediments of the lower River. The conclusions of the report fail to cite the evidence of other loadings that it found in its own analysis and thus mischaracterized the importance of upper River sources to PCBs in the lower River.

## **VI. SEDIMENTATION AND DECHLORINATION ARE IMPORTANT REMEDIAL PROCESSES**

The Report understates the importance and benefits of natural recovery processes, including sedimentation and PCB dechlorination/biodegradation. These processes combine to reduce the availability of PCBs to the water column and biota and reduce the toxicity and bioaccumulation of the PCBs that remain. GE has explained to EPA the importance of sedimentation in previous submittals (HydroQual, 1995, GE/HydroQual, 1996), and we will not repeat these here.

The Report fails to recognize dechlorination as an important risk-reduction process and this failure is reflected in the Report's misplaced emphasis on mass rather than toxicity and bioavailability. The importance of dechlorination is not mass reduction but its effect in reducing the toxicity and bioaccumulation potential of PCBs. The indices used in the Report to measure dechlorination fail to capture the complexity and variability of dechlorination processes and are insensitive measures of dechlorination.

The Report also overlooks microbial PCB dechlorination in the sediment of the Hudson River as a critical tool for distinguishing the source of PCBs to specific receptors. Dechlorination produces unique, congener-specific changes in PCB congener distributions that permit precise source identification, as is described in detail in Appendix C. Briefly, this Appendix identifies several peak ratios that can "fingerprint" PCB sources in more than 30 species of Hudson River fish collected during a 16-year period. This analysis shows that PCBs in the fish of the TIP have not undergone

dechlorination because they have been continually exposed to a supply of fresh PCBs reaching that section of the river from the Hudson Falls source. This finding underscores that the aged, buried, dechlorinated PCBs in "hot spots" are not the predominant source to Upper Hudson River fish. Instead, the fish are accumulating recently deposited PCBs with a composition very similar to unaltered Aroclor 1242 (and with bioaccumulation and toxicity properties similar to those of Aroclor 1242), consistent with a known source of undechlorinated Aroclor 1242 in the vicinity of the GE Hudson Falls plant.

- A. Dechlorination is an important mechanism in reducing the bioaccumulation and toxicity of PCBs.

There are environmentally important benefits to dechlorination:

- Dechlorination reduces the tendency of PCBs to bioaccumulate.
- Dechlorination sharply reduces the levels of the particular PCB congeners that appear responsible for producing potential risks to wildlife and humans.
- Dechlorination of the more heavily chlorinated PCB congeners to lightly chlorinated congeners facilitates biodegradation and provides a route for the ultimate destruction of PCBs.

The benefits of dechlorination are discussed at greater length in Appendix D. In summary, dechlorination reduces both the total chlorine level of the PCB mixture and the concentration of specific coplanar congeners. Reduced chlorine level results in significant reductions in PCB carcinogenic potential (USEPA, 1996). For mixtures containing only mono- through

tetrachlorobiphenyls, carcinogenic potential has been reduced 100 fold. Coplanar congeners can determine acute toxicity, and dechlorination in Hudson River sediments has been shown to reduce the concentration of these congeners by up to 97 percent (Quenson, et al, 1992b). Dechlorination also dramatically reduces the potential for environmental receptors to be exposed to PCBs in PCB-contaminated Upper Hudson River sediments. Dechlorination reduces the bioaccumulation potential of this mixture four to 35 fold. It also facilitates aerobic biodegradation by converting the mixture to readily degradable congeners.

The insensitive dechlorination indices developed in the Report, which only measure the final phases of dechlorination, are incapable of measuring these benefits because potential toxicity, carcinogenicity and exposure are reduced by even modest levels of dechlorination as the initial stages of dechlorination provide disproportionate reductions in these endpoints.

**B. The Report's Dechlorination Indices are Flawed and Insensitive.**

The Report characterizes PCB dechlorination in terms of two indices: a so-called "molar dechlorination product ratio" and a "fractional change in molecular weight". PCB homologue distributions can be affected by other known physical processes, such as the selective extraction into the water column, in addition to microbial dechlorination and by different mixtures of Aroclors. Laboratory experiments show that when water is passed over Aroclor 1242, the extracted PCBs are generally enriched in the lower homologues, particularly BZ 1, 4, 8, 10 and 19 that were used in the

Report in calculating molar dechlorination product ratios, and these same congeners are depleted in the other phases. The enrichments observed in the water phase, relative to the tetrachlorobiphenyls, are about 40-fold for the monochlorobiphenyls, 10-fold for the dichlorobiphenyls and 3-fold for the trichlorobiphenyls. Thus, no simple index of homologue distribution, whether expressed as "product" ratios or as mean molecular weight, can provide definitive information about the dechlorination state of PCBs formed in a water-extract, and all statements regarding the extent of dechlorination in media susceptible to such extraction based on these indices are questionable.

An additional serious shortcoming of the "molar dechlorination product ratio" is its insensitivity, due to the selection of only "terminal" dechlorination products, to assess the extent of dechlorination. Due to this insensitivity, it is capable only of detecting extensive dechlorination in sediments containing the dechlorination activity that carries out near complete removal of *meta* and *para* chlorines from congeners with 2-4 chlorines per biphenyl (described above as the activity limited to the upper Hudson River). It would barely register dechlorination in sediments containing only moderate dechlorination activity, and it would completely miss those sediments containing the dechlorination activity found throughout the upper and lower Hudson that carries out partial dechlorinations of higher PCB congeners (i.e., those with 4-7 chlorine atoms per biphenyl), but producing very little of the lower homologues (with only 1-2 chlorines). As this other dechlorination activity still produces significant reductions in toxicity and exposure, its benefits as well as its detection are completely missed by the analysis in the Report.

An illustration of the insensitivity in this flawed dechlorination index is the impact of dechlorination of BZ 8. The most abundant congener in Aroclor 1242, BZ 8 is dechlorinated to BZ 1. However, this activity would be completely missed in EPA's molecular dechlorination product ratio because the sum of these congeners never changes due to dechlorination. Moreover, many of the other most abundant PCB congeners in Aroclor 1242 would be dechlorinated to BZ 1 *via* BZ 8. Therefore, this methodology would not detect the final chlorine removal step.

C. Dechlorination Occurs at Concentrations Less Than 30 ppm.

The Report relies on the analysis shown in Figure 4-22 to conclude that dechlorination does not occur predictably at PCB concentrations <30 ppm. This misrepresents the data. The data clearly show that the majority of upper river sediments samples register as dechlorinated, even with the insensitive dechlorination index used in the Report. Moreover, the analysis shows that the majority of the lower river samples lie below the line, demonstrating that the approach is inappropriate for the lower Hudson. For the upper Hudson data at <30 ppm (0.8 to 30 ppm), nearly 80% of the samples displayed on the graph are above the molar dechlorination product ratio (MDPR) for unaltered Aroclor 1242. This fraction would only increase as more sensitive dechlorination indices are utilized. For the lower Hudson, ~75% of the samples <30 ppm lie below the MDPR for unaltered Aroclor 1242. It has been well established that the contribution of more highly chlorinated Aroclors increases in the lower Hudson, particularly in the estuary region (EPA Phase 1 Report). The addition of higher Aroclors would both invalidate the application of the MDPR analysis and

predictably drive this measure below that of Aroclor 1242. The peak ratio methods described in Appendix C overcome both of these limitations, as they are a more sensitive index to identify dechlorination (able to detect a variety of dechlorination processes, including Process B, B', C, H, and H' dechlorination), and they are relatively insensitive to partitioning and variable Aroclor compositions.

Numerous studies in the laboratory and the field have detected anaerobic PCB dechlorination over a broad range of concentrations (reviewed in Bedard and Quensen, 1995). Figure 30 shows that anaerobic PCB dechlorination has been observed in controlled laboratory studies at concentrations as low as 10 ppm (Abramowicz *et. al.*, 1993; Fish, 1996, Rhee *et. al.* 1995). Taken together, the studies demonstrate that there is a linear relationship between PCB concentration and dechlorination rate without a threshold concentration.

Although field studies of PCB dechlorination are limited by analytical detection limits at low concentrations, longer incubation times in the field have permitted the detection of PCB dechlorination at even 5 ppm (Table 1, Abramowicz *et. al.*, 1996). These researchers noted that even at the lowest concentration range analyzed (5-10 ppm), 63% of the samples still met the established criteria for extensive dechlorination.

Additional support for environmental dechlorination at low concentrations has been obtained through direct comparisons of surface PCB congener profiles in the Hudson River to Aroclor 1242

and completely dechlorinated Aroclor 1242 congener profiles. A sediment sample was collected from the TIP site known as H7. A fraction of this sample was extracted and analyzed for PCB content and the measured concentration was 6.2 ppm. From the PCB distribution, the number of chlorines per biphenyl (Cl/BP) was 2.71. Since Aroclor 1242 contains 3.26 Cl/BP, even at this low PCB concentration some dechlorination took place in the environment.

The use of intra-homologue peak ratios to assess dechlorination at various PCB concentrations is shown in Figure 31. Four peak ratios are utilized (BZ 56/49, 23-34-/24-25-CB; BZ 60/49, 234-4-/24-25-CB; BZ 66/49, 24-24-/24-25-CB; BZ 74/49, 245-4-/24-25-CB). These ratios represent the change in the dechlorination sensitive tetrachlorobiphenyls (mono-*ortho* substituted) to the more resistant tetrachlorobiphenyl congener 24-25-CB (di-*ortho* substituted). The result of this peak ratio analysis demonstrates that significant dechlorination occurs at all concentrations, even at sub-ppm levels. There is also a clear trend demonstrating more extensive dechlorination at higher PCB concentrations, consistent with laboratory experiments.

D. Dechlorination has not stopped in the Hudson River.

The Report incorrectly states that dechlorination has stopped in the Hudson River, based upon the analysis of high resolution cores (Report at 4-70). This conclusion is flawed since the indices used to monitor dechlorination are insensitive to some dechlorination processes and since it ignores the ongoing dechlorination of fresh Aroclor 1242 in surficial sediments. Evidence for

dechlorination in surficial sediments exists in several forms. First, surficial sediments collected from the "fluff" layer from the TIP display Pattern A dechlorination (described in Appendix C). Second, microcosms that simulate the fate of fresh Aroclor 1242 in Hudson River sediments display Pattern A dechlorination at early time points (4-6 weeks, Fish, private communication). Third, fish in the TIP display a PCB distribution consistent with Pattern A dechlorination. This pattern is likely the result of the initial stages of dechlorination, with more extensive dechlorination occurring over longer time periods, when additional burial sequesters this material.

These surficial biotransformations (Process A initially and Process Y later) and subsurface dechlorinations (Process C) which were observed in microcosm experiments (Fish and Principe, 1994 and Fish, 1996) demonstrate rapid dechlorination and degradation of Aroclor 1242 in Hudson River surface sediments. The changes observed in these physical river models closely correspond to changes observed in the environment.

Additional evidence to demonstrate that dechlorination is still occurring in the upper Hudson is found in Figure 32. This Figure represents the application of the intra-homologue peak ratios to the EPA Phase 2 high resolution sediment cores. To minimize the impact of concentration on the rate of dechlorination, only a narrow concentration range was utilized (all 3-30 ppm core segments from all Upper Hudson high-resolution cores). Note that the extent of dechlorination continues to change in a smooth continuum with increasing depth in the core. This data demonstrates that the extent of dechlorination strongly correlates with increasing depth and increasing age of the sediment,

inconsistent with the Report's claim that dechlorination has stopped in the upper Hudson. These analyses also demonstrate the strength of peak ratios as effective indices of anaerobic PCB dechlorination in environmental media, assessing concentration and temporal effects even under conditions when partitioning, variable Aroclor compositions, or modest level of dechlorination are present, conditions that can confound other dechlorination indices.

## VII. CONCLUSIONS AND RECOMMENDATIONS

In order to evaluate remedial options properly, EPA must understand the sources, transport and fate of PCBs in the Upper Hudson River. This Report provides a geochemical analyses of the data, based on several inconsistent hypothesis, that do not provide a realistic and accurate view of the river system.

The Report offers various hypotheses to explain the spatial and temporal patterns in the PCB data. Many of the hypotheses are incompatible, and the Report chooses from among them to reach overall conclusions. In most cases, the choices are based on qualitative arguments that are not rigorously evaluated. In these comments, we have presented technical arguments that refute the primary hypotheses that form the basis of the Report's conclusions. Our arguments are based on geochemical fingerprinting techniques similar to those used by EPA; a quantitative determination of the PCB fate mechanisms required by the hypothesis; and PCB mass-balance calculations. The last two types of analyses are a requirement of hypothesis-testing because they examine the plausibility of the stated hypothesis.

Because EPA's approach to data interpretation is restricted to a geochemical examination of the data, it is sufficient for developing hypotheses but not for testing them. The Agency must acknowledge this limitation and conduct further analyses to test the hypotheses within the framework of the mass-balance model currently under development. As we have done in our

evaluation of the Report conclusions, the Agency must use the model to examine the consistency of each hypothesis with the estimated rates and magnitudes of relevant fate processes and with historical information regarding the spatial and temporal distributions of PCBs in water, sediment and fish. An integrated interpretation that accounts for all the sources and losses of PCBs is necessary to develop conclusions about the relative importance of the various PCB sources and the rate of recovery.

The utility of the Report and its conclusions are fundamentally undermined by its numerous inconsistent statements. An exhaustive review of each of such statements is beyond the scope of these comments, but the examples set out below demonstrate this shortcoming:

- The Report hypothesizes resuspension of dechlorinated sediments from the TIP despite its own analysis that explains that resuspension is not occurring. On pages 3-62 and 3-63, the Report concludes that resuspension of TIP sediments is of limited importance to the load measured at the TID because there is no evidence of resuspension during low flow and during high flow, when resuspension would be expected, the load above Rogers Island is transported relatively unaffected through the TIP. Notwithstanding this sound conclusion, the Report later hypothesizes that a possible source of the increased load across the TIP seen most prominently during low-flow periods is resuspension of sediments containing highly concentrated, highly dechlorinated PCBs. This hypothesis, presented as one of the primary conclusions of the Report, is obviously inconsistent

with the observation made at 3-62 and 3-63 that resuspension within the TIP is not an important process.

- The Report emphasizes the importance of sediments as PCB contributors to the TIP and de-emphasizes its own analysis that shows that the current sources near Hudson Falls are more important. On page 3-90, the Report describes the mass of PCBs provided by the different internal and external sources in the Upper River in 1993: 370 kg from the sources above Rogers Island; 225 kg from the TIP; 25 kg from the "Schuylerville" source; and 83 kg from scour from the Hoosic-driven scour of surficial sediments during Transect 3. Using these figures, the sources above Rogers Island provide approximately 50% of the annual load during 1993. This fact, however, is ignored in the Report's primary conclusions, which, in particular, attribute increased loads to the TIP sediments):

"The PCB load from the Thompson Island Pool . . . dominates the water column from the Thompson Island Dam to Kingston during low flow conditions" (Report at E-3);

"The sediments of the Thompson Island Pool strongly impact the water column, generating a significant water column load (as documented in Chapter 3) whose congener pattern can often be seen throughout the Upper Hudson" (Report at 4-91).

- The Report dismisses the importance of the more recent load originating near Hudson Falls attributed to 1991 - 1993-era loads from the Allen Mill, which the Report concludes have been essentially eliminated:

“Recent remedial efforts by GE have greatly decreased the PCB loads originating above Rogers Island. As a result, the total annual loads to the water column have decreased but the importance of the TI Pool load has increased.” (Report at 3-91).

Not only are there no data to support this conclusion, it ignores the likelihood that the large releases from the Mill were deposited above and within the TIP, where they are now contributing to the water column.

- The Report is inconsistent in its reliance on different mechanisms above and below the TID. On the one hand, the Report posits a number of possible physical mechanisms within the TIP -- settling or volatilization of the load entering the TIP and porewater diffusion or resuspension of TIP sediments -- to explain the increased loading of PCBs across the pool. At the same time, the Report appears to ignore or discount these same mechanisms in the area below the TID in reaching the conclusion that the load at the TID is transported without significant loss of PCBs to the water column through the rest of the freshwater Hudson. Yet, the sediments in the areas above and below the TID are very similar, and the Report itself identifies an increase in PCB load downstream of the TID during low flows (Report at 3-84). It is unreasonable to invoke these processes where they tend

to support one's conclusions, but ignore them when they do not comport with those same conclusions.

In order to complete a technically defensible remedial analysis, EPA must develop a consistent and physically plausible explanation of the data and then test that explanation against a calibrated and validated model to ensure that the true sources of PCBs to fish, wildlife and humans are identified. The explanation of the data needs to take into account all the processes at work in the river that are relevant to remedial analyses. Where questions central to remedial analyses cannot be answered with the data presently at hand, additional data be obtained to resolve the issues so that we can have full confidence in the conclusions reached on the basis of data interpretation and evaluation.

# APPENDICES

## **APPENDIX A**

### **SUMMARY OF ANALYTICAL BIAS CORRECTIONS FOR USGS AND GE DATABASE**

Corrections for analytical biases in both the USGS and GE water column databases were developed to support the data analyses presented in this document. Summaries of the rationale and data used to develop these corrections are presented below. More detailed reports documenting the development of these corrections will be presented in the future.

#### **A. Quantification of The Analytical Bias in The USGS Data**

The USGS data contains analytical biases, however, we believe that these biases can be bounded and used to "correct" the existing database. The analytical biases within the USGS database relate to the packed column methodology for PCB separation employed during the period of 1977 to 1989. This separation and quantitation method failed to resolve the mono-chlorinated biphenyls as they elute with the solvent peak on the packed column. Based upon the PCB loading patterns observed in the Hudson, this bias would tend to underestimate the PCB loading from sediment porewater, which is enriched in mono-chlorinated biphenyls.

In anticipation of these potential biases, GE analyzed a subset of the water column data collected over a five month period during 1991 by both congener methods (NEA608CAP) and

packed column USGS methods (Schroeder and Barnes, 1983). These paired data provide a means of quantifying the low bias in the USGS data.

Based upon linear regression analysis of the difference between paired USGS and capillary column PCB data and the weight percent of homologues quantified by the capillary column method, the low bias in the USGS data (Figure A-1) appears to be strongly correlated with the concentration of mono-chlorinated biphenyls in the sample (Figure A-2). Addition of dichlorinated biphenyls to the regression strengthens the correlation suggesting that a portion of the bias may also be attributable to an underquantification of the dichlorinated biphenyls (Figure A-3). Therefore, it appears that the bias associated with the USGS data is directly related to the concentration of mono-, and to a lesser extent, the dichlorinated biphenyls. Since there is no direct measure of the mono-chlorinated biphenyls in the historical USGS data, a straight linear regression between capillary column and USGS total PCB concentrations was performed to assess the analytical bias in the USGS data. This regression was performed for each sampling station due to differences observed in mono- and dichlorinated PCB concentrations at the different stations in subsequent congener PCB monitoring programs.

The results of the regression analyses for the different stations appear in Figure A-4. At the Fort Edward station, where water column samples contain only a small amount of mono- and dichlorinated biphenyls, the low bias in the USGS methodology is estimated at 29 percent (bias determined by the slope of the relationship). Similarly, PCB measurements by USGS methodologies underestimate Schuylerville PCB concentrations by an estimated 40 percent. Stillwater and

Waterford correction factors were similar to those of Schuylerville. Biases at downstream stations are greater than those calculated for the Fort Edward station due to the higher proportion of mono-chlorinated biphenyls in samples from these downstream stations. These correction factors were applied to the USGS data for the entire period of record (1977-1995). The corrected data were then used to analyze long term spatial and temporal patterns in PCB loading in the upper Hudson River, specifically, the historical loading observed from the TIP region of the river.

#### **B. Quantification of the Analytical Bias in NEA Peaks 5, 8, and 14**

Comparison of 1993 water column PCB concentrations measured at the Fort Edward and Thompson Island Dam stations by GE with those measured in the EPA Phase II study suggested that analytical biases were present in the GE data set. Although total PCB levels and homologue distributions in the two data sets exhibited consistency in magnitude and temporal trends, examination of specific dechlorination products suggested that analytical biases are manifested in individual PCB congeners. Differences between GE and EPA data for capillary column peak 5 (PK5), which contains PCB congeners 2,2' dichlorobiphenyl (BZ4) and 2,6 dichlorobiphenyl (BZ10), are especially evident in the 1993 data from TID (Figure A-5).

Biases in individual congeners may significantly affect data analyses used in developing an understanding of PCB fate and transport mechanisms in the Thompson Island Pool (TIP). For the case of PK5, the low bias of the GE data (Figure A-5) causes the TIP loading to be underestimated;

and may significantly affect conclusions drawn from data analyses regarding the relative importance of sediment diffusive flux and dechlorination as PCB fate and transport mechanisms.

The primary cause of analytical biases in the GE data is related to the capillary column (DB-1) method used to separate PCB congeners. Coelution of congeners with differing relative response factors (RRFs) causes DB-1 results to be sensitive to the assumption made regarding their relative amounts within the given peak. Also, coeluting congeners can cause the shape of a chromatograph peak to deviate from an ideal Gaussian distribution, resulting in area calculation errors. Biases in the GE data set were also attributed to errors in the original Mullin calibration of the PCB standard used in DB-1 analyses. The weight percent of peak 5 components within the 25:18:18 mixture of Aroclors 1232, 1248, and 1262 of the Green Bay Mass Balance Study mixed Aroclor standard (US EPA, 1987) was apparently miscalculated.

Preliminary attempts to "correct" the GE database for analytical biases were focused on the revised Mullin calibration of the Green Bay Standard (Mullin, 1994). However, temporal trends in 1993 GE water column data recomputed with the revised calibration did not compare well with EPA data. Remaining differences were attributed to differences in RRFs among individual congeners within a given DB-1 peak containing coeluting congeners, as the ratio of coeluting congeners can be altered upon dechlorination or by other processes.

To further explore the coelution issue, peaks with coeluting congeners were first ranked based on their potential for analytical bias. Archived extracts from Hudson River water column

samples were then reanalyzed in the laboratory to separate out coeluting congeners from selected target peaks. Regression analyses were used to quantify single peak analytical biases by relating DB-1 measurements to congener sums.

Peaks targeted for reanalysis were ranked by a surrogate parameter chosen to reflect their contribution to PCB loadings in the TIP and the effects of coelution. For peak  $I$ , containing  $j=1, \dots, n$  coeluting congeners, the potential bias index,  $\Phi$ , was defined as the product of its relative range in congener RRFs and its average weight percent ( $WTID$ ) in 1991-96 summer low flow GE water column PCBs measured at TID:

$$\Phi_x = WTID_x \left( \frac{RRF_{\Phi_{\text{HIG}}} - RRF_{\Phi_{\text{LOW}}}}{\sum_{\alpha=\Phi}^{\Psi} \frac{RRF_{\alpha}}{n}} \right) \times 100\%$$

The DB-1 peaks with the five highest  $\Phi$ 's are listed in Table A-1.

**Table A-1.**

**DB-1 PCB Peaks with the highest potential for analytical bias in the GE water column dataload. Congener RRFs obtained from Table 7-IV (Erickson, 1992).**

| DB-1 Peak # | IUPAC Congener #s |     |     |     | Congener RRFs |       |       |       | Relative Range in RRFs (%) | Avg TID WT% | Φ    |
|-------------|-------------------|-----|-----|-----|---------------|-------|-------|-------|----------------------------|-------------|------|
|             | 1st               | 2nd | 3rd | 4th | 1st           | 2nd   | 3rd   | 4th   |                            |             |      |
| 5           | 4                 | 10  |     |     | 0.037         | 0.262 |       |       | 150.03                     | 10.15       | 1523 |
| 8           | 5                 | 8   |     |     | 0.119         | 0.206 |       |       | 53.54                      | 7.90        | 423  |
| 14          | 15                | 18  |     |     | 0.107         | 0.313 |       |       | 98.10                      | 3.68        | 361  |
| 25          | 20                | 21  | 33  | 53  | 0.724         | 1.060 | 0.361 | 0.447 | 107.93                     | 3.16        | 341  |
| 17          | 16                | 32  |     |     | 0.447         | 0.278 |       |       | 46.62                      | 5.68        | 265  |
| 26          | 22                | 51  |     |     | 1.094         | 0.600 |       |       | 58.28                      | 2.82        | 164  |

1993 water column data for the five peaks listed in Table A-1 were compared with measured values from the EPA data set and the largest biases were found to be in peaks 5 (low), 8 (high), and 14 (low). Therefore, these peaks were selected as target peaks for further analyses.

Laboratory separation of the congeners within target peaks was performed on a CP-SIL 5/C18 (C18) gas chromatograph column, manufactured by Chromopack, Inc. This column was selected primarily on its ability to resolve low molecular weight PCB congeners including those coeluting in peaks 5, 8, and 14.

Historical archived GE Hudson River water column sample extracts selected for laboratory reanalysis included recent samples (1995-1996) with total PCBs greater than 40 ng/L collected from FE, TID, and the Hudson Falls plunge pool, and historical paired samples collected from FE and TID

during the summer low flow periods of 1991-1996. The paired samples chosen for reanalysis exhibited a strong TIP loading signal (i.e., large difference in total PCBs between FE and TID). The selected data set enabled examination of the variation in single peak correction factors for different time periods and sampling locations, and for data that were expected to have significantly different PCB compositions.

Comparison of results from DB-1 analyses of archived extracts with original data indicated that the laboratory achieved good analyte recovery (i.e., storage loss was not significant). Extracts were reanalyzed on the C18 column, and linear regression analyses were performed to relate C18 congener sums with DB-1 results. Regression analyses for the three target peaks (PK5, PK8, PK14) are plotted in Figure A-6. Results from the regression plots suggest that the analytical bias in the target peaks is systematic and independent of sample time and location (i.e., correlation coefficients close to unity and small y-intercepts). Based on these results, correction factors were developed to account for analytical biases in peaks 5 (3X), 8 (0.5X), and 14 (1.5X). Regression statistics for the three target peaks are summarized in Table A-2.

| DB-1 Peak # | Structure of PCB Congeners | Reanalyzed Extract Data |                  |                  | Regression Statistics |                    |                |                         |                          |
|-------------|----------------------------|-------------------------|------------------|------------------|-----------------------|--------------------|----------------|-------------------------|--------------------------|
|             |                            | Number                  | Max Conc. [ng/L] | Min Conc. [ng/L] | Slope                 | y-Intercept [ng/L] | R <sup>2</sup> | Standard y-Error [ng/L] | Significance F (P-value) |
| 5           | 2,2' + 2,6                 | 38                      | 30.7             | 0.0              | 2.94                  | 1.4                | 0.931          | 5.8                     | 1.7E-22                  |
| 8           | 2,3 + 2,4'                 | 38                      | 102.7            | 0.0              | 0.47                  | 0.3                | 0.995          | 0.9                     | 9.9E-44                  |
| 14          | 4,4' + 2,2',5              | 38                      | 83.8             | 0.9              | 1.53                  | -1.2               | 0.996          | 1.6                     | 3.0E-45                  |

The correction factors developed from regression line slopes were applied to the 1993 GE water column data set for comparison with GE data from the same period. 1993 total and target peak PCB water column concentrations are plotted in Figures A-7 and A-8 for the FE and TID sampling stations, respectively. Inspection of Figures A-7 and A-8 suggests that application of the correction factors to the GE data set dramatically improved its comparability with the EPA data. This improvement is most notable for PCB data collected at TID.

A-8.

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## APPENDIX B

### DNAPL SOURCES IN THE VICINITY OF HUDSON FALLS

#### Source Identification:

In September 1991, elevated river water levels of PCBs were detected by GE upstream of the contaminated sediments in the TIP. Intense investigations localized the source area to the eastern shoreline near river mile 196.8, in the vicinity of the GE Hudson Falls plant site. Access to this area was hampered due to complex site geography, the presence of a steep cliff and the Baker's Falls, a 150 year old mill (Allen Mill) in poor structural condition and several hydraulic conduits.

The results of these investigations revealed the presence of active seeps of Dense Non-Aqueous Phase Liquids (DNAPL) along the eastern cliff face and the rock face of the eastern raceway within the Allen Mill. In addition, free phase PCB oil (Aroclor 1242) and oil-contaminated sediments (up to 70,000 ppm) were found within the Mill and in the tailrace tunnel (the tailrace tunnel, a 200 foot tunnel discovered below the Mill in the fall of 1992, outlets into the plunge pool at the base of Baker's Falls).

As part of the reconstruction of the Baker's Falls dam by Adirondack Hydro Development Corporation, the eastern portion of the Falls was dewatered in the first quarter of 1996, revealing additional seeps in the river bottom.

#### Remediation:

A number of different remedial measures have been implemented to mitigate the seepage of PCBs from the vicinity of the plant site to the River. It is now recognized that DNAPL is present in fractured bedrock below the site. Remedial efforts are briefly summarized below: 1) DNAPL seepage from the rock face of the eastern raceway is now routinely captured; 2) hydraulic control of conduits through the Mill was achieved in 1993 to allow access and additional investigation of the Mill; 3) a slurry wall was constructed within the eastern raceway in 1994 to reduce river seeps from this region; 4) removal of DNAPL and oil-contaminated sediments from the Allen Mill containing 50 tons of PCBs was completed in 1995 (this material represents approximately twice the amount of PCBs estimated to reside in all of the TIP sediments); 5) construction of a WWTP to allow expansion of recovery efforts at the site in 1995; 6) installation of DNAPL-recovery wells in the vicinity of the plant site that have recovered >8000L of DNAPL to date; and 7) the ongoing installation of barrier wells utilizing hydraulic control to further reduce DNAPL transport through subsurface fractures. Clearly these remedial efforts have reduced the PCB loading of undechlorinated Aroclor 1242 to the Hudson River, but it is not yet possible to determine the degree of control that has been achieved.

#### Recent Efforts:

Additional chemical characterization of DNAPL fluids from seeps and subsurface wells has recently been undertaken to aid DNAPL control efforts at the site. Chemical characterization of these fluids by GC/MS has identified the major chemical components of the DNAPL in the bedrock at Hudson Falls to be Aroclor 1242 (PCBs), phenyl-xylyl ethane (PXE), bis-(2-ethylhexyl) phthalate

(BEHP) and trichlorobenzene (TCB). The level of PCBs in the DNAPL ranged from 12 to 100 weight percent. The other components also varied considerably. Although there was considerable variation in the composition of the DNAPL recovered from different locations at Hudson Falls, the composition of the DNAPL falls into four distinct categories.

The four categories of DNAPL recovered from 38 different locations, including wells and in-river seeps, can be defined as 1) PCBs only (primarily PCBs), 2) all components (PCBs, PXE, BEHP and TCB), 3) all components less TCB (PCBs, PXE and BEHP), and 4) low PCBs (containing less than 50% PCBs, and variable quantities of PXE, BEHP and TCB). The presence of these four categories of DNAPL suggest that there are at least four unique DNAPL reservoirs present in the vicinity of the plant site. These DNAPL reservoirs are located as follows and are shown in Figure B-1:

| <b>TABLE B-1</b>   |   |
|--|---|
| <b>Chemical characterization of DNAPL reservoirs in the vicinity of the Hudson Falls Plant Site.</b> |   |
| <b>DNAPL composition</b>   | <b>Location</b>   |
| PCBs only  | Seeps 1 & 5; vertical seep control borings in tunnel; Eastern Raceway |
| All components   | Seep 13; RW-104; angled seep control borings in tunnel                |
| All components less TCB  | RW-100 & east of RR tracks  |
| Low PCBs   | Bldg 1 & south of John St.  |

Note that the river seeps fall into two distinct reservoirs. Seep 13 was discovered in the fall of 1996 by divers at the base of Baker's Falls. DNAPL collected from this river seep totaled over 16 liters by early January 1997. This represented ~0.5 lbs/day of potential PCB loading to the river that was being captured since its discovery in late 1996. The location and chemical characterization of this seep was distinct from the other river seeps, suggesting additional controls would be necessary to capture this material. Recovery well RW-104 was installed to capture this material and it quickly began capturing DNAPL with the same chemical composition as that previously collected from Seep 13. Moreover, production ceased from Seep 13 in nearly the same time frame. The new recovery wells in the Eastern Raceway, installed as a portion of the barrier wells near the River's edge, may also be capturing DNAPL that is impacting Seeps 1 and 5.

These recent results suggest that targeted remedial activities at the Hudson Falls site are currently reducing the upstream source responsible for the contamination of surface sediments in the TIP. As these surface sediments represent a source of PCBs to the biota and water column from the TIP, impacting the upstream source (undechlorinated Aroclor 1242) should have a direct benefit on water and fish PCB levels. The negative impact on both of these media was observed after the Allen Mill releases in 1991-1993. We would expect correspondingly positive impacts on both media due to the recent controls implemented on the Hudson Falls plant site.

## APPENDIX C

### APPLICATION OF INTRA-HOMOLOGUE PEAK RATIOS TO CHARACTERIZE PCB SOURCES

#### ABSTRACT

The origin of the persistent PCB levels in Hudson River fish has remained controversial: primarily, we believe, for lack of chemical "fingerprinting" procedures that would permit distinguishing between alternative sources for the fishes' PCBs. Past attempts to provide such fingerprinting via descriptions of PCB congener distribution or principal components analysis have been generally unproductive; largely, it now appears, because of data confounding by variabilities in such processes as elutriation, bioaccumulation, and depuration. Since these processes impact much more heavily on inter-homologue ratios than on intra-homologue, or isomer, ratios, we have explored the use of isomer ratio data sets as information indicators of the environmental alteration state, and hence environmental pathways, taken by the fishes' PCBs. Examination of over 300 such data sets, determined for the PCBs in Hudson River fish belonging to 30 species, 21 genera, and 11 families, collected over a 200-mile stretch of the river over a 16-year period, showed that the resident fishes' isomer ratio "fingerprints" have generally corresponded to those of the local surficial sediments in all sections of the river, except as altered by metabolic processes that were found characteristic of 9 of the 21 genera studied. Since 1977, the PCBs of the fish of the Thompson Island Pool (upper Hudson River Reach 8) have exhibited surficial sediment Pattern A, indicative of recently deposited Aroclor 1242. Those of fish taken a hundred miles downstream in the mid-estuary have instead exhibited subsurficial sediment dechlorination Pattern H', indicative of PCB

compositions, such as hydraulic fluids, that had long been present in the sediments. In between, there has been a smooth transition in pattern, indicating a decrease in the extent of fish PCB dechlorination with decreasing distance from the known source of undechlorinated Aroclor 1242 input at Hudson Falls.

## INTRODUCTION

The Hudson River is the major waterway draining eastern New York State (Figure C-1). Its fish have been known to be carrying elevated levels of PCBs (polychlorinated biphenyls) since 1970 (1). All industrial uses of PCBs ceased in the 1970's and the levels of PCBs in Hudson River fish have declined only slowly since the mid 1980s. Continuing controversies as to the sources of the fishes' PCBs revolve around such questions as: whether the PCBs in upper Hudson fish are coming from old local high level sediment deposits ("hot spots") or from ongoing drainage from rock fractures under a contaminated plant site; whether the PCBs in lower Hudson resident fish are coming from old deposits in the local sediments or from ongoing inputs from the upper Hudson; and whether the PCBs in lower Hudson migratory fish are coming from either of these sources, or from the sediments and sewers of the New York metropolitan area.

The commercial PCB products (e.g. Aroclors) that were released into the environment were complex mixtures of isomers (PCBs of the same Cl-Number) and homologues (PCBs of different Cl-Number), which are generically referred to as congeners. The original distributions of such congeners can be altered by biological processes in each of the environmental compartments through which the PCBs may pass, e.g., by aerobic microbial biodegradation near the sediment surface

(4,5,6); by anaerobic microbial dechlorination in subsurficial sediments (7,8,9,10); by limited microsomal metabolism in some fish species (11); and by more extensive microsomal metabolism in crustaceans, piscivores, and man (11, 12). Since each of these processes alters the PCB congener distribution in a different way, it should, in principle, be possible to identify the set of niches through which any environmental PCB has passed *via* observable alterations in congener distribution.

In practice, this has generally proved difficult, primarily because  $K_{ow}$ -dependent phenomena such as evaporation, elutriation, bioaccumulation, and depuration, as well as variations in Aroclor proportions in the original release, can produce variations in homologue distributions large enough to obscure the effects on congener distribution produced by niche-specific biological activities. It occurred to us, however, that this problem could be minimized by simply using isomer ratios rather than congener levels as indices of chemical composition. Accordingly, we undertook to determine enough PCB isomer ratios on enough types of fish samples to determine whether an isomer ratio data set could indeed provide a robust indicator of PCB source and alteration history.

## MATERIALS AND METHODS

Site Description. - The lower 156 mi. (251 km) of the Hudson River, from Troy to New York City, is a tidal estuary herein referred to as the lower Hudson (see Figure C-1). The next *ca.* 80 mi. (*ca.* 125 km), i.e., the lower part of the upper Hudson, consists of a series of dammed stillwaters called "reaches," numbered in order starting from the Federal Dam at Troy. Distances along the Hudson are measured as "river miles" (RM) starting from the Battery at the southern end of

Manhattan Island (New York City). Several descriptions of the contamination of the Hudson River by PCBs have been published (13, 14, 15, 16, 17).

Fish Data Used. - The fish samples or analytical data used in this study came from collections made by seven other investigators:

1. From R.J. Sloan of the New York State Dept. of Environmental Conservation (DEC) we obtained about 800 archived analytical extracts of fish from his 1977-82 collections (2) that had been returned by his analyst after low resolution packed column analysis. We selected 75 specimens that reflected a variety of fish species, PCB levels, and Aroclor ratios and submitted them to Northeast Analytical Services of Schenectady, NY (NEA) for DB-1 capillary gas chromatographic (GC) analysis by described procedures (18). These analyses revealed that a few of the extracts, notably those of the goldfish and eels, had been allowed to dry out and lost lower congeners, but that most still exhibited homologue distributions in accord with the original "Aroclor" determinations.

2. From P.A. Jones, also of DEC, we obtained splits of the fathead minnow samples collected in his 1985 study (19) of Hudson River PCB uptake by caged minnows, which were analyzed at GE (18).

3. From J.M. O'Connor, then of New York University, we obtained the original packed column GCs of the *gammarus* collected in 1980 as a part of the NYU Hudson River Survey (20).

He also supplied us with a dozen lower Hudson striped bass, collected in 1985, that were analyzed at GE (18).

4. From B.K. Shephard, then of Harza Engineering Co., we obtained both NEA GCs and data for samples of sediments, Hester-Dendy (periphyton) plates, dialysis bags, invertebrates, and fish collected during his 1988-1998 survey of PCBs in the lower Hudson River, New York Harbor, and western Long Island Sound.

5. From J.G. Haggard of General Electric we obtained 90 frozen fish that had been collected from upper Hudson Reaches 1-11 by Law Environmental Services in 1990. These were submitted to NEA for a 118-peak DB-1 analysis (18), along with a separate analysis for congener 77, which is not well resolved from PCB 110 on DB-1.

6. From W.A. Ayling of O'Brien and Gere Engineers, Inc. of Syracuse, NY we obtained NEA chromatograms and data for fish, invertebrates, and sediment surface scrapings collected from the Thompson Island Pool in May, 1992, eight months after the major PCB loading event of September, 1991 (21).

7. From L.J. Field of NOAA, Seattle, WA, we received 145-congener dual column PCB data files for 115 fish samples that he had collected in collaboration with RJ Sloan (DEC) at ten collection stations between RM 40 and 200 on the upper and lower Hudson in the autumn of 1993.

