

**HUDSON RIVER PCBs REASSESSMENT RI/FS
RESPONSE TO PEER REVIEW COMMENTS ON THE
DATA EVALUATION AND INTERPRETATION REPORT (DEIR) AND
THE LOW RESOLUTION SEDIMENT CORING REPORT (LRC)**

NOVEMBER 2000



For

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

**TAMS Consultants, Inc.
TetraTech, Inc.**

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I. INTRODUCTION

The United States Environmental Protection Agency (USEPA) has prepared this Response to Comments from the Peer Review of the Data Evaluation and Interpretation Report (DEIR) and the Low Resolution Sediment Coring Report (LRC) for the Hudson River PCBs Reassessment Remedial Investigation/Feasibility Study (Reassessment). It addresses significant comments made in the Report on the Peer Review of the Data Evaluation and Interpretation Report and Low Resolution Sediment Coring Report for the Hudson River PCBs Superfund Site, which occurred between January and March, 1999. The peer review, which was the second of five separate peer reviews conducted for the Reassessment, was intended to ensure that the USEPA science used in the Reassessment and embodied in the DEIR, LRC and associated Responsiveness Summaries is technically adequate, competently performed, properly documented, and satisfies established quality requirements.

The DEIR, LRC and associated Responsiveness Summaries are incorporated by reference and are not reproduced herein. No revised copies of these documents will be published as such. The comment responses and revisions noted herein are considered to amend the reports. For complete coverage, the DEIR, LRC and associated Responsiveness Summaries and this Response to Peer Review Comments must be used together.

The first part of this Response to Peer Review Comments is the "Introduction" section. This section describes the Reassessment peer review process and explains the organization and format of comments and responses.

The second part, entitled "Peer Review Comments", contains the comment directory and summarizes the final recommendations of each of the Peer Review experts on the DEIR, LRC and associated Responsiveness Summaries. The comments are identified by commentor and comment number, as further explained in the Comment Directory. A summary of the each reviewers' comments is excerpted from the Report on the Peer Review of the Data Evaluation and Interpretation Report and Low Resolution Sediment Coring Report for the Hudson River PCBs Superfund Site (USEPA, 1999a). The full text of the Report on the Peer Review contains additional information on the peer review.

The third part, entitled "Responses to Comments", contains the USEPA responses to the major comments by the peer reviewers. Tables and figures for the responses are found within the text of this Response to Peer Review Comments. This Response to Peer Review Comments also contains three attachments, providing information that has been prepared in response to the peer review

comments. Note that each attachment begins with a table of contents, listing the figures and tables contained in the attachment. The respective tables and figures are contained at the end of each of the attachments.

Recent Developments

Attachment A contains a principal components analysis which examines the relationship among the PCB patterns found in the sediments of the Hudson. This analysis aids in the identification of the major PCB sources to the Hudson, confirming the dominance of GE-related PCB contamination in all freshwater areas of the Hudson south of Hudson Falls. The principal components are closely related to the geochemically-derived parameters used in the DEIR, providing statistical support for the approaches used in the DEIR.

Attachment B contains a revised executive summary of the information found in the DEIR, LRC and Responsiveness Summaries. As part of the Responsiveness Summaries, additional analyses were performed which have made minor changes to the original conclusions of the DEIR and LRC. These alterations are incorporated yielding a single list of conclusions for these two geochemistry reports.

An analysis of the affect of gas exchange in the Upper Hudson on water-column load is presented in Attachment C.

1. PEER REVIEW PROCESS

This section documents and explains the peer review process and the organization of comments and responses in this document. To find responses to particularly comments, the reader should go to the Comment Directory on page CD-1.

The peer review process was managed by Eastern Research Group, Inc. (ERG), including selecting reviewers, briefing the reviewers on the site, and organizing the peer review meeting.

1.1 Selecting the Reviewers

To organize a comprehensive peer review, six independent peer reviewers were selected who are engineers or senior scientists with demonstrated expertise in any combination of the following technical fields:

- River sedimentology
- Low and high resolution sediment coring
- Hydrology and water-column fate and transport
- Geochemistry

- Analytical chemistry of PCBs
- Anaerobic dechlorination of PCBs

The collective expertise of the selected peer reviewers covers the six technical areas (i.e., at least one reviewer has expertise in analytical chemistry of PCBs, at least one reviewer has experience in river sedimentology, and so on). Biographies for the six reviewers can be found in USEPA, 1999a.

To ensure the peer reviewers' independence, ERG only selected individuals who could provide an objective and fair critique of USEPA's work. As a result, the reviewer selection process only included individuals who were not associated in any way with preparing the DEIR or the LRC or individuals associated with GE or any other specifically identified stakeholder.

1.2 Briefing the Reviewers

The six reviewers were provided with the:

- Data Evaluation and Interpretation Report (USEPA, 1997)
- The Responsiveness Summary for the DEIR (USEPA, 1998b)
- Low Resolution Sediment Coring Report (LRC) (USEPA, 1998a)
- The Responsiveness Summary for the LRC (USEPA, 1999d)
- Hudson River Reassessment Database, which contains all of the sampling data used to prepare the above reports.

To focus the reviewers' evaluations of the documents, USEPA developed written guidelines for the technical review. These guidelines, which are commonly referred to as a charge, were presented during the briefing meeting and asked the reviewers to address at least the following topics: whether the main conclusions of the DEIR and LRC are well supported by the data; if the data presented in these reports is sufficient for understanding fate and transport mechanisms in the Upper Hudson River; and if additional analyses should be performed to verify certain findings of the reports. A copy of this charge, which includes many additional topics and questions, is included in USEPA, 1999a as Appendix B.

In the weeks following the briefing meeting, the reviewers prepared their initial evaluations of the DEIR, the LRC, and the Responsiveness Summaries. The premeeting comments were compiled and distributed to the reviewers, and made available to observers during the peer review meeting. The premeeting comments are included in USEPA, 1999a, without modification. It should

be noted that the premeeting comments are preliminary in nature and some reviewers' technical findings might have changed based on discussions during the meeting. As a result, the premeeting comments should not be considered the reviewers' final opinions.

The peer reviewers were asked to base their premeeting comments on the DEIR, the LRC, and the Responsiveness Summaries. Though not required for this review, some reviewers might also have researched site-specific reports they obtained from other sources.

1.3 Peer Review Meetings

The six reviewers attended two meetings, which were both open to the public. The first meeting, which took place in Albany, New York, on January 11-12, 1999, included several presentations and a tour of the Upper Hudson River to familiarize the reviewers with the site and its environmental history. The second peer review meeting, which was held at the Albany Marriott Hotel in Albany, New York, on March 16-18, 1999, was attended by the six expert reviewers and at least 30 observers. The discussions were held to answer the questions in the charge. The charge, specific and general questions for the Peer Review, and the reviewers' responses to the general and specific charge questions are included in the Peer Review Report, USEPA, 1999a.

2. ORGANIZATION OF COMMENTS AND RESPONSES TO COMMENTS

2.1 Identification of Comments

Each comment submitted for a Report was assigned a dual letter code. The letters stand for the initials of the commentor. The comments are numbered sequentially for each commentor. For example, Reinhard Bierl's comments are RB-1 through RB-5. The letter codes were assigned for the convenience of readers and to assist in the organization of this document; priority or special treatment was neither intended nor given in the responses to comments. The alphanumeric code associated with each reprinted written submission is marked within the text in the Comments section.

2.2 Location of Responses to Comments

The Comment Directory, in the following section, contains a complete listing of all commentors and comments. This directory allows readers to find responses to comments. The comment directory table is organized as follows:

- The columns list the comment number, the recommendation and the names of the commentors.
- Each of the comments recommendations is coded, RB-1 is Reinhard Bierl's (RB) first comment. The text of this comment can be located under the Comments section.

Responses are answered in the order given by the comment number in the Responses section. For many of the recommendations, several commentors commented on the same or very similar items. These comments are answered by one common response that addresses the common issue being raised. Thus, a comment is not necessarily answered by an individualized response.

II. PEER REVIEW COMMENTS

1. COMMENT DIRECTORY

Comment No.	Recommendation	Reinhard Bierl	Per Larsson	Keith Maruya	Ron Mitchum	Ken Reimer	J. Bruno Risatti
1	Use multivariate statistical analyses of the data to support the conclusions of the DEIR and LRC.	RB-1	PL-2	KM-2	RM-2 RM-6	KR-3	
2	More prominently acknowledge uncertainty in conclusions; use data ranges to present findings that might be highly uncertain; discuss the implications of analytical variability	RB-3		KM-3 KM-8	RM-3 RM-5	KR-2 KR-5	BR-1
3	Publish a concise summary of the information in the DEIR, LRC and Responsiveness Summaries			KM-1		KR-1	
4	Consider the limnology of the TIP and other pools in the Hudson River (e.g., how primary production affects PCB fate and transport)			KM-5			
5	Validate the conceptual models and other findings with more recent water column sampling data	RB-4		KM-4			
6	Use two-phase partition coefficients until enough data are available to derive three-phase coefficients			KM-6			
7	Modify the conclusion regarding the 30 ppm threshold for anaerobic dechlorination			KM-7	RM-4	KR-4	BR-4
8	Further consider how elevated PCB concentrations in near-shore sediments might affect inventory estimates			KM-9			
9	Use more sophisticated statistical analyses to estimate PCB inventory	RB-2					
10	Provide additional details on the analytical methods used in the various sediment coring studies	RB-4					

Comment No.	Recommendation	Reinhard Bierl	Per Larsson	Keith Maruya	Ron Mitchum	Ken Reimer	J. Bruno Risatti
11	Review more recent sampling data and consider implementing ongoing sediment monitoring studies in order to more fully understand the system (research such as better characterizing the partitioning of PCBs between the suspended and dissolved phases)	RB-5					
12	Describe the data analysis methodology in the reports		PL-3				
13	Consider other compartments in the PCB mass balance (e.g., evaporative losses, photo chemical degradation, aerobic degradation)				RM-1		BR-3
14	Conduct sedimentological studies concurrent with water column sampling						BR-2
15	Conduct an experiment to characterize the extent of cross contamination in "vibracoring" samples.						BR-6
16	Establish guidelines for writing future reports						BR-7
17	Include a basic model to estimate the source loading of the sediments from the TIP to the water column		PL-1				
18	The MDPR may underestimate the extent of dechlorination since the ratio is based on congeners that are more susceptible to transport from the sediments.						BR-5

Note:

The text of the final recommendations are indicated under Recommendations.

2. SUMMARY OF PEER REVIEW COMMENTS ON THE DEIR/LRC

A summary of the reviewers' final recommendations is provided below. The commentor's recommendations as cited in this document are in bold text in parenthesis, i.e. **(KM-1)**. See Comment Directory to find the report section which discusses the recommendation.

5.0 REVIEWERS' OVERALL RECOMMENDATIONS

After answering the specific and general questions in the charge, and after listening to the second set of observer comments, the reviewers reconvened to provide their final findings on EPA's reports. The reviewers decided to offer these findings as individual statements, during which other reviewers did not discuss or debate each reviewer's final recommendations. Section 5.1 summarizes each peer reviewer's final statements, and the Comment Directory on page CD-1 identifies common themes among these final recommendations.

5.1 Peer Reviewers' Final Statements

The peer review meeting concluded with each peer reviewer providing closing statements on the reports, including an "overall recommendation" in response to the final question in the charge: "Based on your review of the information provided, please identify and submit an explanation of your overall recommendation for both the DEIR and LRC.