The sediment reference samples for A, B, C, H and H' alterations were taken from individual core sections that exhibited these patterns as previously described (7-9).

Data Processing. From each PCB congener data set we calculated, if not already provided, the total PCB level, the PCB/lipid ratio, the levels of the homologue groups, the ratios between successive homologue groups, and the ratios of about 40 of the stronger single congener peaks to those of a selected isomeric reference congener, as well as site and species averages. The selected reference congener(s) were, for the tri-CB (hereinafter CB(s) = chlorobiphenyl(s)), the sum of PCBs 28 + 31 (these are normally the highest and second highest level tri-CBs, respectively; but they elute so closely on a DB-1 column that we were concerned about the reliability of the peak splitting calculation); for most tetra-CBs, PCB 49 (which maintains a relatively constant level during the early stages of dechlorination); for the tetra-CB PCB 70, which is readily metabolized by the AP-ICT activity, the non-metabolized PCB 74 (which is also more similar in  $K_{ow}$  to PCB 70 than PCB 49); for most penta-CBs, the rather slowly dechlorinated PCB 110, with PCB 99 as a non-metabolizeable alternate; and for the hexa-CBs, PCB 153.

Adjustment for Reference Congener Depuration - We noted that the ratio between isomers 74 and 49, which differ somewhat in water solubility, became elevated in individual fish that were heavily depurated, as indicated by low levels of di- and tri-CB's. In such fish the elevation in log (PCB 74/PCB 49) averaged about 0.2 times that in log (tetra-CB/tri-CB). Accordingly, a possible depuration adjustment to the 74/49 ratio was calculated on that basis.

## RESULTS

Table C-1 lists the fish species examined, abbreviations used, and metabolic alteration patterns observed. Table C-2 presents the mean values of the upper and lower Hudson River fish PCB homologue levels and selected PCB isomer ratios for the 1977-78, 1990, 1992, and 1993 fish collections, along with reference values for a 90:10 Aroclor 1242:1254 mix and Hudson River sediments exhibiting alteration patterns A, B, C, H, and H'. The variability of all tetra-CB and some penta-CB homologue levels, and the upper Hudson PCB isomer ratios involving penta- and hexa-CBs was low (5 - 20% Relative Standard Deviation (RSD)). Tri- and hexa-CB homologue levels, and the other isomer ratios involving tetra-, penta-, or hexa-CBs displayed somewhat greater variability (20 - 40% RSD). Generally, however, the % RSD's were only about half as great for the isomer ratios as for the homologue levels. Much of this remaining variance in the Table C-2 isomer ratio data, which arose from measurements of the PCBs in many different species of fish, taken over large geographical ranges, could be correlated with specific variables. These will be considered in turn.

Variations arising from PCB depuration. - Some of the individual fish collected from the upper Hudson in November, 1990 showed levels of tri-CBs that were reduced to as little as 10% of their usual values, and displayed even greater reductions in di-CBs. Such reductions in lower homologue levels occurred most frequently in walley (WAL), smallmouth bass (SWM), and largemouth bass (LMB), and significantly influenced the average lower homologue levels reported for 1990, since SMB had been selected as the species to be measured in triplicate in every reach of the upper Hudson. The depurative losses could have resulted from either a late-season cessation of

feeding, or from periods of feeding in uncontaminated tributary streams. These losses were much less prominent in the 1977-1978, 1992, and 1993 collections. However, the observation of the effects they might have on the PCB 74/49 isomer ratio prompted the inclusion of a possible 74/49 ratio adjustment for depuration in Table C-2.

Variations arising from atypical Aroclor inputs. Occasional fish in most collections exhibited congener profiles clearly divergent from the majority. Thus, most of the very lightly contaminated (<1ppm) fish taken from above Glens Falls showed only the broad homologue distribution pattern and DDE content characteristic of atmospheric deposition, as did also the local sediments, those of the Mohawk River, and those of some mountaintop peat from the summit of Mt. Algonquin (elev. 5114') in the Adirondacks. However, two (out of 17) of the 1993 NOAA fish collected in this area exhibited patterns resembling Aroclor 1242, one showed the pattern of Aroclor 1268, and one 1990 fish showed Aroclor 1260; all probably reflecting exposure to local areas of low level contamination with these Aroclors. One of the 1990 Reach 8 LMB showed the low total PCB level and broad homologue distribution of the upstream region, indicating recent translocation. Both the 3 - 4 year age group of the 1982 Albany pumpkinseed (PKS) and the 1980 NYU *gammarus* collections from several lower Hudson stations showed substantial levels of Aroclor 1260, indicating the occurrence of a significant, but short-lived, Aroclor 1260 contamination event around 1980.

Of more general significance, the homologue distributions in Table C-2 showed that there were higher levels of penta-, hexa-, and hepta-CBs in the lower Hudson than in the upper section, and also higher ratios of hexa- and hepta- to penta-CBs, which would not have been effected by

elutriative, evaporative, or depurative losses of lower congeners. Evidently, the original source of the lower Hudson River fish PCBs had been an Aroclor mix containing higher proportions of more heavily chlorinated Aroclors than that contaminating the upper Hudson.

Variations correlatable with fish species or genus. The PCBs in certain of the fish species showed consistent depletions of particular groups of congeners, thus defining an alteration pattern (AP), presumably arising from a species-specific PCB metabolizing activity (Table C-1). The commonest, Pattern AP-ICT (for *Ictalurus*, the first genus in which noted) was previously designed "P450-1A-like" (11); however, that term now seems better restricted to the somewhat different pattern seen in higher animals (12). AP-ICT shows a marked reduction in PCB 70 (and hence the 70/74 ratio) and lesser reductions in PCBs 16, 17, 18, 22, 27, 33, 40, 49, 56, 91, 97, and possibly 101, 110, and 174; all of them congeners with adjacent unsubstituted 4-positions. By contrast, AP-PET (for *Petromyzon*) showed reduced levels of the 4,4'-substituted PCBs 28, 74, 118, 105, 128, 167, and 156, and also of PCBs 49, 52, and 174, leaving the peak given by the coeluting pair, PCBs 64 + 71, as the strongest in the chromatogram. Pattern AP-ESX (for *Esox* where it appeared occasionally) showed clear reductions in every resolved congener carrying a 2, 3-dichlorophenyl group, i.e., PCBs 22, 40, 42, 44, 56, 82, 84, 97, and 129. Pattern AP-LEP (for *Lepomis*) showed clear reductions in just two of the above, namely, PCBs 40 and 44. Finally in AP-CAT (for *Catostomus*) the only clear reduction was in congener 52. Thus, the only observed fish alteration patterns that would affect a PCB 74/49 isomer ratio were AP-ICT and AP-PET.

A very different set of variations was observed in the anadromous (migratory) fish of the lower Hudson River. The STB (for Striped Bass) and AMS (for American Shad) all showed substantial levels of DDE, sometimes accompanied by DDD or DDT; *trans*-nonachlor, sometimes accompanied by  $\alpha$ - and  $\gamma$ -chlordane; and other pesticides as well, generally producing enough interfering peaks in the tri- through hexa-CB range to make calculation of isomer ratios from GC-ECD data problematical. The observed pesticide/PCB ratios generally corresponded to those seen in the sediments of the New York metropolitan area, including western Long Island Sound, which is where these species overwinter. Conversely, the two Atlantic tomcod (ATT) examined, both collected at RM 41 in January, 1978, showed only low levels of Aroclor 1242-like PCB contamination, without any pesticides, not even the low level of DDE present in the lower Hudson.

Variations due to biodegradation/dechlorination state. Congener distributions in Hudson River subsurface PCB dechlorination Patterns B and C (7,8,10) and H and H' (9,10) have been previously described. Generally speaking, Pattern C dechlorination, which gives the most extensive conversion to mono- and di-CBs, is seen in the most heavily contaminated sediments of the upper Hudson; Patterns B and B' are seen in somewhat less heavily contaminated sediments as far downstream as Albany; and the rather selective Patterns H and H' are uncommon in the upper Hudson, but dominant in most of the more lightly contaminated lower Hudson (9). Bedard has argued that these patterns may all result from the dechlorination activities of just three microbial strains, all separable in anaerobic laboratory cultures, designated M, Q, and H or H' (10), with most dechlorination of the higher congeners coming from the H/H' activity. This could explain why the patterns of higher congener loss are essentially identical for the observed alternative patterns B, C,

H, and H', even though the distributions of the more lightly chlorinated PCB congeners formed are quite different.

The columns on the left side of Table C-2 present the homologue distributions and selected PCB isomer ratios for some representative specimens of subsurface sediment PCBs exhibiting those patterns, along with comparable data for a 90:10 Aroclor 1242:1254 mix, selected as a representative example of an unaltered Aroclor release. The marked compositional changes effected by anaerobic dechlorination are evident.

Geographical variations in dechlorination state. Surficial PCB alteration Pattern A was noted as far back as 1984 (7), but was not seen free from admixed Pattern B until recently. It has now been observed in the 0-1 cm. sediment layers and "fluff" layers collected in the Thompson Island Pool at the same time as the 1992 fish sampling, and repeatedly reproduced in the upper (0-5mm.), presumably microaerobic, sediment layers in laboratory microcosms where upper Hudson sediments were spiked with fresh Aroclor 1242 (21). The Pattern A alteration appeared in the microcosms within six weeks. Its microbiological basis is uncertain; one speculation is that it arises from a combination of an oxygen-tolerant, *meta*-selective dechlorination process followed by an aerobic biodegradation of the most of the dechlorination products. In sediments, it appears to effect limited removal of PCBs 17, 18, 33, 97, 99, 101, 153, and 167 without attacking 40, 44, 56, 60, 66, 70, 74, 87, 105, 114, or 128, and to result in increases in 47, but not in 19 or 27. Its most sensitive indicator is a depression in the ratio 33/28+31, or if separately measurable, just 33/28. Such depressions,

usually paralleled by increases in the 47/49 ratio, are almost universally observed in PCBs recovered from aquatic environments.

Table C-2 shows that in general the isomer ratios observed in upper Hudson fish fell between the values for fresh Aroclor and Pattern A altered PCB, with no obvious contribution from the subsurface Pattern B and C PCBs, with their high levels of dechlorination product PCBs 19 and 27, and low levels of readily dechlorinated PCBs 74, 87, 97, and 105. By contrast, the Table C-2 data for isomer ratios in lower Hudson River fish generally fell between the values for dechlorination patterns H and H', indicating as much dechlorination as in the local sediments.

The 1993 NOAA analyses by a dual column procedure permitted resolution of a number of congeners that were less readily quantified by the NEA single column analyses. Table 3 presents mean isomer ratios, calculated from the NOAA data, for 17 PCB isomers known (9) to be sensitive to Pattern H/H' dechlorination at various stations between the Thompson Island Pool (RM ~192) and Iona (RM 40). The levels of all of the dechlorination-sensitive congeners were found to decrease with distance downstream: most rapidly in the case of the toxic coplanar PCB 77; quite slowly for congeners 118 or 138; and with the major mono-*ortho* tetra-CBs 56, 60, 66, 74, and penta-CB 105 in between.

The 1993 EPA water and sediment analyses by the same procedure, as presented graphically in Figs. 3-73 to 3-80 of a recent report (17), were noted to show the same changes for congeners 56, 60, 66, 70, and 74. Their levels in upper Hudson water at RM 177.8 were similar to those in

undechlorinated Aroclor 1242, while those in lower Hudson Pattern H/H' - dechlorinated sediments at RM 143.5, 88.5 or 43.2 were only half as great.

Figure C-2 shows the trend for unadjusted 74/49 ratios not only for the 1993 NOAA fish, but also for the 1990 and 1992 fish collections, the 1985 caged minnow study, and the 1989 *gammarus*, periphyton, and dialysis bags. In all cases there appeared a smooth transition between values characteristic of the Pattern A sediment surface of the Thompson Island Pool and the Pattern H/H' dechlorinated sediments and water of the lower Hudson.

## DISCUSSION

Utility of isomer ratio analysis. The above results show that PCB isomer ratio analysis can be used to identify and quantify the niche-specific biological alteration processes to which an environmental PCB release may be subjected. These processes include the ubiquitous but enigmatic, possibly microaerophilic, microbial alteration process A at the sediment surface; the well-characterized subsurficial anaerobic microbial dechlorination processes leading to alteration patterns B, C, H or H'; the genus-dependent fish PCB alteration processes leading to the patterns AP-ICT, AP-PET, AP-CAT, AP-ESX, and AP-LEP described above; and the microsomal P4502B-like alteration process exhibited by many crustaceans (which are frequently prey of the fish examined here) as well as by higher vertebrates (12). Characterization of such processes can be useful in defining the set of environmental niches through which a PCB composition has passed on its way from point of release to accumulation in a fish.

One complication of isomer ratio analysis is interferences between the effects of different processes, especially as they effect the reference congeners used. For example, reference tri-CB 31, reference tetra-CB 49, and possibly penta-CB 110 are all potentially subject to metabolism by the AP-ICT system, and the first two of these also to losses under conditions of heavy depuration. We have presented here a procedure for correcting the 74/49 ratio for such losses of PCB 49 as a possible adjustment. An alternative would be to simply avoid the use of heavily depurated individuals, or of lampreys, eels, ictroids or goldfish, in making quantitative determinations of local PCB alteration state *via* isomer ratio analysis.

Previously, the most popular approach to handling environmental PCB congener distribution data has been by principal components analysis. This defines PCB composition in terms of two or three enigmatic "principal components." These may permit the grouping of samples into related sets, but do little to explain the chemical nature of the differences. It is now evident why this happens: there are simply many more significant alteration processes affecting PCB composition than there are mathematically resolvable "components," so that the resolved "components" inevitably represent combinations of the effects of multiple alteration processes in various proportions.

Sources of the PCBs in Hudson River fish. The PCB (and pesticide) "fingerprinting" provided by isomer ratio analysis, along with data from other environmental studies, shows that the PCBs in Hudson River fish originate from four readily distinguished sources.

The first, and least important of these, is atmospheric deposition. This PCB source is characterized by homologue and pesticide distributions that are very different from those of the other sources, and is responsible for the low level PCB (and DDE) contamination seen in the fish and sediments of the upper reaches of the Hudson, the Mohawk River, and presumably other tributaries as well.

The second identifiable source consists of the sewers and sediments of the New York Metropolitan area, which is where two important anadromous fish of the lower Hudson, the striped bass (STB) and the American shad (AMS) spend the winter before migrating upriver to spawn. These sediments are known to contain substantial levels of DDT-derived, chlordane-derived, and other pesticide residues (13), as well as PCB mixtures reflecting heavy contributions from Aroclors 1254 and 1260, which were particularly extensively used in railroad and substation transformers in that area. The 1978, 1982, and 1985 STB and AMS in our collection generally showed PCB homologue distribution and pesticide/PCB ratios comparable to those of the sediments of New York Harbor and western Long Island Sound, indicating the significance of those sources.

The third distinguishable source consists of the moderately Pattern H/H'-dechlorinated PCBs of the sediments of the lower Hudson, which exhibit an isomer ratio "fingerprint" closely matching that of the lower Hudson resident fish. These PCBs have been there a long time. Radionuclide dating has shown that most were deposited in the 1950's and 1960's (14) and elevated levels in fish were seen in 1970 and 1973 (1), all before the removal of the Ft. Edward dam and sediment scouring/redeposition events of 1974-76 caused the heavy PCB contamination of the upper Hudson

(16). One original source is the formerly extensive industrial usage of PCB-based hydraulic systems in many of the riverside communities. Available Monsanto sales records for 1957-1977 document purchases by such users of over  $3 \times 10^6$  lbs. of PCB products, especially the hydraulic fluid Pydraul A-200, an Aroclor 1242-1248 blend. Releases of such compositions into the river would result in the moderate elevations in higher homologue levels exhibited by lower Hudson sediments and fish (Table C-2). A less plausible source would be inputs of dissolved PCBs eluted from upstream deposits, since these are depleted, rather than enriched, in the higher homologues (17), and substantially undechlorinated, as noted above.

The fourth fingerprintable source of the 1977-1993 Hudson River fish PCBs consists of Aroclor 1242-like compositions that have been on the surface of the sediments of the Thompson Island pool only long enough to have undergone a limited Pattern A alteration, thus indicating a continuing deposition. The ultimate source of this PCB input may be Aroclor 1242 seeping from the fractured bedrock near the former capacitor manufacturing plant at Hudson Falls. Seepage from this reservoir is now known to have been entering the River as droplets of undechlorinated oil-phase Aroclor 1242 that contaminate surface sediments of the Thompson Island Pool. There, the PCBs soon undergo Pattern A alteration and partial extraction into the water column and its biota, leading to the appearance of undechlorinated Pattern A PCBs in the fish. Eventually, of course, ongoing sedimentation covers each increment of PCB and allows anaerobic microbial dechlorination to the Pattern B- or C-dechlorinated PCBs of the local subsurface accumulations.

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## APPENDIX D

### BENEFITS OF PCB DECHLORINATION

**Reduced Toxicity.** The toxic effects produced by PCBs in inbred strains of laboratory rodents, and possibly in a few wildlife species, are now generally recognized to be mediated by binding to a particular cytoplasmic protein, called the Ah-receptor (AhR), which has the ability to induce expression of cytochrome P450 isozymes 1A1, 1A2 and 1B1, and several Phase 2 drug-metabolizing enzymes as well. The magnitude of this AhR-agonist activity is most commonly determined by measuring the ability of a PCB congener (or other toxicant of concern) to induce the expression of cytochrome P4501A1 in a test animal or cell culture, as indicated by ethoxyresorufin-O-deethylase (EROD) activity, and generally reported as "toxic equivalency," e.g., the ratio of the EROD activity exhibited by the test congener to that exhibited by dioxin, which is the strongest known AhR agonist. Using this test, and direct measures of toxic response, the particular PCB congeners that are the most active of Ah-receptor agonists have been found to be those lacking *ortho* substituents, such as the "coplanar" congeners having substitution patterns 34-34, 345-34, and 345-345 (Safe, 1992). Several "near coplanar" analogs of these congeners, i.e., mono-*ortho* substituted analogs such as 234-34, 245-34, and 2345-34, may also have some AhR-agonist activity [Safe, 1992], but this is much weaker than that of the coplanar congeners in rodents, and often undetectable in other species.

The particular types of PCB dechlorination activities present in the subsurface "hot spots" of the upper Hudson have been found to result in dramatic reductions in the levels of the toxic

coplanar and near coplanar congeners (Quensen *et al*, 1992a; Quensen *et al*, 1992b). The net effect of these reductions, as measured by the EROD activity of the dechlorinated mixture, was a 97% loss of toxic equivalency. In general, the percent toxicity decrease was much greater than the percent decrease in *meta* and *para* chlorine level. It has also recently been shown that microbial dechlorination markedly reduced or eliminated the adverse effects observed with Aroclor 1242 on mouse gamete fertilization (Mousa *et al*, 1996). The reductions in concentrations of coplanar PCB congeners in environmental samples due to microbial anaerobic dechlorination has now been documented in several sediments, including the Hudson River, Sheboygan River, Waukegan Harbor, and Lake Keteelmeer (reviewed in Bedard and Quensen, 1995).

In the case of the lower Hudson River fish PCBs, Table C-3 of Appendix C shows that the relative levels of the one coplanar congener measured (PCB 77; 34-34 CB) were only 10-20% of those in the PCBs of Thompson Island Pool fish, and those of several "near coplanar" congeners between 10 and 35% of such values, indicating a >80% overall loss of toxic equivalency, despite the very modest level of dechlorination in the local sediments.

**Reduced Carcinogenicity.** Currently, the EPA employs a default assumption, that any positive finding in a high dose rodent bioassay implies a proportionate human cancer risk. In the most recent statement of application of this policy to PCB risk assessment (USEPA, 1996) the Agency recognizes that Aroclors 1016, 1242, and the higher Aroclors 1254/1260 can differ considerably in their calculated carcinogenic potency, with upper-bound cancer slope factor (CSF) values of 0.07, 0.4, and 2.0 per mg/kg-day, respectively. However, the Aroclor 1242 CSF value of

0.4 is applicable only for Aroclor 1242 uptake by inhalation. For sediments or fish contaminated by Aroclor 1242, EPA uses the CSF value (2.0) as it would if they were contaminated with Aroclor 1254 or 1260. Likewise, the guidance document recognizes that the CSF may be sharply increased, and in proportion to toxic equivalency, by the presence of coplanar or near coplanar congeners with AhR-agonist activity, but does not allow for a reduction in the CSF when the levels of toxic congeners have been reduced. Thus, although the current guidelines permit the risk assessor to ignore the beneficial effects of PCB dechlorination upon presumed cancer risk, they also clearly indicate the presumed cancer risk is dependent upon both the overall degree of PCB chlorination (which may be moderately reduced by dechlorination) and the content of toxic congeners (which is sharply reduced by dechlorination, as indicated above).

**Reduced Exposure via Aerobic Degradation.** The aerobic bacterial biodegradation of PCBs is widely known and has been well studied (Abramowicz 1990; Bedard, 1990; Alder, 1993; Bedard and Quensen, 1995; Furukawa, 1986). Numerous microorganisms have been isolated that can aerobically degrade a wide variety of PCBs, although the more lightly chlorinated congeners are preferentially degraded. These organisms attack PCBs via the well known 2,3-dioxygenase pathway, converting PCB congeners to their corresponding chlorobenzoic acids. These chlorobenzoic acids can then be readily degraded by indigenous bacteria, resulting in the production of carbon dioxide, water, chloride, and biomass. (Harkness, 1993).

The ability of native microbes to aerobically metabolize PCBs has been demonstrated in a field test in the Hudson River. There are two lines of evidence that strongly indicate that natural

aerobic PCB biodegradation is occurring in the upper Hudson River. First, significant aerobic PCB biodegradation was observed in the field without the addition of microorganisms, nutrients, or supplemental oxygen (although mixing was performed) in the field test. (Harkness, 1993) This result suggested that these sediments contain all the necessary elements for *in situ* aerobic activity. To prove this hypothesis, a sensitive analytical method was developed to detect chlorobenzoic acids, the intermediate products of aerobic PCB biodegradation, in undisturbed cores taken from the River. PCB metabolites were found in all PCB contaminated samples, but not in any of the uncontaminated sediments from further upstream (Flanagan and May, 1993). Moreover, the concentrations and congener distributions of the observed chlorobenzoic acids closely matched the predicted degradation products from the PCBs mixture in the samples .

The detection of chlorobenzoic acids of aerobic PCB biodegradation in contaminated upper Hudson River sediments provides persuasive evidence that aerobic PCB biodegradation occurs naturally in the environment. This finding is consistent with previous studies indicating that aerobic PCB-degrading bacteria with broad congener specificities are widely distributed in contaminated soils and sediments. It could be argued that the PCB biodegradation metabolites observed by the Flanagan and May (1993) study represent evidence of ongoing aerobic biodegradative activity, remnants of past activity, or both. There is evidence to suggest that the metabolites are formed in ongoing biodegradative activity since in a microcosm study, designed to mimic unperturbed Hudson River conditions, the same chlorobenzoic acids are formed and then degraded in the course of approximately 3 months. (Fish, 1996).

**Reduced Bioconcentration.** The lightly chlorinated PCB congeners resulting from dechlorination in Hudson River sediments (e.g., 2-CB and 2-2-CB) display an approximately 450-fold reduction in their tendency to bioconcentrate in fish, as compared to the more highly chlorinated tri- and tetra-chlorinated PCBs present in the original Aroclor 1242 mixture. (Abramowicz, 1994). Thus, natural anaerobic PCB dechlorination reduces the potential risk associated with PCBs via direct reductions in carcinogenic potency, dioxin-like toxicity, and exposure.

**Reduced Bioavailability.** An additional reduction in PCB exposure results from long-term contact of PCBs with sediment particles, and consequent reductions in bioavailability. It is well established that the desorption of many nonionic organic compounds from sediment display bimodal kinetics; a "labile fraction" of the contaminant desorbs readily, while a "resistant fraction" desorbs orders of magnitude more slowly (Karickhoff and Morris, 1985). This phenomenon has been observed with PCBs both in spiked and environmentally contaminated sediments (Carroll et al., 1994, Coates and Elzerman, 1986; Witkowski, et al., 1988). The desorption kinetics of PCBs from environmentally-contaminated Hudson River sediment and spiked sea sand using XAD-4 (polystyrene bead resin) as a "PCB sink" is shown in Figure D-1. PCB levels on the y-axis are normalized to the starting PCB levels of the sand and sediment before desorption (13 and 25 ppm, respectively). PCBs from Aroclor 1242 spiked sand were readily desorbed (85% in 8 hours). In contrast, roughly half of the PCBs from H-7 sediment desorbed within the first 8 hours (the labile fraction), with little additional desorption observed over the remaining 162 hours (Carroll et al., 1994). The slowly desorbing fraction represents the proportion of PCB molecules that have diffused into the organic material of the sediment over an extended period of time. Under these conditions

PCB molecules are not available to bacteria and other river biota making them resistant to uptake and degradation. Longer-term desorption experiments demonstrated that resistant fraction PCBs desorb from Hudson River sediment with a half life of approximately 1 year (Carroll et al., 1994).

The bioaccumulation model developed by HydroQual for GE was used to compute total PCB concentrations in fish for a variety of sediment and water column homologue compositions and concentrations. Depending on the relative concentrations in the sediment and water, as well as on the structure of the food web, dechlorination can lead to reductions in total PCB concentration of between 4 and 35-fold lower than with relatively undechlorinated exposure sources.

## APPENDIX E

### ADDITIONAL COMMENTS AND CLARIFICATIONS

#### 1. Dechlorination Pattern H/H'

The Report recognizes that a variety of more highly chlorinated PCB congeners are very susceptible to losses (pg. 3-119), but instead of recognizing this as a widespread example of anaerobic dechlorination (pattern H and H'), it hypothesizes an unknown selective degradation process that favors these tetra-chlorinated congeners (BZ 56, 60, 70, and 74). In fact, the data displayed to demonstrate this unknown selective degradation (Figures 3-73 to 3-75) are further evidence that dechlorination occurs at low concentrations (down to 1 ppm). Due to the insensitivity of the dechlorination indices used by EPA, the Report fails first to identify this process as process H/H' PCB dechlorination, and more important, fails to recognize its widespread occurrence. Although this pattern is uncommon in the upper Hudson, it is widespread in areas of low contamination in the lower Hudson. Process H/H' dechlorination does not produce significant levels of the terminal PCB dechlorination products, but even such modest dechlorination significantly reduces potential exposure, toxicity, and carcinogenicity, as the initial stages of dechlorination provide disproportionate reductions in these endpoints.

#### 2. Partitioning

One major failing of the analysis of equilibrium partitioning performed by the TAMS/CADMUS/Gradient group is the inclusion of the Remnants and Rogers Island Stations in the determination of global partition coefficients. The stations above the TI Dam show much

different behavior from those below the dam. Figure E-1 shows the average and range of total PCB partition coefficients for Transects 002-006 vs. river mile. Note the relatively constant values for  $K_p$  beginning at the TI Dam of about 50000 l/kg and the distinctly higher values upriver. This difference cannot be attributed to a change in organic content of the solids. Figure E-2 shows estimated log  $K_{OC}$  values plotted against log  $K_{OW}$  (as reported by Hawker and Connell). For the Thompson Island Dam, Schuylerville, and Waterford stations, the  $K_{OC}$  pattern is relatively uniform throughout all transects, and is reasonably well represented by  $K_{OW}$ . The Fort Edward station estimates show a much different pattern, being generally higher than the other stations and exhibiting a higher degree of variability.

The Report states on pp. 3-13 and 3-14: "Noticeable in all transects are the generally consistent values for  $K_{p,a}$  and  $K_{POC,a}$  estimates for most congeners within a given transect beginning at Station 5, the TI Dam (RM 188.5). This suggests that approximate equilibrium conditions are established within the Pool and remain consistent throughout the remainder of the freshwater Hudson. The results for Rogers Island, Station 4, are distinctly different from those downstream and probably reflect its proximity to the Hudson Falls source resulting in a lack of water column equilibrium partitioning." The Report further states on p. 3-20, "All congeners tend to show increased estimates of  $K_{POC,a}$  at RM 196.8 (Rogers Island) [note: Rogers Island is actually at RM 194.6], which may represent presence of non-equilibrated sediment in these samples."

This observation of markedly different partitioning above and below the TI Dam is apparent and the conclusion of partitioning non-equilibrium above the TI Dam and equilibrium below is valid.

With this conclusion, it is incorrect to include Remnant and Rogers Island data in the determination of equilibrium partition coefficients. Estimates including this data will yield partition coefficients well above equilibrium.

The analysis of the temperature dependence of partition coefficients (p 3-16) is based upon historical data reported in Warren, et al (1987). It is not clear why this data was used to determine the temperature dependence of partition coefficients when the Phase 2 data collected covers a sufficient range in temperature to determine temperature dependence directly. Figures E-3 and E-4 show  $\log K_{oc}$  vs  $1/T$  for congeners 10 and 27.

It should be noted that these values of temperature have been corrected to ambient river temperature. Figures E-3b and E-4b show  $\log K_{oc}$  vs  $1/T$  for congeners 10 and 27 based on the temperature reported in the Phase 2 data. That this temperature is not ambient is evident by the large temperature differences within transects as well as the reporting of high (~20 degC) temperatures in the early Spring surveys. Figure E-5 shows a comparison of ambient TI Dam water temperature data collected by OBG as compared to those reported in the Phase 2 transect data. In all transects the reported Phase 2 temperature is higher than ambient. It is not clear when and where the Phase 2 temperatures were taken, especially in relation to the time of filtration of water samples. If the filtration was performed before samples reached equilibrium at the higher temperatures, values of  $K_{oc}(20)$  will be biased high.

### 3. Volatilization

The equation used to determine PCB volatilization during low-flow conditions is inappropriate for river systems. Eq. 3-33 (Report at 3-55) is an empirical model developed by Hartman and Hammond from their studies of San Francisco Bay. This model is driven solely by wind shear and is only appropriate for large open water bodies such as lakes and bays where water velocities are minimal and there exists sufficient fetch to generate appreciable surface shear forces. Even under extreme low-flow conditions in the Hudson River (~1000cfs) flow-induced shear dominates gas exchange. The equation developed by O'Connor and Dobbins (Eq. 3-34) is an appropriate model for rivers.

Additionally, these models only estimate the liquid film transfer coefficient. Prevailing theory holds that gas exchange across a gas-liquid interface is subject to both a liquid and gas film resistance. For substances with a high Henry's constant, such as oxygen, the liquid film resistance dominates and it can be assumed that the overall transfer coefficient is equal to the liquid film transfer coefficient. This assumption is incorrect for PCBs and other chemicals with much smaller Henry's constants. Gas film resistance must be considered for PCB volatilization.

The conclusion at 3-56 in the Report that there exists no seasonal dependence on gas exchange is not accurate. Both ice cover and temperature variations play a major role in volatilization, whereas wind does not. As the Report states at 3-55, "during the winter months when ice cover is extensive, the effective gas-exchange rate is reduced to near zero." At 3-56, it further states, " $K_L$  increases by approximately a factor of two between 0°C and 25°C as a result of the

temperature dependence of water viscosity." Both these observations are accurate. Wind, however, will not appreciably affect gas exchange in the Hudson River for reasons discussed above. The net effect is a significant seasonal variation in PCB volatilization.

#### 4. Analytical Issues (EPA Appendix C)

##### Pg 1 - 14.

The congener-specific PCB analysis method lists 126 congeners which can be measured, as listed in Table 1-4. Inspection of the list reveals some whose possible reported presence should be regarded with suspicion: PCBs 12 and 126 should appear in Aroclors at very low levels, and their ECD response factors are low, making any reported detection suspect, especially as they have no *ortho*-chlorines and would not be expected to build up as bacterial dechlorination products of other, more abundant congeners. PCB 20 coelutes with PCB 33 on the HP-5 column and with PCB 28 on the octyl column, and would therefore appear difficult or impossible to quantify in the system described.

PCBs 23, 58, 69, 96, 140, 143, 169, and 184 have been found to be present at only trace levels in Aroclors, and are unlikely dechlorination products, (Frame, G.M., Cochran, J.W., and Bøwadt, S.S., J. High Res. Chromatogr., 19, (1996) 657 - 668), so any reported values of these should be viewed with skepticism.

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Principal target congeners are listed as **1, 4, 8, 10, 18, 19, 28, 52, 101, 118, 138**, and 180. Those in bold and underline have some analytical problems acknowledged in the report and additional ones noted here below.

Those underlined only are measurable only with the octyl/Apiezon system, and some of the values might be affected by the problems of retention time instability noted both by Aquatec and GE-CRD in 1993 with octyl columns.

**PCB 1.** This is a critical congener contributing substantially to the dechlorination index defined by PCBs 1,4,8,10 and 19 *using dechlorination products only*. PCB 1 has a very low ECD relative response factor, and interferences or substandard detector operation can introduce large errors into its quantitation. In section A.5.4, mention is made that SDG 169803 samples did not display peaks for BZ-1 on the octyl column, but the results from the HP-5 column were accepted on the grounds that the peak is expected. The octyl non-detect probably represents substandard operation of the detector on that column at that time rather than a column problem, and highlights the potential for detection and quantitation problems for this congener when using ECD quantitation.

**PCB 8.** This congener was separable from PCB 5 on octyl/Apiezon L only, and considerable problems in quantitation confirmation were encountered until the coelution criterion with PCB 5 was relaxed.

**PCB 18.** This is a critical congener assessing the amount of Aroclors 1016/1242 present. Data had to be requalified for this congener (see pg A-26) based on the known general presence of this in these sediments, and GC-ITD confirmation. Note however that quantitation of this congener is suspect, even if its presence is reasonable on the grounds of its general appearance in these sediments and the GC-ITD confirmation. In section A.5.2.7 it is stated that "TAMS/Gradient considered quantitative differences between the GC-ITD and GC-ECD results less than a factor of 5 acceptable, while differences greater than five times were considered unacceptable and associated results rejected." Quantitative uncertainty of this magnitude may not require rejection of a finding of detection of this key congener, but it renders its use in quantitative modeling highly suspect.

**PCB 118.** When the shift was made from octyl to Apiezon L, the potential for a small difference due to coelution with PCB 122 on Apiezon which does not occur on octyl was ignored. This will likely cause only a minor quantitative error.

**PCB 138.** The fact that PCB 138 coelutes on both octyl and HP-5, but not on Apiezon L, with substantial amounts of PCB 163 when they come from Aroclors 1254 or 1260, was not recognized. This could cause discrepancies between data collected before and after 1993, when the shift from octyl to Apiezon L was made. In some fish the relative rates of metabolic clearance of 138 and 163 differ strongly, so failure to realize that both could be present in the peak in varying amounts can result in quantitative difference errors if calibration was only against a 138 standard.

In the listing of 126 congeners measurable in the dual column system in Table 1-4, it is not clear why PCB 46, 2,2',3,6-tetrachlorobiphenyl, (present at ~0.4 weight% in Aroclor 1242, and cleanly resolvable from all other Aroclor congeners on both the HP-5 and octyl columns) was dropped from the list of non-target congeners as noted at the top of page A-12. This congener should have been clearly identified and reported in this study.

Section A.5.2.2. pg. A-12.

In the corrections to relative response factors obtained by measurement of the actual congeners in 1993 and 1994 for congeners previously quantified only against the PCB 52 response, there is no indication of how stable and comparable the previous responses being corrected actually were. Individual congener's ECD response factors can easily vary by as much as a factor of 2 on different detectors at different times, especially if temperature and/or carrier make-up flows are changed. One needs to know how well these variables were controlled over the whole period of data gathering to assess how consistent the quantitation and the quantitative correction which was retroactively applied to the non-target congeners is.

On pg A-3 it is stated for core tops collected in 1992 that "RPI dried and archived core tops (0-2 cm) from these cores for eventual PCB congener analysis." Aquatec subsequently analyzed a small subset. The behavior and congener distributions of PCBs in the topmost layers of Hudson River sediments is critical to evaluation of competing models of their fate and transport. How were these samples dried? Excessive drying, especially in air with heat, can result in uncontrolled losses of *mono-* and *di-* chloro PCBs which are major components of EPA's dechlorination index.

On pg. A-4 appears the statement "Aquatec extracted sediment samples with hexane, and performed applicable cleanup procedures prior to analysis by GC/ECD, as detailed in Appendix A3 of Phase 2A SAP/QAPP." Reference to the latter document reveals that the protocol for sediments requires Soxhlet extraction with hexane/acetone. Which solvent was used? Hexane extraction alone is inadequate to remove all PCBs from sediments unless they are previously dried so strenuously as to risk losing by evaporation substantial amounts of lower congeners, which are critical to assessing dechlorination processes. A call to Kurt Young of ITS Environmental in Colchester, VT (successor company to Aquatec Chemistry Division) on 3/14/97 elicited the statement that the information to answer this question was stored in a warehouse, not instantly accessible, and in any event would require EPA authorization to be made available. A request for information to resolve this question was made orally by phone to Douglas Tomchuck of the EPA on the same date. As of 4/1/97 no reply has been received by GE-CRD.

#### 5. Miscellaneous Issues

Report at 4-49: The document states that remobilization by sediment resuspension or porewater displacement can serve to return PCBs to the water column long after any point source contributions have been eliminated.

Response: EPA failed to determine the depths of the scour and porewater displacement contribution to the water column. Answering these questions will give an index of relative sediment PCB importance as a function of depth.

Report at 4-50: The document states that in general, aerobic processes affect only the lightest congeners, and are ineffective at altering heavy congeners under environmental conditions.

Response: It should be pointed out that several microorganisms including MB1, H850 and L400 have been enriched from the Hudson River and are capable of degrading PCBs containing as many as six chlorines. In addition, there are several later remarks suggesting significant amounts of degradation may have taken place in some instances. It should be pointed out that Flanagan and May (1993) showed that PCB metabolites have been found throughout the river even in relatively deep sediments and that these metabolites are short lived, with lifespans on the order of weeks (Fish, 1996) in physical models of the Hudson River. This points to the possibility that biodegradation does take place even in non-surficial sediments.

Report at 4-50: The document states that in the absence of oxygen, the only biotransformation possible is dechlorination.

Response: It has been repeatedly found in surface sediment microcosm sediments that both aerobic and anaerobic PCB biodegradation takes place (Fish, 1994; 1996). This has a significant impact because the surface sediments are where the newest releases of PCBs are settling and where the fish are getting their PCBs from. There is the potential for decrease in chlorine content and mass reduction in this layer.

Report at 4-51: The document states that the dechlorination process is more effective on the heavier PCB homologues.

Response: No generalizations about PCB dechlorination are valid except that there is no conclusive evidence for *ortho*- dechlorination in the Hudson River. A good review of the literature offered in Bedard and Quensen (1995).

Report at 4-51: The document states that there is no reduction in the total number of PCB molecules.

Response: There is ~3 mole% of PCBs that can be reductively dechlorinated to biphenyl and then easily degraded, namely the dioxin-like congeners including 34-4-CB, 4-4-CB, 34-34-CB, 345-34-CB. The dechlorination of these congeners would significantly reduce the risk associated with toxicological effects.

Report at 4-51: More chlorinated congeners are often associated with carcinogenic endpoints while the literature suggests that less chlorinated congeners are more likely to produce neurological impairment and developmental damage.

Response: The Battelle rat bioassay demonstrated that chlorine content does affect potential carcinogenic potential in rats, and that potency is markedly reduced as compared to previous estimates. This study served as a basis for EPA's recent reassessment of PCB cancer slope factors.