1. Acceptable as is
2. Acceptable with minor revision (as indicated)
3. Acceptable with major revision (as outlined)
4. Not acceptable (under any circumstance)"

A detailed summary of the peer reviewers' final statements, in the order they were given, follows:

Dr. Keith Maruya. Dr. Maruya indicated that he accepted the main conclusions of the reports, though he did have suggestions and recommendations for improving them. First, he suggested that EPA publish a concise summary of the information provided in the DEIR, LRC, and the Responsiveness Summaries. **(KM-1)** He recommended the use of multivariate statistical analyses to make certain conclusions in these reports more convincing. **(KM-2)** Dr. Maruya also recommended the reports more prominently acknowledge the uncertainty in some key findings, like the estimated mass loss of PCBs. **(KM-3)**

Focusing specifically on the DEIR, Dr. Maruya first reiterated a recommendation he had mentioned earlier in the meeting: EPA should validate the findings of the conceptual

models with more recent water column sampling data. He thought such validation would better quantify PCB sources between Roger's Island and Waterford during times when upstream sources of PCBs are negligible. (KM-4) Dr. Maruya then suggested that EPA consider the limnology of the TIP and other pools in the Hudson River for a better understanding of PCB transport (e.g., how primary production affects partitioning, fate, and transport of PCBs). (KM-5) On the topic of partition coefficients, Dr. Maruya recommended that EPA only use the two-phase coefficients derived in the DEIR until sufficient data are available to estimate the three-phase coefficients. (KM-6) Dr. Maruya did not think the data in the DEIR supported a 30 ppm threshold below which PCB dechlorination reportedly does not occur. (KM-7)

Commenting on the LRC, Dr. Maruya first concluded that the comparisons between the PCB inventories in 1984 and 1994 were reasonable and the data from 1977 were not sufficient for inventory estimates. He thought the analytical variability contributed to considerable uncertainty in the inventory estimates, which the LRC did not acknowledge. (KM-8) Dr. Maruya thought EPA should further consider how elevated PCB concentrations in near-shore sediments might have affected the inventory estimates. (KM-9) Finally, Dr. Maruya maintained that the sampling data suggest that widespread burial of PCBs does not occur.

Overall, Dr. Maruya thought the DEIR and LRC were both "acceptable with minor revisions."

Dr. Ken Reimer. Dr. Reimer concluded that the weight of evidence of the data presented in the DEIR and LRC generally support the reports' main conclusions, especially as they were modified in the Responsiveness Summaries. He thought the data collected for the reports provided an adequate basis for EPA to proceed with its Reassessment.

Dr. Reimer then listed several suggestions and recommendations. First, noting that the public might have difficulty identifying the basic messages of the DEIR and LRC, Dr. Reimer recommended that EPA prepare a succinct summary of the major findings of these reports. (KR-1) Second, he strongly recommended that EPA's reports present quantitative findings in appropriate context, particularly with respect to uncertainty. Dr. Reimer suggested that EPA consider presenting ranges of data when the actual values are not known. He cautioned EPA about "over interpreting" data. (KR-2)

Focusing on the main conclusions of the reports, Dr. Reimer indicated that they were generally supported by the data, but with a few caveats. He thought the conceptual models used to interpret the water column transect studies could be improved, for example, with the use of multivariate analyses to "fingerprint" sources of PCBs. (KR-3) Further, Dr. Reimer suggested that the reports not infer that anaerobic dechlorination of PCBs does not occur at PCB concentrations less than 30 ppm. (KR-4) He added, however, that dechlorination is "a very minor issue" in terms of the overall problem of contaminated sediments. Dr. Reimer then discussed the issue of estimating PCB mass loss in the sediments: he thought the 1984 and 1994 were sufficient for making these estimates; he cautioned against presenting firm estimates of the mass loss; and he also

cautioned against using the 1977 sediment coring data for this purpose. **(KR-5)** Finally, Dr. Reimer concluded that the data suggest that widespread burial of PCBs does not occur in the TIP and that the TIP sediments act as a source of PCBs to the water column.

Overall, Dr. Reimer found the DEIR and LRC to be "acceptable with minor revisions."

Dr. Reinhard Bierl. Dr. Bierl opened his final statements by indicating that the data reported in the DEIR and LRC are sufficient for EPA to proceed with its reassessment, but he identified several aspects of the reports that should be improved to make them more convincing. Regarding the statistical methods used in the reports, Dr. Bierl recommended the use of multivariate analyses to quantify certain trends **(RB-1)** and additional statistical analyses to calculate changes in PCB inventories. **(RB-2)** Dr. Bierl then suggested that EPA qualify its quantitative estimates of PCB mass loss to put these figures into perspective. **(RB-3)** Dr. Bierl added that he wanted to see more information in the reports on the PCB analytical methods (e.g., quality assurance plans and standard operating procedures). He thought this information was particularly lacking for the previous sediment coring studies. **(RB-4)**

Noting the time gaps between the various sediment coring studies, Dr. Bierl recommended that EPA consider reviewing more recent sampling data and possibly even consider implementing ongoing monitoring studies. He thought future studies should focus on characterizing how PCBs partition between the suspended and dissolved phases, among other research topics. **(RB-5)**

Overall, Dr. Bierl found the DEIR and LRC to be acceptable with revisions, but he was not sure whether his recommended revisions should be considered "minor" or "major."

Dr. Per Larsson. Dr. Larsson concluded that the data summarized in the DEIR and LRC identified major source areas of PCBs in the Hudson River and characterized the extent of contamination in these areas. Dr. Larsson found that the data indicate a loss of PCBs from the river sediments, but he thought the exact amount of losses are difficult to quantify. He reminded the reviewers, however, that even "a very small percentage" loss of PCBs might have very serious consequences on downstream ecosystems.

Dr. Larsson then reviewed his responses to selected questions in the charge. First, he found that the river sediments in the TIP undoubtedly act as a source of PCBs to the water column; he recommended that EPA include a basic model in the final report to estimate the source loading of the sediments. **(PL-1)** Second, Dr. Larsson commended EPA's work on differentiating dissolved phase PCBs from suspended phase PCBs--a distinction he thought would be important for future analyses of bioavailability. Third, Dr. Larsson noted that he and other reviewers had questions about the mechanisms that cause PCBs to enter the water column; he suspected that particle transport (rather than bioturbation or pore water diffusion) is probably the primary mechanism affecting PCB transport. Finally, Dr. Larsson addressed the findings of PCB mass loss and sediment burial. He was convinced that PCBs are gradually transporting with the sediments, and he speculated that the river sediments will continue to redistribute in the future. Noting that

the Hudson River is a dynamic system, Dr. Larsson cautioned against assuming data trends from a 10-year time frame are representative of river conditions over the longer term.

Based on his review of the documents, Dr. Larsson thought two specific revisions were necessary. He recommended the use of multivariate statistics for identifying and quantifying trends and patterns among the large volume of congener-specific data. **(PL-2)** He also recommended the reports thoroughly describe the data analysis methodology, such that the statistical analyses are transparent and easier to follow. **(PL-3)**

Overall, Dr. Larsson thought the DEIR and LRC were "acceptable with minor revisions."

Dr. Ron Mitchum. Dr. Mitchum split his comments into those specific to the DEIR and those specific to the LRC. Beginning with the DEIR, Dr. Mitchum noted that many of the report's original conclusions had been "softened" in the Responsiveness Summary. He then offered several suggestions for future work on the site and improving the DEIR. He first recommended that EPA include in its ongoing analysis some assessment of evaporative losses and photochemical degradation of PCBs. **(RM-1)** Dr. Mitchum then suggested that EPA use multivariate statistical analyses to verify many of the findings in the report. **(RM-2)** He also suggested that the report's conclusions include discussions about uncertainty, particularly in regard to sampling and analytical variability. **(RM-3)** Dr. Mitchum thought the DEIR's original conclusion of a concentration threshold for anaerobic dechlorination was not well founded. **(RM-4)**

Dr. Mitchum then summarized his major findings pertaining to the LRC. First, he concluded that EPA did "the best job possible" in comparing the 1984 and 1994 sediment coring data. Dr. Mitchum added, however, that sampling and analytical variability limited the confidence he had in the estimated PCB inventories. Regardless of the uncertainty, Dr. Mitchum believed the 1984 and 1994 data sets support EPA's conclusion that the hot spots in the river have lost PCBs. **(RM-5)** He cautioned EPA against using the 1977 sediment coring data in the ongoing reassessment. Finally, Dr. Mitchum suggested that use of multivariate statistical analyses was needed to verify conclusions in the LRC. **(RM-6)**

Overall, Dr. Mitchum thought the DEIR and LRC were both "acceptable with minor revisions."

Dr. J. Bruno Risatti. During his final statements, Dr. Risatti provided general comments about both reports, followed by comments specific to the individual reports. Dr. Risatti thought the data collected for the reports provide a background for a better understanding of PCB transport in the Hudson River, but he did not think the reports should be considered as an "all encompassing" study. In general, Dr. Risatti was uncertain about some findings in the reports, due largely to the analytical variability in the data. **(BR-1)** He thought the PCB transport processes could be further characterized by conducting sedimentological studies concurrent with water column sampling. **(BR-2)** Though he found the reports extensive, Dr. Risatti thought they should have more thoroughly

addressed the fate of PCBs by considering aerobic degradation and evaporative losses. **(BR-3)**

Focusing specifically on the DEIR, Dr. Risatti's primary finding was that EPA should reconsider its conclusions regarding anaerobic dechlorination, particularly the finding of a 30 ppm threshold below which dechlorination does not occur. **(BR-4)** He then reiterated that the MDPR might underestimate actual dechlorination, since the MDPR is calculated from concentrations of lower homologue PCBs that are more likely to transport from the sediments. **(BR-5)**

When presenting his comments on the LRC, Dr. Risatti suggested that the study had some evidence of cross contamination of the "vibracore" samples, and he recommended that EPA conduct a basic study to quantify the potential extent of this cross contamination. **(BR-6)** Noting that he had difficulties reading the LRC (and the DEIR), Dr. Risatti also recommended that EPA develop guidelines for writing technical reports in a format similar to articles in scientific journals. **(BR-7)**

Overall, Dr. Risatti found the DEIR and LRC to be acceptable with revisions, but he was not sure whether his recommended revisions should be considered "minor" or "major."

5.2 Summary of Peer Reviewers' Final Recommendations

The reviewers' final recommendations, which are detailed in Section 5.1, are summarized by peer reviewer the Comment Directory on page CD-1 (Note that this table does not incorporate any additional recommendations the reviewers made during earlier portions of the meeting.)

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RESPONSE TO COMMENTS

Comment 1: Use multivariate statistical analyses of the data to support the conclusions of the DEIR and LRC.

Response 1: In response to this recommendation, USEPA has performed several multivariate analyses of the data. In response to the concerns of the peer reviewers for the DEIR and LRC, a principal components analysis was performed on the sediment and water data presented in the two reports. Specifically, this analysis was performed on the congener-specific USEPA data collected on sediments (high resolution cores (1992), ecological sediments samples (1993) and low resolution cores (1994)) and on a subset of the water samples (both transect and flow-averaged samples). The analysis supports the findings of the DEIR and the LRC that the sediments between Schuylerville and Fort Edward are the primary source of PCBs to the freshwater Hudson, and also supported the use of the Molar Dechlorination Product Ratio to evaluate dechlorination of PCBs in the river. The analysis is described in detail in Attachment A of this Response to Peer Review Comments.