Furthermore there have been questions regarding the validity of the neurological impairment studies as these studies are generally considered flawed and they have not been reproduced in six separate attempts.

Report at 4-51: The document states that little evidence has been demonstrated for anaerobic degradation in sediments.

Response: As discussed above, the presence of metabolic PCB biodegradation products in anaerobic sediments is indicative of degradation processes even at low oxygen concentrations. The transient nature of these metabolites also indicates that at least some low level of the degradation process occurs.

Report at 4-52: The document states that the issue of anaerobic dechlorination will be revisited in a Phase 3 report, incorporating the results of both high and low resolution coring.

Response: This provides EPA and its contractors with an opportunity to develop and use more sensitive dechlorination indices.

Report at 4-88: The document concludes that the degree of *in situ* PCB dechlorination is not a function of time but rather dependent upon the total PCB concentration within the sediment.

Response: This conclusion is based in part on the use of an insensitive index of dechlorination, and the lack of understanding dechlorination biochemistry. A more detailed analysis of the data using a more appropriate index of dechlorination would show that concentration effects the rate as has been shown in lab studies (Abramowicz et al., 1993; Rhee et al., 1995) and microcosm studies (Fish, 1996). Sokol et al. (1994) and Rhee et al. (1995) indicate that the belief that *in situ* dechlorination may not occur in areas with relatively low PCB contamination is based on "dechlorination potential" and by definition is flawed. The phrase dechlorination potential is defined as relating to the length of the lag phase before which dechlorination occurred. This definition is not an indication of the dechlorination potential of a congener at a given concentration, but an indication of the acclimation time for anaerobic microorganisms to respond in laboratory studies. Note that this investigation only addressed BZ 138 and BZ 21. In the case of BZ 138 which is 0.15-0.54 wt % of Aroclor 1242, no dechlorination was detected below 35 ppm, but the investigators probably did not run the experiment long enough to overcome the lag time for acclimation observed in these experiments. In comparison, these investigators looked at the concentration effects of dechlorination of BZ 21, which does not exist in Aroclor 1242, but they did show a 70% decrease in concentration in 7.5 months of incubation. Even at 4 ppm in the latter paper, the concentrations used to evaluate the concentration were somewhat high, but complement rates found by Abramowicz et al. (1993) who used a mixture of Aroclors 1242, 1254 and 1260, and Fish (1996) who used much lower concentrations of Aroclor 1242 in test tube microcosms. When all of these data are combined, they produce an interesting correlation that passes through the origin as discussed above.

Report at 4-52: The document introduces the concept of measuring the degree of dechlorination resulting from PCB storage based on PCB sources and usage.

Response: This dramatically overestimates the usefulness of simply comparing final products to the starting congener mix and underestimates the complexity of the task. It ignores the fact that there are a variety of selectivity processes and sets the stage for using an inappropriate index of dechlorination. Even if this methodology did work, it would rely upon the homogeneous mixing of the Aroclors throughout the Hudson River with a single pair of reference points, namely Aroclor 1242 and completely dechlorinated Aroclor 1242. Earlier in the document, it is stated that as much as 25% of the load south of Waterford is Aroclor 1254. Thus, their estimate of molecular weight is underestimated by ~6%. This may at first glance appear to be trivial, but is most likely part of the reason for the unusually low (<0% dechlorination) indices calculated for the lower Hudson River. There is also an extensive discussion of PCB partitioning to porewater and the water column on a congener basis. After such an extensive discussion on these principles, it is surprising that the indices of dechlorination do not account for "washout" of the lighter congeners from sediment and porewater. In fact, congeners used to calculate MDPR are up to 10x more likely to be lost to the water column than are the heavier ones.

Report at 4-49 to 4-56. The use of BZ 8 as an indicator peak itself poses some serious problems. First of all it is the most abundant congener in Aroclor 1242. Thus even at the onset of dechlorination, small changes in a large peak of the chromatogram will meet with uncertainty. In addition, if BZ 8 is dechlorinated to BZ 1 there would be no change in the MDPR.

Report at 4-56: The document states that MDPH is a measure of the number of affected PCB molecules.

Response: MDPH is a measure of the last one or two dechlorination steps for mixtures containing 3.26-3.7 chlorines/biphenyl. Dechlorination via processes H' and H that are active in the lower Hudson River (where the PCB concentration is generally lower) primarily attacks higher homologues and will not be picked up by this index of dechlorination. Therefore, a significant percentage of PCB molecules could be affected by these processes and still be missed by EPA's analysis.

Report at 4-57: The document states that due to the lack of *ortho*-chlorine removal, the dechlorination process is theoretically limited in its ability to reduce the PCB sediment inventory.

Response: The dechlorination processes that are known to occur in the Hudson River serve to reduce the ability of PCBs to bioaccumulate an important risk-reduction benefit. This also ignores the possibility of other loss mechanisms, such as photo-destruction and biodegradation. In fact, the latter two are mentioned later to account for the <25% of the PCB alterations in the lower river. If the Agency believes that these are the processes responsible for <25% of the PCB alterations in the lower river, there is no reason to believe that they are not also occurring in other parts of the river. Furthermore, Fish (1994, 1996), has shown that in surface sediments, combined reductive dechlorination and aerobic degradation serve to reduce a significant amount of mass in as short as 140 days. Both indices of dechlorination will tend to account for this as either no net mass loss or

even as mass gain (in the case of aerobic degradation with little dechlorination) as shown in MDPR vs.  $\Delta MW$  at low concentrations in the lower Hudson River samples.

Report at 4-59: The mean molecular weights of Phase 2 sediment samples with low concentrations of dechlorination products have been found to be close to that of Aroclor 1242, indicating that processes other than dechlorination have not greatly modified the sample PCB content.

Response: Alternatively, both higher and lower homologues are lost due to process H' and H or moderate process C, M or Q (as their chromatograms indicate) plus loss of lighter congeners from degradation and partitioning. The Agency's analysis could result in insignificant changes in MDPR and  $\Delta MW$ .

Report at 4-60: The document states that the sensitivity of MDPR has a larger range (relative to  $\Delta MW$ ), and thus is more sensitive to changes in the PCB congener composition.

Response: The congeners used to measure the MDPR have the lowest response factors by electron capture detection and are the most insensitive measure and thus most susceptible to uncertainty, especially for BZ 1. In addition, any dechlorination due to *para* attack on BZ 8 will not be evident from the calculation. This is 7.65 weight percent of the total PCBs in Aroclor 1242.

Report at 4-62: The document states: "The Lower Hudson sample MDPRs tend to cluster just below the Aroclor 1242 value of 0.14. The mean MDPR for the Lower Hudson is 0.11, suggesting the presence of a minor contribution by heavier Aroclors, or more likely, possible loss of BZ 1, 4, 8, and 19 prior to deposition due to their generally greater solubility and degradability. The congener pattern comparisons made in Chapter 3 (Subsection 3.3.3), suggest that both processes probably occur to some degree. It is important to note the absence of any significant degree of dechlorination in the sediments of the Lower Hudson. Based on this observation, it would appear that dechlorination will not decrease the sediment PCB inventory of the Lower Hudson.

Response: The paragraph immediately discusses the Upper Hudson and ignores the possibility that same loss mechanisms (partitioning and degradation) would reduce mass. It is scientifically invalid to have one set of paradigms for one reach of the river and another set for other parts.

Report at 4-65: The document states that there is a maximum decrease of 26% mass due to dechlorination.

Response: This does not account for any of the degradation that was suggested earlier in the document, for which Flanagan and May (1993) have found evidence. Furthermore, Fish (1994, 1996) have shown this in a physical model of the Hudson River in the laboratory.

Report at 4-69: The document states that no significant change in  $\Delta MW$  occurs in PCB concentrations less than 30000 ug/kg.

Response: If there were slow steady-state dechlorination with steady washout of mono-trichlorobiphenyls, one would expect the plots of  $\Delta MW$  vs. PCB concentration to look as they do.

Report at 4-70: This presents a discussion on the age of sediments and degree of dechlorination as a function of sediment age. The document does not address the upstream source and low-level recent contamination of the newest sediments. Also the "sampling" is skewed: there are >2x the number of "new sediment samples" than "old sediments" used to construct Figure 4-28a. Furthermore, the discussion of concentration effects on dechlorination should take into account the different processes and end products expected as a function of concentration. In particular, processes B,B' and C are common in the Upper Hudson and can lead to non-selective extensive dechlorination, whereas processes H' H and A are more selective with different end products.

Table C-1. Species-Characteristic PCB Alteration Patterns Observed in the Hudson River.

| <u>Family</u>                  | <u>Common name</u> | <u>abbr.</u> | <u>Species name</u>            | <u>Alt'n. Pattern</u> |
|--------------------------------|--------------------|--------------|--------------------------------|-----------------------|
| Lampreys (Petromyzontidae)     | Sea Lamprey        | SLP          | <i>Petromyzon marinus</i>      | AP-PET                |
| Freshwater Eels (Anguillidae)  | American Eel       | AME          | <i>Anguilla rostrata</i>       | AP-ICT                |
| Herrings (Clupidae)            | American Shad      | AMS          | <i>Alosa sapidissima</i>       | None                  |
| Bullhead/Catfish (Ictaluridae) | Brown Bullhead     | BRB          | <i>Ictalurus nebulosus</i>     | AP-ICT                |
|                                | Yellow Bullhead    | YBH          | <i>Ictalurus natalis</i>       | AP-ICT                |
|                                | White Catfish      | WCF          | <i>Ictalurus catus</i>         | AP-ICT                |
| Suckers (Catostomidae)         | Northern Hogsucker | NHS          | <i>Hypentelium nigricans</i>   | AP-CAT                |
|                                | White Sucker       | WSR          | <i>Catostomas commersoni</i>   | AP-CAT (a)            |
| Minnows (Cyprinidae)           | Carp               | CAR          | <i>Cyprinus carpio</i>         | None                  |
|                                | Goldfish           | GLF          | <i>Carassius auratus</i>       | AP-ICT                |
|                                | Golden Shiner      | GSH          | <i>Notemigonis crysoleucas</i> | None                  |
|                                | "Minnows"          | MMM          | <i>Cyprinia spp.</i>           | None                  |
|                                | Fathead Minnow     | FHM          | <i>Dimorphales promelas</i>    | None                  |
| Pikes (Esocidae)               | Chain Pickerel     | CHP          | <i>Esox niger</i>              | AP-ESX (a)            |
|                                | Northern Pike      | NOP          | <i>Esox lucius</i>             | None                  |
| Codfish (Gadidae)              | Atlantic Tomcod    | ATT          | <i>Microgadus tomcod</i>       | AP-ICT                |
| Temperate Bass (Moronidae)     | Striped Bass       | STB          | <i>Morone saxatilis</i>        | None (b)              |
|                                | White Perch        | WPR          | <i>Morone americana</i>        | None (b)              |
| Sunfishes (Centrarchidae)      | Largemouth Bass    | LMB          | <i>Micropterus salmoides</i>   | None (b)              |
|                                | Smallmouth Bass    | SMB          | <i>Micropterus dolomieu</i>    | None (b)              |
|                                | Rock Bass          | RKB          | <i>Ambloplites ropestris</i>   | None                  |
|                                | Black Crappie      | BLC          | <i>Pomoxis nigromaculatus</i>  | None                  |
|                                | White Crappie      | WCR          | <i>Pomoxis annularis</i>       | None                  |
|                                | Bluegill           | BLG          | <i>Lepomis macrochirus</i>     | AP-LEP                |
|                                | Longear Sunfish    | LSF          | <i>Lepomis megalotis</i>       | AP-LEP                |
|                                | Pumpkinseed        | PKS          | <i>Lepomis gibbosus</i>        | AP-LEP                |
|                                | Redbreast Sunfish  | RBS          | <i>Lepomis auritus</i>         | AP-LEP (b)            |
| Perches (Perchidae)            | Yellow Perch       | YPR          | <i>Percha flara</i>            | None                  |
|                                | Walleye            | WAL          | <i>Stizostedion vitreum</i>    | None                  |
|                                | Tessellated Darter | TES          | <i>Etheostoma olmstedii</i>    | None                  |

(a) Distinction alteration seen in some, but not all, individuals

(b) Some individuals showed weak and variable AP-ICT-like depressions in PCB 70, and occasionally also P45D2B-like depressions in PCB 110, presumably altered in prey species.

| Parameter                    | Reference Distributions |                         |       |       |       |       | Upper Hudson River Means |          |             |          |             |          |             |          | Lower H.R. Means |          |             |          |
|------------------------------|-------------------------|-------------------------|-------|-------|-------|-------|--------------------------|----------|-------------|----------|-------------|----------|-------------|----------|------------------|----------|-------------|----------|
|                              | Aroclor<br>90:10<br>Wt% | Dechlorination Patterns |       |       |       |       | 1977-1978                |          | 1990        |          | 1992        |          | 1993        |          | 1977-1978        |          | 1993        |          |
|                              |                         | A                       | B     | C     | H     | H'    | Mean<br>Wt%              | %<br>RSD | Mean<br>Wt% | %<br>RSD | Mean<br>Wt% | %<br>RSD | Mean<br>Wt% | %<br>RSD | Mean<br>Wt%      | %<br>RSD | Mean<br>Wt% | %<br>RSD |
| Footnotes --                 | 1                       | 2                       | 2     | 2     | 2     | 2     | 2                        | 3        | 4           | 5        | 6           | 7        | 8           | 7        | 8                | 7        | 8           |          |
| No. of Fish in Mean -        |                         |                         |       |       |       |       |                          | n=18     | n=29        | n=15     | n=36        | n=15     | n=45        |          |                  |          |             |          |
| <b>Homolog Distribution</b>  |                         |                         |       |       |       |       |                          |          |             |          |             |          |             |          |                  |          |             |          |
| % 1 Cl                       | .40                     | 8.51                    | 7.20  | 20.84 | .90   | 1.03  | .20                      | **       | .37         | **       | .21         | **       | .47         | **       | .04              | **       | .01         | **       |
| % 2 Cl                       | 12.96                   | 13.89                   | 33.76 | 48.01 | 15.77 | 10.79 | 3.88                     | *        | 1.80        | **       | 2.52        | *        | 2.26        | *        | 2.41             | **       | 1.44        | *        |
| % 3 Cl                       | 42.14                   | 31.72                   | 33.38 | 19.38 | 38.36 | 42.72 | 23.48                    |          | 18.38       |          | 24.35       |          | 18.79       |          | 18.56            |          | 16.93       |          |
| % 4 Cl                       | 30.95                   | 32.11                   | 16.02 | 5.95  | 23.88 | 28.75 | 45.44                    |          | 46.19       |          | 46.26       |          | 48.90       |          | 43.79            |          | 36.84       |          |
| % 5 Cl                       | 9.05                    | 8.79                    | 5.81  | 2.66  | 11.89 | 11.28 | 15.95                    |          | 19.54       |          | 15.95       |          | 21.53       |          | 20.02            |          | 24.35       |          |
| % 6 Cl                       | 3.88                    | 3.83                    | 3.03  | 2.01  | 6.50  | 3.64  | 8.42                     |          | 10.26       |          | 7.69        |          | 7.04        |          | 11.25            |          | 13.95       |          |
| % 7 Cl                       | .81                     | .85                     | .55   | .70   | 1.27  | 1.22  | 2.07                     |          | 2.66        | *        | 2.23        | **       | 1.61        |          | 3.26             |          | 4.88        | *        |
| % 8 Cl                       | .01                     | .18                     | .15   | .18   | .24   | .26   | .40                      |          | .55         | **       | .60         | **       | .36         | *        | .48              | *        | 1.33        | *        |
| % 9 Cl                       | .00                     | .05                     | .10   | .16   | .10   | .31   | .17                      | *        | .12         | **       | .15         | **       | .05         | **       | .17              | **       | .23         | *        |
| Mean %RSD all 2Cl-9Cl        |                         |                         |       |       |       |       | 38                       |          | 54          |          | 68          |          | 36          |          | 45               |          | 42          |          |
| <b>Isomer Ratios PCB/PCB</b> |                         |                         |       |       |       |       |                          |          |             |          |             |          |             |          |                  |          |             |          |
|                              | Mean                    | Mean                    | Mean  | Mean  | Mean  | Mean  | Mean                     | RSD      | Mean        | RSD      | Mean        | RSD      | Mean        | RSD      | Mean             | RSD      | Mean        | RSD      |
| <b>Trichlorobiphenyls</b>    |                         |                         |       |       |       |       |                          |          |             |          |             |          |             |          |                  |          |             |          |
| 18/28+31                     | .06                     | .10                     | .49   | 1.76  | .08   | .04   | .07                      | **       | .08         | **       | .02         | **       | .08         | *        | .06              | **       | .10         |          |
| 18/28+31                     | .68                     | .29                     | .43   | .97   | .93   | .55   | .15                      |          | .12         | *        | .13         |          | .16         |          | .27              | *        | .34         |          |
| 17/28+31                     | .31                     | .23                     | .42   | .27   | .48   | .33   | .21                      |          | .13         | *        | .13         |          | .12         |          | .22              | *        | .26         |          |
| 27/28+31                     | .06                     | .09                     | .28   | 1.18  | .10   | .06   | .10                      |          | .06         | **       | .03         | *        | .08         | *        | .11              | **       | .12         |          |
| 26/28+31                     | .08                     | .14                     | .32   | .33   | .21   | .18   | .18                      |          | .12         |          | .10         |          | .16         |          | .16              |          | .24         |          |
| 33/28+31                     | .43                     | .35                     | .22   | .36   | .20   | .12   | .11                      |          | .25         |          | .24         |          | .21         |          | .12              |          | .20         |          |
| 22/28+31                     | .19                     | .33                     | .07   | .10   | .15   | .07   | .11                      |          | .28         |          | .27         |          | .17         |          | .11              |          | .11         |          |
| <b>Tetrachlorobiphenyls</b>  |                         |                         |       |       |       |       |                          |          |             |          |             |          |             |          |                  |          |             |          |
| 52/49                        | 1.40                    | 1.36                    | 1.32  | 1.80  | 1.24  | 1.00  | .99                      |          | 1.29        |          | 1.24        |          | 1.01        |          | 1.06             |          | .97         |          |
| 47/49                        | .39                     | .56                     | .74   | 1.12  | .70   | .79   | 1.06                     |          | .72         |          | .64         |          | .51         |          | .85              |          | .56         |          |
| 44/49                        | 1.26                    | 1.37                    | .08   | .27   | .68   | .28   | .48                      |          | .78         |          | .98         |          | .51         |          | .64              |          | .44         |          |
| 40/49                        | .36                     | .34                     | .04   | .07   | .25   | .19   | .13                      |          | .15         |          | .16         |          | .08         | *        | .11              |          | .02         | **       |
| 74/49                        | .61                     | .73                     | .04   | .25   | .33   | .22   | .70                      |          | .94         |          | .83         |          | .78         |          | .50              |          | .38         |          |
| Adj. ratio 74/49             | .61                     | .71                     | .06   | .39   | .38   | .26   | .52                      |          | .58         |          | .62         |          | .52         |          | .34              |          | .26         |          |
| 77/49                        | .13                     |                         |       |       |       |       | .13                      |          | .12         | *        |             |          | .10         |          |                  |          | .03         |          |
| 70/74                        | 2.21                    | 2.76                    | 1.86  | 1.15  | 1.52  | 1.64  | .76                      |          | 1.89        |          | 2.30        |          | 1.41        |          | .72              | *        | 1.17        |          |
| <b>Pentachlorobiphenyls</b>  |                         |                         |       |       |       |       |                          |          |             |          |             |          |             |          |                  |          |             |          |
| 101/99                       | 1.69                    | 1.93                    | 3.07  | 3.04  | 1.80  | 1.89  | 1.31                     |          | 1.69        |          | 1.76        |          | 1.50        |          | 1.40             |          | 1.42        |          |
| 87/101                       | .87                     | 1.03                    | .53   | .35   | .33   | .22   | .49                      |          | .80         |          | .82         |          | .48         |          | .42              |          | .61         | *        |
| 101/110                      | .91                     | .53                     | .49   | .55   | .76   | .99   | 1.15                     |          | .71         |          | .68         |          | .96         |          | .99              |          | 1.08        |          |
| 99/110                       | .54                     | .28                     | .17   | .18   | .42   | .53   | .88                      |          | .42         |          | .41         |          | .64         |          | .67              |          | .75         |          |
| 97/110                       | .48                     | .29                     | .06   | .08   | .21   | .19   | .36                      |          | .31         |          | .28         |          | .36         |          | .25              |          | .28         |          |
| 87/110                       | .61                     | .54                     | .26   | .19   | .25   | .22   | .55                      |          | .57         |          | .55         |          | .46         |          | .41              |          | .63         | *        |
| 118/110                      | .98                     | .87                     | .63   | .72   | .89   | 1.13  | 1.69                     |          | 1.28        |          | 1.15        |          | 1.19        |          | 1.22             |          | 1.26        |          |
| 106/110                      | .59                     | .74                     | .17   | .21   | .25   | .31   | .69                      |          | .91         |          | .83         |          | .63         |          | .38              |          | .49         |          |
| <b>Hazachlorobiphenyls</b>   |                         |                         |       |       |       |       |                          |          |             |          |             |          |             |          |                  |          |             |          |
| 146/153                      | .14                     | .26                     | .00   | .73   | .15   | .28   | .22                      |          | .24         |          | .27         |          | .34         |          | .21              |          | .36         |          |
| 141/153                      | .18                     | .41                     | .00   | .00   | .12   | .07   | .12                      |          | .26         |          | .29         |          | .16         |          | .13              |          | .10         |          |
| 138+163/153                  | 1.10                    | 1.43                    | 3.83  | 1.81  | 1.04  | 1.17  | 1.29                     |          | 1.27        |          | 1.34        |          | 1.38        |          | 1.15             |          | 1.04        |          |
| 128/153                      | .25                     | .25                     | .17   | .09   | .19   | .16   | .22                      |          | .22         |          | .21         |          | .26         |          | .15              |          | .15         |          |
| 187/153                      | .11                     | .03                     | .00   | .06   | .09   | .07   | .09                      |          | .03         |          | .03         |          | .06         |          | .07              |          | .10         | **       |
| 156+171/153                  | .17                     | .42                     | .16   | .12   | .14   | .15   | .23                      |          | .32         |          | .38         |          | .19         |          | .14              |          | .12         |          |
| Mean %RSD (28 Ratios)        |                         |                         |       |       |       |       | 17                       |          | 30          |          | 26          |          | 22          |          | 29               |          | 38          |          |

- Mixture of Aroclors 1242:1254 in ratio of 90:10
- Means (n = ) of sediment core values: A (3); B (3); C (1); H (3); H' (1)
- 6 BRB, 12 LMB, 1977-78, Upper Hudson Mile 175
- 1 AME, 3 BLC, 3 CAR, 2 CHP, 1 LMB, 1 NOP, 2 PKS, 3 RBS, 3 RKB, 3 SMB, 3 WAL, 1 WSR, 3 YPR. Autumn 1990, Upper Hudson Mile 181
- 2 BRB, 2 CHP, 2 PKS, 2 RKB, 2 SMB, 2 WSR, 1 YPR. May 1992, Upper Hudson Miles 174, 188, 192
- 6 LMB, 13 PKS, 6 RBS, 6 TESS, 4 YPR. NOAA Autumn 1993, Upper Hudson Mile 182
- 5 BRB, 3 LMB, 2 SMB, 2 WCF, 3 WPR. 1977-78, Lower Hudson Miles 112, 126, 153
- 3 BRB, 3 LMB, 8 PKS; 6 RBS, 3 SMB, 3 WCF, 19 WPR. NOAA Autumn 1993, Lower Hudson Miles 143, 135, 123, 88, 40
- ADJ = 74/49 ratio adjusted for greater elution of PCB 49, as estimated from trichlorobiphenyl/tetrachlorobiphenyl ratio change
- \* Indicates RSD in range of 50% - 70%; \*\* indicates RSD > 70%

Table C-2. Mean Values of PCB Homologue Levels and Isomer Ratios in Upper and Lower Hudson River Resident Fish Collected 1977-1993.

| Isomer CI Level -<br>No. of Ortho- Cls - |            |             |       | Tetrachlorobiphenyls |       |       |       |       |       |       | Pentachlorobiphenyls |         |         |         | Hexachlorobiphenyls |         |         |         |         |         |
|--|------------|-------------|-------|----------------------|-------|-------|-------|-------|-------|-------|----------------------|---------|---------|---------|---------------------|---------|---------|---------|---------|---------|
|  |            |             |       | 1                    | 1     | 1     | 1     | 1     | 1     | 0     | 1                    | 1       | 1       | 1       | 2                   | 2       | 1       | 1       | 2       | 1       |
| BZ#/BZ#                                  |            |             |       | 56/49                | 60/49 | 63/49 | 66/49 | 67/49 | 74/49 | 77/49 | 105/110              | 114/110 | 118/110 | 123/110 | 128/153             | 138/153 | 156/153 | 157/153 | 158/153 | 167/153 |
| NOAA Station                             | River Mile | Species     | (no.) |                      |       |       |       |       |       |       |                      |         |         |         |                     |         |         |         |         |         |
| 2,3,4                                    | 192        | Pumpkinseed | (13)  | .37                  | .37   | .11   | 1.13  | .06   | .69   | .09   | .40                  | .07     | .82     | .01     | .26                 | 1.43    | .17     | .03     | .17     | .08     |
|  |            | All Species | (36)  | .42                  | .44   | .12   | 1.25  | .07   | .78   | .10   | .47                  | .09     | .90     | .01     | .26                 | 1.38    | .16     | .03     | .16     | .09     |
| 8  | 176        | Pumpkinseed | (5)   | .28                  | .26   | .08   | .85   | .04   | .55   | .05   | .33                  | .04     | .73     |         | .21                 | 1.35    | .13     | .02     | .12     | .07     |
|  |            | All Species | (11)  | .29                  | .29   | .09   | .89   | .04   | .59   | .05   | .39                  | .06     | .83     |         | .20                 | 1.31    | .13     | .02     | .11     | .06     |
| 10                                       | 143        | Pumpkinseed | (4)   | .21                  |       | .08   | .64   | .02   | .44   | .04   | .31                  | .03     | .76     |         | .16                 | 1.12    | .10     | .01     | .09     | .20     |
|  |            | All Species | (18)  | .20                  | .19   | .08   | .65   | .04   | .46   | .04   | .32                  | .04     | .81     |         | .15                 | 1.05    | .09     | .01     | .09     | .10     |
| 11                                       | 135        | White Perch | (4)   | .25                  | .18   | .09   | .74   | .05   | .56   | .04   | .29                  | .05     | .69     | .00     | .16                 | 1.11    | .10     | .02     | .11     | .06     |
| 12                                       | 123        | White Perch | (5)   | .18                  | .15   | .08   | .54   | .02   | .40   | .03   | .24                  | .04     | .71     |         | .14                 | .95     | .08     | .01     | .09     | .09     |
| 15                                       | 88         | Pumpkinseed | (4)   | .10                  |       | .06   | .31   | .00   | .24   | .01   | .17                  | .00     | .61     |         | .12                 | .92     | .07     |         | .07     | .04     |
|  |            | All Species | (19)  | .09                  | .10   | .08   | .42   | .02   | .31   | .01   | .23                  | .02     | .72     |         | .17                 | 1.08    | .08     | .02     | .09     | .11     |
| 17                                       | 40         | White Perch | (5)   | .12                  | .05   | .05   | .35   | .02   | .21   | .02   | .14                  | .01     | .52     |         | .13                 | .85     | .06     | .01     | .07     | .06     |

(a.) Ratios of PCB isomer levels as reported by Aquatech; not translated into Northeast Analytical equivalents as in Table 2.

Table C-3. Downstream Declines in 1993 NOAA Fish PCB Isomer Ratios (a.) that are Reduced by Subsurface Dechlorination Processes.

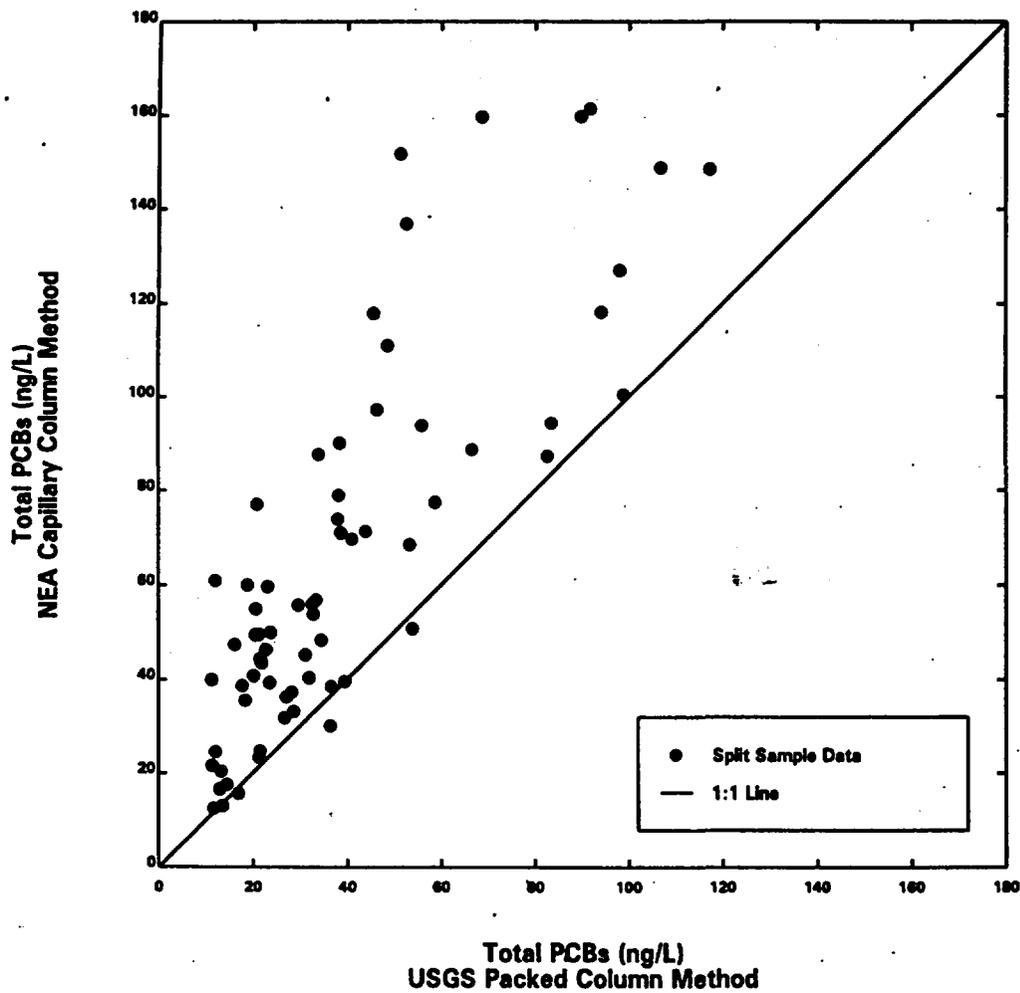


Figure A-1. Comparison of water column PCB concentrations calculated by the NEA capillary column method versus the USGS packed column method.

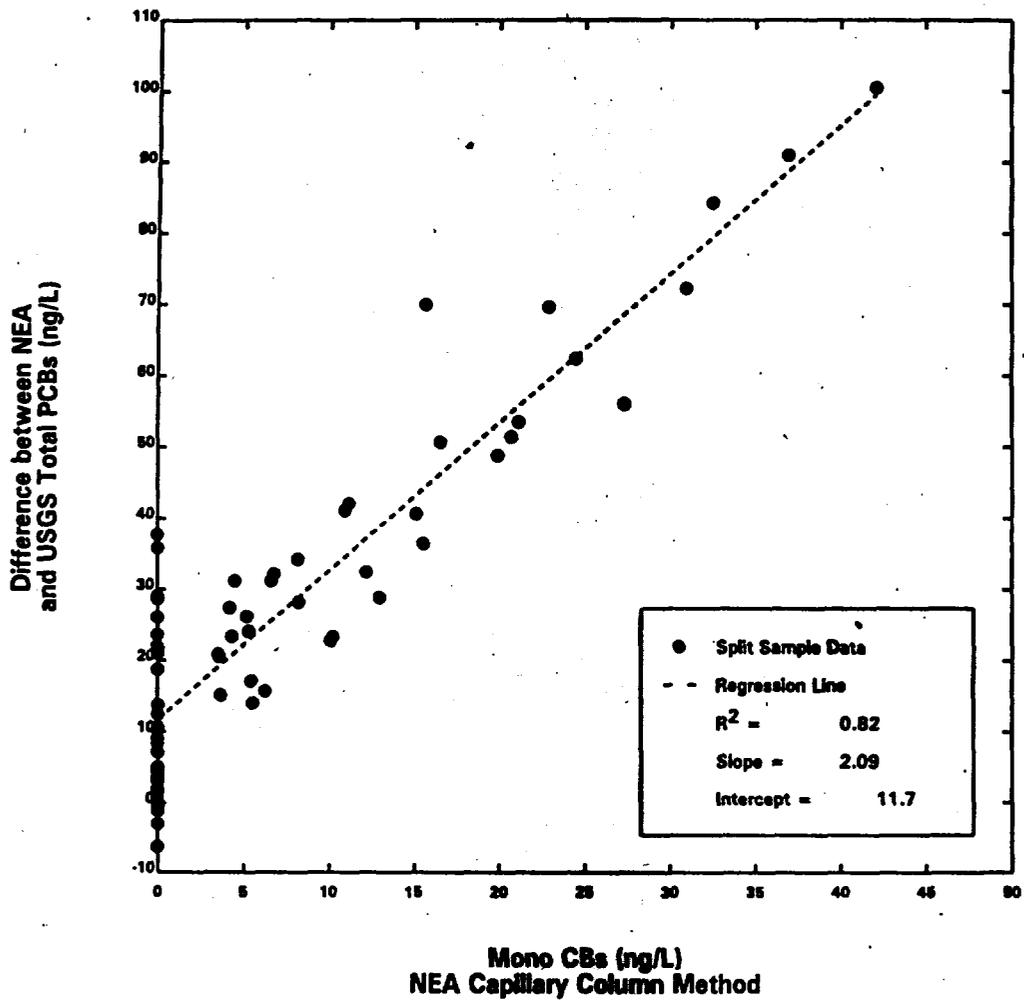


Figure A-2, The correlation of differences between NEA and USGS total PCBs and monochlorobiphenyls.

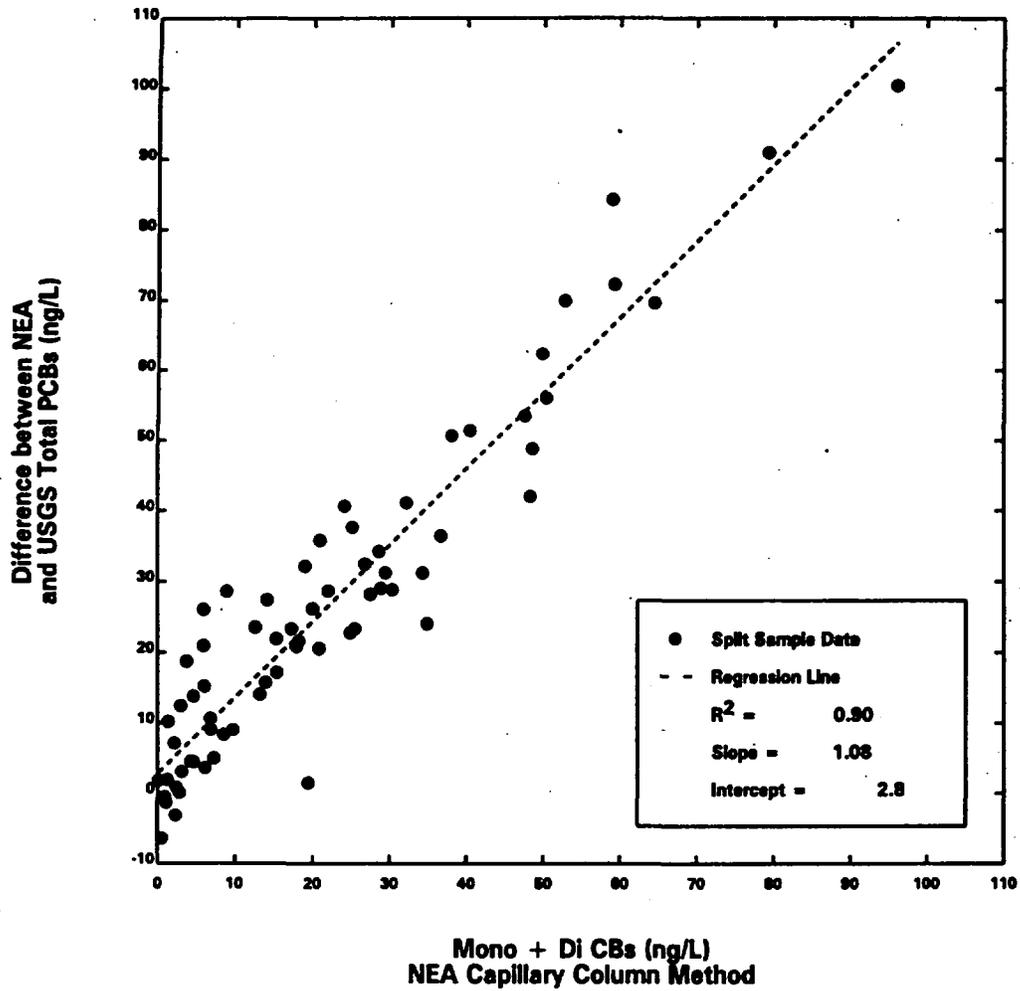


Figure A-3. The Correlation of differences between NEA and USGS total PCBs and monochlorobiphenyls plus dichlorobiphenyls.