In addition, a principal components analysis was included in the Baseline Ecological Risk Assessment (USEPA, 1999c). In that analysis, the PCB congener patterns of fish, benthic invertebrates, water (both dissolved and suspended matter) and sediments were examined utilizing several sets of congeners. The analysis yielded several important conclusions regarding the nature of PCBs in Hudson River fish and the relationship of fish body burdens to the other media. This work is presented in Appendix K of the Ecological Risk Assessment.

Comment 2: More prominently acknowledge uncertainty in conclusions; use data ranges to present findings that might be highly uncertain; discuss the implications of analytical variability.

Response 2: USEPA acknowledges that in the presentation of the findings it is appropriate to express uncertainty, to discuss the implications of analytical variability and to use data ranges for highly uncertain findings. USEPA had made an effort to do so in the subsequent Reassessment RI/FS reports. See the revised executive summary for the DEIR and LRC provided as Attachment B to this Response to Peer Review Comments.

Comment 3: Publish a concise summary of the information in the DEIR, LRC and Responsiveness Summaries.

Response 3: USEPA has prepared a revised executive summary for these reports which reflects revisions made in the Responsiveness Summaries as well as revisions based on the peer review. The executive summary is provided as Attachment B to this report.

Comment 4: Consider effects of limnology of the TIP and other pools in the Hudson River (*e.g.*, how primary production affects PCB fate and transport).

Response 4: USEPA is aware of studies on the Great Lakes that demonstrated such effects, but is unaware of appropriately matched PCB and primary production data for the Upper Hudson which might be useful for this purpose. In general, primary production is most likely to affect the partitioning of PCBs to solids and the solids settling rate. Partitioning has already been examined as part of the DEIR and shown to vary with temperature, which could be due in part to primary production. However, USEPA is unaware of PCB partitioning data relating to primary production in the Hudson.

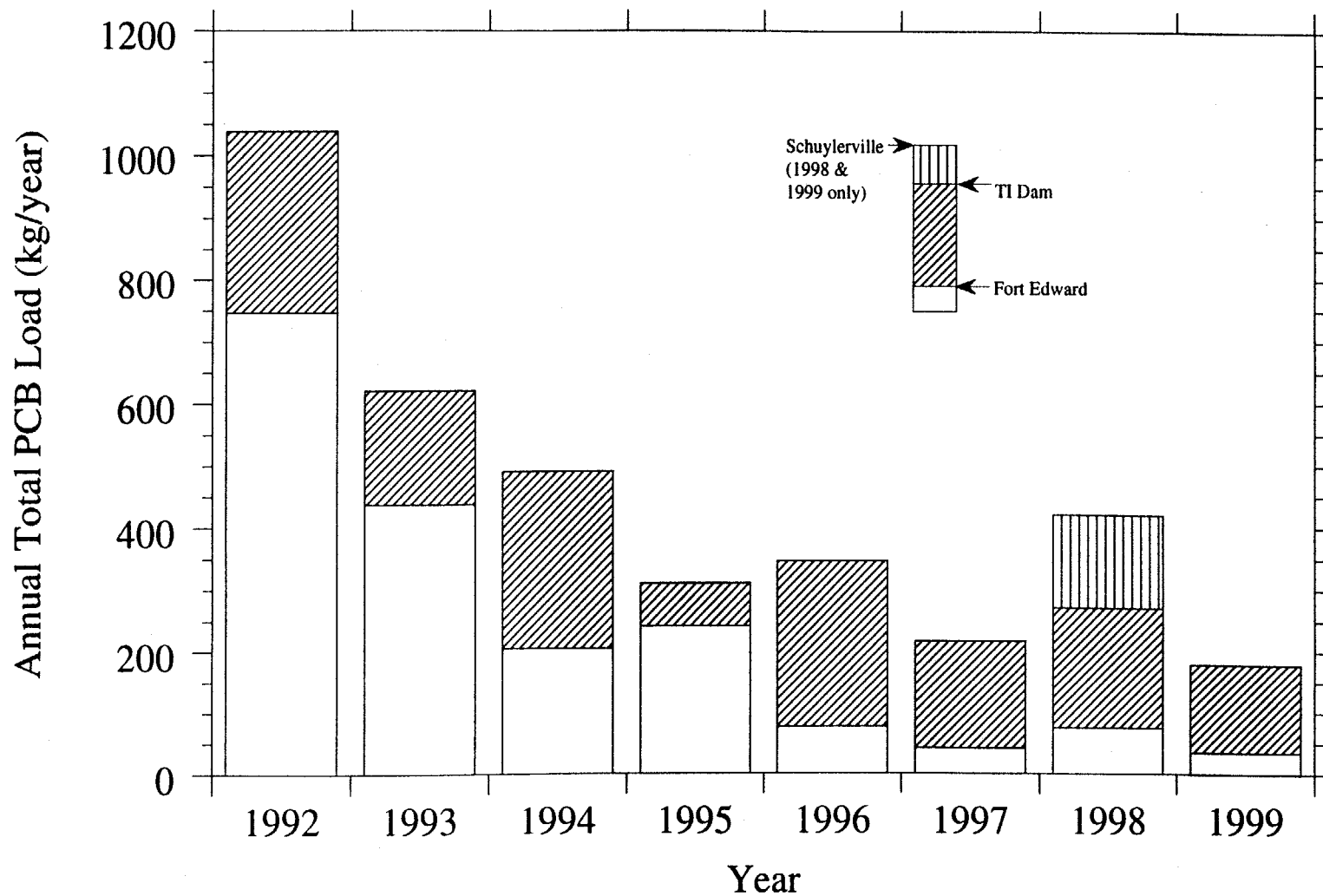
Further consideration of such effects was conducted in the modeling efforts. However, the modeling did not explicitly consider primary production because 1) there was not data to support such consideration, 2) it was not believed that primary production made a substantial effect on the system.

Comment 5: Validate conceptual models and other findings with more recent water column sampling data.

Response 5: Since the completion of the Phase 2 sampling efforts, there have been no similar intensive surveys of the Upper Hudson to directly extend the Phase 2 results. However, as was done in the DEIR, other data sets have been utilized so as to extend and confirm the DEIR findings. To this end GE and USGS data were examined up to 1996 in estimating water column concentrations. The Revised Baseline Modeling Report continued this analysis by including data up to 1997 in its calibrations and utilized more recent data (from 1998 and 1999) as part of model verification. USEPA will continue to review new data as it becomes available, as appropriate. Additionally, the modeling analysis for the Reassessment also serves to examine and validate the conceptual models applied in the DEIR and LRC.

In response to this comment, more recent data obtained by GE on water column concentrations at Rogers Island, Thompson Island Dam and Schuylerville were reviewed. These results were examined for the purposes of examining the incremental load increases between these stations to see if the TI Pool sediments continue to release substantial amounts of PCBs. Water column total PCB annual loads were calculated based on GE weekly water samples and USGS flow data at Rogers Island, TI Dam and Schuylerville using a ratio estimator method (USEPA, 1997). Loads at the TI Dam were corrected to estimate center channel conditions based on the contamination and flow conditions at Rogers Island as mentioned in the Responsiveness Summary for Low Resolution Sediment Coring Report (USEPA, 1999d).

In the conceptual model of the Upper Hudson, TI Pool sediments and, to a lesser degree, sediments between TI Dam and Schuylerville, contribute substantial amounts of PCBs to the water column during the warmer months of the year. Thus, if this is true, then water column load should increase substantially relative to Rogers Island each year. This has already been examined to a degree by GE and its consultants (QEA, 1998). The evaluation below, serves to update the QEA analysis. Figure 5-1 compares the water column load for the three stations. Clearly evident in the most current data available is the substantial load gain between Rogers Island and TI Dam. A smaller load gain



Note: No data were available for Schuylerville prior to 1998.

In 1999 the load at Schuylerville was essentially identical to that at TI Dam.

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Figure 5-1
Water Column Total PCB Annual Load at Fort Edward, TI Dam, and Schuylerville from GE Data
(Ratio Estimator)

is evident between TI Dam and Schuylerville (only 1998 and 1999 data are available for Schuylerville; in 1998, load in Schuylerville was greater than in TI Dam, while in 1999, there was a loss of PCBs between the TI Dam and Schuylerville of -3 kg/year). These calculations confirm the results reported in the DEIR and Appendix C of the Low Resolution Sediment Coring Report Responsiveness Summary. Specifically, these results confirm the continued release of PCBs from the sediments of the Upper Hudson as extensively discussed and documented in the previous USEPA reports. USEPA will continue to evaluate data including water-column monitoring data collected by GE with respect to the remnant deposits as required under the July 21, 1990 Consent Decree entered in U.S. v. General Electric Company, Inc., Case No. 90-CV-575 (N.D.N.Y.).

Comment 6: Use two-phase partition coefficients until enough data are available to derive three-phase coefficients.

Response 6: USEPA recognizes the substantially greater uncertainty involved in using three-phase partition coefficients rather than two-phase. In particular, the two phase coefficients can be more readily measured since no separate DOC phase needs be characterized. Nonetheless, the estimation of three-phase coefficients for Hudson River conditions was performed in a rigorous manner for the DEIR and was in fact applied in the modeling analysis performed for the Baseline Modeling Report (USEPA, May 1999). The use of three-phase coefficients in the model was necessary to account for different degrees of partitioning in the DOC-enriched porewater as compared to the low DOC levels of the overlying surface water. In addition, the FISHRAND model (USEPA's mechanistic bioaccumulation model based on Gobas' 1995 model) requires a "freely dissolved" concentration which can be predicted out of the fate and transport model HUDTOX (USEPA, 2000) using three-phase partition coefficients. It is also noted that the three-phase estimates derived for the Hudson have been published in a peer-reviewed journal (Butcher *et al*, 1998). Recognizing the uncertainty in these estimates, USEPA still determined it was necessary to apply them as a best means to approximate PCB partitioning behavior in the Hudson.

Comment 7: Modify the conclusion regarding the 30 ppm threshold for anaerobic dechlorination.

Response 7: USEPA clarifies its conclusion regarding a dechlorination threshold, restating the relevant text of the executive summary of the DEIR as follows:

Below a concentration of 30,000 µg/kg (30 ppm), dechlorination mass loss does not occur predictably in the Upper Hudson. Evidence of dechlorination as a substantive mass loss and a shift in congener pattern was essentially absent from the Lower Hudson. The extent of dechlorination in sediments higher than 30 ppm total PCB mass was found to correlate well with the log of the sediment PCB concentration. Below 30 ppm, no correlation with PCB mass could be found. No dechlorination threshold was determined but the results indicate that relatively low levels of PCB contamination are unaffected by the dechlorination process.

Comment 8: Further consider how elevated PCB concentrations in near-shore sediments might affect inventory estimates.