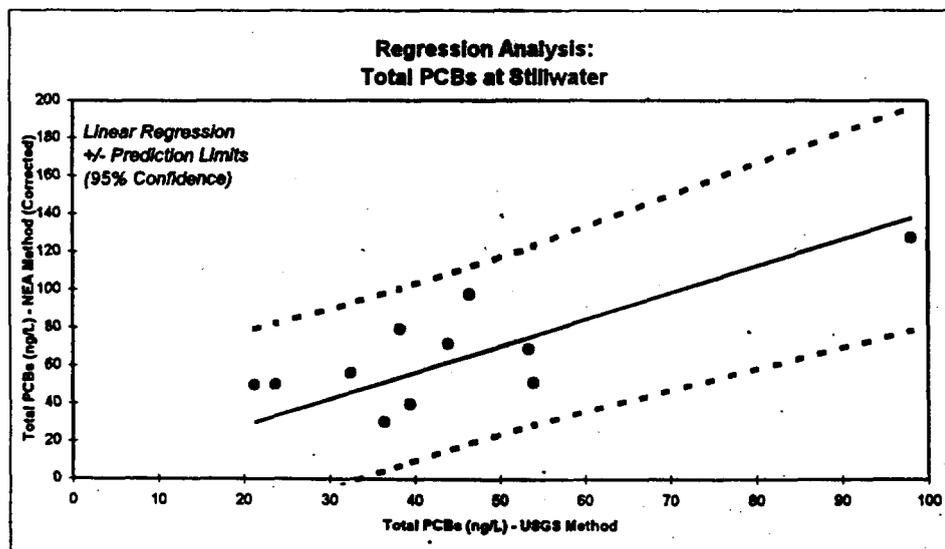
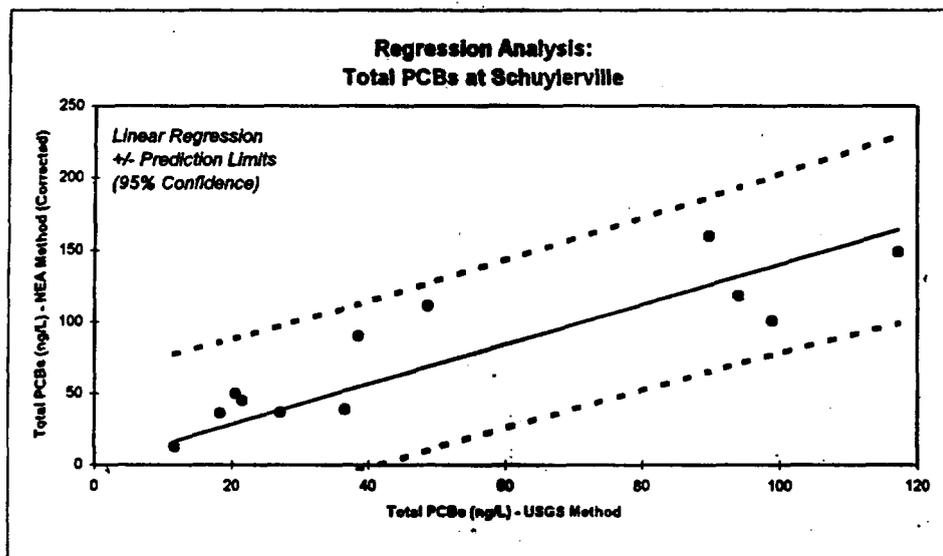
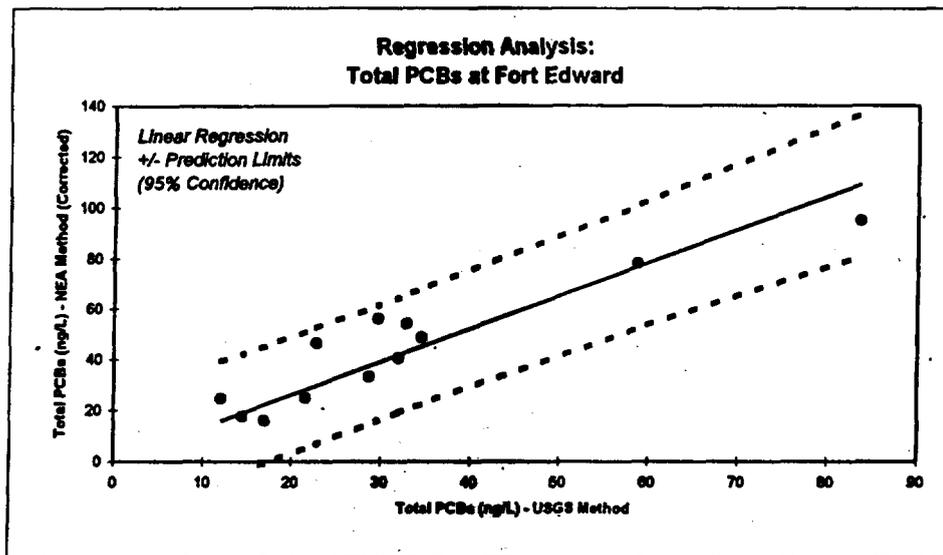


Figure A-4. Comparison of total water column PCB concentrations calculated by the NEA capillary column method versus the USGS packed column method at Fort Edward, Schuylerville and Stillwater.

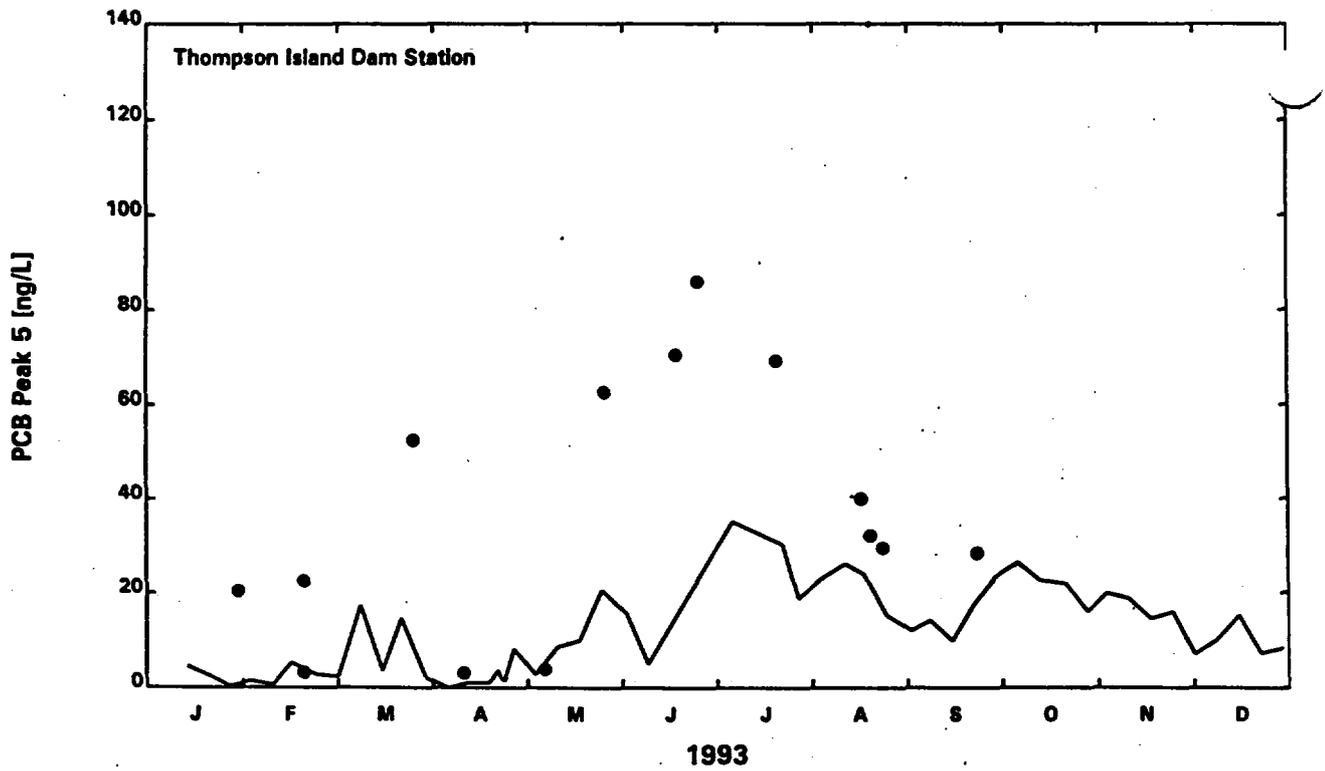
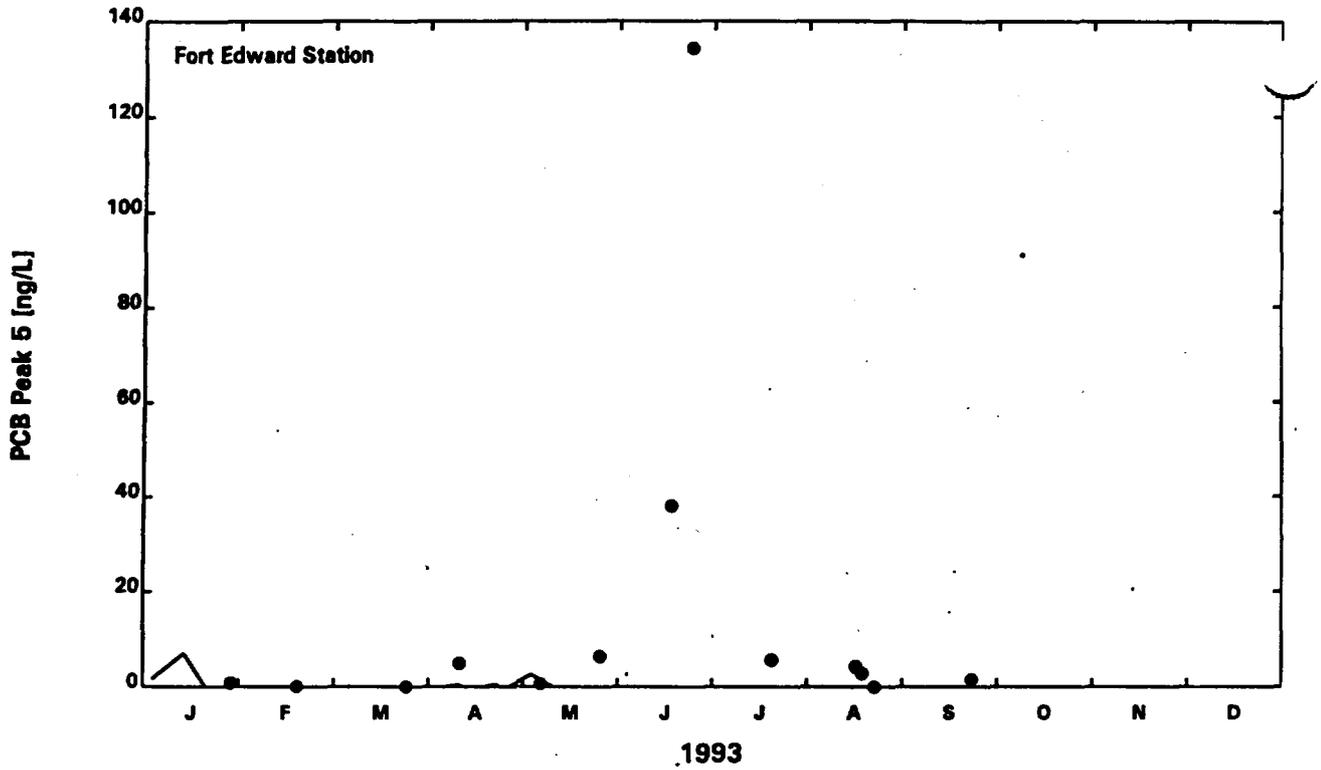


Figure A-5. Comparison of GE and EPA analyses of 1993 water column DB-1 capillary column peak 5 components (BZ#4 plus BZ#10) collected at Fort Edward and the Thompson Island Dam.

● EPA Data      — GE Data

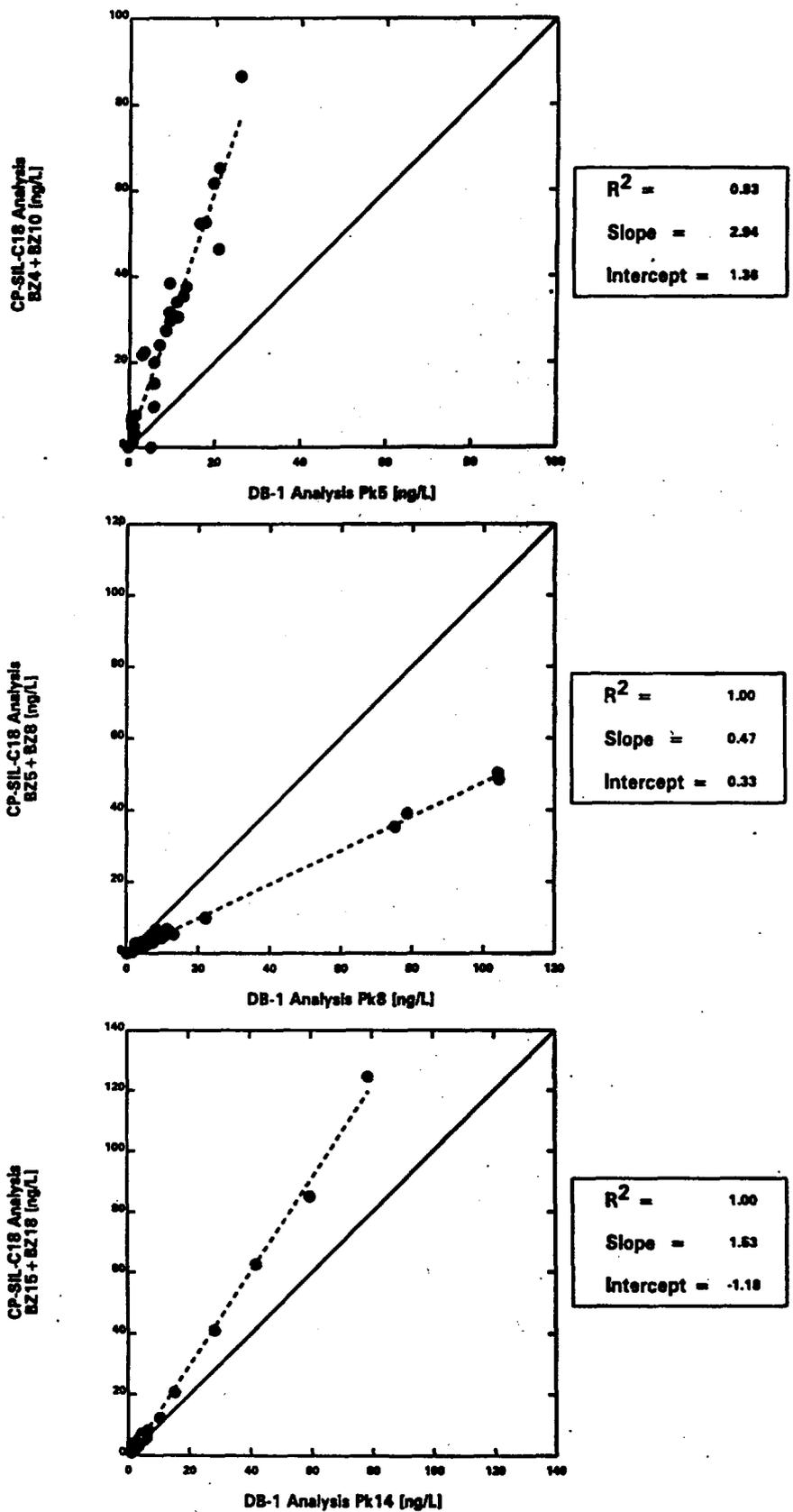


Figure A-6. Comparisons of top: CP-Sil-C18 BZ#4 plus BZ#10 analysis to DB-1 peak 5 analysis; middle CP-Sil-C18 analysis of BZ#5 plus BZ#8 to DB1 peak 8 analysis; bottom, CP-Sil-C18 analysis of BZ#15 plus BZ#18 to DB1 peak 14 analysis.

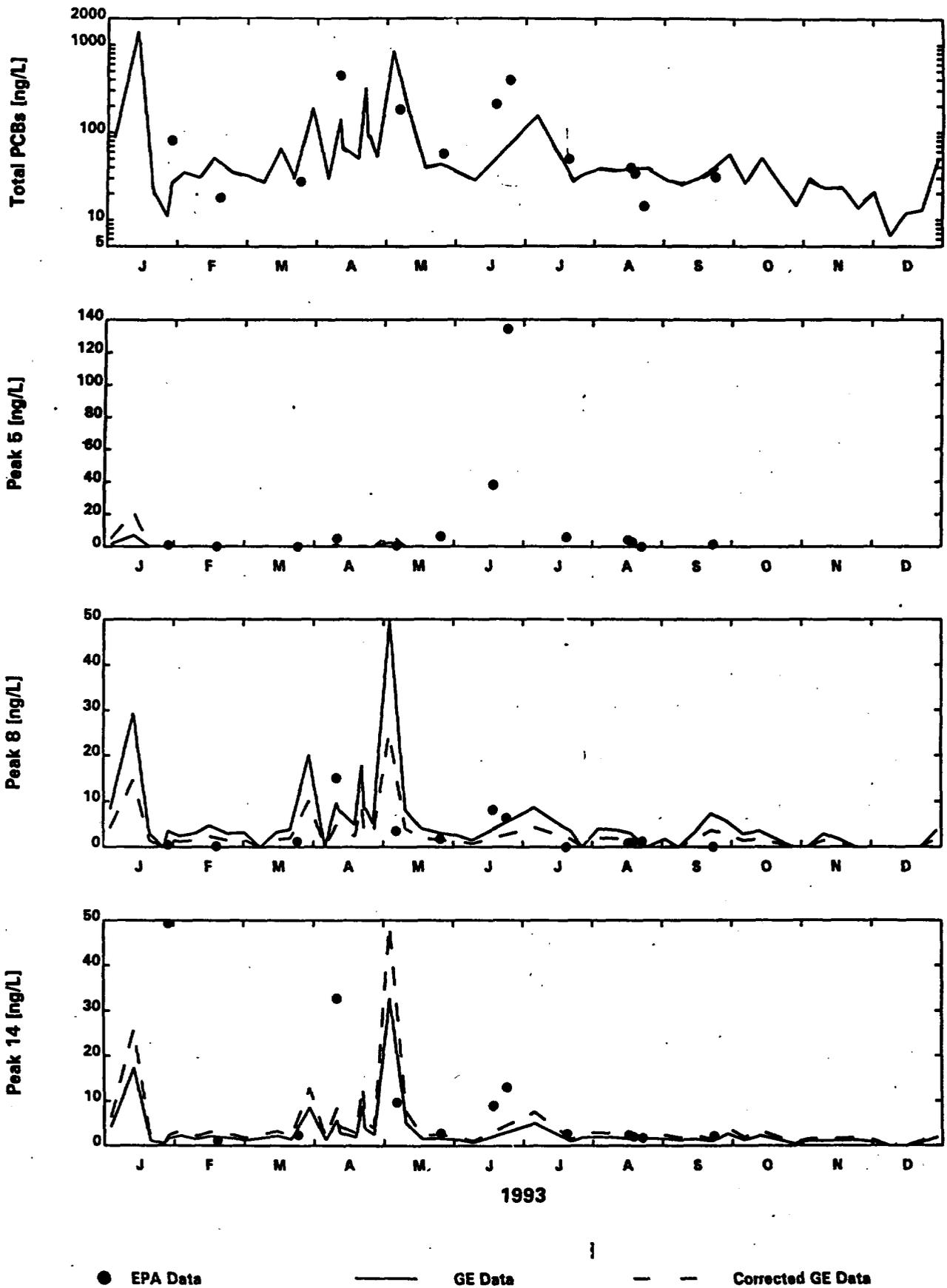


Figure A-7. Comparisons of EPA, GE and corrected GE temporal 1993 water column concentrations of total PCBs, peak 5 (BZ#4 plus BZ#8), peak 8 (BZ#8) and peak 14 (BZ#15 plus BZ#18) at Fort Edward.

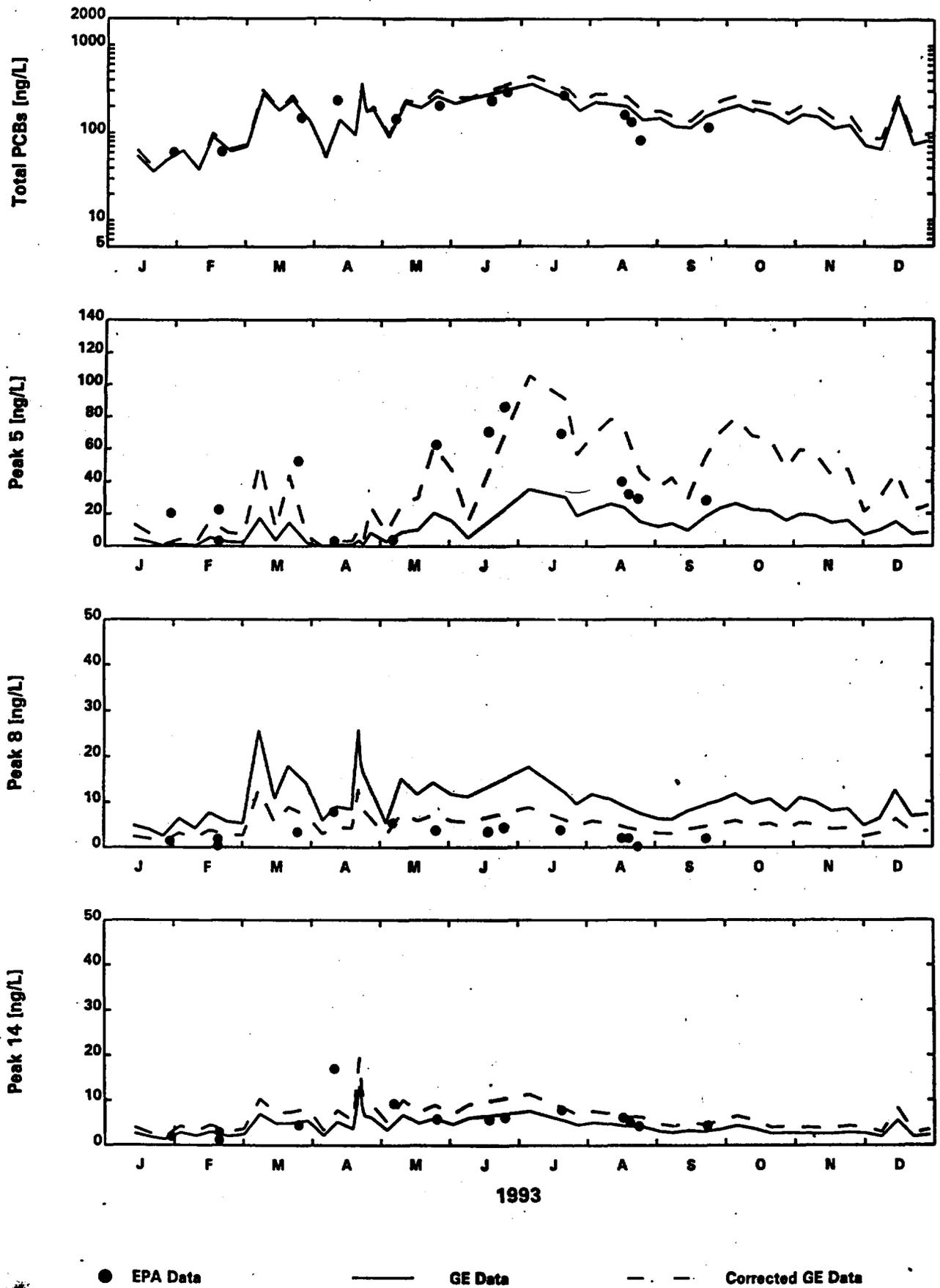
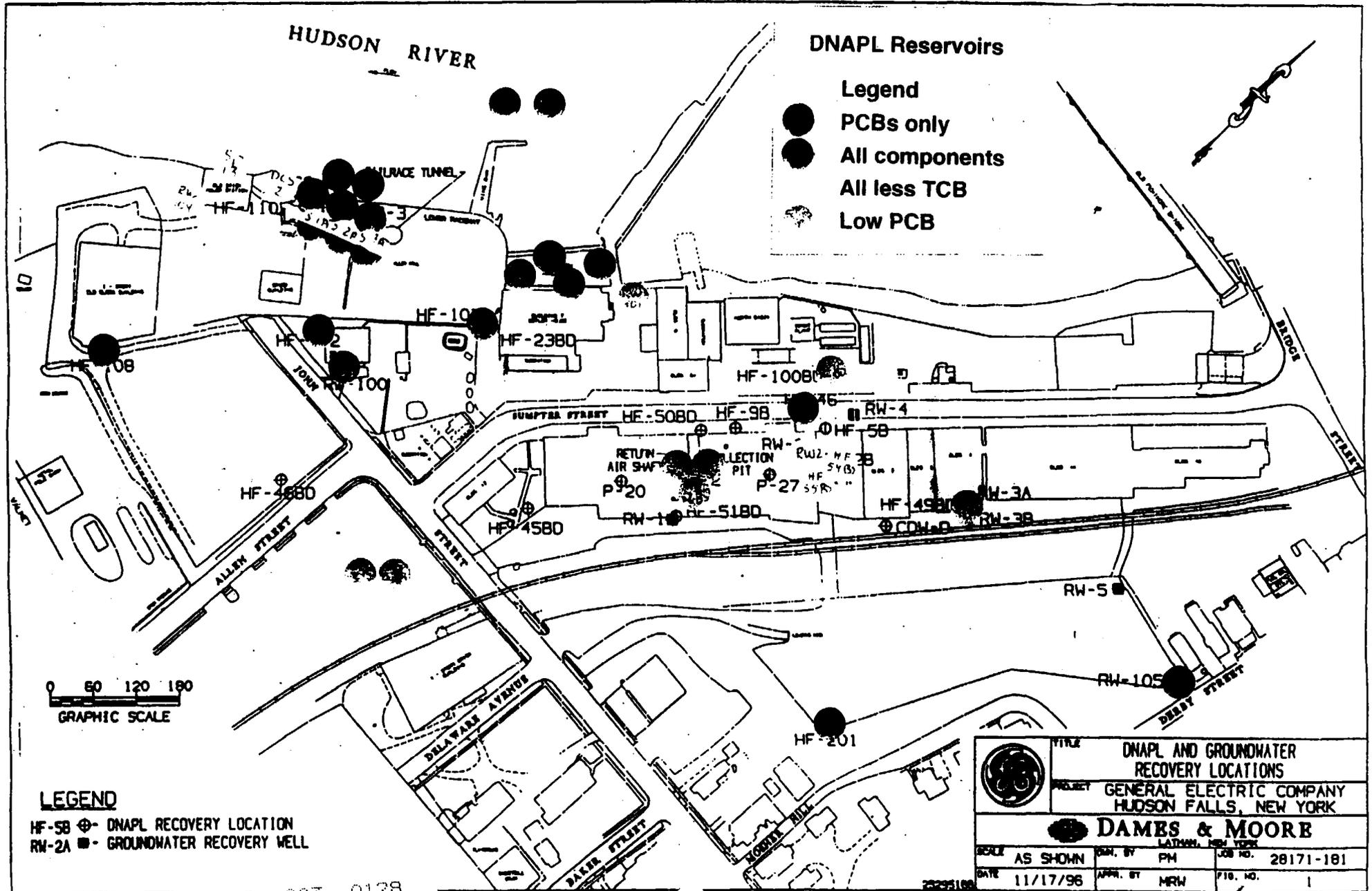
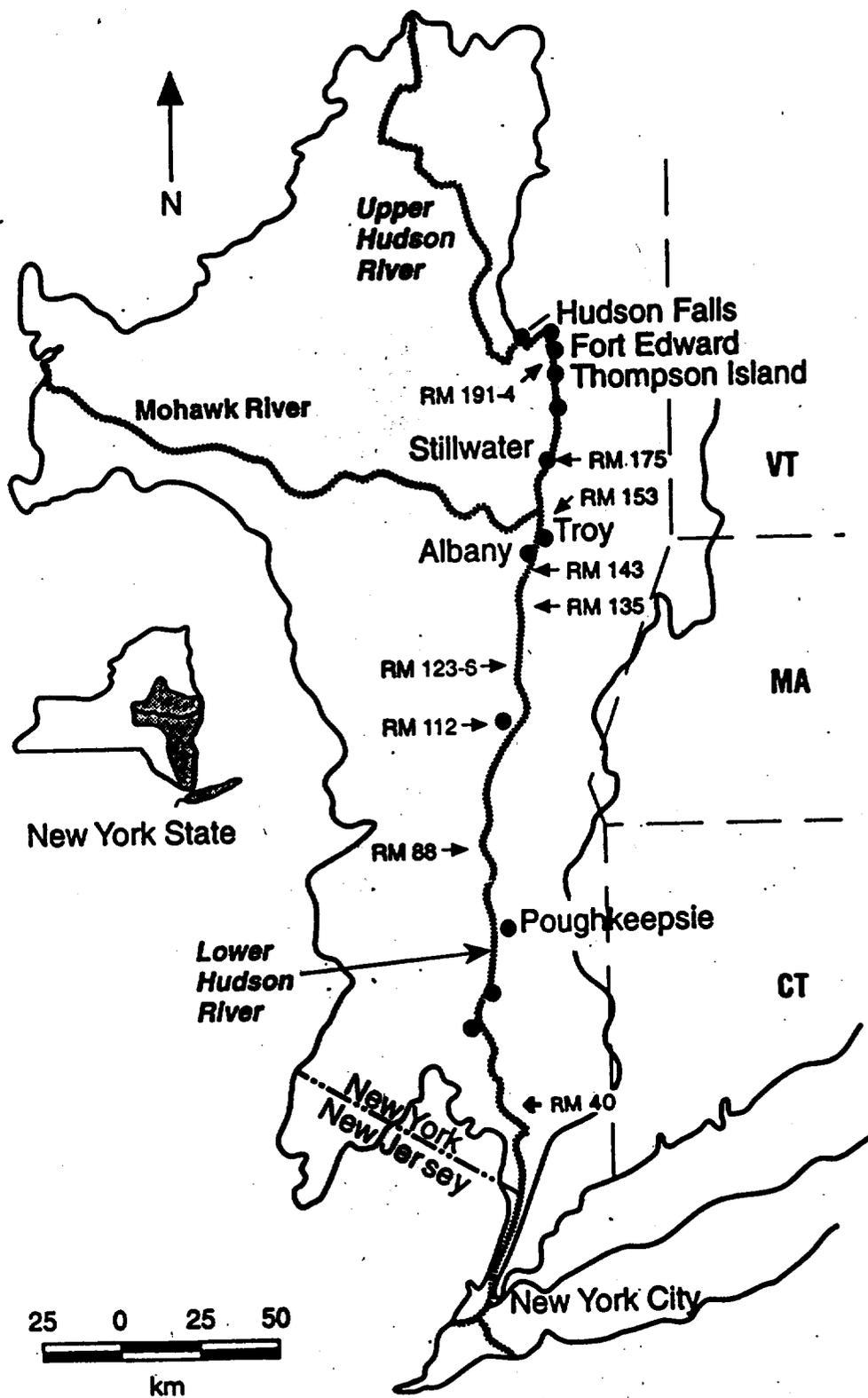


Figure A-8. Comparison of EPA, GE and corrected GE temporal 1993 water column concentrations of Total PCBs, peak 5 (BZ#4 plus BZ#8), peak 8 (BZ#8) and peak 14 (BZ#15 plus BZ#18) at the Thompson Island Dam.

Figure B-1. Map of Hudson Falls plant site indicating locations of DNAPL and groundwater recovery locations which are color coded for composition.





RM Indicates Fish Collection Site River Mile

Figure C-1. Hudson River Drainage Basin.

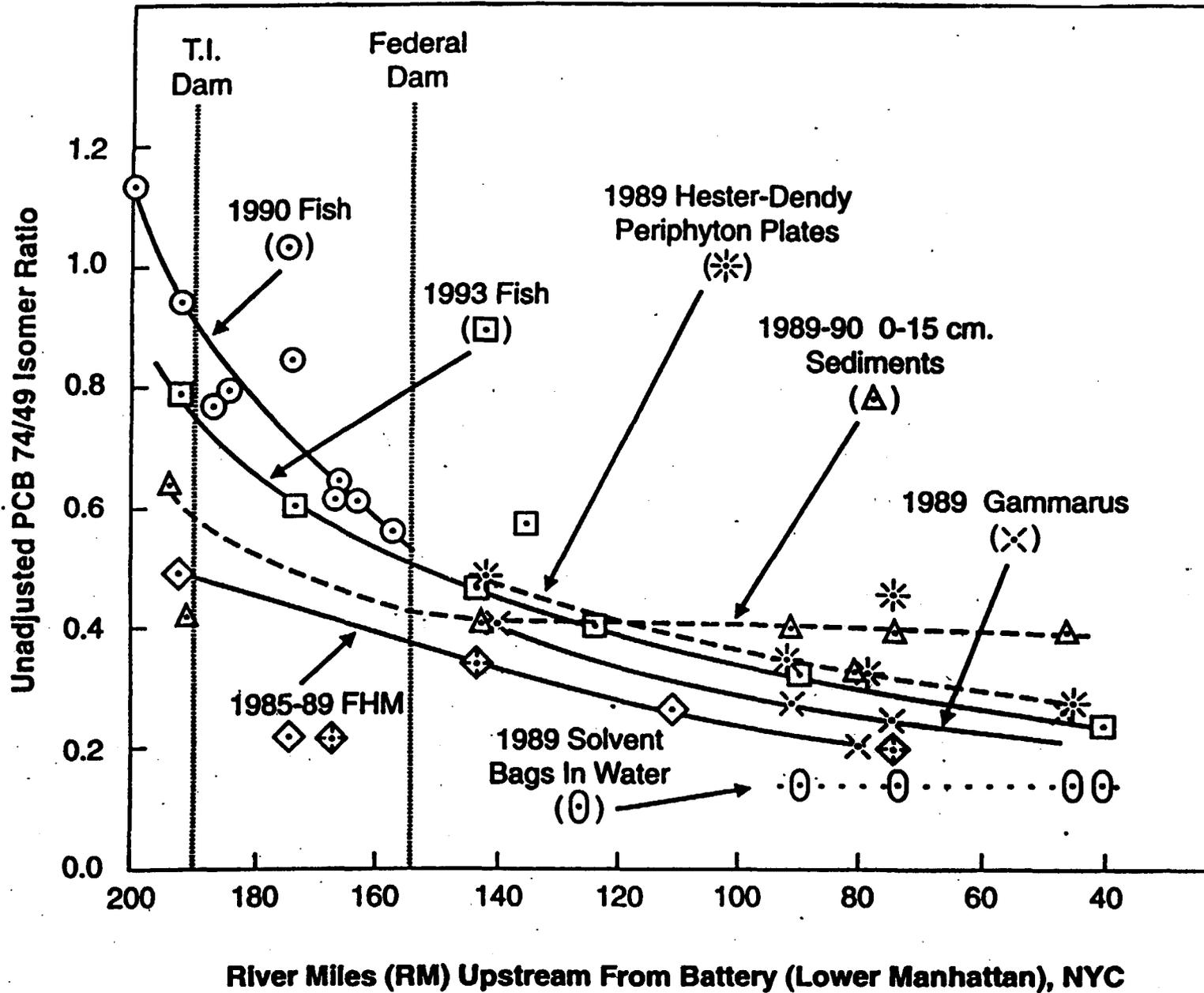


Figure C-2. Unadjusted PCB BZ#74/BZ#49 ratios in Hudson River Biota, Sediment Water, 1985-1993, River Miles 40-203.

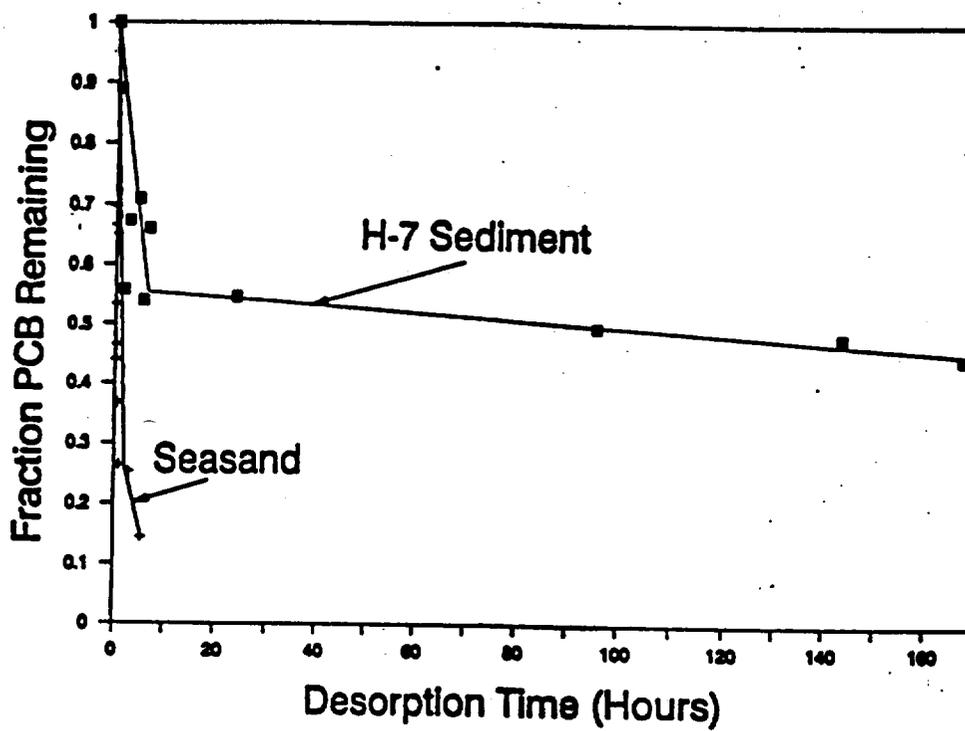


Figure D-1. Desorption of PCBs from H7 sediment compared to spiked sea sand.

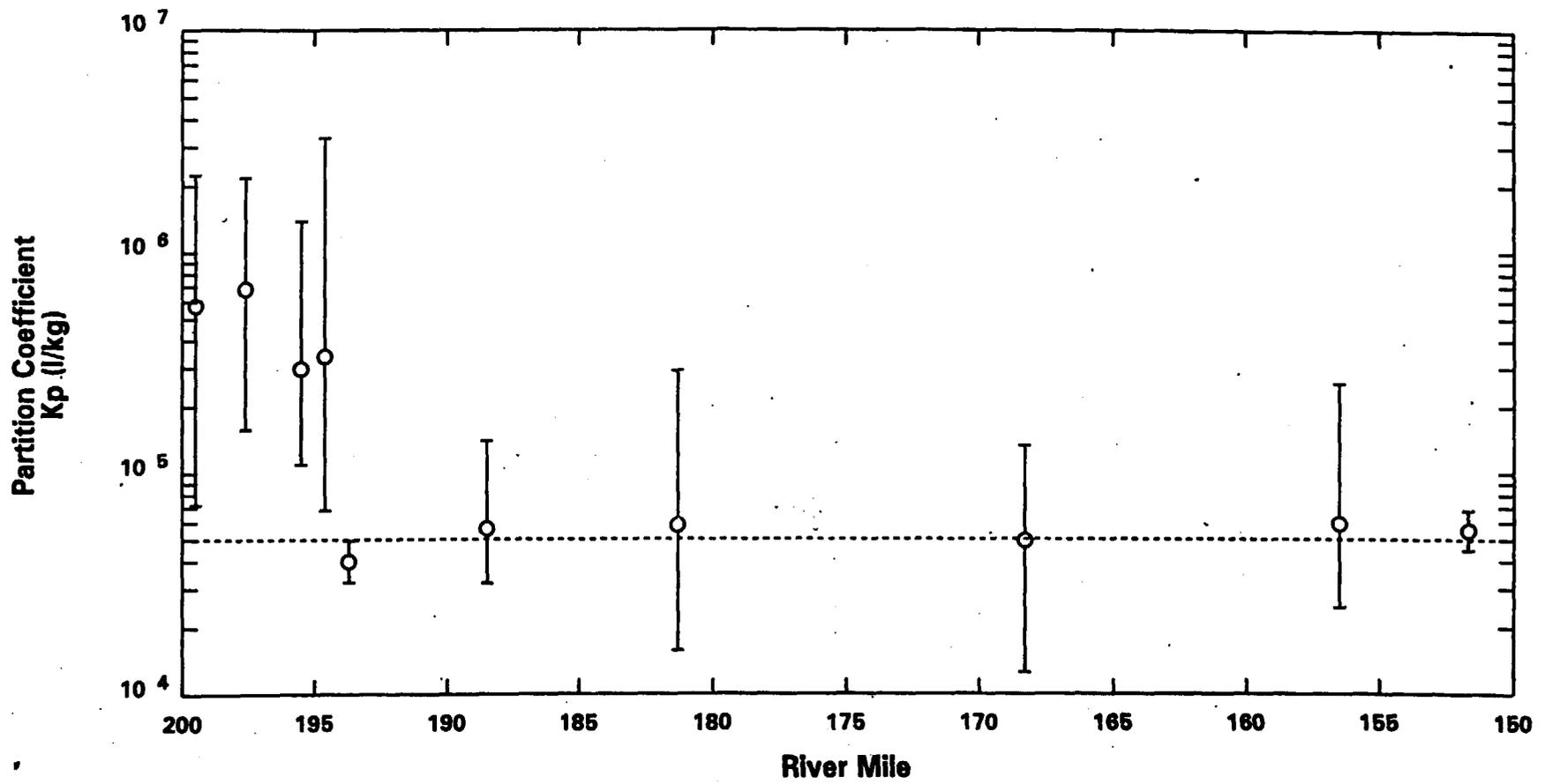


Figure E-1. Partition coefficients as a function of river mile calculated from EPA Phase 2 water column monitoring transect studies 2-6.