Response 8: USEPA lacks sufficient data to characterize these regions of the Hudson. However, it is possible to examine the potential impact of a misrepresentation of the near-shore inventories based on the data provided in Table 4-13 of the LRC and Table B-2 of Appendix B to the Responsiveness Summary for the LRC. These tables are reproduced here for convenience as Table 8-1. Before beginning the upper bound calculation, some assumptions are necessary. Based on the maps of the TI Pool and the results of the geophysical investigation, the TI Pool contains some 2.0 km² of sediments. The cohesive (fine-grained) and noncohesive (coarse-grained) areas represent 29 percent (0.59 km²) and 71 percent (1.41 km²) of the TI Pool sediments, respectively. For the purposes of the calculation, the near-shore environment is considered to be the zone within 50 feet of shore. This zone contains approximately 22 percent (0.44 km²) of the sediment area. However, the near-shore environment contains a disproportionately larger fraction (36 percent) of the cohesive sediment areas.

The total PCB inventory as estimated in Appendix B of the Responsiveness Summary for the LRC is 14.9 metric tons with 8.7 tons in the cohesive areas and 6.2 tons in the noncohesive areas. Thus the PCB mass per unit area of TI Pool in the cohesive areas is as follows:

$$\text{MPA}_{\text{cohesive}} = 8.7 \text{ tons} / 0.59 \text{ km}^2 = 14.8 \text{ g/m}^2$$

Similarly for the noncohesive areas

$$\text{MPA}_{\text{noncohesive}} = 6.2 \text{ tons} / 1.41 \text{ km}^2 = 4.4 \text{ g/m}^2$$

Note that g/m² are equivalent to tons/km². The sediments of the near-shore environment, unlike the TI Pool as a whole, are 48 percent cohesive (0.21 km²) and 52 percent noncohesive (0.23 km²) sediment. This is expected since the near-shore environment is characterized by lower water velocities where deposition of finer-grained material can be deposited and accumulate.

In Table 4-13 (as shown in Table 8-1), the arithmetic mean of PCB concentrations in the 1984 fine grained samples from the near-shore environment is 52 mg/kg. The upper bound estimate of the mean concentration based on the near-shore low resolution cores is 151 mg/kg, or essentially three times the 1984 estimate. Since the mass estimates of the TI Pool are based on the 1984 survey data, a conservative estimate of the actual mass per unit area in the near-shore cohesive sediments would be three times the mass per unit area estimate given above (*i.e.*, 3 * 14.8 g/m² or 44.5 g/m²).

Table 8-1
Estimates of PCB Concentration in Shallow, Near-Shore Sediments
and Thompson Island Pool Sediment Total PCB Inventory

Estimates of PCB Concentration in Shallow, Near-Shore Sediments

Concentrations in mg/kg.	Low Resolution Near-Shore Clusters ¹	Low Resolution Fine Sediment Cores ^{1,2}	1984 Fine Sediment Samples ^{1,2,6}	Original 1984 Shallow Sediment Estimate
Number of Samples	11	19	100	
Minimum	10	0.4	0	
Maximum	281	281	778	
Geometric Mean	46	19	13	
Arithmetic Mean	68	45	52	
MVUE ³	68	68	75	
95% UCL ⁴ on Arithmetic Mean	151	264	135	66 ⁵

Previous and Revised Thompson Island Pool Sediment Total PCB Inventory Estimates

Sediment Type	Previous Total PCB Mass Estimate (metric tons) ⁷	Revised Total PCB Mass Estimate (metric tons)	Tri and Higher PCB Mass Estimate (metric tons) ⁸
Cohesive		8.7	8.2
Noncohesive		6.2	5.9
Total	14.5	14.9	14.1

Notes:

1. Sampling locations within 50 ft of shoreline. Shoreline based on Normandeau, 1976.
2. Sediment classification as fine sediment assigned based on side-scan sonar results.
3. Minimum Variance Unbiased Estimator of the arithmetic mean is given by:

Where:

χ = MVUE of the arithmetic mean

y = Mean natural logarithm of the data

S_y^2 = Variance of the natural logarithms of the data

$$(y + S_y^2 / 2)$$

$$\chi = e$$

4. Upper Confidence Limit
5. Cited from Phase I Report. Interim Characterization And Evaluation (TAMS/Gradient 1991)
6. Zero values were set to 0.5 mg/kg for calculation of log-based statistics.
7. From USEPA, 1997 - Based on the kriging analysis of the Thompson Island Pool.
8. Based on correction factor developed in Appendix E of the LRC (USEPA, 1998).

These values are believed to represent the most accurate inventory of the Thompson Island Pool.

This estimate represents the sum of trichloro to decachloro homologues only.

From these assumptions a conservative upper bound estimate of the total TI Pool inventory can be created as follows:

	Area of TI Pool (km ²)	PCB Mass per Area (g/m ²)	Total Mass (tons)
Cohesive inventory outside the near shore =	(0.59 - 0.21)	* 14.8	= 5.64
Non-cohesive inventory outside the near-shore =	(1.41 - 0.23)	* 7.75	= 5.17
Cohesive inventory inside the near-shore =	0.21	* 44.5	= 9.29
Non-cohesive inventory inside the near-shore =	0.23	* 7.75	= 1.02

Upper Bound TI Pool PCB Inventory = 21.1 tons

While this estimate is quite conservative, it is still within the range of historical estimates although it is substantially beyond the estimates created with the statistical techniques employed by USEPA (*i.e.*, 14.5 tons via kriging, 19.6 tons via polygonal declustering or 14.9 tons via sediment classification and polygonal declustering). Nonetheless, the estimate suggests that the near-shore may have a disproportionately large fraction of the TI Pool PCB inventory if its concentrations have been underestimated. USEPA has considered the near shore sediment inventory during the preparation of the Feasibility Study for the site.

Comment 9: Use more sophisticated statistical analyses to estimate PCB inventory.

Response 9: USEPA does not agree with the reviewer that more sophisticated techniques for this purpose are warranted. While more sophisticated statistical analyses may refine the sediment inventory estimates for the study years 1984 and 1977, they do not provide a current estimate. In particular, the ongoing modeling analysis is best suited for estimating current sediment inventories since it is able to track the various processes which modify the inventory over time. The statistical analyses are limited in this regard since they can really only characterize the instantaneous "snap shot" of the sediment inventory. If additional sediment sampling is required to monitor natural attenuation or for a remedial design (after the Record of Decision), USEPA will consider more sophisticated statistical analyses at that time.

Comment 10: Provide additional details on the analytical methods used in the various sediment coring studies.

Response 10: USEPA has provided extensive detail on its Phase 2 analytical methods in the Phase 2 sampling and analysis plans and quality assurance plans (SAP/QAP). Four of these were prepared in all, covering all aspects of sample collection, laboratory methods and data validation. These

documents are in the site files, and therefore, details of the analytical methods were not incorporated in the DEIR and LRC.

Comment 11: Review more recent sampling data and consider implementing ongoing sediment monitoring studies in order to more fully understand the system (research such as better characterizing the partitioning of PCBs between the suspended and dissolved phases).

Response 11: USEPA has followed this recommendation in that it continues to review sampling and monitoring data as becomes available from NYSDEC, GE and others (see Response 5, above, for example). However, the Agency believes that it currently has a sufficient understanding of the system (recognizing the uncertainties) on which to base a decision for the site. USEPA does not believe that conducting additional field monitoring would have provided a definitive understanding of the system within a reasonable time frame for purposes of the Reassessment. Therefore, USEPA decided not to implement additional monitoring studies as suggested by the peer reviewers.

USEPA also believes that the monitoring program currently maintained by GE provides sufficient data to assess changes in river conditions, and USEPA continues to review this data as it becomes available. If the data suggest that substantive changes are occurring in river conditions, then the Agency will address those changes in the final Responsiveness Summary to be issued with the Record of Decision in 2001.

Comment 12: Describe the data analysis methodology in the reports.

Response 12: Since USEPA will not reissue the DEIR and LRC reports, USEPA will not directly revise the text of the reports to address this comment. However, as part of its responses to the peer review, USEPA has prepared a principal components analysis to address the request for a multivariate statistical analysis. This analytical approach is described in Attachment A of this Response to Peer Review Comments and is written with this comment in mind. With regard to future analyses, USEPA will strive to provide similar descriptions of the analytical approach as an aid to the reader.

Comment 13: Consider other compartments in the PCB mass balance (e.g., evaporative losses, photo chemical degradation, aerobic degradation).

Response 13: USEPA recognizes the importance of other compartments in the PCB mass balance for the Hudson. To address these compartments, USEPA has developed a geochemical fate-and-transport model for the Upper Hudson (HUDTOX) (USEPA, 2000). Expressions representing gas exchange, sediment resuspension, particle settling and other processes affecting PCBs have been incorporated in HUDTOX. While USEPA recognizes the potential for aerobic degradation and photochemical degradation, the magnitudes of these processes in the water column are not well constrained for PCBs and thus are difficult to parameterize in the model. Additionally, the importance of these processes in the Upper Hudson may be limited by the relatively short residence time of water and PCBs in this region of the river (typically 3 to 10 days, depending on flow). Given that many of the other better-known processes are themselves somewhat poorly constrained, the direct addition of these processes to the model is most likely to add to the model complexity without adding understanding.

In addition to the model analysis, USEPA has also estimated the gas exchange rate for several of the transect events where detailed information on flow, PCB concentration, and other conditions are well-known for the transect period. The results of these calculations are discussed in Attachment C of this Response to Peer Review Comments. The basic finding of these calculations is that the observed patterns of PCB loss from the water column are not a close match to those expected from gas exchange. Additionally, the scale of congener losses from the water column estimated from gas exchange are of the same magnitude as the observed losses but the gas exchange estimates are consistently higher than the observations. The implications of these findings are to suggest the possibility of other mechanisms of PCB loss from the water column, such degradation, while also signaling the addition of PCBs to the water column from the sediments below Schuylerville. The magnitude of these additions is clearly smaller than the loads originating upstream of Schuylerville and TI Dam.

Comment 14: Conduct sedimentological studies concurrent with water column sampling.

Response 14: USEPA recognizes that additional sampling always has the potential to improve the understanding of PCB transport. Nonetheless, USEPA does not feel that additional sampling for PCBs beyond the current monitoring efforts conducted by NYSDEC and GE are needed to complete the Reassessment. Additionally, concurrent sampling of river sediment and water is not seen as essential to the effort due to the vastly different residence times of PCBs in the water (approximately 10 days or less in the Upper Hudson) vs. that in the sediments (on the scale of years). Thus, from the perspective of sediment residence times, the Phase 2 program provided water and sediment data which were essentially concurrent. More specifically, it is unlikely that the week-to-week and month-to-month variations seen in water column PCB concentration are a direct reflection of changes in the surface sediment PCB concentrations. Rather the variations are due to temporal changes in the processes that serve to release the PCBs from the sediments to the water column.

Comment 15: Conduct an experiment to characterize the extent of cross contamination in "vibracoring" samples.

Response 15: While USEPA recognizes that the cross-contamination issue limited the use of the low resolution coring data to some degree, the issue did not affect the data used toward the major goal of the program, *i.e.*, estimation of sediment PCB inventory. For this reason, USEPA does not plan to revisit the cross-contamination issue at this time. However, in the event that additional coring work is required for subsequent stages in the remedial efforts, USEPA will take measures to avoid or prevent sample cross-contamination at that time.

Comment 16: Establish guidelines for writing future reports.

Response 16: USEPA did not create guidelines for future Hudson River Reassessment reports because relatively few were left to be completed subsequent to the peer review, although many of the suggestions of the peer reviewers were kept in mind when writing the remaining reports. Note, however, that EPA's Phase 3 (Feasibility Study) report will be prepared in accordance with EPA's existing Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA (OSWER Directive 9355.3-01) (October 1988).

Comment 17: Include a basic model to estimate the source loading of the sediments from the TIP to the water column.

Response 17: USEPA has completed such a model (HUDTOX) and reported its initial results in the Baseline Modeling Report (USEPA, 1999b). Revisions to the modeling were released in the Revised Baseline Modeling Report (USEPA, 2000). A peer review of the Revised Baseline Modeling Report was held in March 2000.

Comment 18: The Molar Dechlorination Product Ratio (MDPR) may underestimate the extent of dechlorination since the ratio is based on congeners that are more susceptible to transport from the sediments

Response 18: This issue was explored by the examination of other congener ratios as discussed below. It was also explored in a principal components analysis whose results are summarized in Attachment A of this Response to Peer Review Comments.

As addressed in DEIR, the process of dechlorination has the net effect of reducing the mass of PCBs within the sediments without reducing the total molecular PCB concentration except in limited cases where the process removes all chlorine atoms. Thus, by dechlorination a more-chlorinated congener molecule may be converted to a less-chlorinated congener molecule but the same number of chlorinated biphenyl molecules remain in the sediments. If the loss of lighter congeners occurs through aerobic degradation or partitioning into aqueous phases, the total molecular PCB concentration in the sediment would decrease as well.

The individual mole fraction for each of 126 congeners analyzed in the High Resolution Coring study were examined on the basis of its correlation to MDPR. Only freshwater high-resolution sediment core samples for post-1954 deposition were used in this examination.

Of the 126 congeners, 11 congeners demonstrated an increased mole fraction with higher MDPR, specifically BZ#1, 4, 5, 6, 7, 8, 9, 10, 19, 24 and 27 (see Figure 18-1). Many of these congeners have been documented as dechlorination products such as in Brown *et al.* (1987). All of these congeners can be shown to be dechlorination products of various congeners contained in Hudson River sediment and so would be expected to increase as dechlorination progressed. BZ#1, 4, 8, 10, 19 have already been described as final or intermediate products of dechlorination process in the DEIR and are included in the MDPR. BZ#5, 6, and 7 can be also regarded as intermediate dechlorination products since they are di-chlorobiphenyl and are not present in Aroclor 1242 at important levels. BZ#24 and 27 are tri-chlorobiphenyls and contribute to the mass of Aroclor 1242 in a higher degree. BZ#24 and 27 have several potential parents in the suite of 126 congeners based on the chemical structure. Thus, these congener concentrations should increase with MDPR as was noted. This correlation also is noted in the PCA analysis in Attachment A. The fact that few Hudson River samples have progressed to a fully dechlorinated state is evident in the fact that the intermediate dechlorination products BZ# 5, 6, 7, 8, 24 and 27 all tend to increase with MDPR. If dechlorination regularly went to completion (*i.e.*, no meta or para chlorines) then these congeners would exhibit an arc-like pattern with the MDPR since they would first increase from the initial dechlorination steps and then decrease as they were converted to the final dechlorination products.

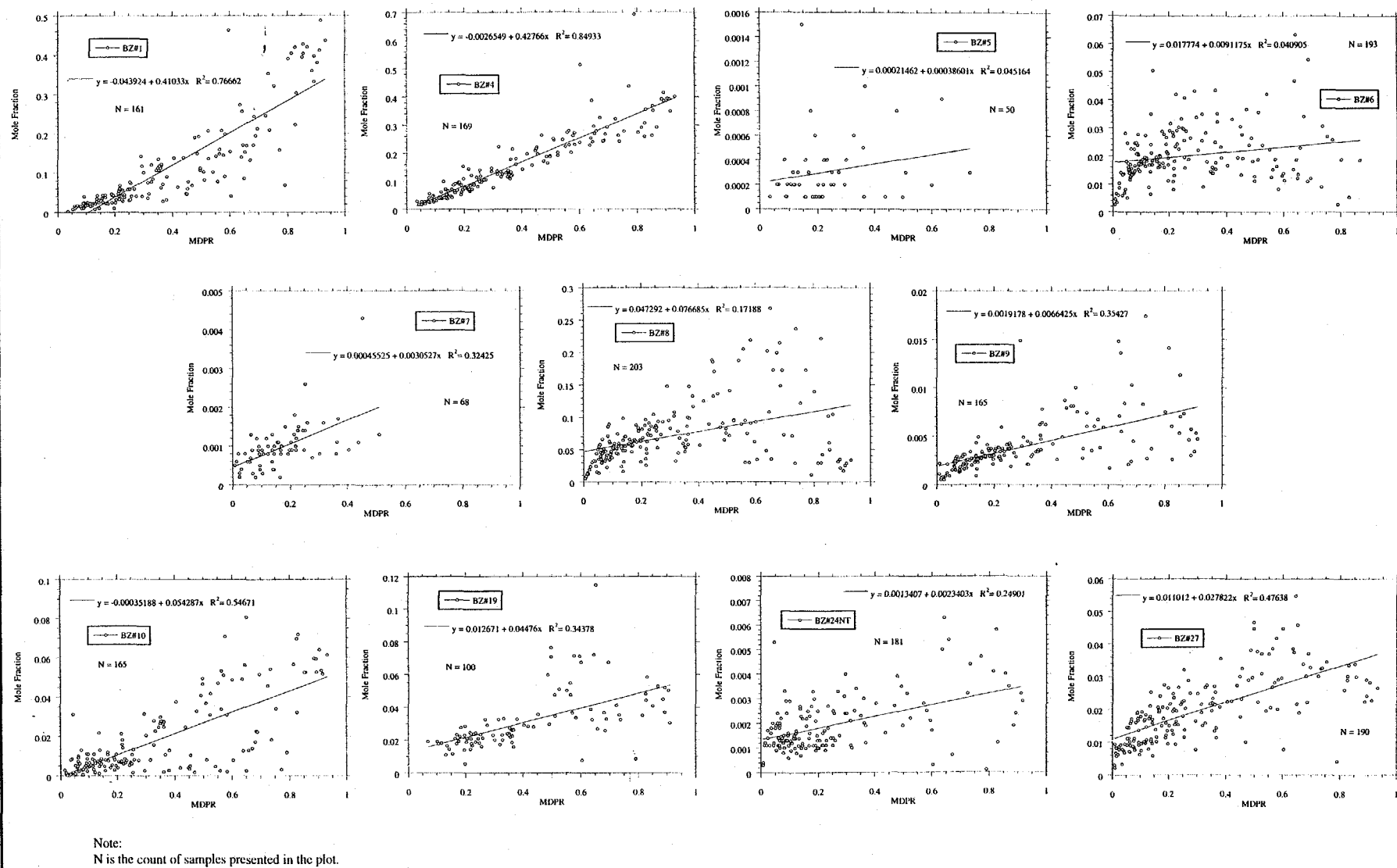
As can be seen in Figure 18-1, none exhibit such a simple behavior although scatter with MDPR does increase for these congeners. Only the results for BZ#6 suggest an arc-like trend.

Among the remaining 115 congeners, the majority of them show a decreasing mole fraction with the increase of MDPR. Figure 18-2 shows several representative congeners, one for each of the homologue groups (dichloro to octachloro). It can be seen that although the rate of decrease varied among the congeners, they all decreased while dechlorination level increased. Additionally, most decreased linearly with the MDPR, supporting the use of the MDPR as a measure of the degree of dechlorination.

A few congener mole fractions were found to show no trend with the MDPR. These are shown in Figure 18-3. The relatively constant mole fraction of these congeners indicates that they are recalcitrant to the dechlorination process and the molecular concentration of these congeners does not change over time. As mentioned above, if lighter congeners were lost from sediment, the total molecular PCB concentration in the sediment would decrease. Therefore, the mole fraction of these recalcitrant congeners should increase since the numerator stays constant while denominator decreases. But, it is not the phenomenon shown in Figure 18-3, which suggests that the molecular concentration of total PCB in the sediment does not change over time, or at a minimum, there is no substantive preferential loss of lighter congeners relative to heavier congeners over time. These results indicate the absence of processes which would preferentially extract lighter congeners from the sediments. Processes such as resuspension and sediment scour which would remove the entire suite of congeners from the sediments are not constrained by these findings.

USEPA agrees with the reviewer that lower-chlorinated congeners are potentially subject to aerobic degradation and partitioning into aqueous phases. However, the upward trend of the dechlorination product congener mole fractions with MDPR, the downward trend of the remaining majority of congener mole fractions with MDPR suggest the absence of preferential loss of the dechlorination products. This information, coupled with the tight correlation of the molecular weight with the MDPR, strongly support the use of the MDPR as an accurate measure of the extent of dechlorination. Because of the simplicity of its construction as well as its strong correlation with total PCB mass, USEPA sees no need to revise its calculations regarding the MDPR nor the need to find a replacement measure for it.