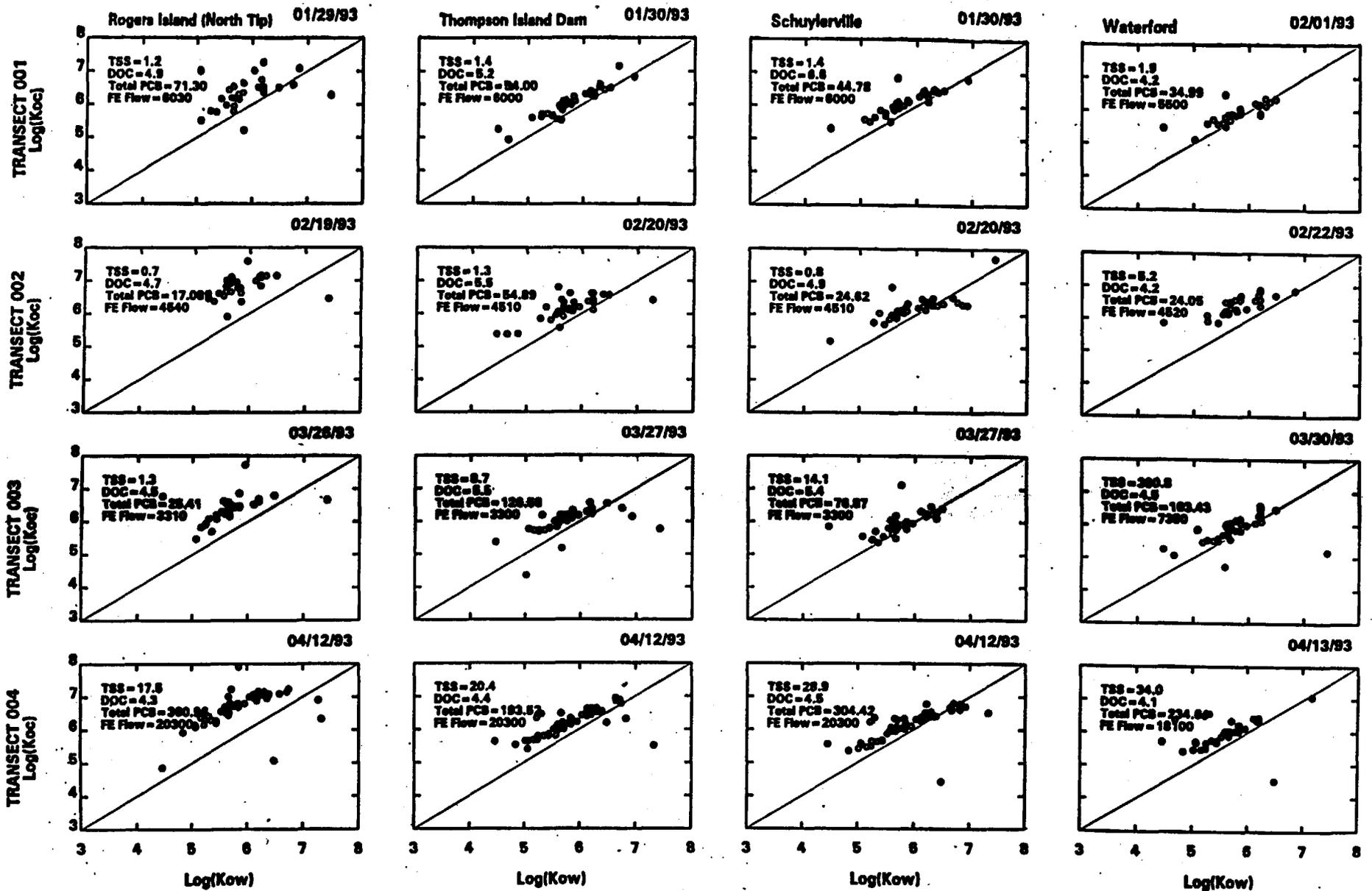


Figure E-2. The relationships between  $K_{oc}$  and  $K_{ow}$  at Rogers Island, the Thompson Island Dam, Schuylerville and Waterford from Transects 1-8; Tss in mg/L, Total PCBs in mg/L and Fort Edward in cfs.

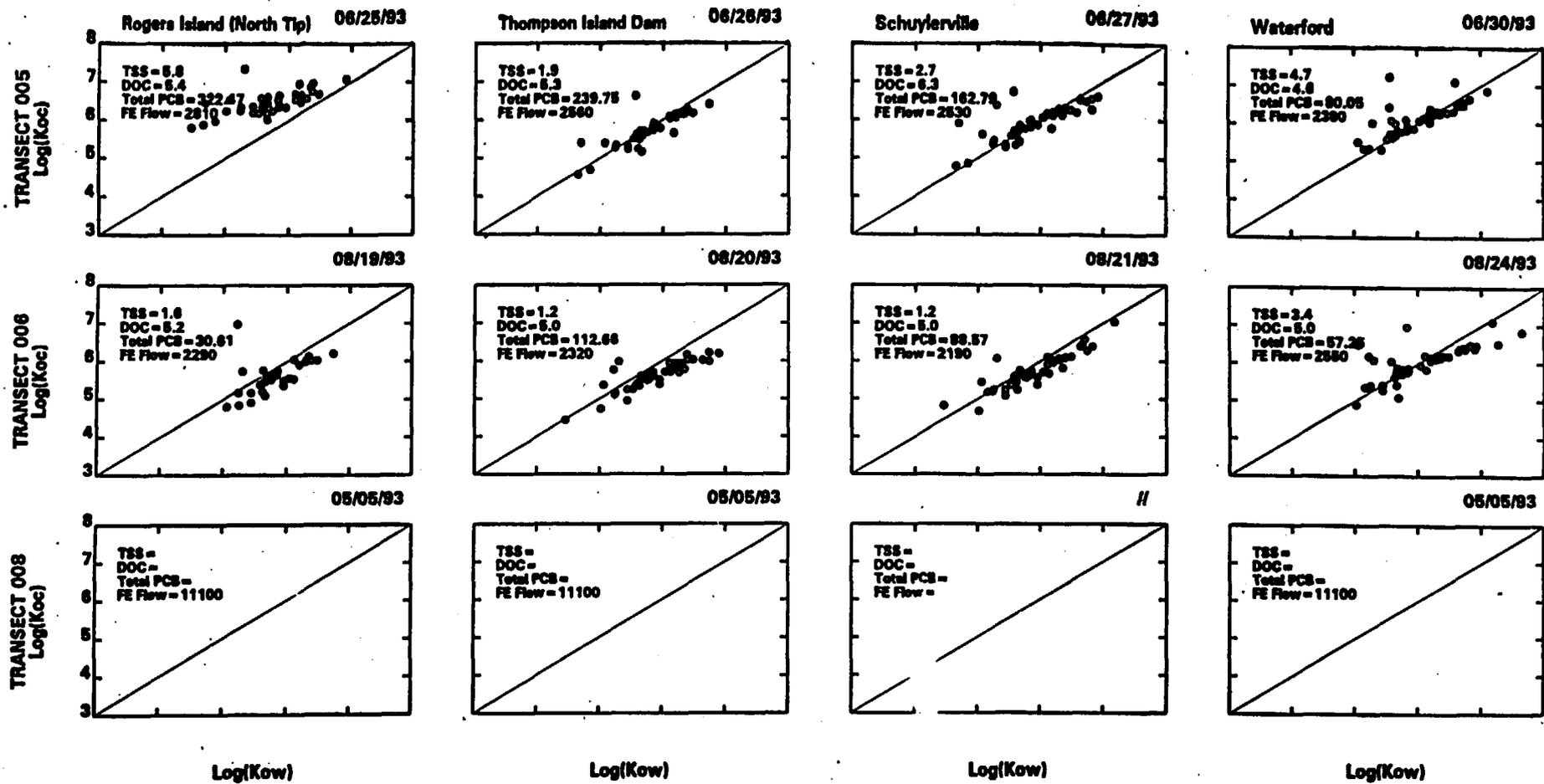


Figure E-2  
(continued).

The relationships between  $K_{oc}$  and  $K_{ow}$  at Rogers Island, the Thompson Island Dam, Schuylerville and Waterford from Transects 1-8; Tss in mg/L, Total PCBs in ng/L and Fort Edward flows in cfs.

HRP 003 0134

Log K<sub>oc</sub> as a function of inverse Temperature

Congener 10

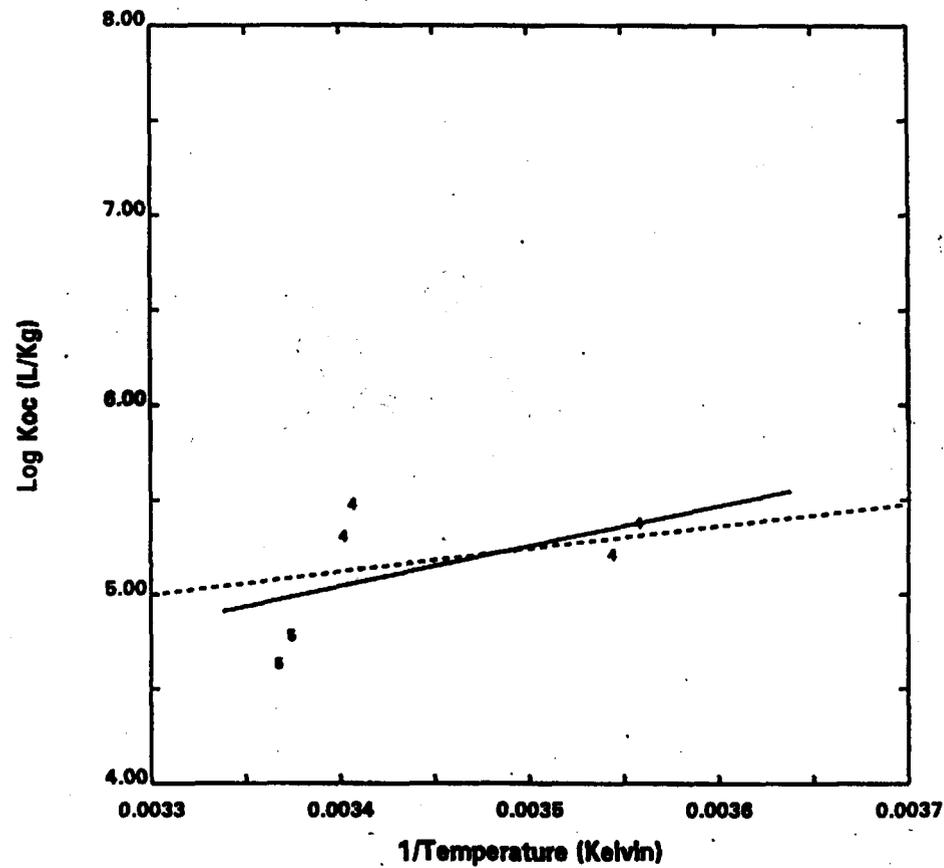
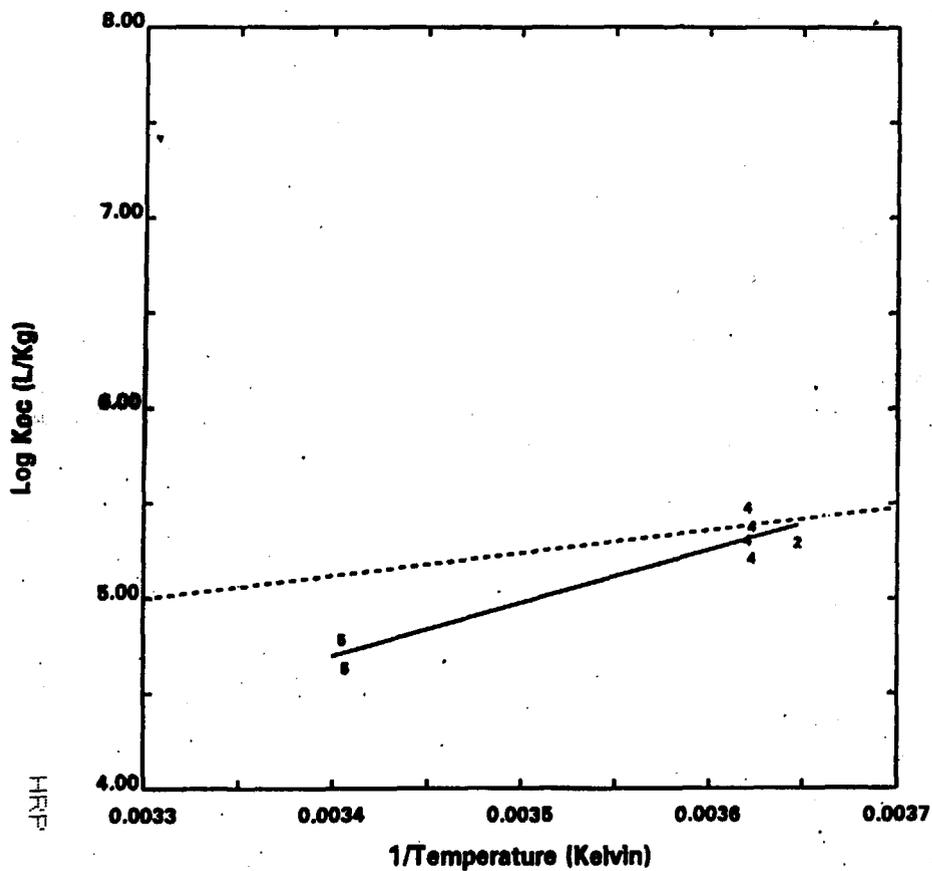


Figure E-3. Log K<sub>oc</sub> of BZ#10 as a function of inverse temperature. Only Transect studies 1-6 from the Thompson Island Dam to Waterford: Left, with temperature correction; Right, without temperature correction.

Log K<sub>oc</sub> as a function of inverse Temperature

Congener 27

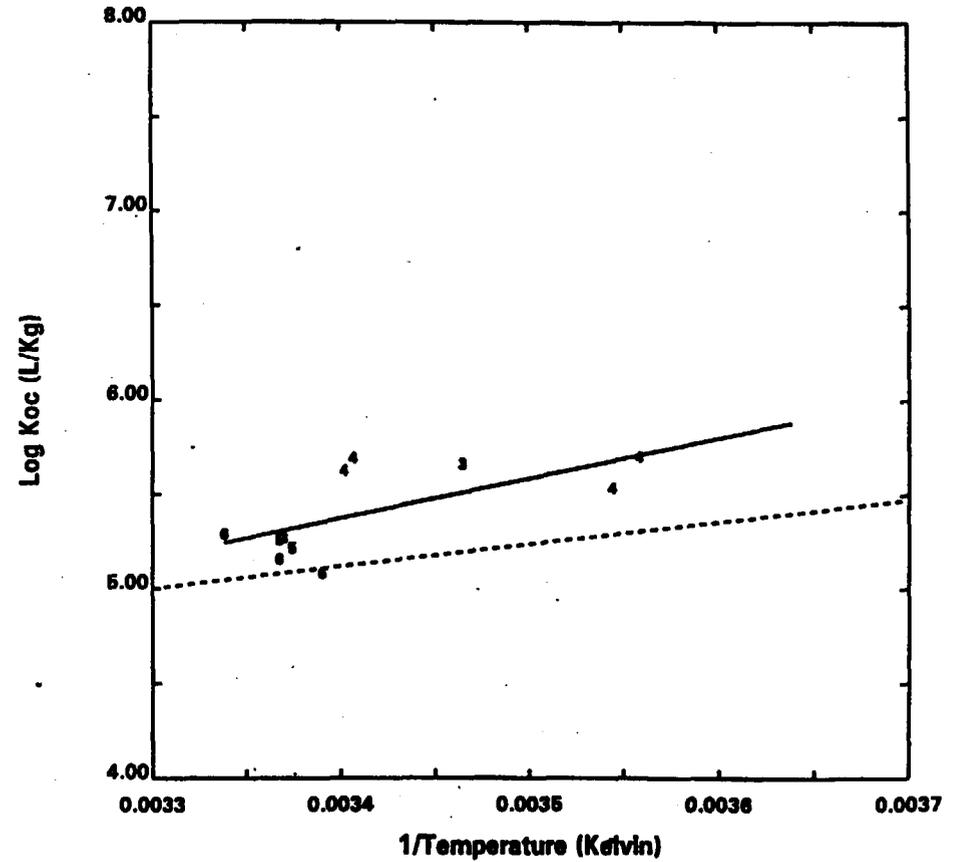
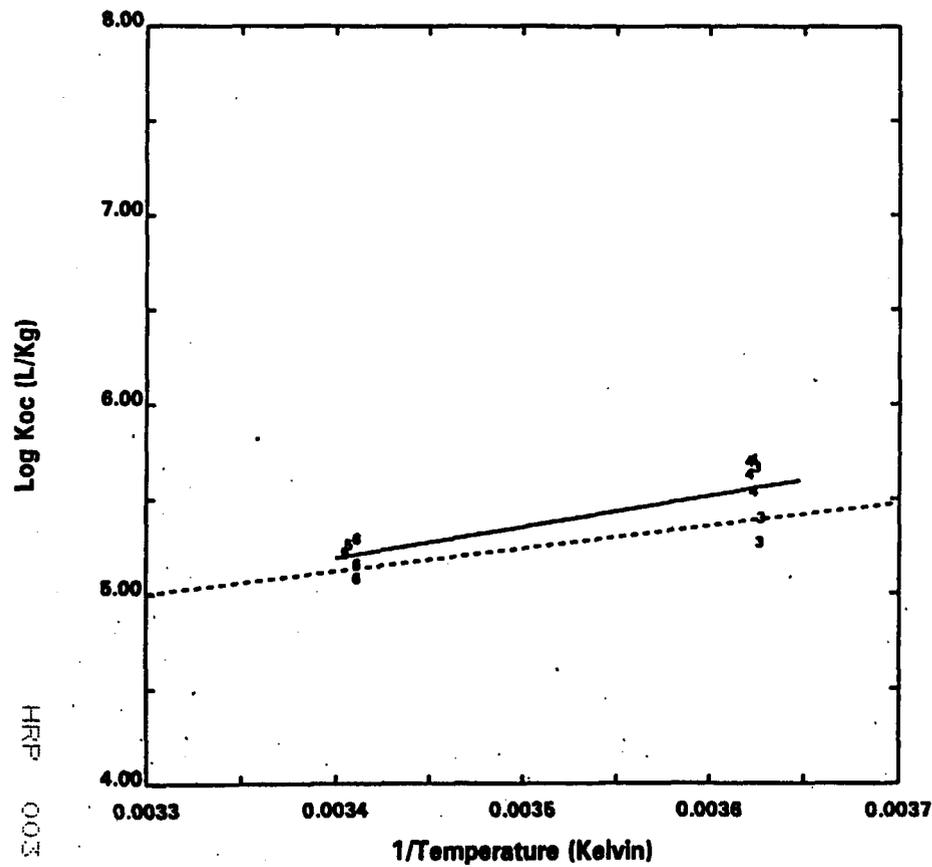


Figure E-4. Log K<sub>oc</sub> of BZ#27 as a function of inverse temperature. Only Transect studies 1-6 from the Thompson Island Dam to Waterford: Left, with temperature correction; Right, without temperature correction.

HRP 003 0136

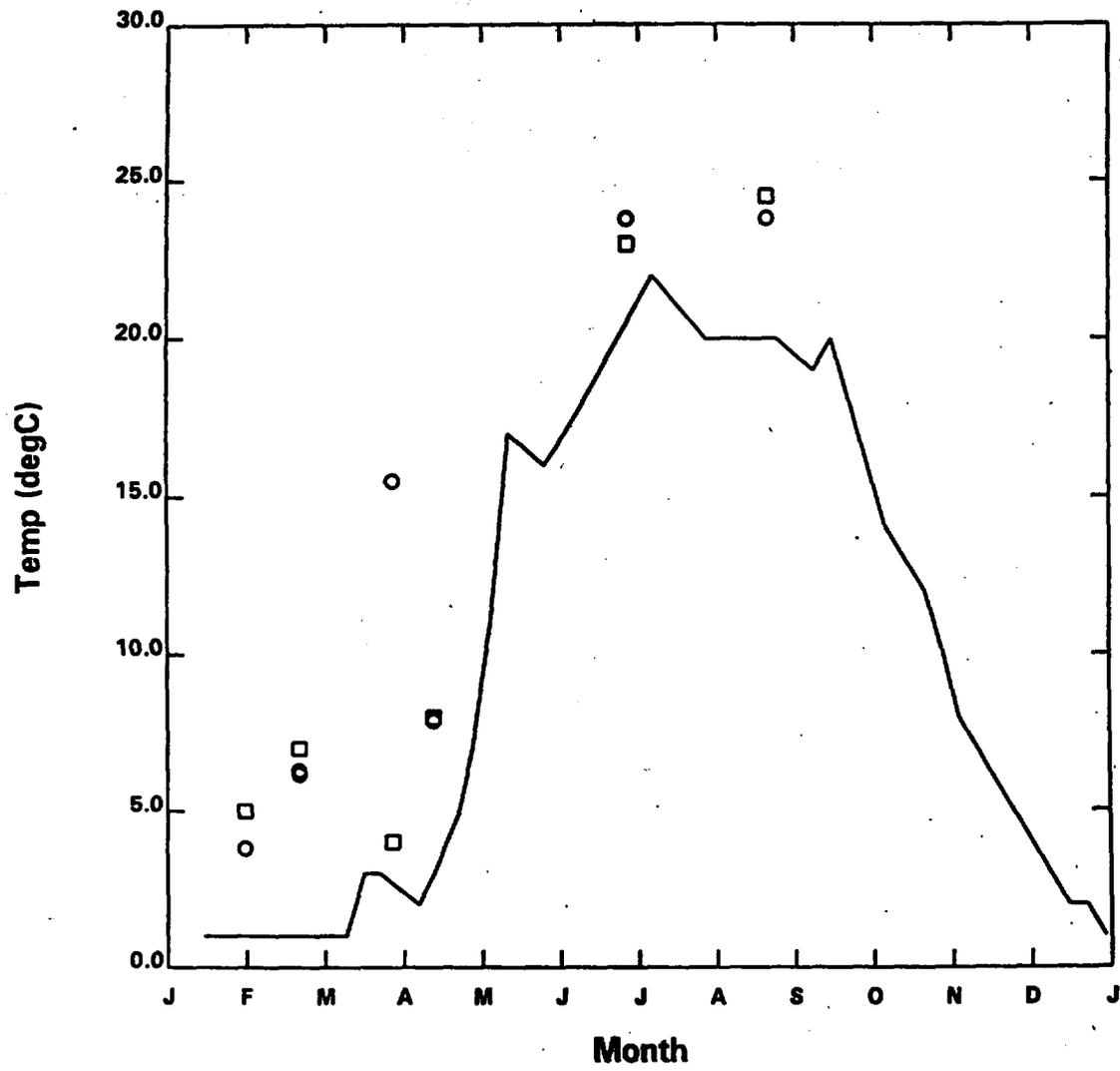


Figure E-5. Temporal temperature profile in 1993 at the Thompson Island Dam: Line GE data, ○ EPA pH meter, □ EPA DO probe.

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## REFERENCES

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# TABLES

| Table 1.  |  |  |  |
|---|--|--|--|
| Surface Sediment PCB Reservoir Depletion under 1993-1996 Average<br>Thompson Island Pool Load |  |  |  |
| Homologue   | Mass of PCBs in TIP<br>Surface Sediments in<br>1984 <sup>(1,2)</sup><br>(MT) | Load from TI<br>Pool <sup>(3)</sup><br>(MT/year) | Time to deplete the<br>sediment reservoir<br>(Years) |
| 1   | 0.58   | 0.055  | 1995   |
| 2   | 1.4  | 0.117  | 1996   |
| 3   | 1.0  | 0.062  | 2000   |
| 4   | 0.41   | 0.016  | 2009   |
| 5   | 0.13   | 0.002  | 2040   |
| Sum   | 3.52   | 0.25<br>= 0.69 kg/day                            |  |

(1) Mass of total PCB in surface sediments = surface sediment concentration\* x specific weight of sediments\* x 8 cm depth x area of TI Pool\*

\* Values based on EPA analysis.

(2) Homologue mass based on homologue composition of EPA low resolution cores

(3) Load from TI Pool = Load at TI Dam - load at Rogers Island; all GE data, 1993-1996.

| <b>Table 2.</b>  |                                 |                                   |
|--|---------------------------------|-----------------------------------|
| <b>Average PCB Loading Across Thompson Island Pool from 1993 to 1996<sup>1</sup></b> |                                 |                                   |
| <b>Year</b>  | <b>Number of Paired Samples</b> | <b>Average PCB Load [kg/year]</b> |
| 1993   | 49                              | 202.2                             |
| 1994   | 34                              | 296.9                             |
| 1995   | 45                              | 84.3                              |
| 1996   | 57                              | 406.6                             |
| <b>Overall</b>   | <b>185</b>                      | <b>253.9</b>                      |

<sup>1</sup>Loadings calculated from GE database (corrected for bias), based on daily average flows measured at Fort Edward and differences between paired water column PCB concentrations from samples collected at Fort Edward and Thompson Island Dam.

**Table 3.****Magnitude and Composition of the Unaccounted for Summer PCB Load from Thompson Island Pool**

| Year | Unaccounted for PCB Load [kg/day] | Unaccounted-for Solid Phase PCB Homolog Distribution (WT%) |      |      |      |      |     |     |     |     |     |
|------|-----------------------------------|--|------|------|------|------|-----|-----|-----|-----|-----|
|      |                                   | Mon  | Di   | Tri  | Tet  | Pen  | Hex | Hep | Oct | Non | Dec |
| 1991 | 0.05                              | 5.9  | 0.1  | 38.8 | 32.1 | 22.8 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1992 | 0.56                              | 11.8   | 19.9 | 42.1 | 23.4 | 1.8  | 1.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1993 | 0.99                              | 7.5  | 17.8 | 28.8 | 31.7 | 12.1 | 2.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1994 | 0.97                              | 9.3  | 22.4 | 33.8 | 28.0 | 6.4  | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1995 | 0.23                              | 2.3  | 14.8 | 29.1 | 35.4 | 15.0 | 3.3 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1996 | 1.18                              | 4.4  | 18.3 | 36.9 | 29.4 | 9.4  | 1.6 | 0.0 | 0.0 | 0.0 | 0.0 |

**Table 4.**

**Magnitude and Composition of the Unaccounted-for  
Monthly PCB Load from Thompson Island Pool During 1996**

| Month<br>of 1996 | Unaccounted-<br>for PCB Load<br>[kg/day] | Unaccounted-for Solid Phase PCB Homolog Distribution [WT%] |      |      |      |      |     |     |     |     |     |
|------------------|--|--|------|------|------|------|-----|-----|-----|-----|-----|
|                  |  | Mon  | Di   | Tri  | Tet  | Pen  | Hex | Hep | Oct | Non | Dec |
| Jan              | 0.54                                     | 3.6  | 17.4 | 43.1 | 31.9 | 3.7  | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| Feb              | 0.13                                     | 0.6  | 26.2 | 36.9 | 28.6 | 7.5  | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| Mar              | 0.60                                     | 3.4  | 15.6 | 33.5 | 35.3 | 11.2 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Apr              | 2.05                                     | 4.3  | 11.6 | 38.3 | 38.2 | 6.7  | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 |
| May              | 1.80                                     | 5.6  | 19.6 | 34.7 | 31.5 | 7.8  | 0.8 | 0.0 | 0.0 | 0.0 | 0.0 |
| Jun              | 2.06                                     | 4.9  | 15.6 | 35.9 | 30.9 | 11.1 | 1.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| Jul              | 0.68                                     | 4.9  | 28.4 | 35.1 | 21.2 | 8.7  | 1.7 | 0.0 | 0.0 | 0.0 | 0.0 |
| Aug              | 0.92                                     | 3.9  | 19.1 | 40.3 | 30.4 | 4.7  | 1.7 | 0.0 | 0.0 | 0.0 | 0.0 |
| Sep              | 0.56                                     | 2.3  | 17.9 | 33.0 | 32.3 | 13.7 | 0.8 | 0.0 | 0.0 | 0.0 | 0.0 |
| Oct              | 0.27                                     | 23.9   | 42.0 | 12.7 | 16.0 | 4.9  | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nov              | 0.38                                     | 19.2   | 40.1 | 19.1 | 12.4 | 8.3  | 0.8 | 0.0 | 0.0 | 0.0 | 0.0 |
| Dec              | 0.19                                     | 0.0  | 35.6 | 38.2 | 10.2 | 13.7 | 2.2 | 0.0 | 0.0 | 0.0 | 0.0 |

**Table 5.**

**Information Sources for Homolog-Specific Parameters of the Bioaccumulation Model**

| <b>Parameter</b>  | <b>Data Source</b>   |
|---|--|
| Benthic invertebrate sediment accumulation factors                          | EPA invertebrate data, unsorted total, all samples           |
| Water column invertebrate/water column particulate trophic transfer factors | Green Bay zooplankton/phytoplankton trophic transfer factors |
| Water column particulates/dissolved partition coefficient                   | EPA partitioning data as analyzed by HydroQual               |
| Assimilation efficiencies at the gut and gill                               | Values applied in the Green Bay model                        |

| <b>Table 6.</b>   |   |   |  |  |
|---|---|---|--|--|
| <b>Exposure Sources for Homologue-Based Bioaccumulation Model for TIP</b> |   |   |  |  |
| <b>Figure #</b><br><b>(Simulation #)</b>                                  |   |   |  |  |
|   | <b>18</b><br><b>(h24)</b>                       | <b>19</b><br><b>(h23)</b>                       | <b>20</b><br><b>(h25)</b>                        | <b>21</b><br><b>(h26)</b>                              |
| Exposure basis:   | Realistic water, top 2 cm of sediment bed       | Realistic water, top 5 cm of sediment bed       | Realistic water, heavily dechlorinated sediments | Heavily dechlorinated sediments and water              |
| Water column dissolved tPCB concentration                                 | 20 ng/L (TIP late 1980s)                        | 20 ng/L (TIP late 1980s)                        | 20 ng/L (TIP late 1980s)                         | computed from water column particulates <sup>(1)</sup> |
| Water column dissolved homolog composition                                | Avg of summer data 91-96 at Ft.Edward and TIDam | Avg of summer data 91-96 at Ft.Edward and TIDam | Avg of summer data 91-96 at Ft.Edward and TIDam  | Computed from water column particulates <sup>(1)</sup> |
| Water column particulate tPCB concentration                               | Computed from dissolved <sup>(1)</sup>          | Computed from dissolved <sup>(1)</sup>          | Computed from dissolved <sup>(1)</sup>           | Same as sediment bed particulates                      |
| Water column particulate homolog composition                              | Computed from dissolved <sup>(1)</sup>          | Computed from dissolved <sup>(1)</sup>          | Computed from dissolved <sup>(1)</sup>           | Same as sediment bed particulates                      |
| Sediment particulate tPCB concentration                                   | 400 ug/gOC (TIP late 1980s, fate model)         | 400 ug/gOC (TIP late 1980s, fate model)         | 400 ug/gOC (TIP late 1980s, fate model)          | 400 ug/gOC (TIP late 1980s, fate model)                |
| Sediment particulate homolog composition                                  | TIP EPA hires cores, top slice                  | TIP 1991 GE data, top slice                     | TIP EPA hires core slices with <2 Cl/BP          | TIP EPA hires core slices with <2 Cl/BP                |

(1) Water column dissolved composition was computed from particulate composition (and vice versa) using partition coefficients based on analysis of EPA data.

# FIGURES

| Area ID | Area (sq. ft.) |
|---------|----------------|
| A1      | 4832           |
| A2      | 53974          |
| A3      | 65993          |
| A5      | 47595          |
| A6      | 129309         |
| A4      | 8206           |
| A7      | 166642         |
| A8      | 41458          |
| A9      | 5936           |
| A10     | 223165         |

Total Area = 69,409 sq. m

(Total TIP = 1.93E+06 sq. m)

**Legend**

-  EPA PCB > 100 ppm
-  Mile Markers
-  Shore Line

**Area of Interest**

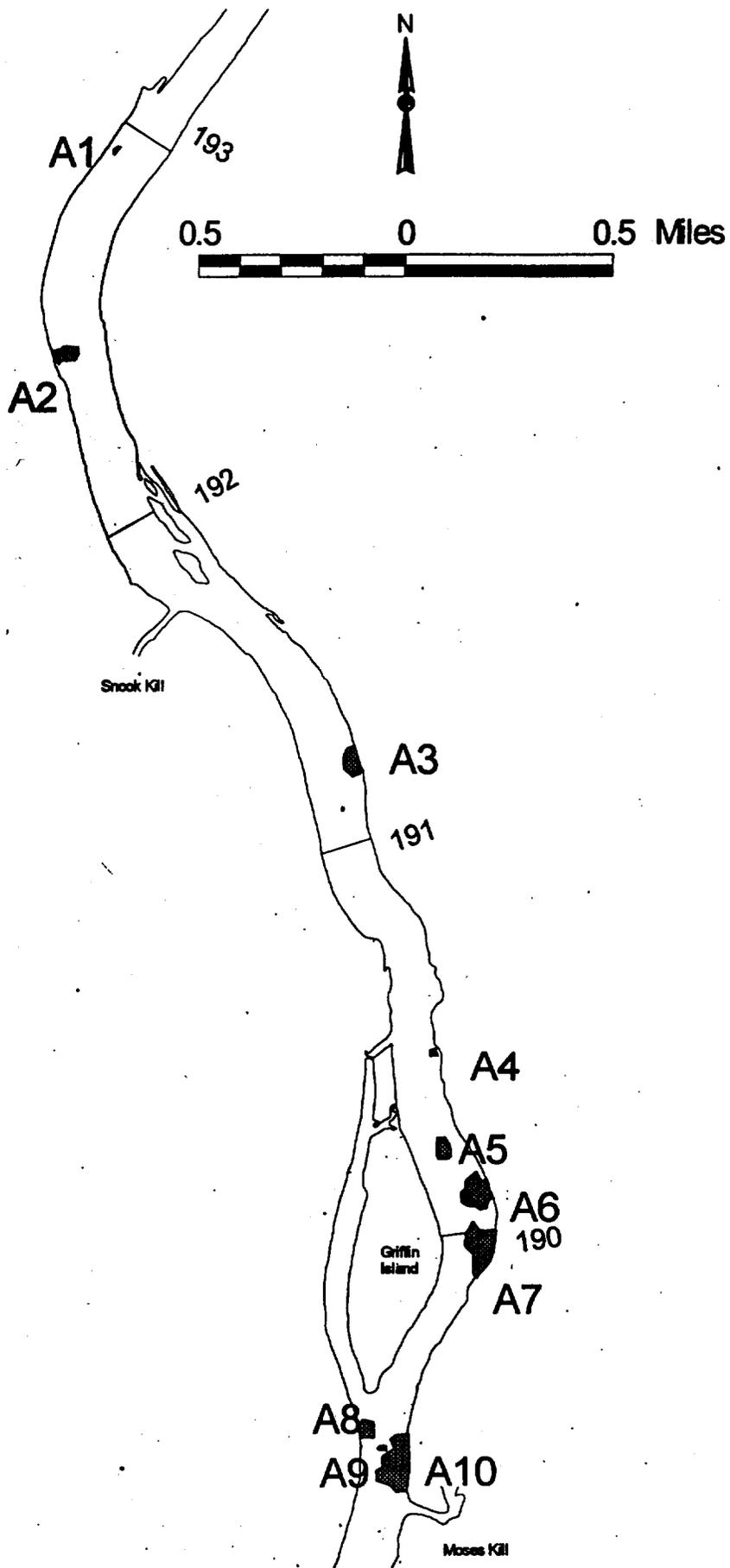



Figure 1. Areas of TIP with surface sediment PCB concentrations greater than 100 ppm.

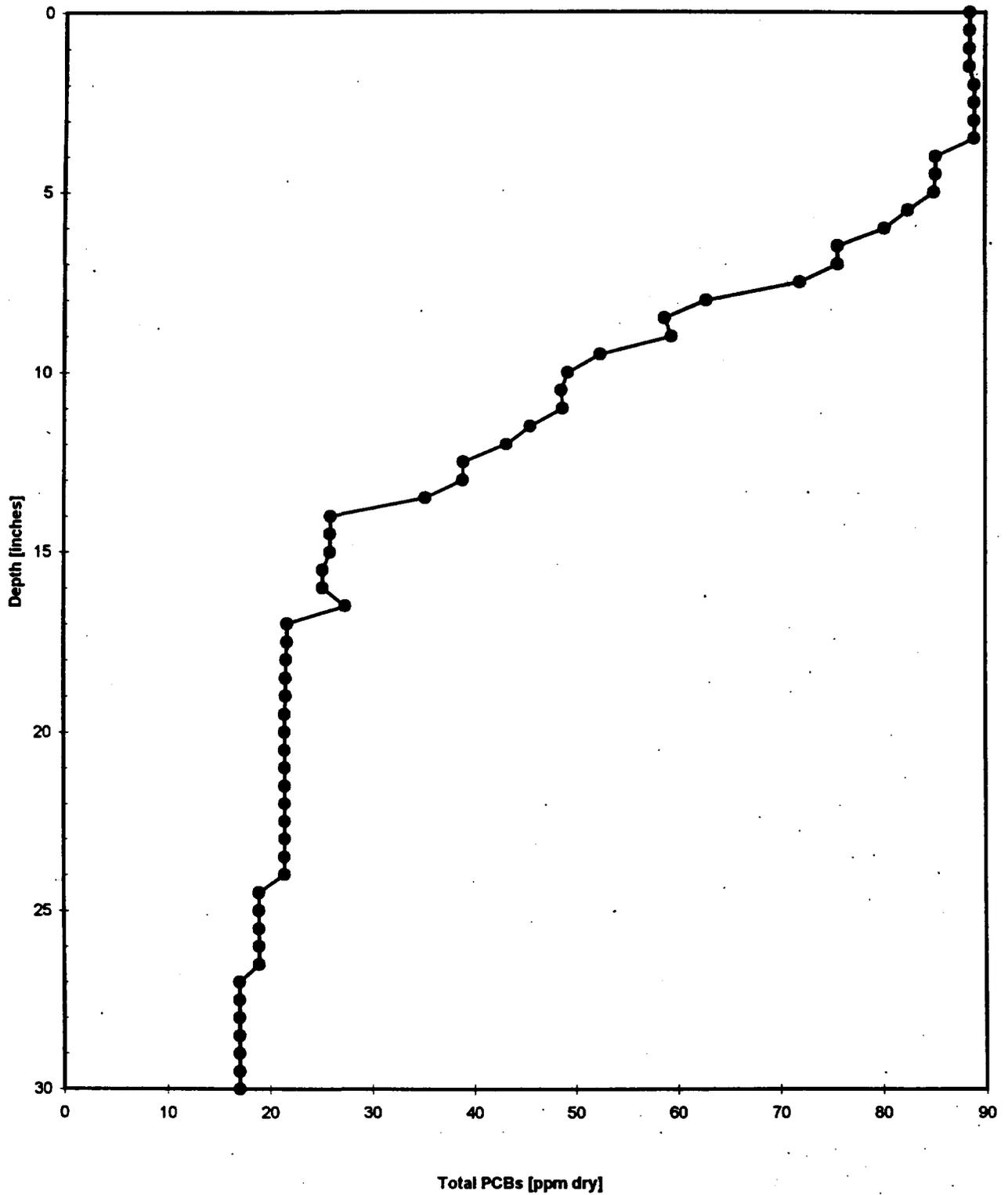


Figure 2. Average 1984 sediment PCB profile for areas with surface sediment PCBs greater than 100 mg/Kg.