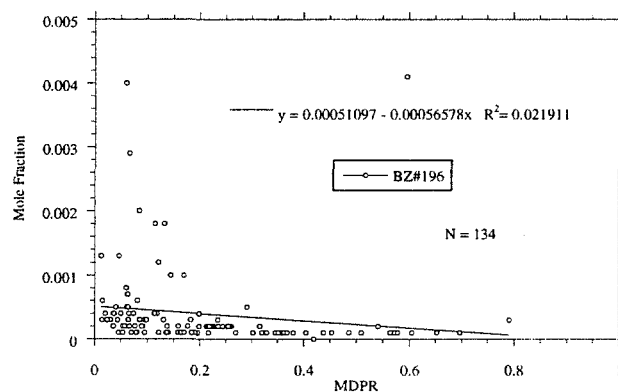
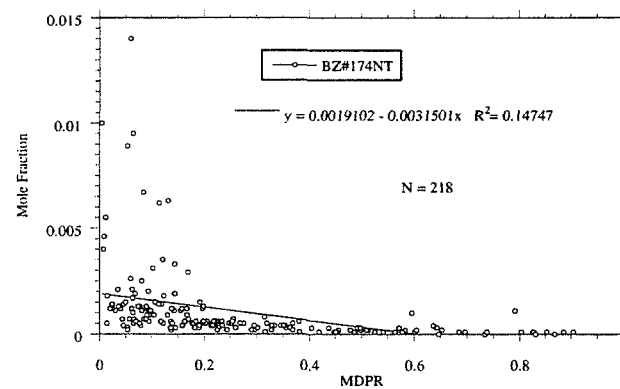
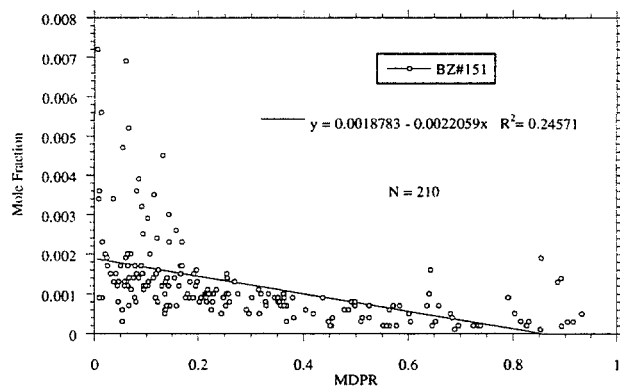
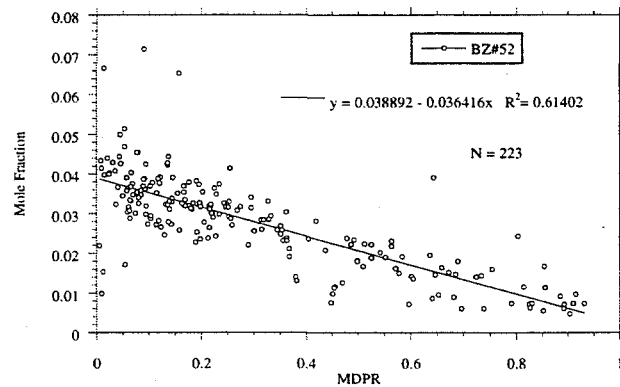
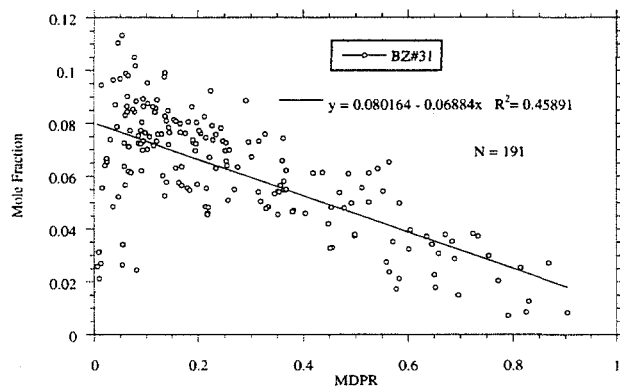
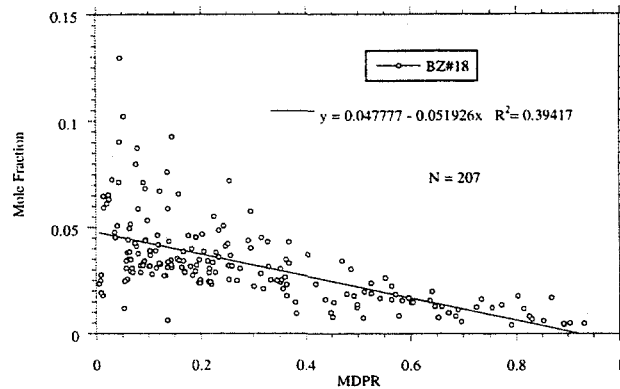
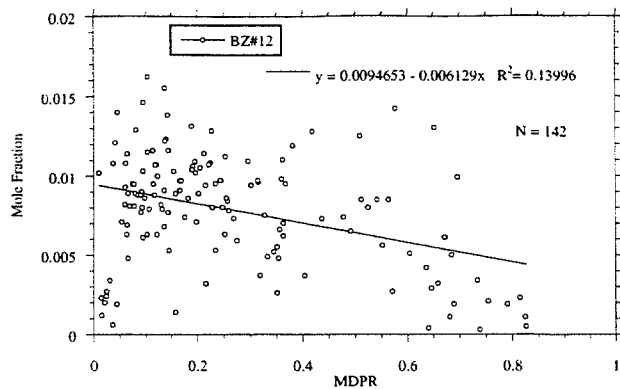
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Hudson River Database Release 4.1

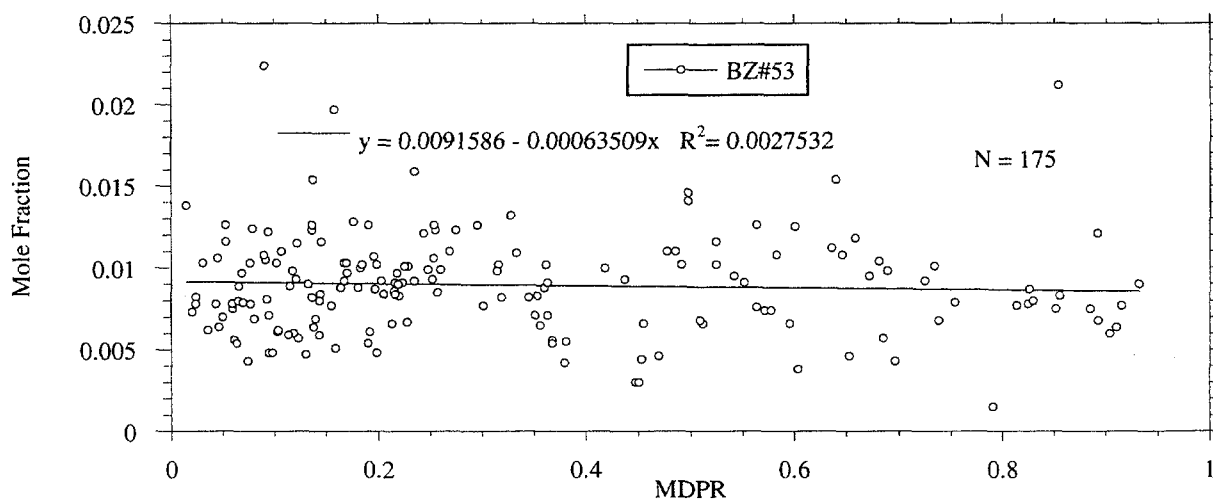
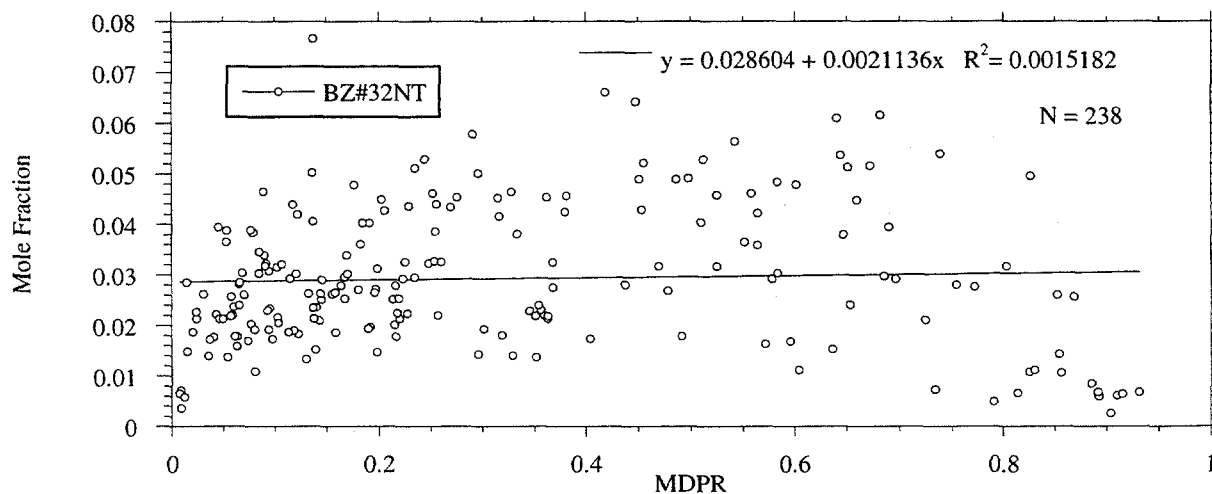
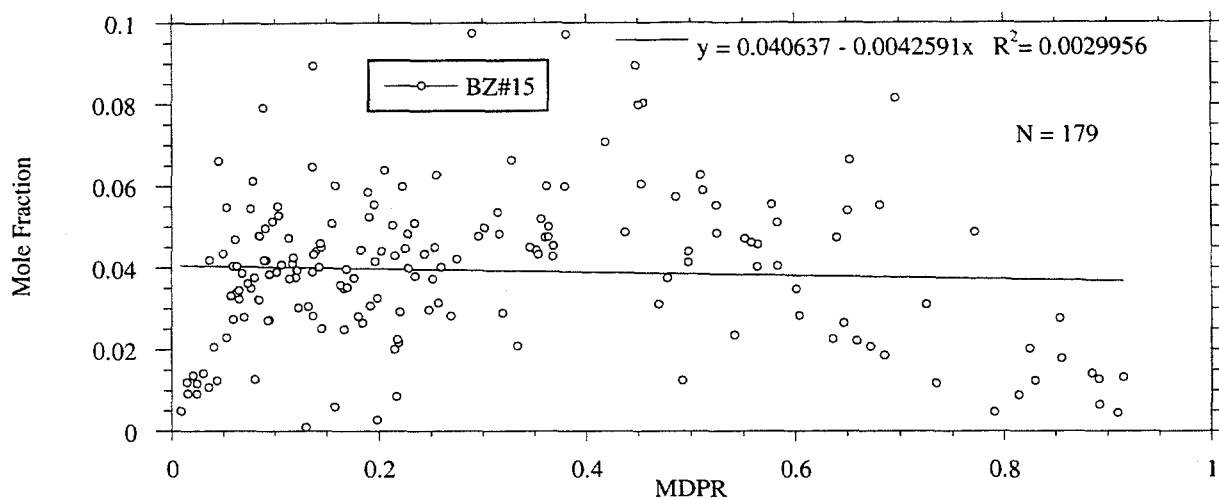
Figure 18-1
Mole Fraction versus MDPR for Final and Intermediate Dechlorination Product Congeners

TAMS



Note:
N is the count of samples presented in the plot.

Figure 18-2
Representative Congener Trends with MDPR for Hudson River Sediments



Note: N is the count of samples presented in the plot.

Figure 18-3
Recalcitrant Congener Trends with MDPR

REFERENCES

- Achman, Dian R., Hornbuckle, Keri C., and Steven J. Eisenreich. 1992. "Volatilization of Polychlorinated Biphenyls from Green Bay, Lake Michigan", *Environ.Sci. Techno.*, Vol 27, No. 1, 1993, pp. 75-87.
- Bopp, Richard F. 1983. "Revised Parameters for Modeling the Transport of PCB Components Across an Air Water Interface", *Journal of Geophysical Research*, Vol. 88, No. C4, pp. 2521-2529, March 20, 1983.
- Brunner, Siegfried, Hornung, Eduard, Santl, Wolff, Egmont and Piringer, Otto G. 1990. "Henry's Law Constants for Polychlorinated Biphenyls: Experimental Determination and Structure - Property Relationships", *Environ. Sci. Technol.*, Vol. 24, No. 11, 1990, pp. 1751-1754.
- Butcher, Jonthan. B., Eaward. A. Garvey and Vick. J. Bierman, Jr., 1998. "Equilibrium Partitioning of PBC Congeners in the Water Column : Field Measurements From the Hudson River", *Chemosphere*, Vol. 36, No. 15, pp. 3149-3166
- Chapra, S.C. 1997. "Surface Water-Quality Modeling", McGraw Hill. New York, New York
- Cirpka, Olaf, Reichert, Peter, Wanner, Oskar, Muller, Stephan R. and Schwarzenbach, Rene P. 1993. "Gas Exchange at River Cascades: Field Experiments and Model Calculations", *Environ.Sci. Techno.*, Vol 27, No. 10, 1993, pp. 2086-2097.
- Clark, Jordan F., Schlosser, Peter, Wanninkhof, Rik, and Simpson, H. James, Schuster, William S. F., Ho, David T. 1994. "Gas transfer velocities for SF₆ and ³He in a small pond at low wind speeds", *Geophysical Research Letters*, Vol., 22, No. 2, pp. 93-96, January 15, 1995.
- Clark, Jordan F., Wanninkhof, Rik, Schlosser, Peter, and Simpson, H. James, 1994. "Gas exchange rates in the tidal Hudson river using a dual tracer technique" *Tellus 46B*, 274-285, ISN0280-6509.
- QEA, 1998 Thompson Island Pool Sediment PCB Source, Prepared for General Electric Co.Albany, New York. March
- "Handbook of Chemistry and Physics", 60th Edition (1979-1980), editor Robert C. Weast, Ph.D., published by CRC Press, Inc.
- Mackay, Donald, Shiu, Wan Ying, Ma Kuo Ching, 1991, "Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals", Volume 1, published by Lewis Publishers, Inc (1992).
- O'Connor, Donald J. and Dobbins, William E. 1956. "Mechanism of Reaeration in Natural Streams", in American Society of Civil Engineers *TRANSACTIONS*. Paper No. 2934, pp. 641- 666.
- Perry, Robert H. & Chilton, Cecil H. 1973. "Chemical Engineers' Handbook", Fifth Edition, McGraw-Hill Chemical Engineering Series, McGraw-Hill Book Company.