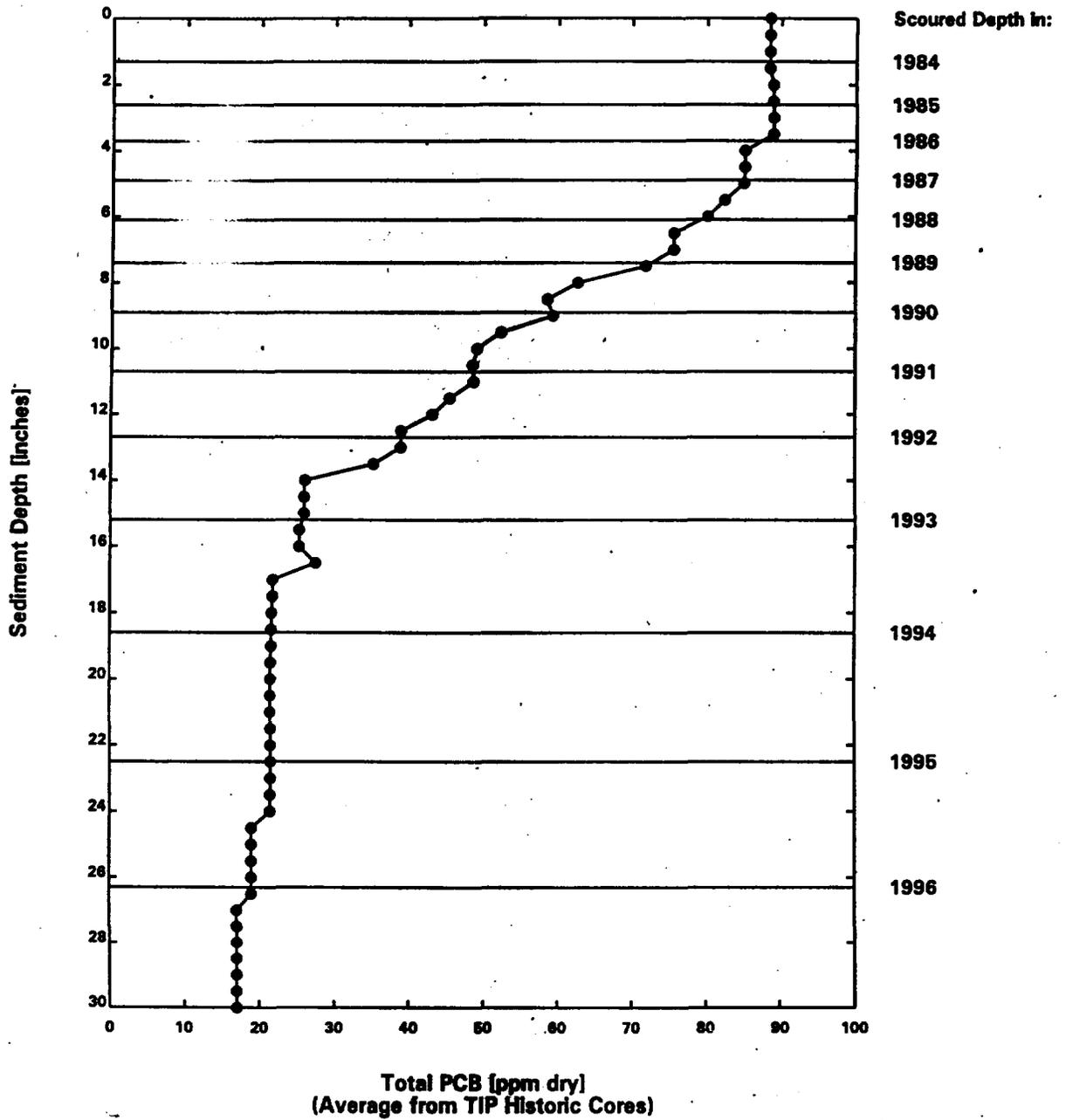


Figure 3. Annual sediment scour depths required to achieve water column concentrations necessary to maintain the TIP load.

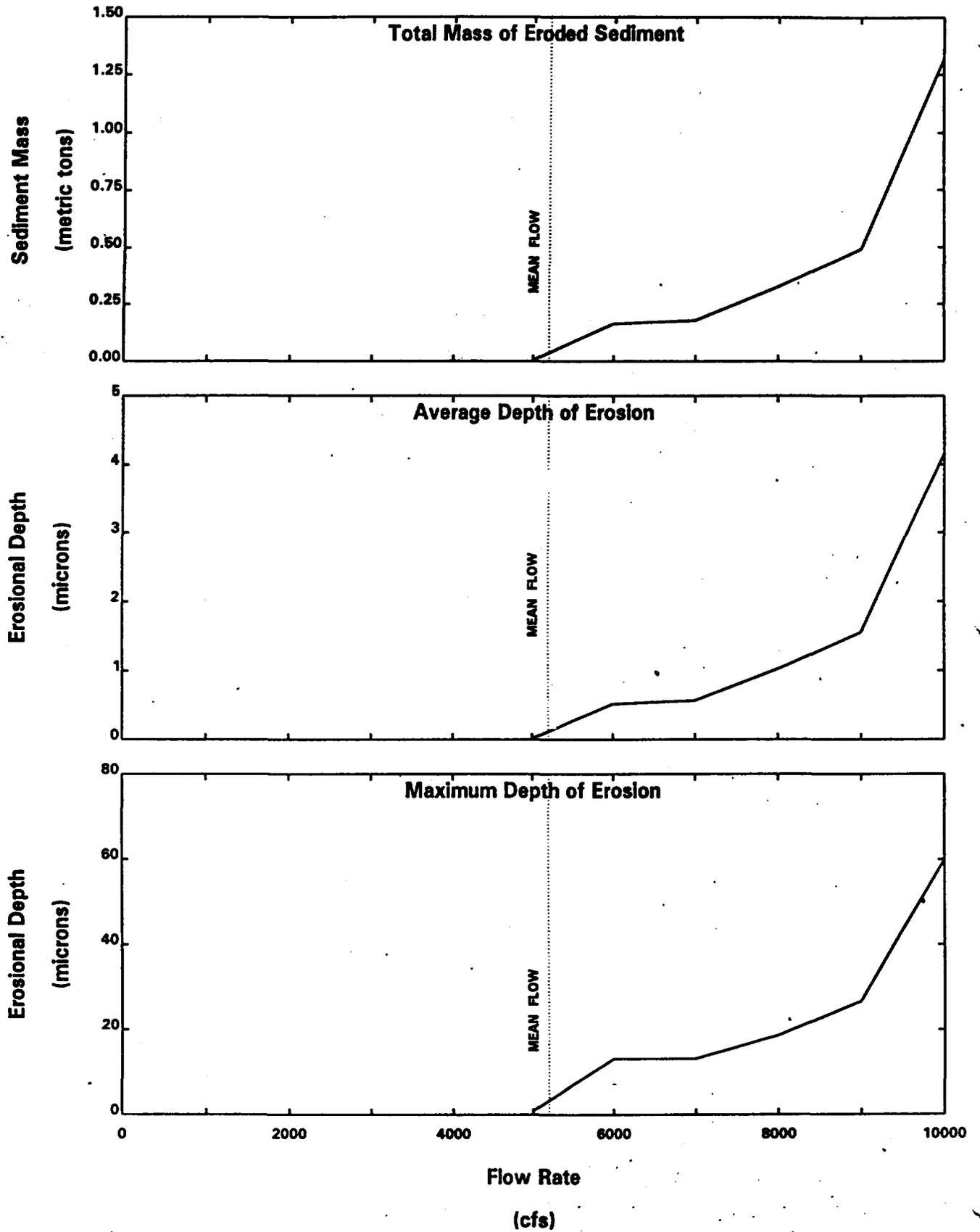
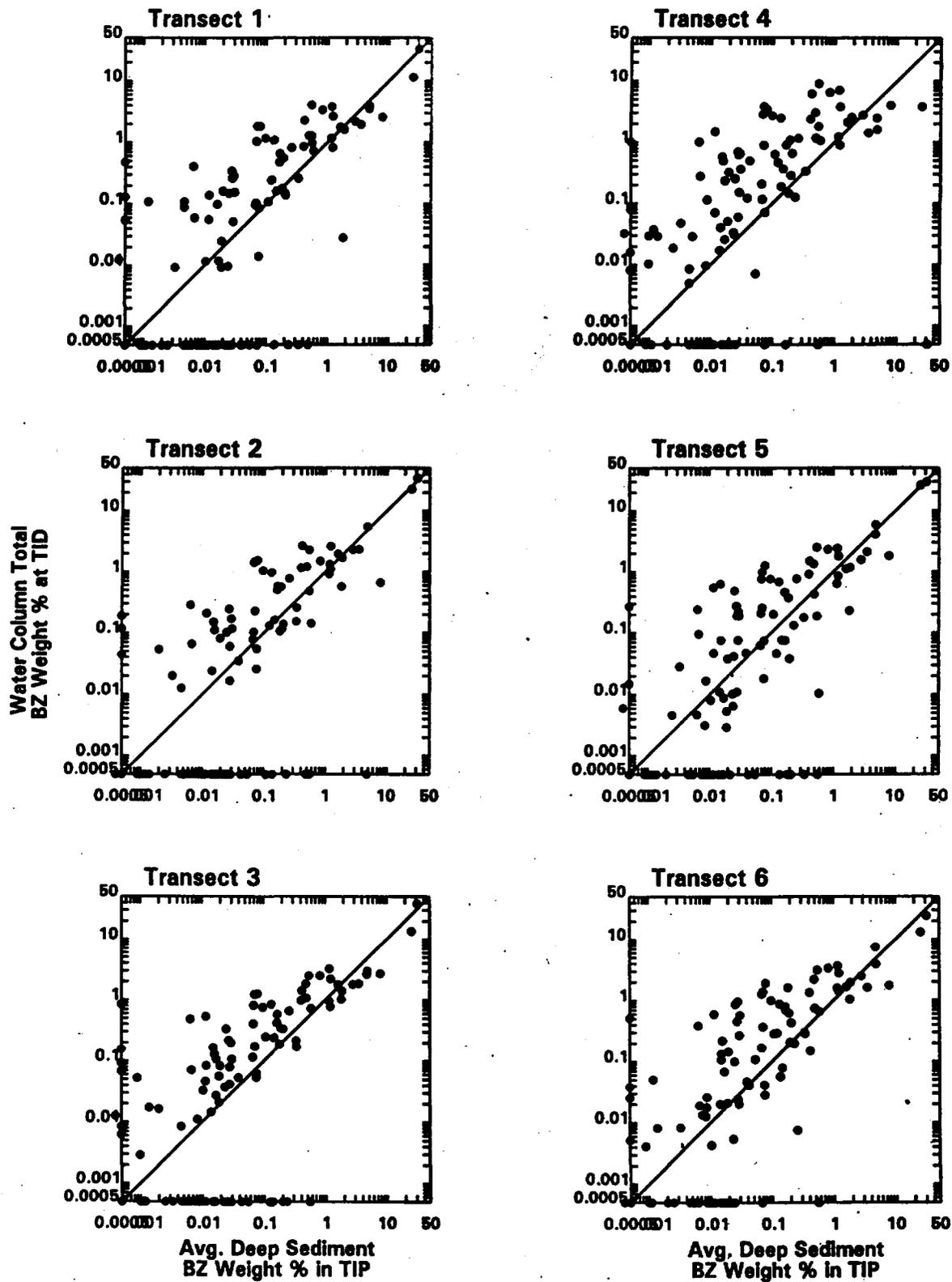


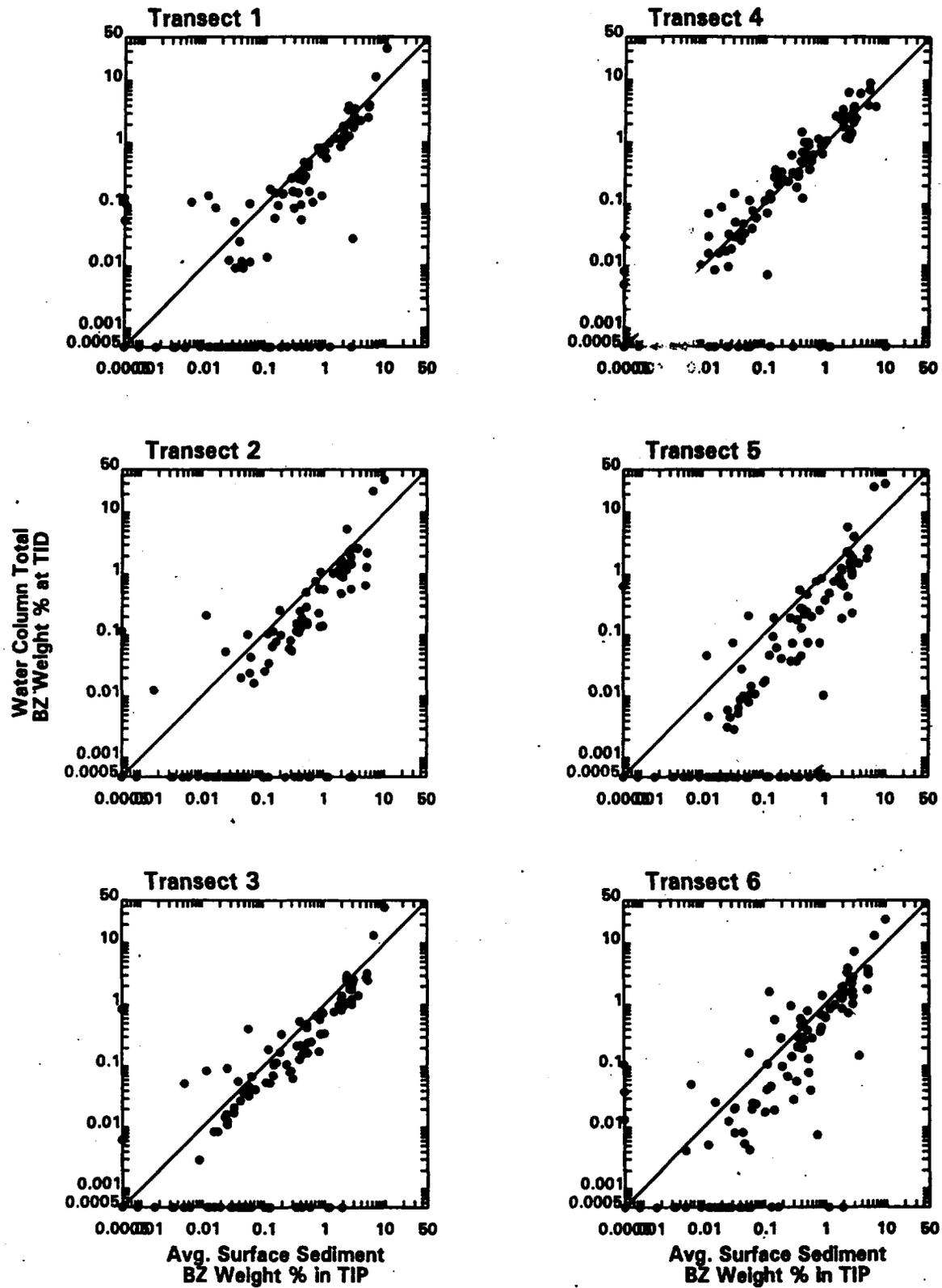
Figure 4. Predicted cohesive sediment bed erosion in the TIP under low flow conditions.



Total Water Column Data Source: EPA Phase 2 Transect Studies at TID

Deep Sediment Data Source: EPA Phase 2 High Res Core slices in TIP  
with tPCB > 100 ppm

Figure 5. Comparison of TID water column PCB signature with TIP deep dechlorinated sediment.



Total Water Column Data Source: EPA Phase 2 Transect Studies at TID  
 Surface Sediment Data Source: EPA Phase 2 High Resolution Surveys at TIP

Figure 6: Comparison of TID water column PCB signature with TIP surface sediments.

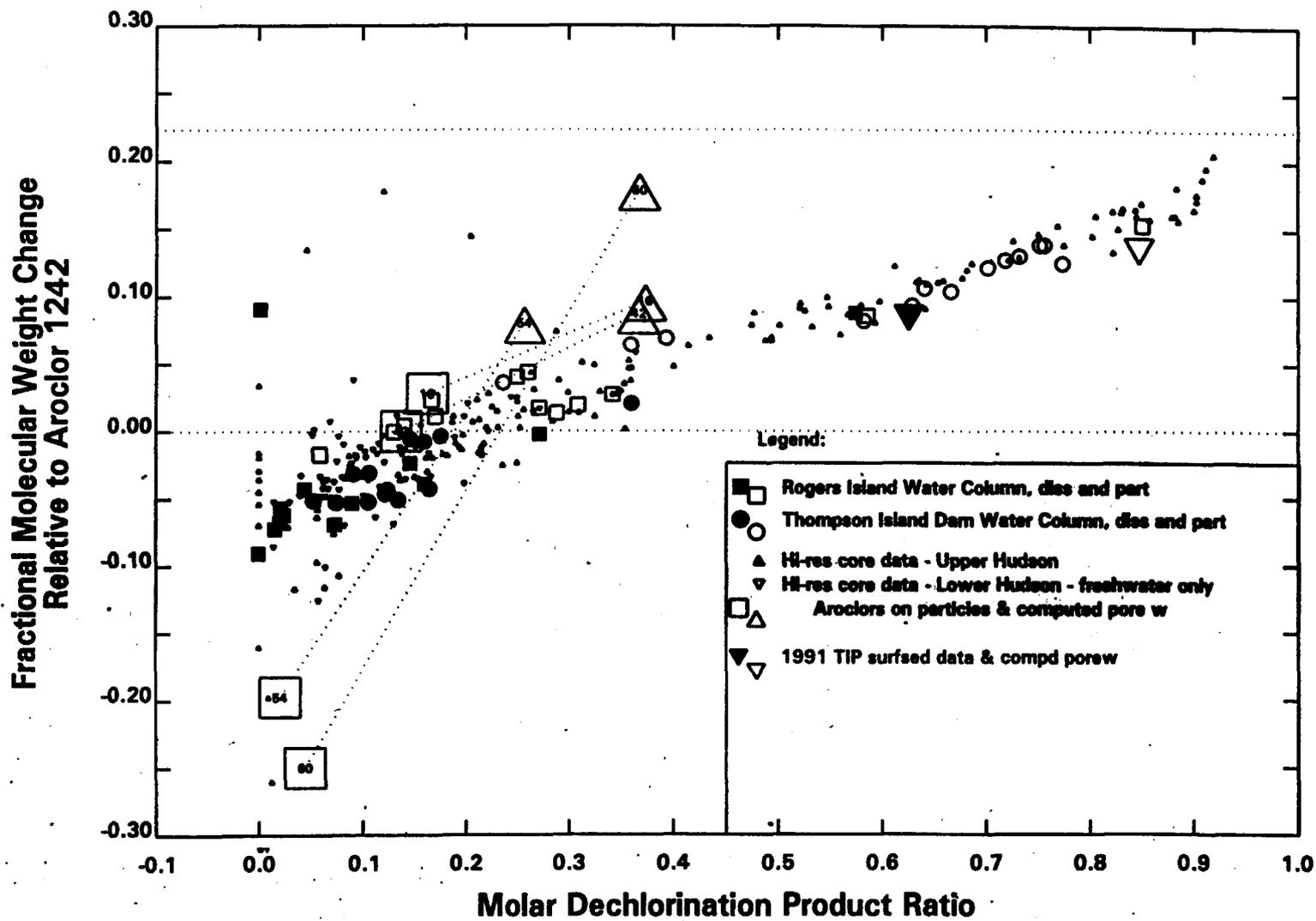


Figure 7. Molar dechlorination product ratio versus fractional molecular weight change relative to Aroclor 1242.

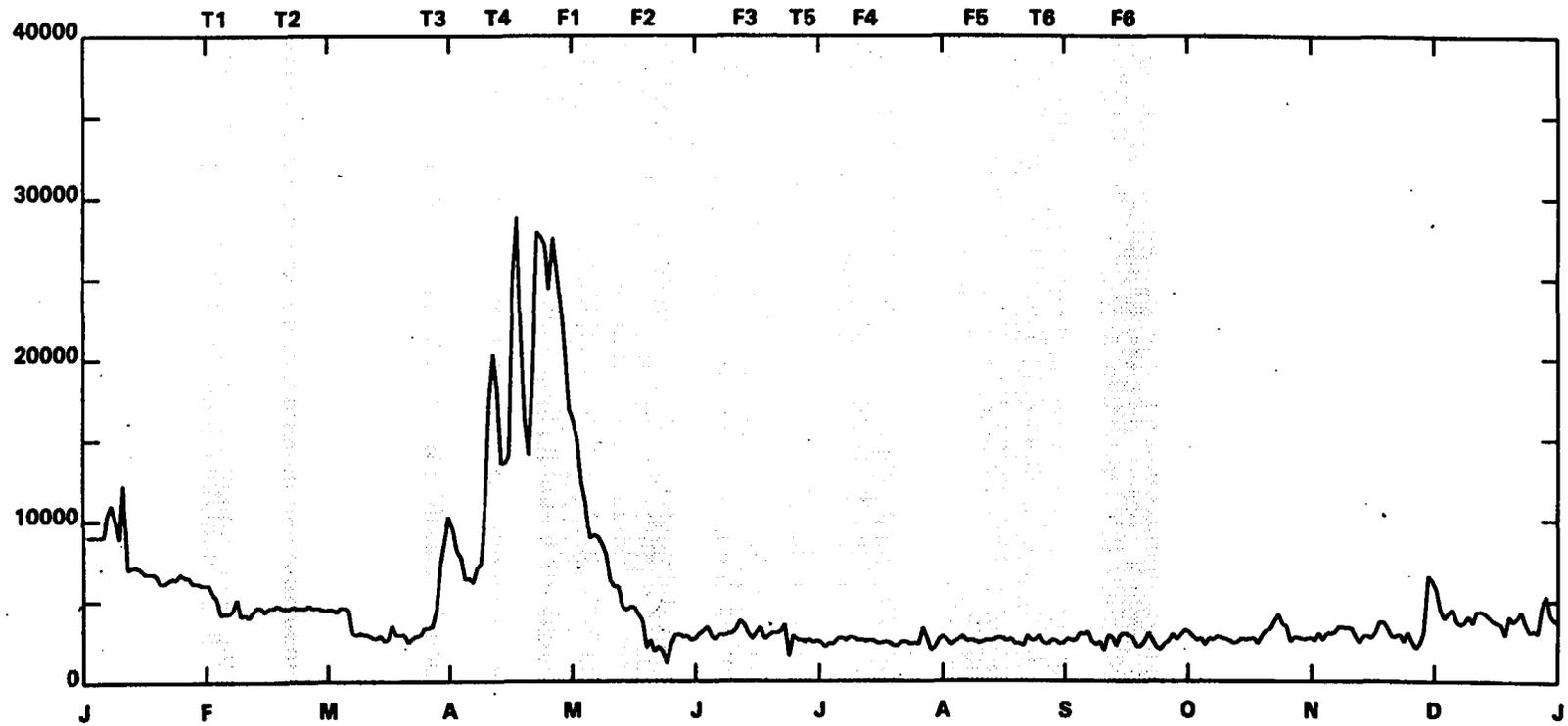
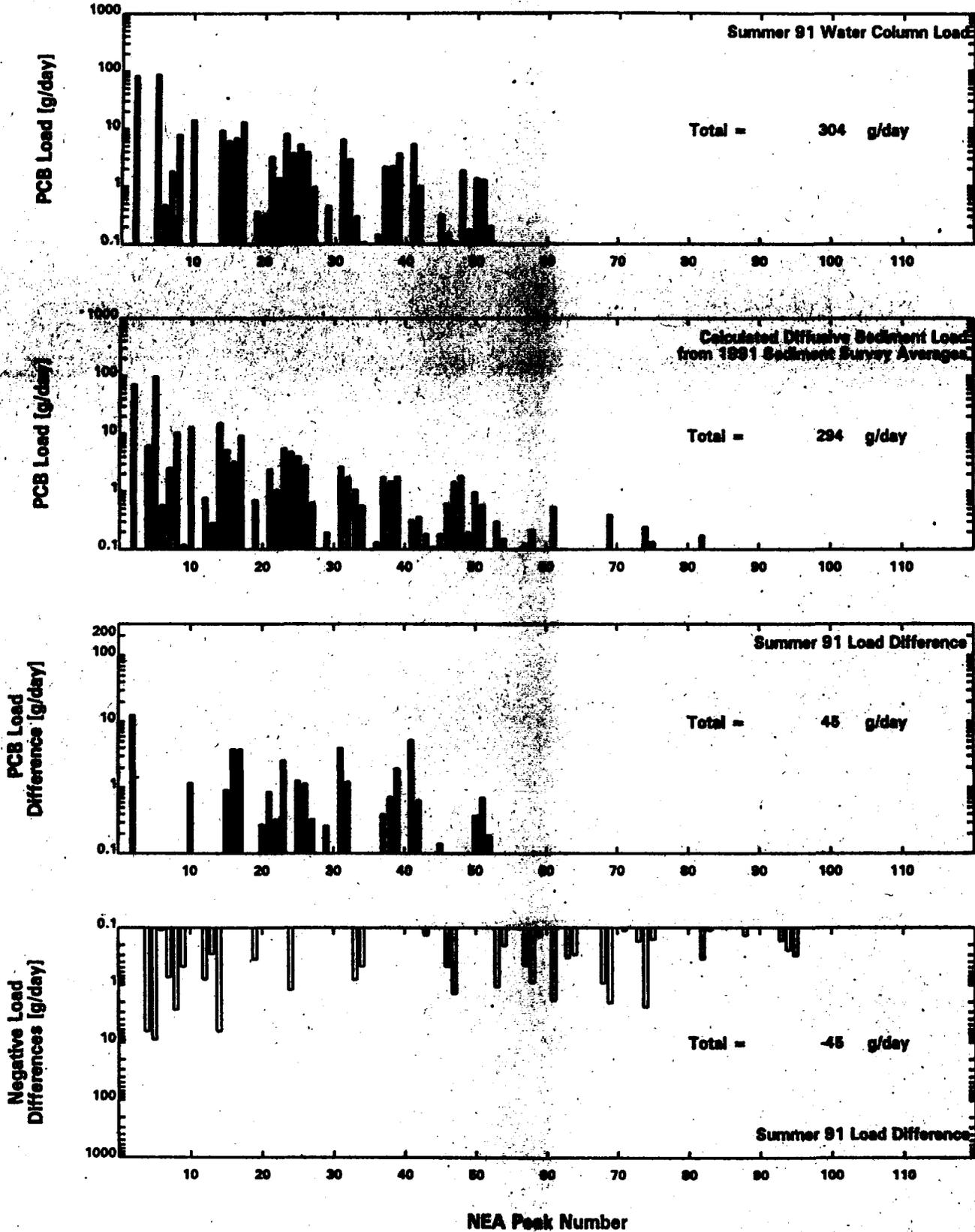


Figure 8. Location of EPA sampling events relative to 1993 hydrograph.

Corrected for Analytical Bias in NEA Peaks  
5, 8, and 14 for Water and Sediment)



$K_f = 0.005$  m/day. Note, negative water column loads are not included.

Figure 9. Summer 1991 congener peak TTH PCB loading - a) water column load; b) calculated diffusive sediment load; c) unaccounted-for load; d) negative congener loadings.

Corrected for Analytical Bias in NEA Peaks 5, 8, and 14 for Water and Sediment  
Congener Kocs Corrected for Temperature Dependence

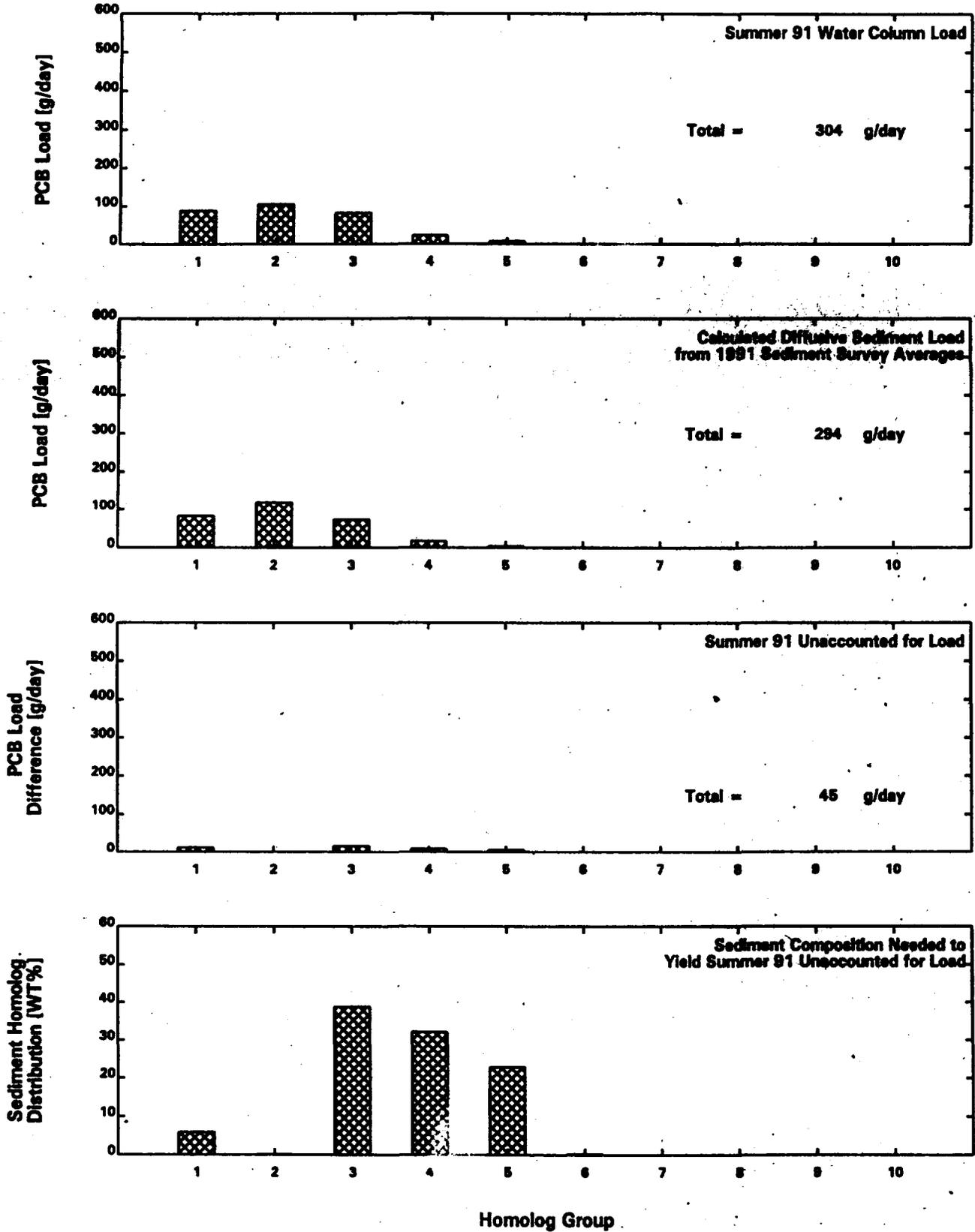


Figure 10. Summer 1991 TIP PCB homologue loading - a) water column derived load; b) calculated diffusive sediment load; c) unaccounted-for load; d) sediment composition required to yield unaccounted-for load.

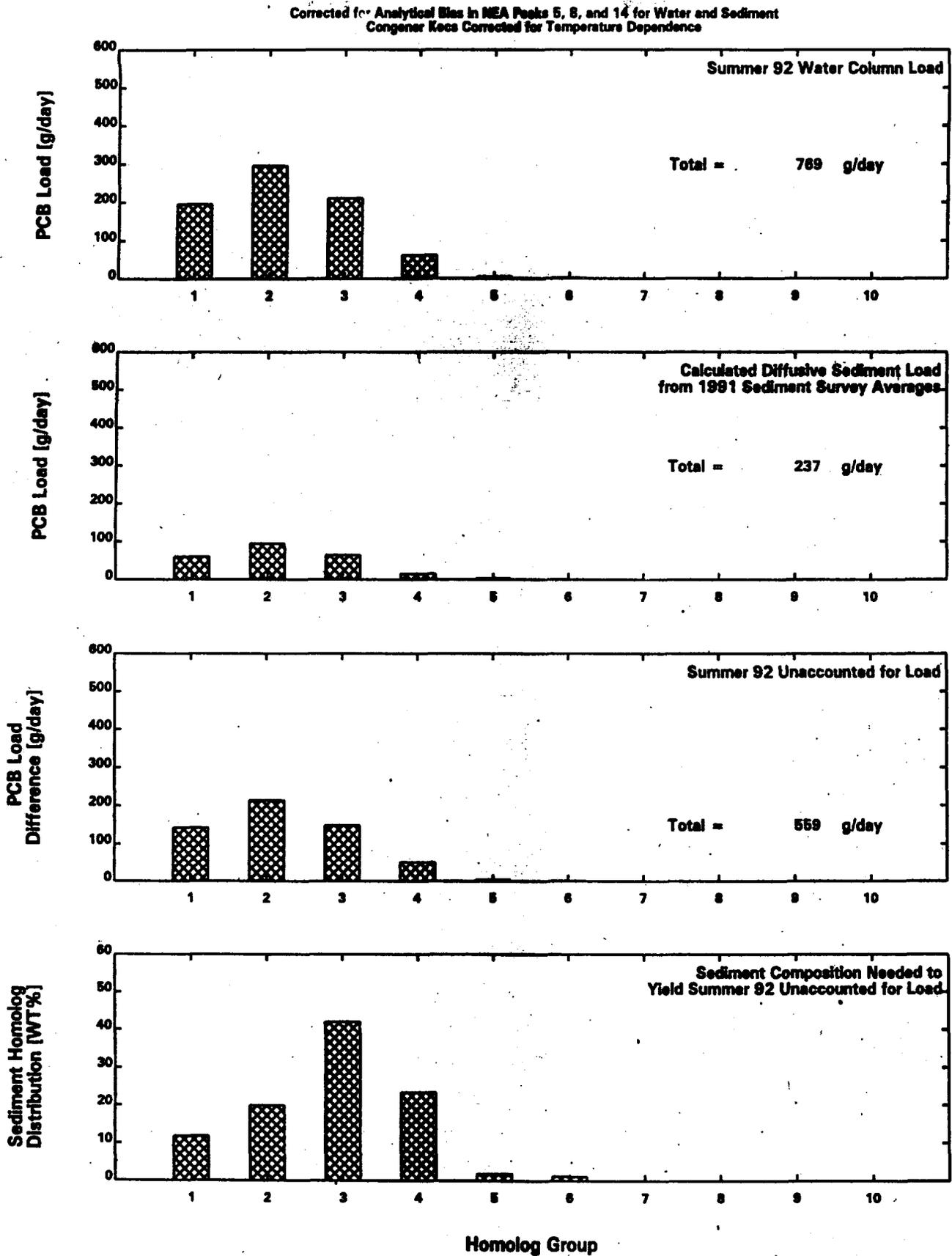


Figure 11. Summer 1992 TIP PCB homologue loading - a) water column derived load; b) calculated diffusive sediment load; c) unaccounted-for load; d) sediment composition required to yield unaccounted-for load.

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Corrected for Analytical Bias in NEA Peaks 5, 8, and 14 for Water and Sediment  
Congener Kocs Corrected for Temperature Dependence

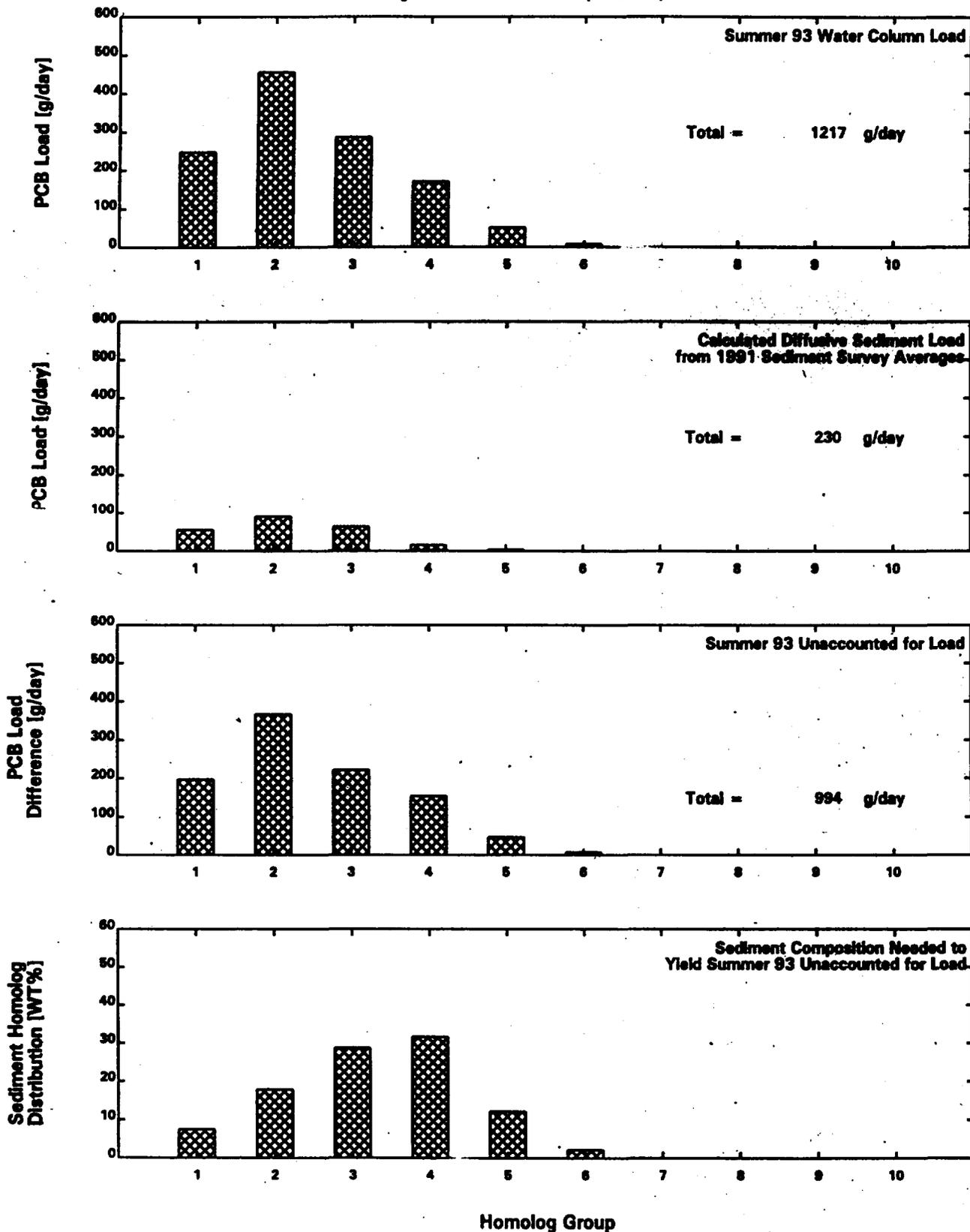


Figure 12. Summer 1993 TIP PCB Homologue loading - a) water column derived load; b) calculated diffusive sediment load; c) unaccounted-for load; d) sediment composition required to yield unaccounted-for load.

Corrected for Analytical Bias in NEA Peaks 5, 8, and 14 for Water and Sediment  
Congener Kees Corrected for Temperature Dependence

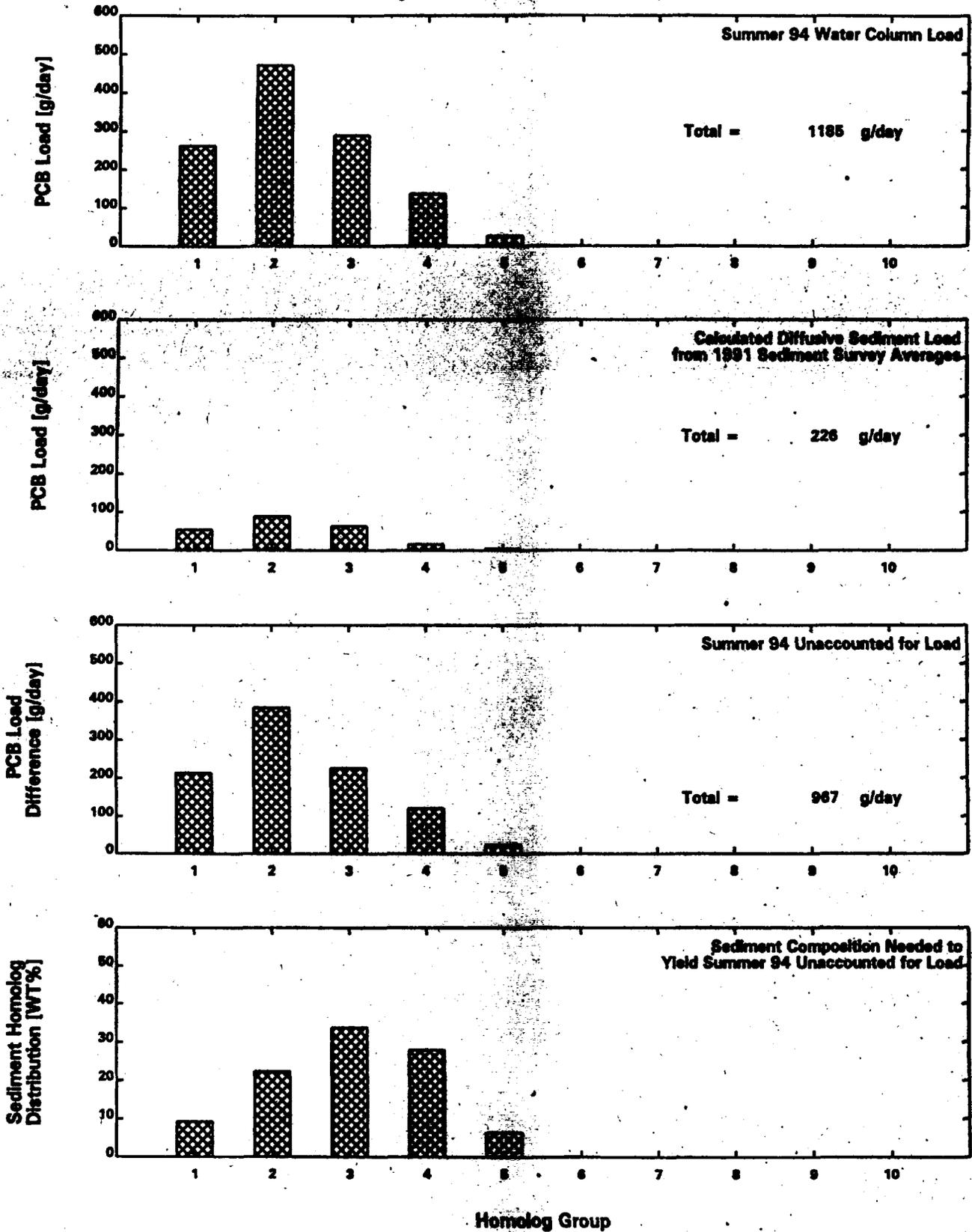


Figure 13. Summer 1994 TIP PCB homologue loading - a) water column derived load; b) calculated diffusive sediment load; c) unaccounted for load; d) sediment composition required to yield unaccounted-for load.

Corrected for Analytical Bias in NEA Peaks 5, 8, and 14 for Water and Sediment  
Congener Kocs Corrected for Temperature Dependence

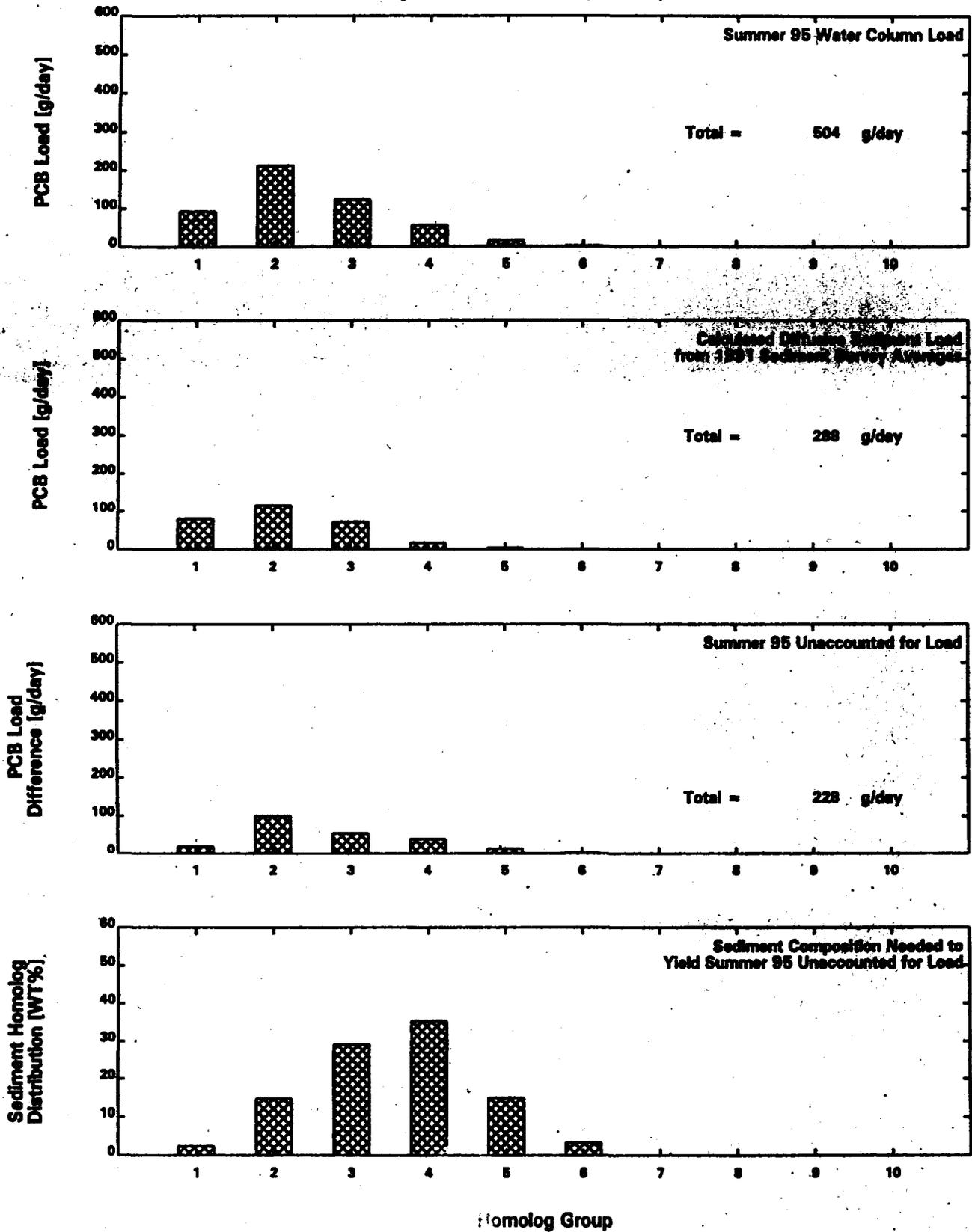


Figure 14. Summer 1995 TIP PCB homologue loading - a) water column derived load; b) calculated diffusive sediment load; c) unaccounted for load; d) sediment composition required to yield unaccounted for load.

Corrected for Analytical Bias in NEA Peaks 5, 8, and 14 For Water and Sediment  
Congener Kace Corrected for Temperature Dependence

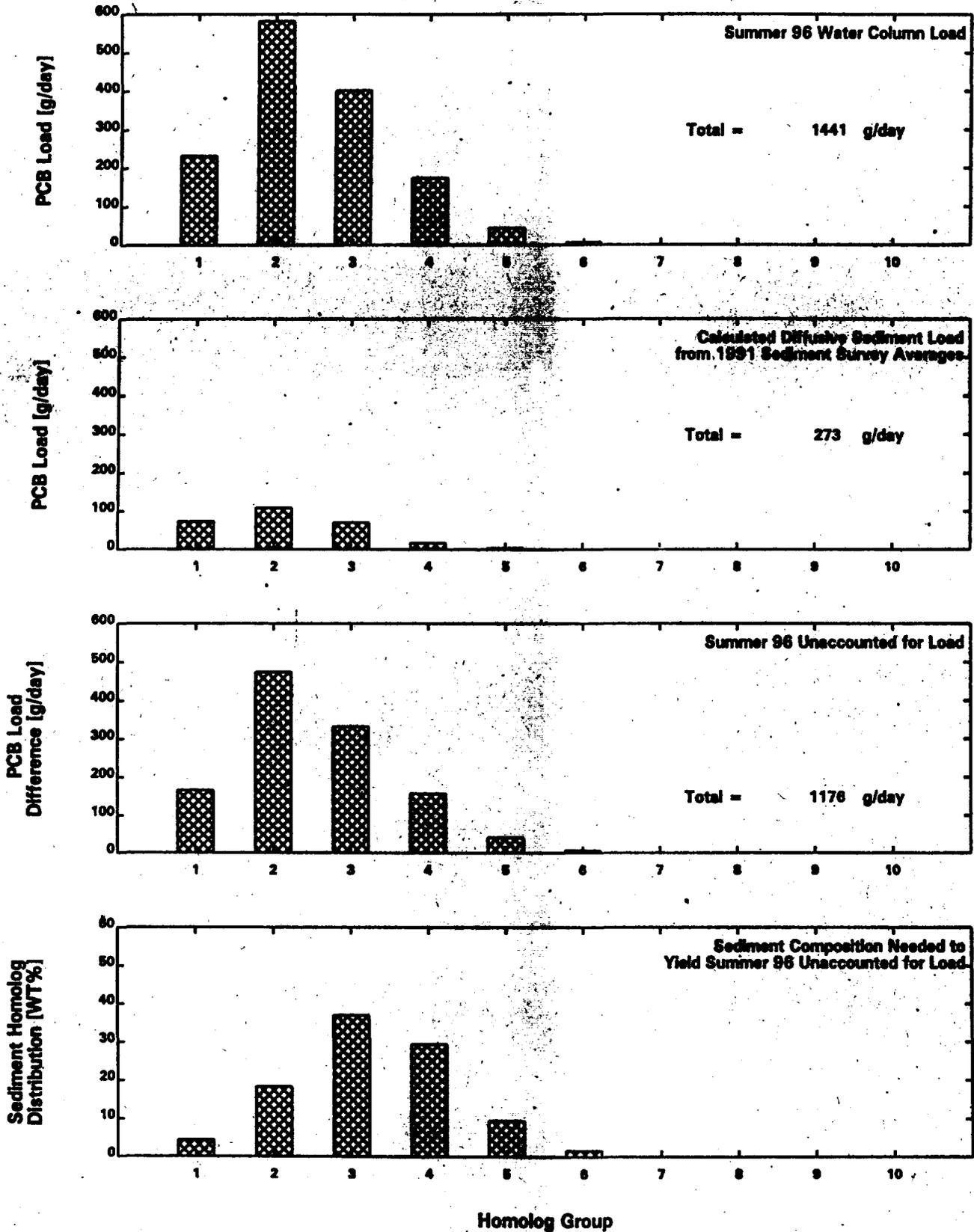


Figure 15. Summer 1996 TIP PCB homologue loading - a) water column derived load; b) calculated diffusive sediment load; c) unaccounted for load; d) sediment composition required to yield unaccounted-for load.

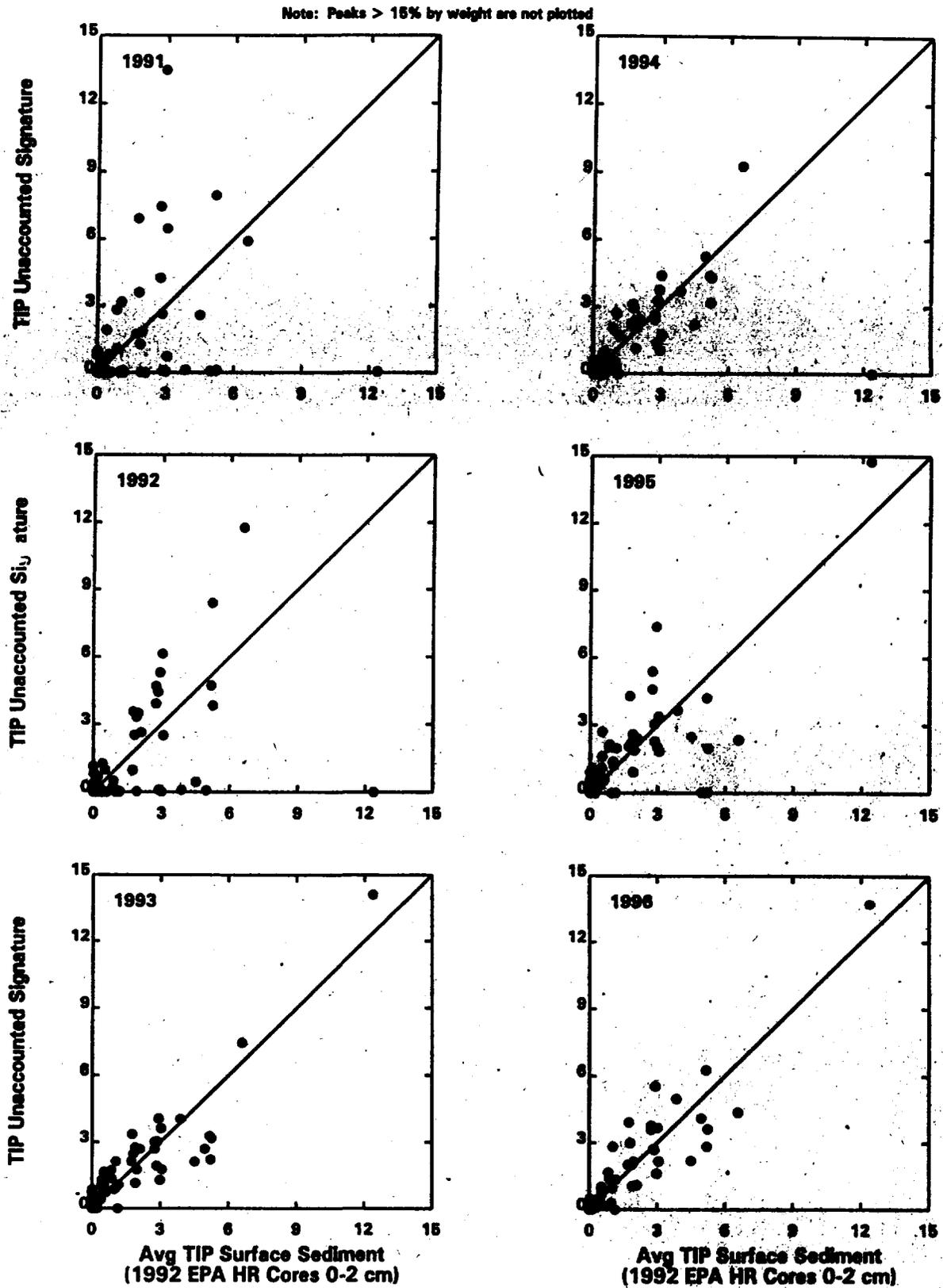


Figure 16. Comparison of PCB congener composition between average TIP surface sediments and unaccounted-for TIP load (summer 1991 - 1996).

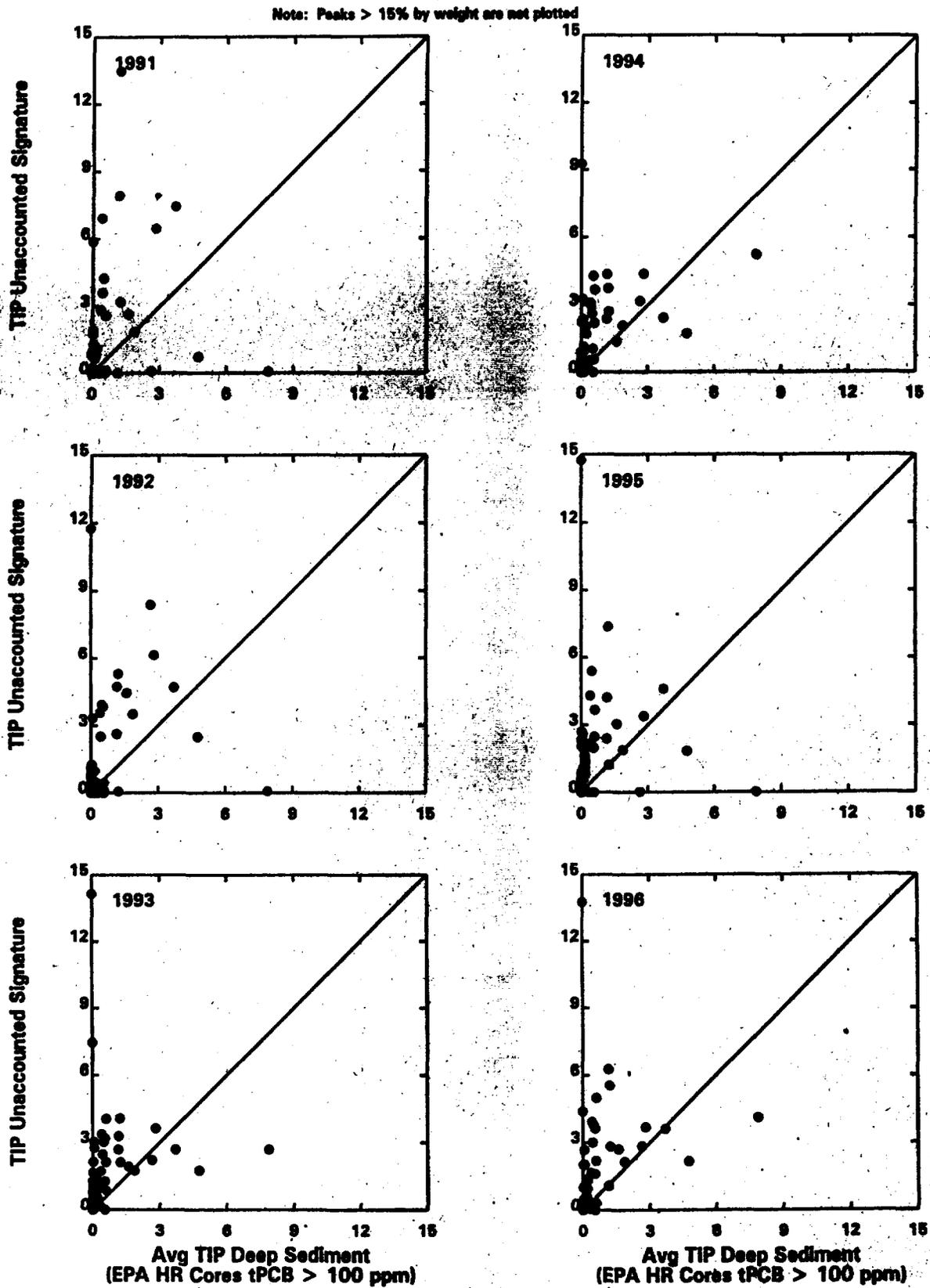


Figure 17. Comparison of PCB congener composition between average TIP deep dechlorinated sediments and unaccounted-for TIP load (summer 1991 - 1996).

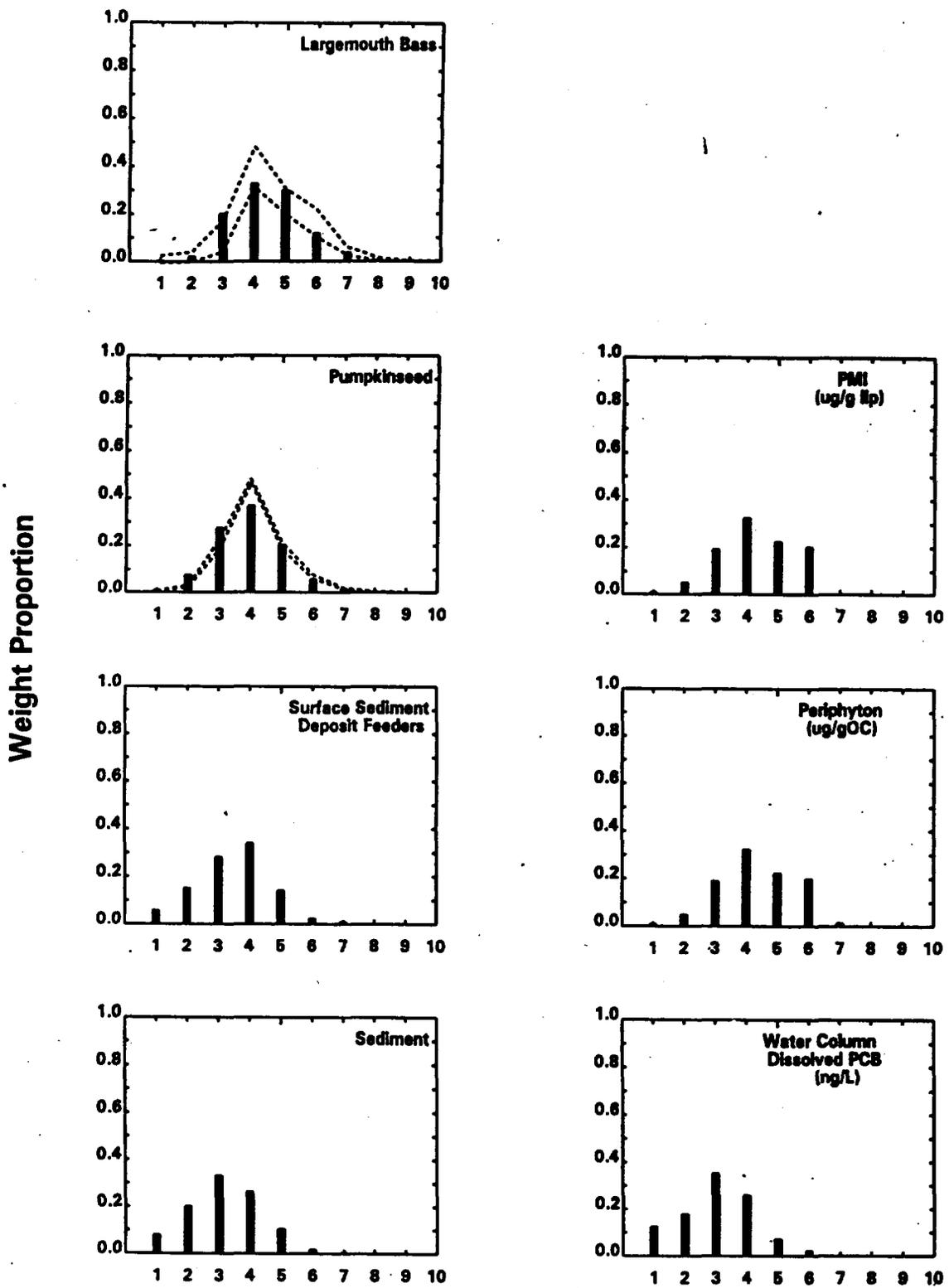


Figure 18. Steady state food web model simulation of TIP (exposure: realistic water, top 0-2 cm of sediment, see Table 6).

Weight Proportion

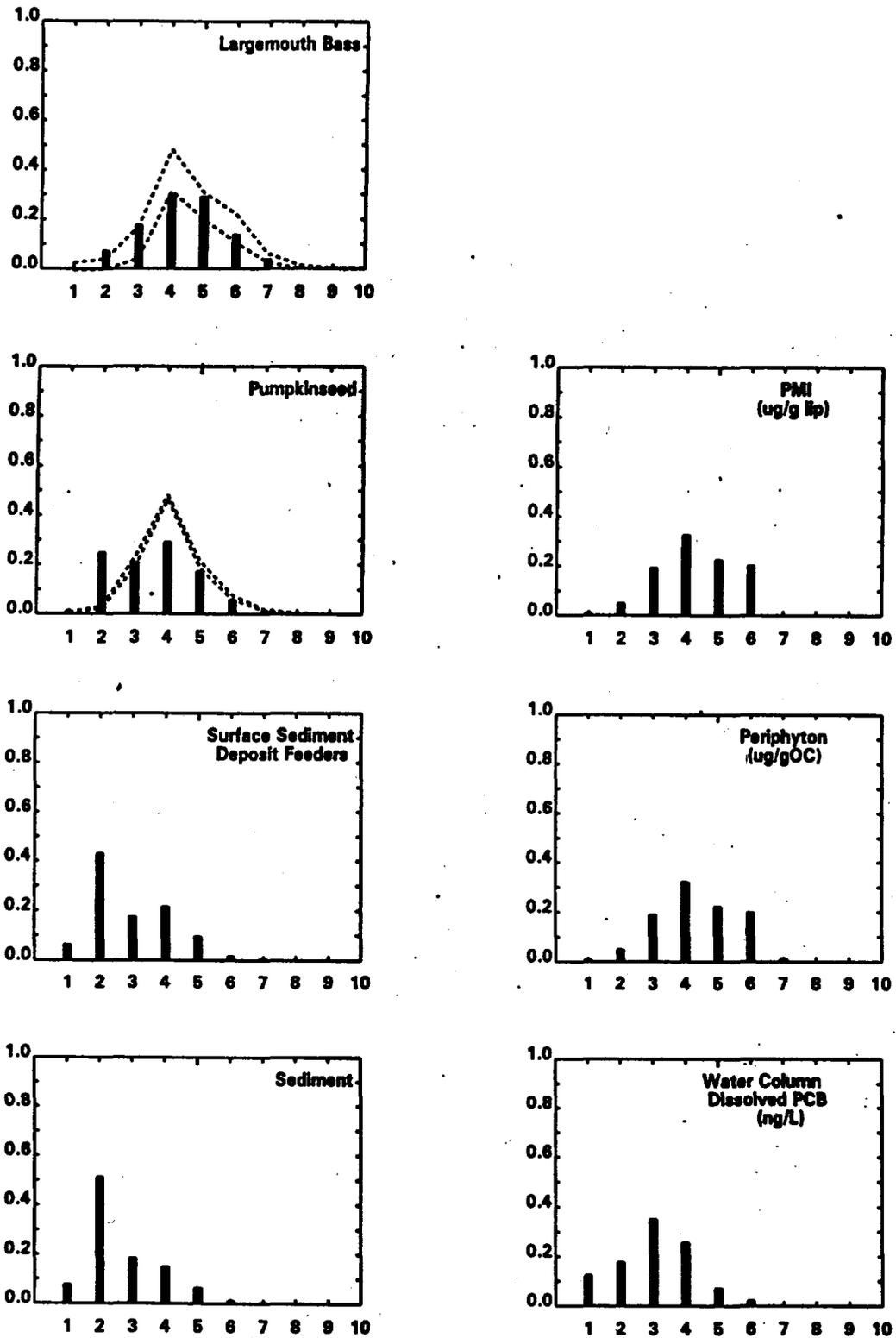


Figure 19. Steady state food web model simulation of TIP (exposure: realistic water, top 0-5 cm of sediment, see Table 6)

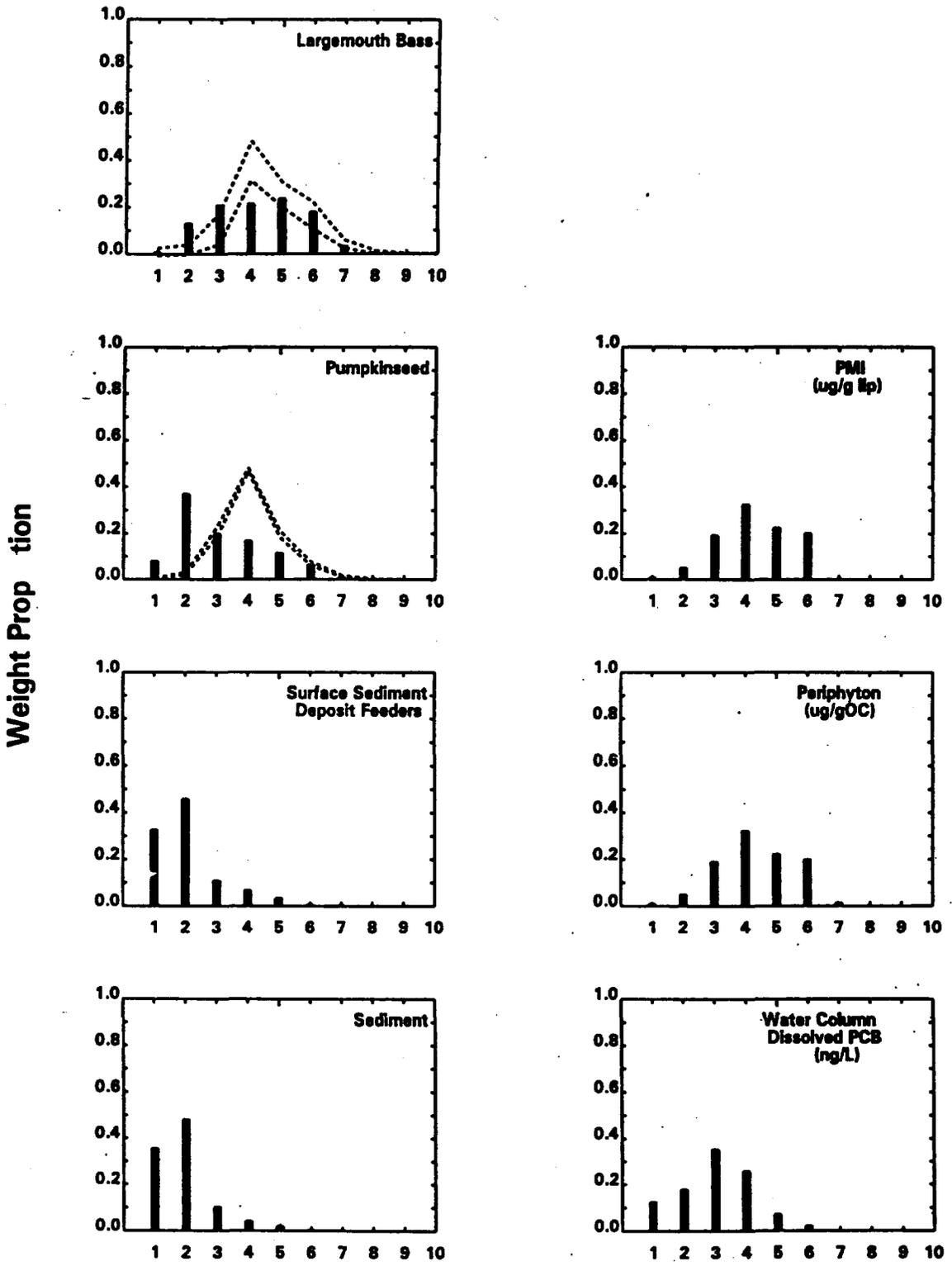


Figure 20. Steady state food web model simulation of TIP (exposure: realistic water, heavily dechlorinated sediments, see Table 6).

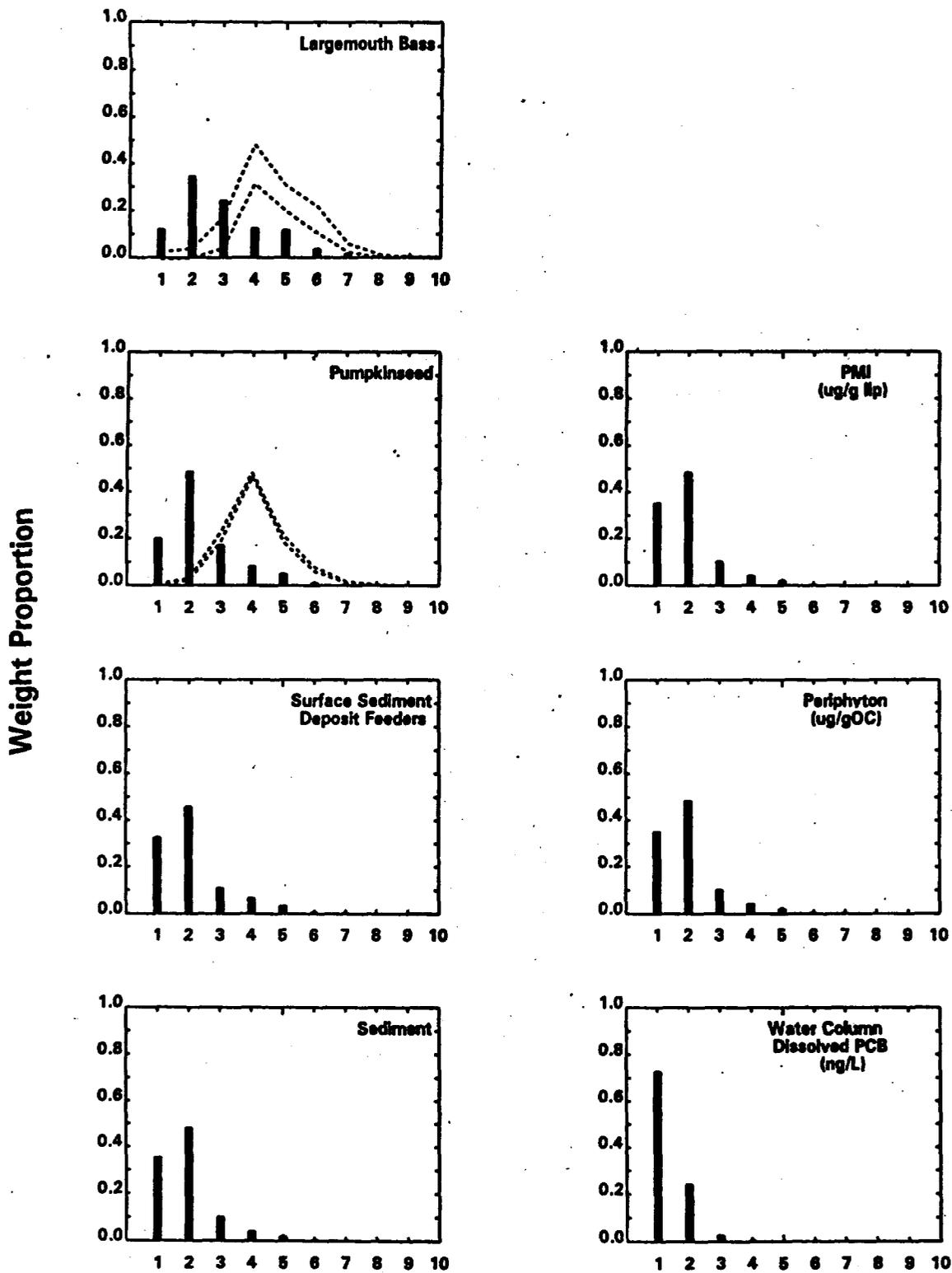
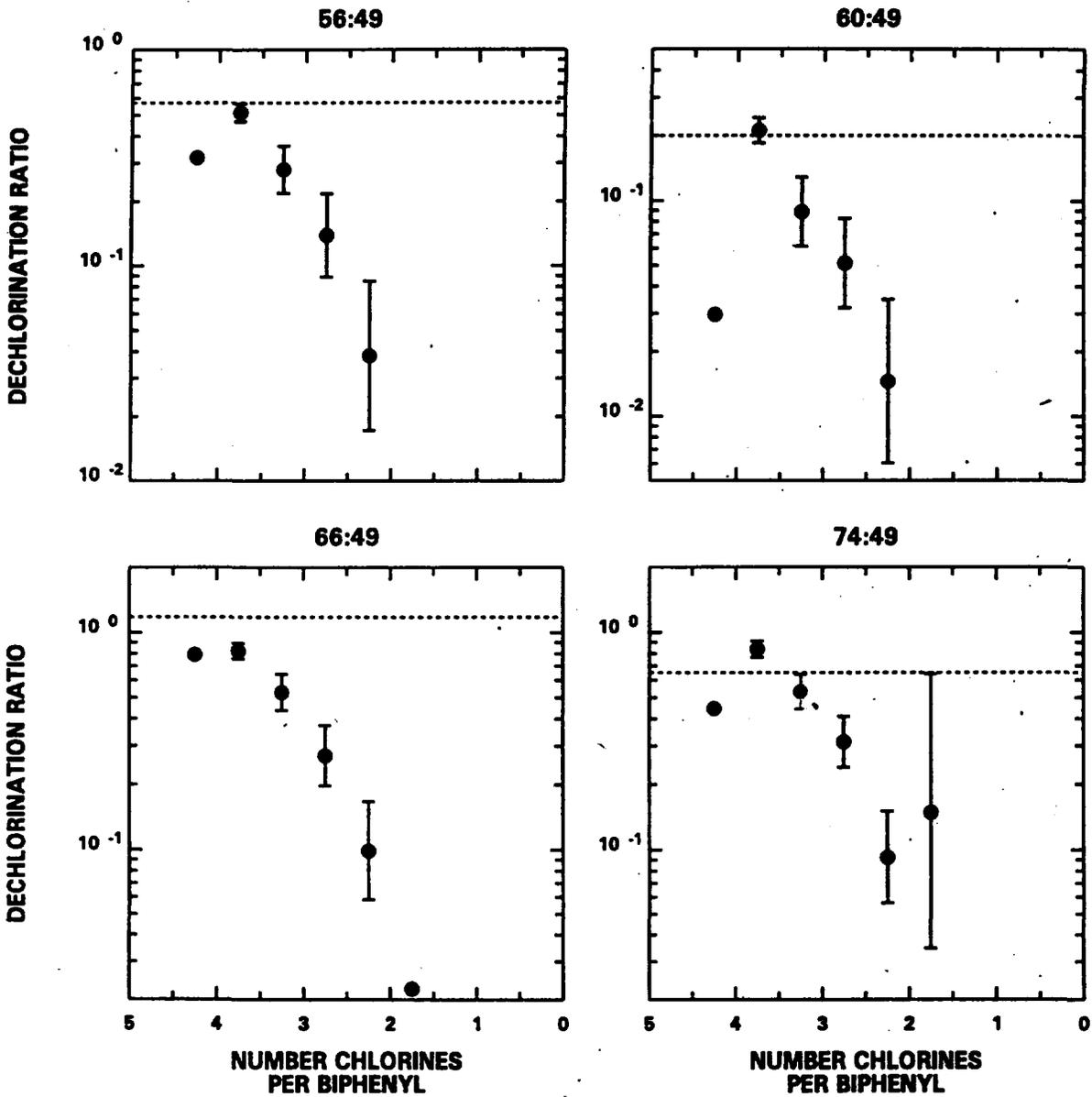
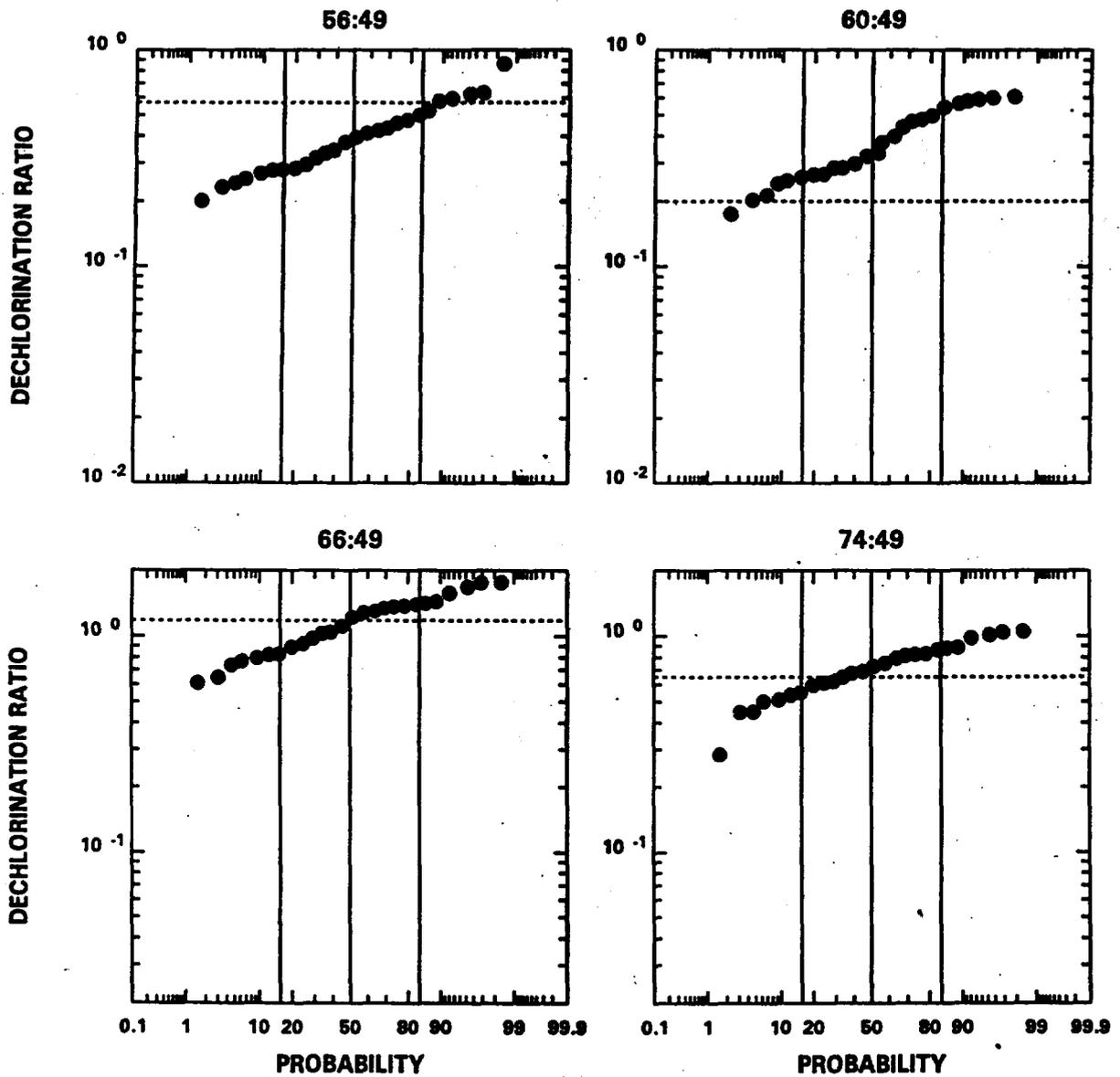


Figure 21. Steady state food web model simulation of TIP (exposure: heavily dechlorinated sediments and partitioned water, see Table 6).