United States Environmental Protection Agency (USEPA). 1997 Phase 2 Report, Further Site Characterization and Analysis, Volume 2C - Data Evaluation and Interpretation Report, Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II, New York. Prepared by TAMS *et al.* February, 1997.

USEPA, 1998a. Low Resolution Sediment Coring Report. Phase 2 Report, Volume 2C-A. Prepared by TAMS Consultants, Inc. and Tetra Tech, Inc., July.

USEPA, 1998b. Hudson River PCBs Reassessment RI/FS Responsiveness Summary for Volumes 2A: Database Report, 2B: Preliminary Model Calibration Report, and 2C: Data Evaluation and Interpretation Report. Prepared by TAMS Consultants, Inc., Limno-Tech, Inc., Tetra Tech, Inc., and Menzie-Cura & Associates, Inc., December.

USEPA, 1999a. Report on the Peer Review of the Data Evaluation and Interpretation Report and Low Resolution Sediment Coring Report for the Hudson River PCBs Superfund Site. Prepared by Eastern Research Group, Inc., June.

USEPA, 1999b. Hudson River PCBs Reassessment RI/FS, Draft, Phase 2 Report, Further Site Characterization and Analysis, Volume 2D - Baseline Modeling Report. Prepared by Limno-Tech, Inc., Menzie Cura & Associates, Inc., and Tetra-Tech, Inc.

USEPA, 1999c. Hudson River PCBs Reassessment RI/FS, Draft, Phase 2 Report, Further Site Characterization and Analysis, Volume 2E - Baseline Ecological Risk Assessment. Prepared by TAMS Consultants, Inc. and Menzie Cura & Associates, Inc.

USEPA, 1999d. Responsiveness Summary for the Low Resolution Sediment Coring Report, USEPA, Region 2, New York. Prepared by TAMS/Gradient/Tetra Tech. February, 1999.

USEPA, 2000. Hudson River PCBs Reassessment RI/FS, Draft, Phase 2 Report, Further Site Characterization and Analysis, Volume 2D - Revised Baseline Modeling Report. Prepared by Limno-Tech, Inc., Menzie Cura & Associates, Inc., and Tetra-Tech, Inc.

Wanninkhof, R., J. Ledwell, and J. Crusius, Gas transfer velocities on lakes measured with sulfur hexafluoride, in *Proceedings of the Second International Symposium on Gas Transfer at Water Surfaces*, edited by S. C. Wilhelms and J. S. Gulliver, pp. 441-455, American Society of Civil Engineers, New York, 1991.

Attachment A

Multivariate Statistical Analysis of Phase 2 Sediment and Water Column Data for PCB Congeners

Attachment A

Multivariate Statistical Analysis of Phase 2 Sediment and Water Column Data for PCB Congeners

General Approach

A principal components analysis was undertaken to examine the relationship among PCB patterns found in the sediments of the Hudson. Since the sediments are the ultimate recorders of PCB loads and sources to the river, the analysis should aid in the identification of the major PCB sources to the Hudson. The analysis is described in detail below. The following outline describes the major steps of the principal components analysis:

A. Principal Components Analysis Using High Resolution Cores and Water Samples

1. Selection of Samples for Analysis.
 - Main stem high resolution core samples (cesium-137 bearing)
 - Tributary high resolution core samples (cesium-137 bearing)
 - Main stem water-column samples from Rogers Island, Thompson Island Dam (TI Dam) and Schuylerville.
2. Selection of Congeners for Inclusion in the PCA
 - Only those with a high (60%) frequency of detection
 - Congeners must also have very low rejection frequency (<2 %)
3. Examination of the Congener Composition of First Two Principal Components
 - Interpretation of primary characteristics
4. Examination of Principal Components Results for Sediments and Water
 - Comparison to Aroclors
 - Examination by river domain (Upper Hudson, Freshwater Lower Hudson, Salt Front to New York Harbor)
 - Identification of end members, likely sources and unrelated (background) samples

B. Principal Components Analysis Using Main Stem High Resolution Cores Only

1. Samples for Analysis Include Main Stem High Resolution Cores (cesium-137 bearing) and Suspended Matter Samples from Rogers Island, TI Dam and Schuylerville
2. Selected Congeners are the Same as in the Initial Analysis
3. Examination of Congener Composition of First Two Principal Components
 - Interpretation of primary characteristics

4. Examination of Principal Components Results for Sediments and Water
 - Comparison to Aroclors
 - Examination by river domain (Upper Hudson, Freshwater Lower Hudson, Salt Front to New York Harbor)
 - Identification of end members and likely sources
 5. Examination of 0-2 cm Sediments and Upper Hudson Suspended Matter
 - Examine relationship among most recent deposition and water column suspended matter PCBs
 6. Examination of Relationships Between the Principal Components and Other Geochemical Measures
 - Total PCB mass
 - Molar Dechlorination Product Ratio
 - Molecular Weight
- C. Principal Components Analysis Using Main Stem High Resolution Cores, Low Resolution Cores, Ecological Sediment Samples (0-5 cm) and Upper Hudson Suspended Matter
1. Samples for Analysis Include All USEPA Sediment Samples and Suspended Matter Samples from Rogers Island, TI Dam and Schuylerville
 2. Selected Congeners are the Same as in the Initial Analysis
 3. Examination of Congener Composition of First Two Principal Components
 - Interpretation of primary characteristics
 4. Examination of Principal Components Results for Sediments and Water
 - Comparison to Aroclors
 - Examination by river domain (Upper Hudson, Freshwater Lower Hudson, Salt Front to New York Harbor)
 - Identification of end members and likely sources
 - Comparison among sampling programs and sample collection techniques

Principal Components Analysis Using High Resolution Cores and Water Samples

Selection of Samples for Analysis: In the initial principal components analysis (PCA), the sample set consisted of the following sample groups:

- Phase 2 high resolution cores from the main stem Hudson plus all tributaries and background cores, cesium-137 bearing sediments only
- Phase 2 whole water from Rogers Island and TI Dam
- Phase 2 suspended matter samples from Rogers Island, TI Dam and Schuylerville

These groups represented a well-understood set of samples and were deemed most likely to provide the greatest value to the PCA. The high resolution sediment core samples represented the entire Hudson River from RM 206 to RM-2 as well as the major Upper Hudson tributaries and the Mohawk River. The whole water samples from Rogers Island and TI Dam represented the characteristics of the likely GE-related sources (*i.e.*, direct discharges and sediment-based release). Finally, the suspended matter samples represented the materials most likely to end up in downstream

sediment cores. This suspended matter was also considered to be characteristic of sediments whose PCB contamination was derived from GE-related discharges, either by direct discharge or by re-release of upstream sediment contamination. Because of the limited number of suspended matter samples at TI Dam (only the six transects had such data), suspended matter from Schuylerville was also included to more extensively characterize this medium.

Selection of Congeners for Inclusion in the PCA: The selection of congeners represented an important step in the PCA process. The set of samples involved in the congener selection process included all Upper Hudson, cesium-137-bearing high resolution cores, all cesium-137-bearing high resolution cores from the freshwater Lower Hudson and all transect plus flow averaged water samples, including main stem and tributary samples. Samples from the saline Lower Hudson were not involved at this point but were included later in the analysis. Since sediment samples from a wide range of environments (and potentially PCB sources) were to be included, it was important to select a broad range of congeners so as to be able to characterize the PCB patterns of the possible sources. For this reason, a relatively low frequency of detection was applied (60 percent). This criterion was met by 73 out of a possible 126 PCB congeners. In this manner, the most important congeners from all areas above the salt front were likely to be included.

A second and equally important criterion was the frequency of rejected results for each congener. Rejected results for a sample are interpreted as a missing measurement. The PCA process requires that all samples have reported values for all congeners used in the analysis. Thus, if a sample contains a single rejected result for any selected congener, the sample is eliminated from the PCA analysis. Because of this effect, the power of the PCA analysis is decreased as if many congeners are kept with high rates of rejected results. For this reason, congeners had to have a rejection frequency lower than 2 percent. Using the two criteria, a total of 57 congeners were selected for the analysis.

As a last criterion, an initial principal component analysis was run with the 57 congeners. Any congener which failed to contribute at least 0.1 percent to either of the first two principal components was eliminated. This eliminated six additional congeners, yielding a final total of 51. The list of congeners used is given in Table A-1. This approach retained 209 of 244 freshwater Hudson and tributary sediment samples and 31 of 37 water samples. Although they were not used in the selection process, this congener selection process also retained 99 out of 130 possible sediment samples from the saline Lower Hudson.

Examination of the Congener Composition of the First Two Principal Components: The PCA results for the selected samples and 51 congeners yielded two principal components whose properties were readily interpretable from a geochemical perspective and directly supported the bivariate analyses presented in the DEIR. Figure A-1 presents the congener loadings for the first two principal components. Principal component 1 is represented in the uppermost diagram and can be described as the ratio of the dechlorination product congeners BZ# 1, 4, 6, 8, 10 and 27 to the remaining congeners in the sample. Notably, congeners 6 and 27 are included in this grouping. These congeners, like BZ#8, represent intermediate dechlorination products since subsequent dechlorination will reduce each of these congeners to BZ#1. Congener BZ#15 is also associated with this group and may represent the dechlorination result of congeners without ortho-chlorines. Congener BZ#53 is also associated with this group and may represent a dechlorination intermediate as well. BZ#19, another dechlorination product congener was screened out by the selection criteria

and not included in this analysis. Nonetheless it should be noted that the statistically derived principal component 1 is quite similar to the theoretical molar dechlorination product ratio (MDPR) constructed for the DEIR (*i.e.*, the molar ratio of the sum of BZ#1, 4, 8, 10 and 19 to total PCBs in the sample).

The fact that this complete examination of the congener patterns in all high resolution sediments from the Hudson yields a principal component which closely matches the molar dechlorination product ratio constructed for the DEIR confirms the approach developed from a geochemical perspective. Further, it strengthens the conclusions developed from the MDPR. Both approaches confirm that the degree of dechlorination is an important basis for examining Hudson River PCBs. As will be shown later, extensive dechlorination is limited to the Upper Hudson and little dechlorination is present in the Lower Hudson, as reported in the DEIR as well.

The second principal component is shown in the lower diagram of Figure A-1. This component represents the ratio of the lower molecular weight congeners (mono to tetrachlorohomologues) to the higher molecular weight congeners (penta to nonachlorohomologues). This division occurs essentially at the tetra-penta homologue boundary, since BZ#82 represents the first pentachlorohomologue in the set of congeners. This component is related to the molecular weight of the PCB mixture and is essentially a measure of the Aroclor 1242 components to the sum of the Aroclor 1254 and 1260 components. This can be seen by comparing the loadings for component 2 against the mass fractions for Aroclors 1242, 1254 and 1260 (see Figure A-2).