Data are Geometric Means + Standard Errors (0.5 CL/BP bins)  
 Horizontal Dashed Line Represents Ratio in Aroclor 1242

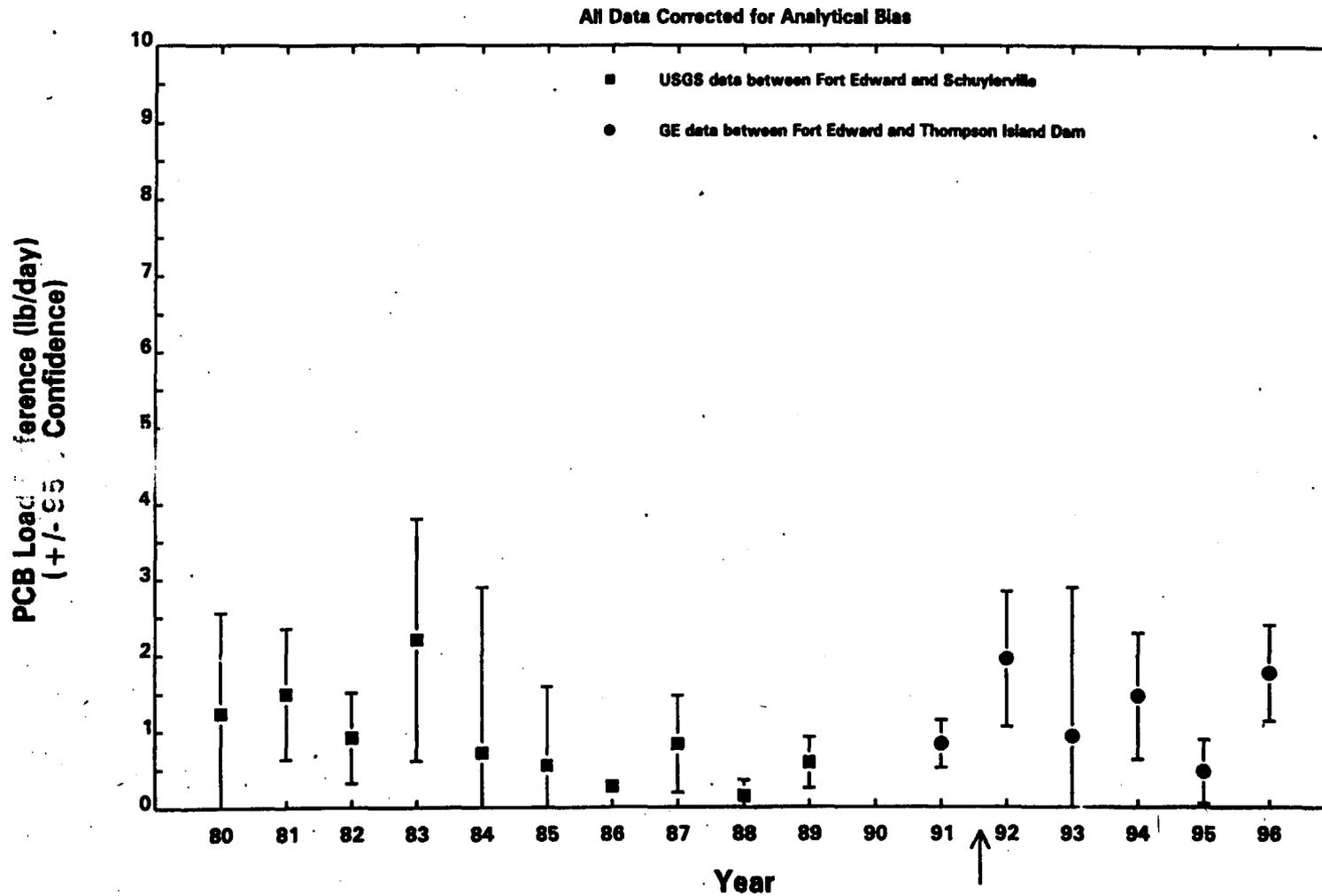
Figure 22. Relationship between PCB congener dechlorination ratios and number of chlorines per biphenyl in EPA Phase 1 high resolution sediment cores.



Upper Hudson (RM > = 153)

Figure 23. Probability distribution of PCB congener dechlorination ratio in 1993 NOAA fish samples.

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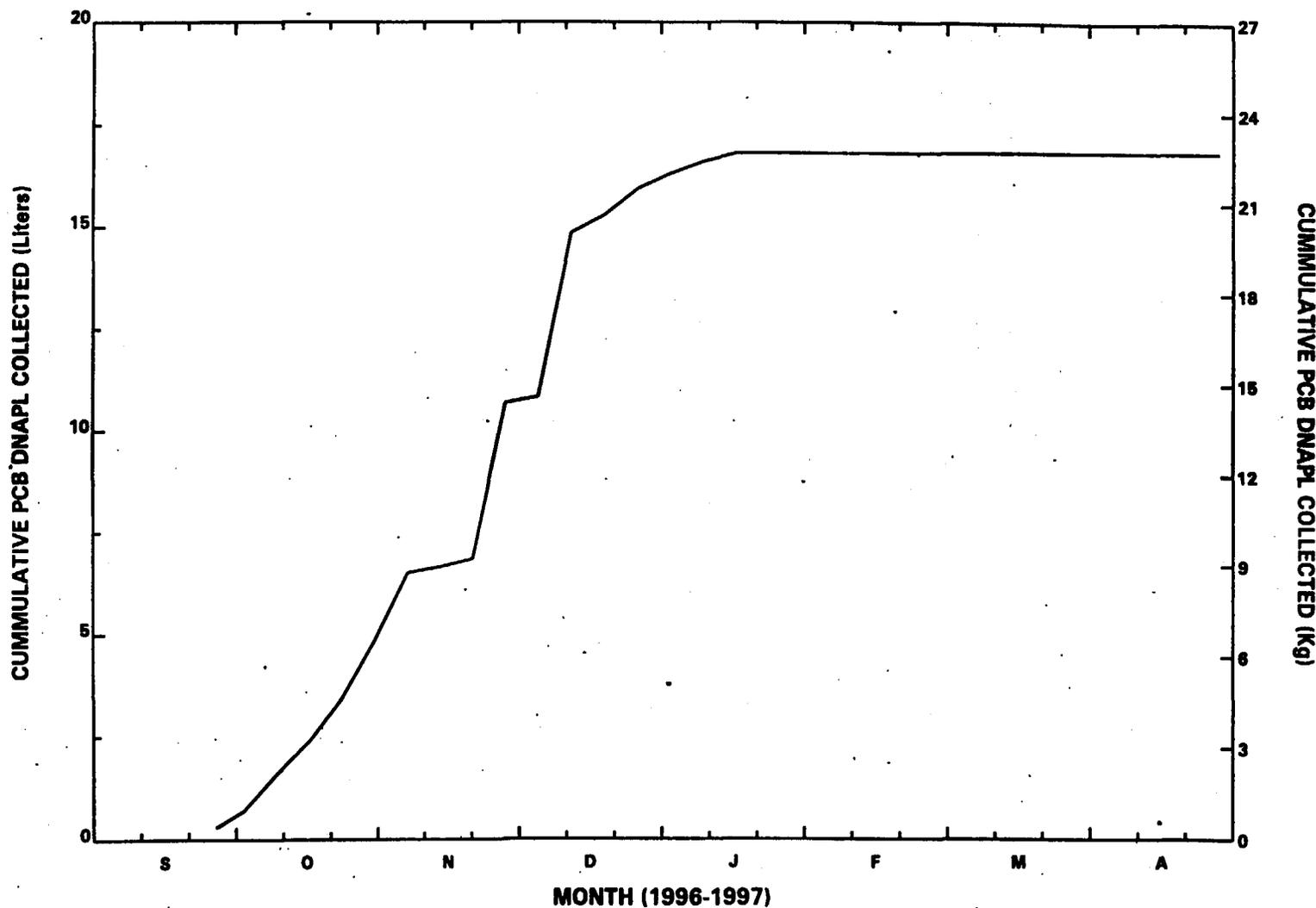
Flow at Fort Edward < 10,000 cfs, High loads from 9/91 to 12/91 excluded

Figure 24. Annual average TIP region loading (1980-1996)

# GENERAL ELECTRIC COMPANY

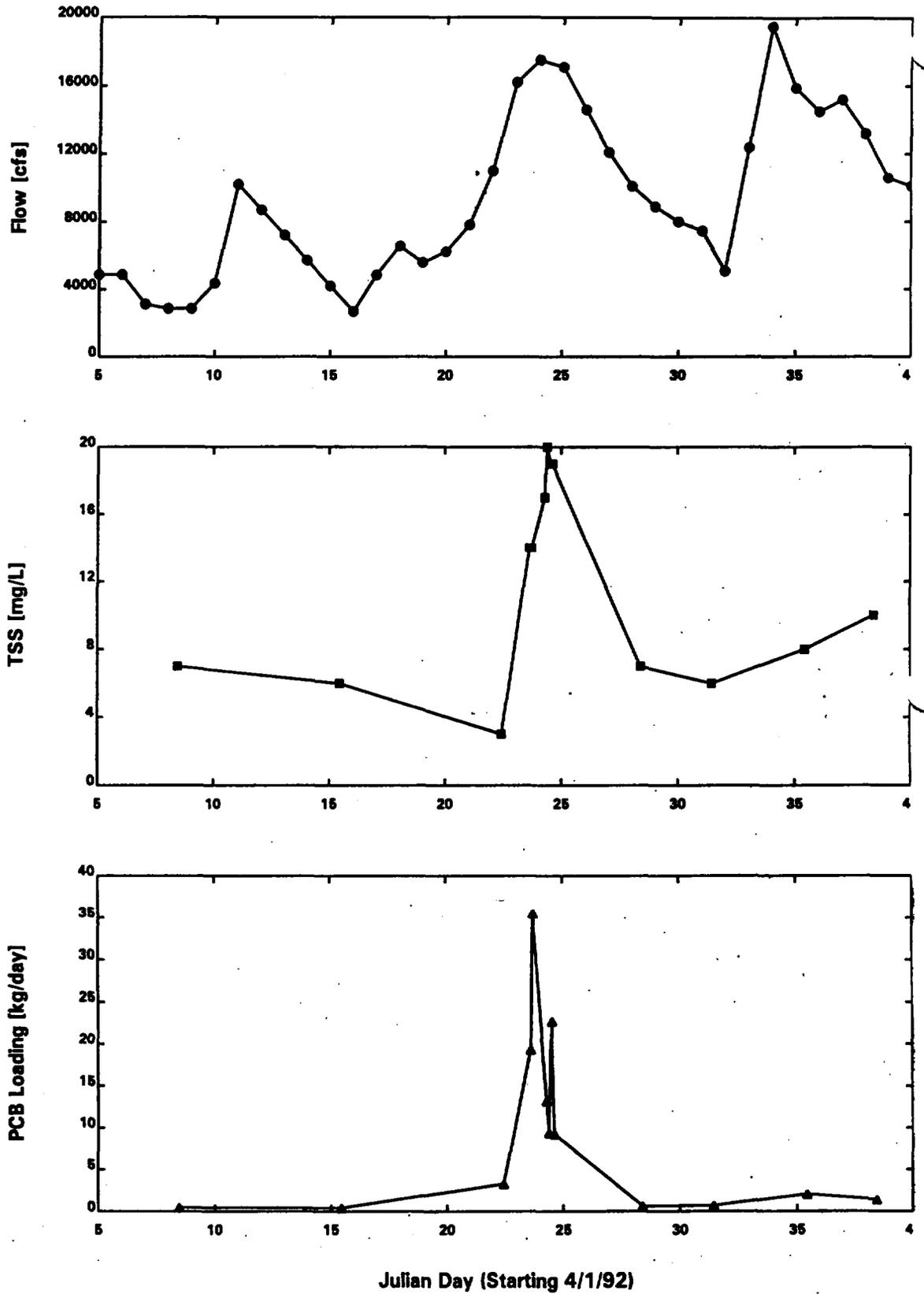
HUDSON FALLS PLANT SITE

Seep 13 DNAPL Recovery



HRP 003 0176

Figure 25. Cumulative PCB DNAPL oils collected from seep 13 (1996-1997).



PCB data are corrected for analytical bias

Figure 26. PCB and solids transport during 1992 spring high flow.

### Fluorescent Particle Mass Balance

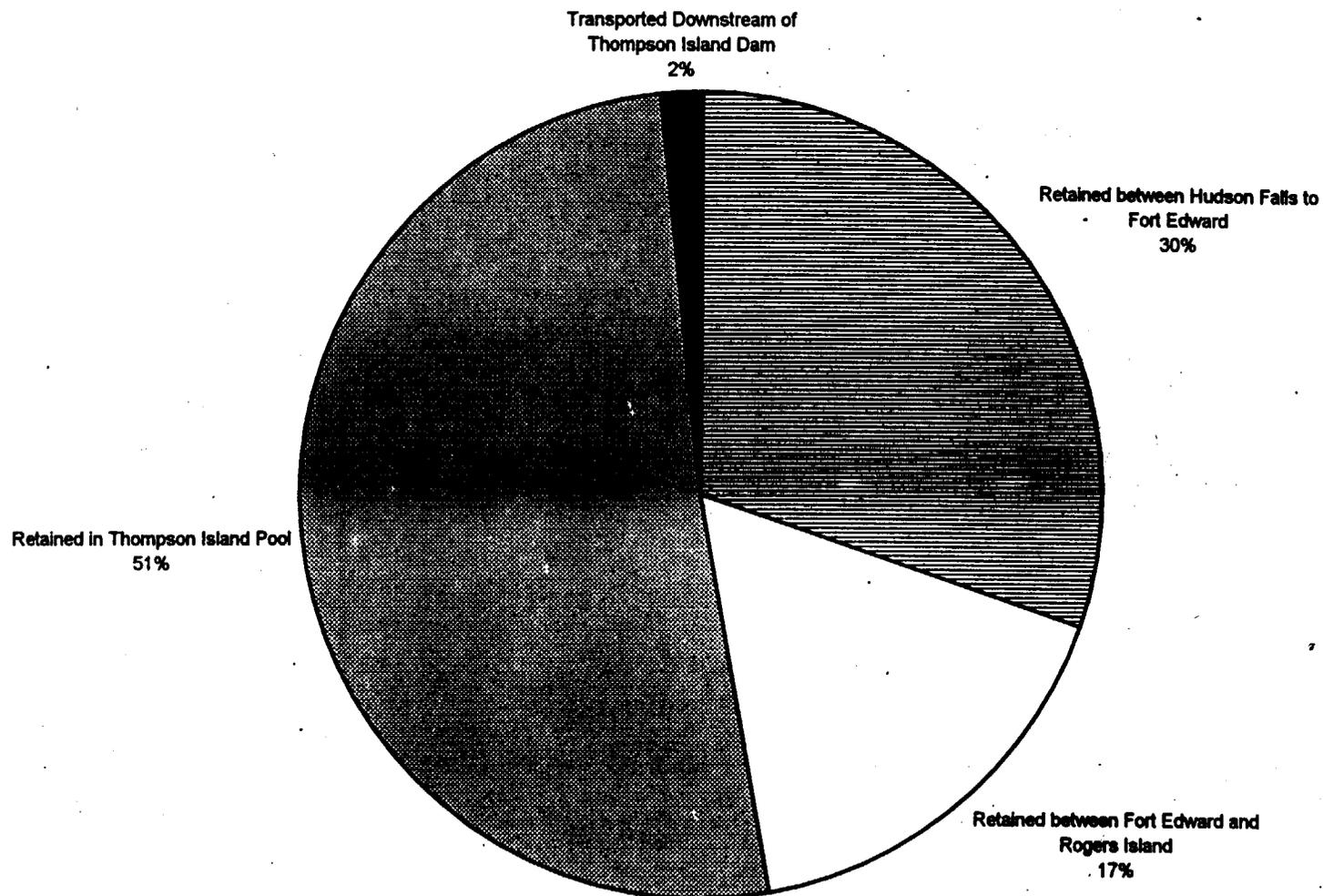


Figure 27. PCB DNAPL transport study fluorescent particle mass balance.

HRP 003 0178

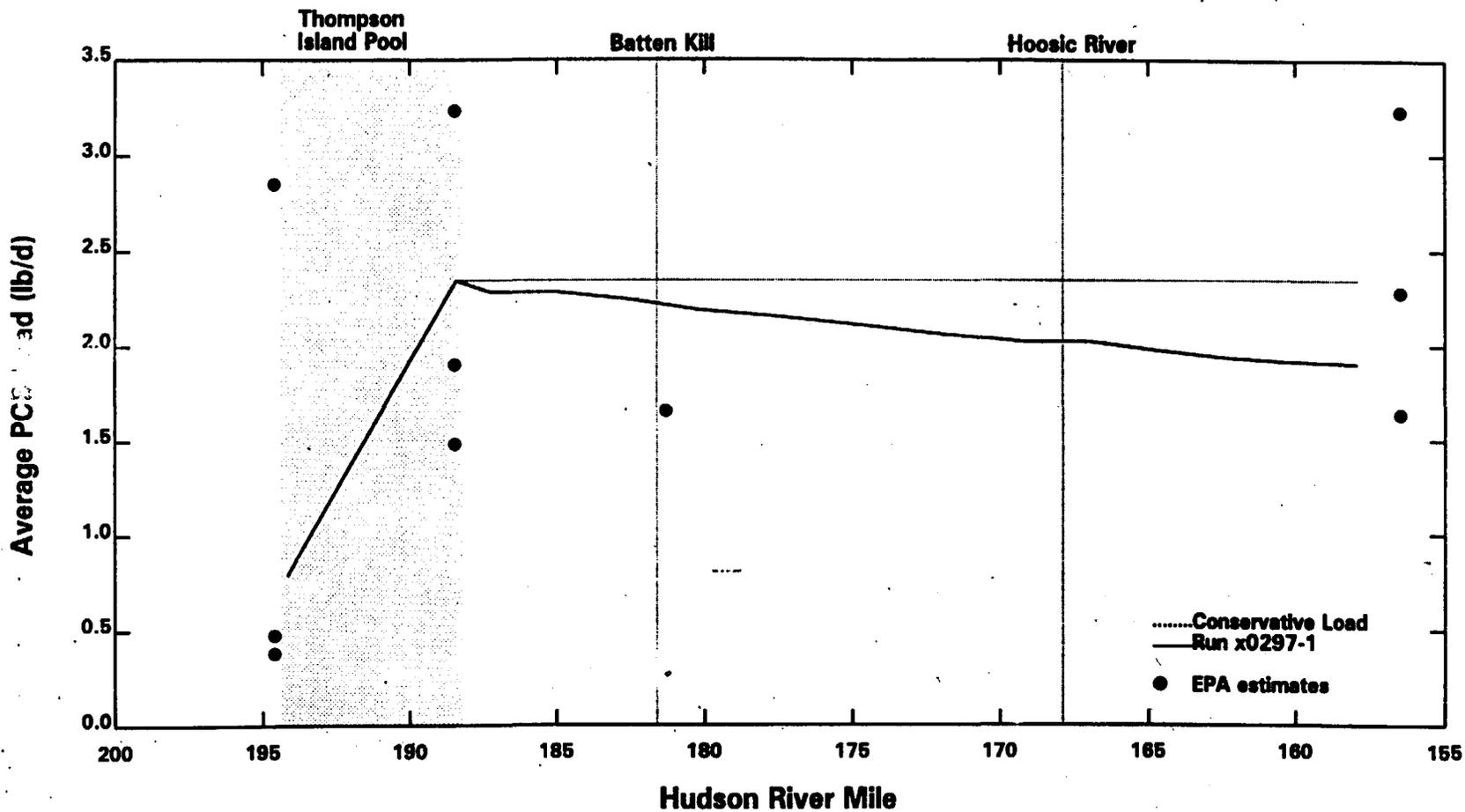


Figure 28. Predicted average June-August 1993 Hudson River PCB loading profile (river mile 195 - 155).

HRP-003 0179

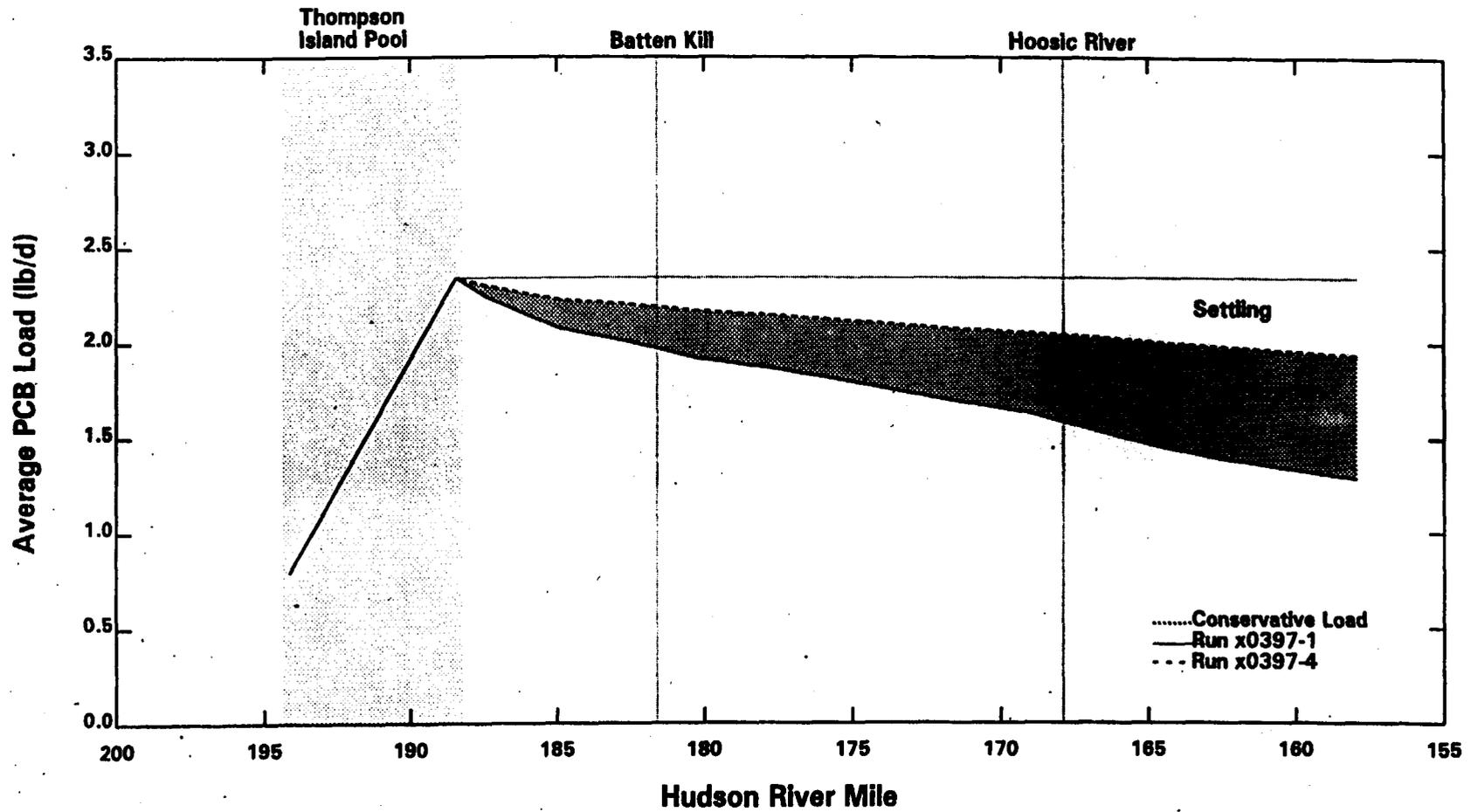


Figure 29. Predicted settling and volatilization components of average June-August 1993 Hudson River PCB loading profile (river mile 195-155).

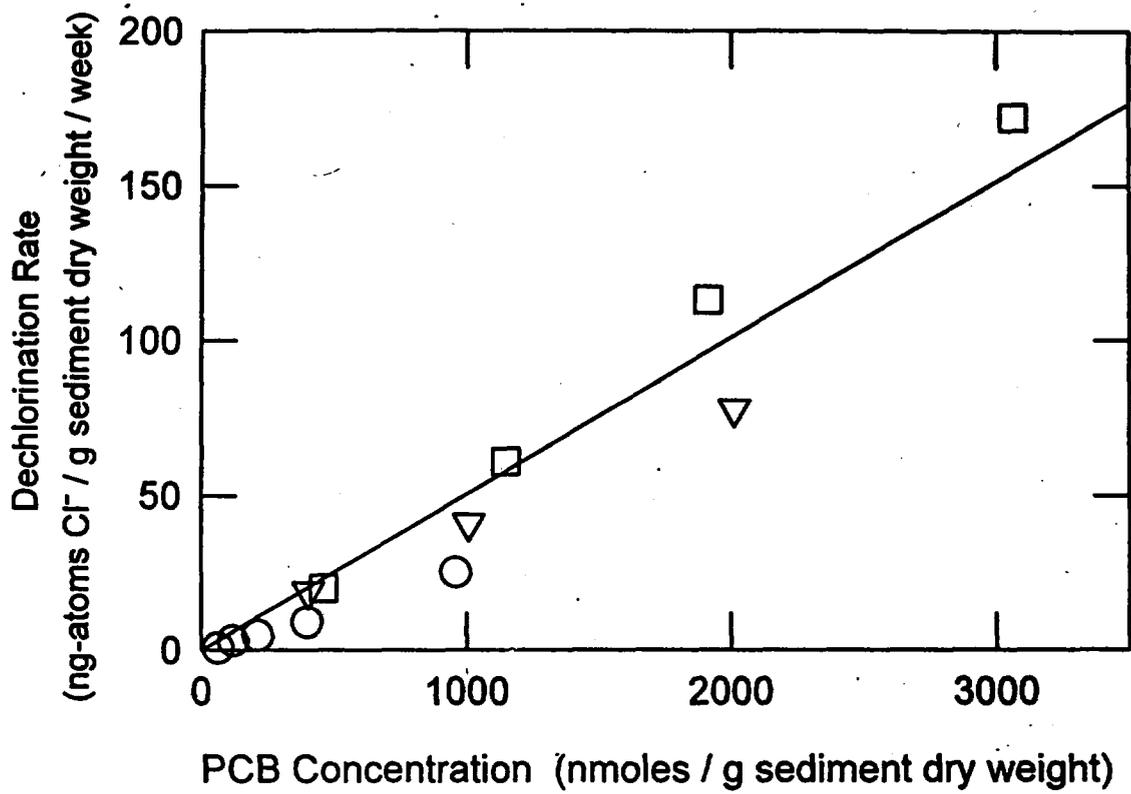
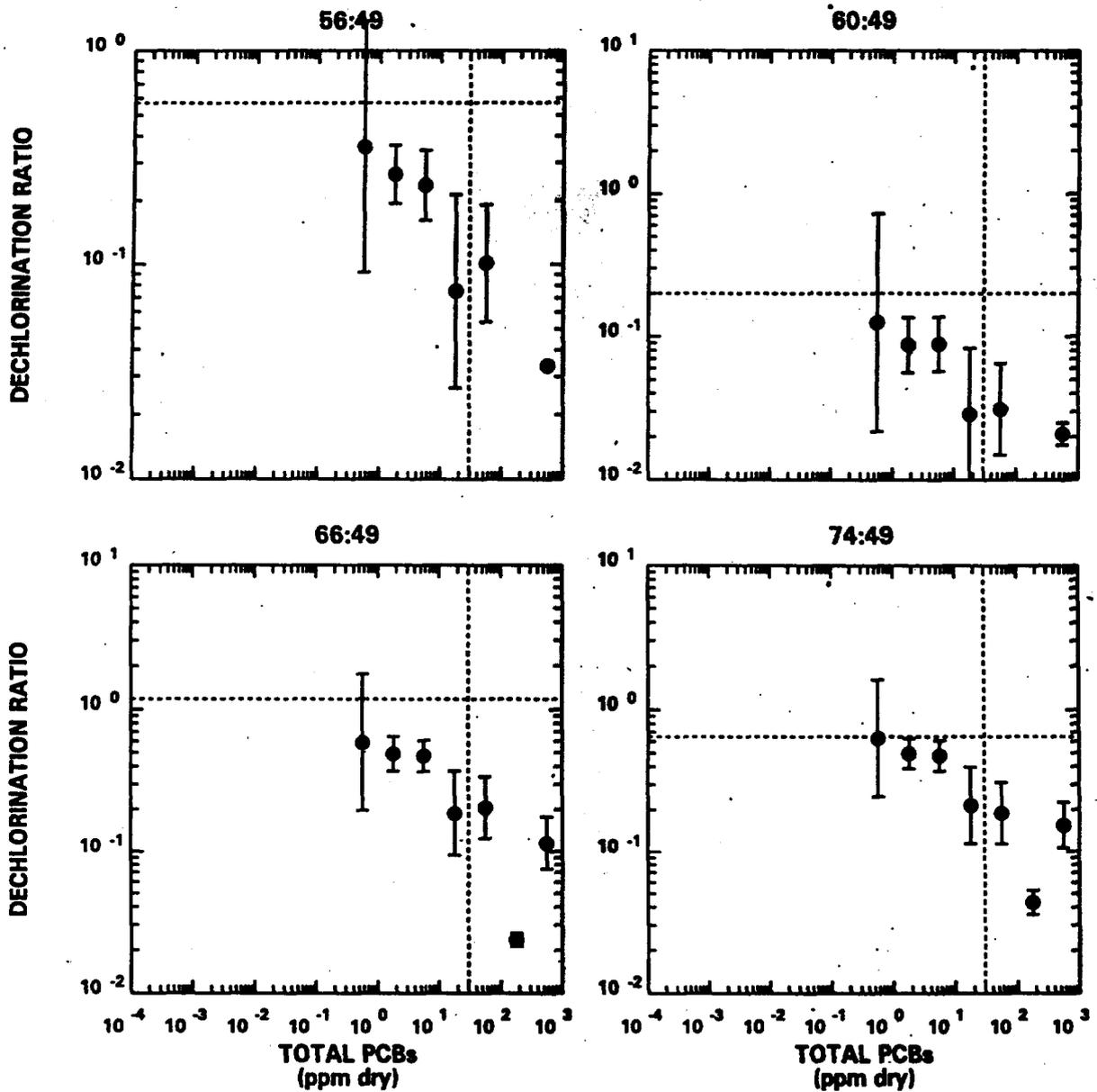


Figure 30. Absolute amount of chlorines removed from PCBs as a function of concentration.



USEPA Phase II High Resolution Sediment Core Data (UPPER HUDSON)  
 Data are Geometric Means +/- 2 Standard Errors (0.5 log unit bins)  
 Vertical Dashed Line Represents Total PCBs = 30 ppm dry  
 Horizontal Dashed Line Represents Ratio in Aroclor 1242

Figure 31. Intra-homologue PCB dechlorination peak ratio as a function of PCB concentration.

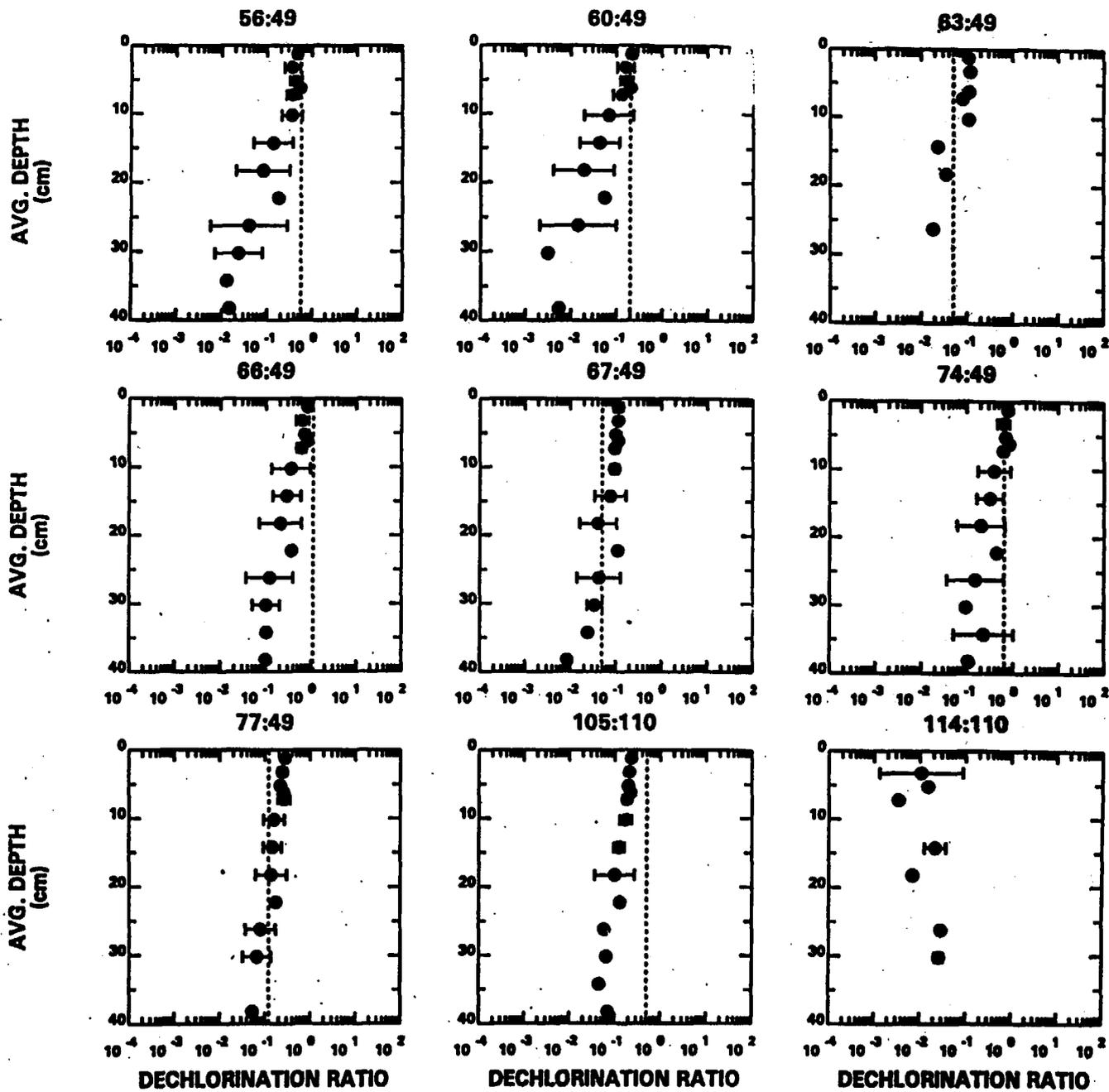


Figure 32. Intra-homologue PCB dechlorination peak ratio as a function of sediment depth for core segments with total PCB less than 30 ppm.