The second principal component also has a small dependence on the two final dechlorination congeners, BZ#1 and 4. Thus this component will also respond to dechlorination when the dechlorination process is nearly complete and these two congeners dominate the sample mixture. This will be further explored below.

Examination of Principal Components Results for Sediments and Water: The results for the first principal component analysis are presented in Figure A-3. This diagram presents the sediment and water column results plotted as a function of the two principal components. The symbols on the diagram have been color coded by river domain. Additionally, background and tributary samples have been denoted by the first letter in their respective names. Symbols representing the Aroclors in the principal components space are also shown for comparison. Note that the Aroclors were not included in the PCA itself. Taken together, these two principal components represent 48 percent of the total variability within the sample set, with the first principal component responsible for 32 percent.

A review of the diagram shows that the main stem Hudson River samples form an arc with Upper Hudson samples forming the left arm and saline Lower Hudson samples forming the right. The apex of the arc is principally constituted by freshwater Lower Hudson samples with some contribution from each of the other Hudson areas. Also plotted on the diagram are symbols representing several Aroclors. Notably, the apex of the arc falls close to Aroclor 1242 while the left arm extends from Aroclor 1242 to 1221 and the right arm extends from Aroclor 1242 toward 1254. Thus the left arm represents sediments with low molecular weight (*i.e.*, low values for principal component 1) and therefore a high degree of dechlorination. The right arm represents samples with a high molecular weight, suggesting little or no dechlorination and the presence of higher molecular

weight Aroclors. It is interesting to note as well that although the apex of the arc falls close to Aroclor 1242, it is in fact shifted to the right of this Aroclor. This indicates that the apex, which will be shown to be characteristic of the source to the sediments, represents a mixture which primarily consists of Aroclor 1242 but also contains heavier Aroclors as well.

This analysis also serves to clearly identify main stem and tributary samples, similar to the analysis presented in Figure 4-21 of the DEIR. Notable in the diagram is the nearly complete separation of the background and tributary samples from those of the main stem Hudson. The only exception to this are the samples from the Mohawk River and Newtown Creek which fall near the end of the right arm of the arc. These results will be explored further when the results are reviewed by river domain.

Water column samples are plotted as well. The whole water samples from Rogers Island fall above the arc, suggesting they do not directly form the source of the PCB contamination found in downstream Hudson sediments. Whole water samples from TI Dam fall along the left arm, reflecting the fact that these samples tend to resemble the dechlorinated sediments from the Upper Hudson. Suspended matter samples from Rogers Island, TI Dam and Schuylerville fall with the main portion of the arc near the apex, indicating that the suspended matter from these locations are most similar to the sediments of the river. This can be seen more clearly when the individual river domains are examined.

In Figure A-4, sediments from the main stem Upper Hudson and its tributaries are plotted as a function of the two principal components. From this diagram, it is clear that the PCBs of the main stem Upper Hudson bear little resemblance to the background or tributary contamination. This rules these areas out as significant contributors of PCB contamination to the Hudson, reinforcing the conclusion that GE-related PCB discharges are the only significant source to the Upper Hudson. Additionally, the Upper Hudson results form a clear trend extending from the suspended matter samples from the Upper Hudson to a low value in both principal components at the far left of the diagram. This trend in fact represents the degree of dechlorination of the PCB mixture in the sediment. From this diagram, it is clear that the degree of dechlorination is the main factor differentiating samples in the Upper Hudson, indicating that the PCB contamination can be described by a single source that is subjected to varying degrees of dechlorination.

Also notable in the diagram is the somewhat closer fit of the TI Dam and Schuylerville suspended matter to the sediment trend relative to the suspended matter and whole water samples at Rogers Island. The Rogers Island values fall above the sediment trend, suggesting that the mixtures on the suspended matter at this location undergo modification during their passage through the TI Pool and prior to their deposition in the river bottom. The suspended matter found at TI Dam and Schuylerville appear to characterize the relatively unaltered end-member of the Upper Hudson sediment contamination. This suggests that the sediment in the TI Pool currently represents the major source of GE-related contamination to locations downstream. As noted in the discussion of Figure A-3, this end-member most closely resembles Aroclor 1242 although heavier congeners resulting from heavier Aroclors in the GE-related releases are present as well.

In Figure A-5, the results from the freshwater Lower Hudson, RM 154 to RM 88.5, are presented as a function of the two principal components. Results for the suspended matter from the Upper Hudson are presented as well. These results, unlike those of the Upper Hudson, do not form

a linear trend and instead cluster around the suspended matter samples and just below and to the right of Aroclor 1242. Only a few samples extend away from the cluster toward the dechlorination end-member evident in Figure A-4. The absence of a substantive trend toward lower values in principal component 1 is indicative of the absence of substantive dechlorination in the Lower Hudson as was noted in the DEIR.

As seen in Figure A-4, the suspended matter from TI Dam and Schuylerville more closely match the sediment results than the results from Rogers Island. This indicates that the suspended matter from these stations is also characteristic of PCB contamination in this region of the Hudson. As additional support for this assertion, sediment results from the Mohawk are also plotted on the diagram. These results fall well away from the cluster of points representing the freshwater Lower Hudson, indicating the Mohawk cannot be a significant source to the Lower Hudson since its congener pattern is not seen in the Lower Hudson. This is an important statement since these results represent the integration of just under half of the total watershed area to Troy, NY. Thus this analysis shows that the large, relatively more urban and more densely populated Mohawk watershed does not substantively contribute PCBs to the Lower Hudson. Additionally, the results show the Lower Hudson contamination is attributable to the Upper Hudson, closely matching the pattern of contamination seen in Upper Hudson locations. As can be seen in Figure A-3, the congener pattern of the freshwater Lower Hudson closely overlaps the unaltered congener pattern of the Upper Hudson as represented by the principal components. These results confirm the following conclusion of the DEIR, that is, GE-related PCB contamination represents the major source of PCB contamination for the entire freshwater Hudson.

Although nearly all points in Figure A-5 cluster around the Upper Hudson source pattern, four points can be seen outside of this cluster, indicating the presence of heavier congeners in the sediments. These results were also noted in the DEIR in the core from the Albany area (RM 143.5). These sediments indicate the occurrence of a heavier Aroclor release in the early 1980s in the Albany area. This pattern is not seen downstream, indicating that this was a local release and did not affect a broad area of the river. More importantly, it was also limited in time, extending over only a few years. This source is apparently ceased seven to eight years prior to the collection of the high resolution cores and nearly 15 years ago today.

The congener pattern of the sediments of the saline Lower Hudson (RM 60 to RM -2) is represented in Figure A-6 along with suspended matter from the Upper Hudson and the various Aroclors. This region is distinct from the upper river sections in that the sediment PCB congener patterns in this region show a trend toward higher molecular weight. The extension of this trend leads to the PCB patterns of Newtown Creek as well as Aroclor 1254. As discussed in the DEIR, Newtown Creek sediments are contaminated by New York City sewage effluent and most likely represent the pattern of metropolitan New York PCB loads. This is the only section of the river where the trend to a non-GE-related PCB mixture is in evidence. The trend originates with sediments similar in pattern to Aroclor 1242 and is well represented by the suspended matter of the TI Dam and Schuylerville. The major portion of the results then form a general trend toward Newtown Creek, indicative of a second end-member in the New York harbor area. Also notable in the diagram is a second trend, consisting of relatively fewer samples, just to the right of the main trend. These results suggest the presence of an additional source in the saline Lower Hudson. This source appears to be more Aroclor 1248-like than the GE or harbor-related sources since the trend is closer to Aroclor 1248 on the diagram.

The areas affected by the two apparent sources to the Lower Hudson are made evident in Figure A-7. Data from the first core upstream of the salt front (core 10 at RM 88.5) has been added as well to represent the freshwater end-member. From this diagram, it can be seen that the sediments approach the Newtown Creek congener pattern with decreasing river mile and as proximity to the creek increases. These results indicate that the end-member represented by Newtown Creek samples originates within the lower harbor, *i.e.*, river mile less than 10. However, the second trend, to the right of the main trend between RM 88.5 and the harbor is most evident in the sediments from RM 59.6 and RM 54.0. These results suggest a PCB source in this area of sufficient size to affect a small region of Hudson, perhaps 10 river miles. This source does not apparently affect a large number of samples or a large area of the river and suggests that this source is much smaller in magnitude than either of the other important sources to this region, *i.e.*, the upriver GE-related source and the metropolitan New York-related discharges. In total, the sediment contamination in this region of the Hudson can be well described by a three end-member mixing system with sediments in any location representing a linear combination of the three source types. It should be noted that even at the lowest downstream core, the congener pattern indicates a substantive contribution from the upriver source, implying that GE-related contamination is still an important portion of the overall PCB burden 200 miles downstream of the original discharge point.

Also notable in Figure A-7 is the range in principal component space for any given river mile. The results indicate that for any given 10 river mile range, there is a noticeable range in the principal component values. Since these coring results represent historical deposition patterns, this suggests that within each 10 mile segment, the relative contributions of GE and local sources have varied over time. This is not surprising given the large, documented changes in GE-related transport over time as well as the gradual diminishing of other PCB sources over time as PCB use was phased out.

This analysis has served to support essentially all of the conclusions of the DEIR with respect to PCB loads and the importance of the GE-related discharges to the Hudson River. This analysis also supported the conclusions regarding the spatial extent of dechlorination. This issue will be further examined in the next section of this Attachment. Evidence for an additional source below the salt front was uncovered in this analysis. A related analysis completed for the Ecological Risk Assessment Responsiveness Summary (comment **EG-1.39c**) also suggested the presence of this source.

Principal Components Analysis Using Main Stem High Resolution Cores Only

In the previous section, the PCA included all high resolution cores. In this section, the PCA is repeated using only the main stem Hudson, high-resolution sediment results. In this manner, differences among the main stem samples will be emphasized, since the deviations stemming from the background vs. main stem samples will not be included.

Selection of Samples for Analysis: This analysis excluded samples from tributary and background sites. All cesium-137-bearing main stem samples were included. Water column suspended matter samples from Rogers Island, TI Dam and Schuylerville were also included.

Selection of Congeners for Inclusion in the PCA: The same 51 congeners were used in this analysis as in the prior analysis.

Examination of the Congener Composition of First Two Principal Components: This PCA yielded results which were quite similar to those seen in the PCA described above, with perhaps some refining of the component loadings. Figure A-8 presents the congener loadings for the 51 congeners for the first 2 principal components. Again the first component represents the ratio of the mass of the dechlorination product congeners (BZ#1, 4, 6, 8, 10, 27) plus BZ#15 and BZ#53 to the remainder of the congeners in the sample. The second principal component represents a similar mass ratio to that of the second principal component derived above. In this instance, this principal component is made up of three distinct domains. The first set of loadings (the small group of negative loadings) represents the final dechlorination congeners, BZ#1, BZ#4 and BZ#10 and is better defined than in the prior PCA. This grouping is clearly a measure of the degree of final dechlorination. The second set of loadings represents the congeners belong to Aroclor 1242, as can be seen by comparing Figure A-8 with Figure A2. Again the split between the Aroclor 1242 congeners and the heavier group occurs at BZ#82, the tetra-penta boundary. The latter group reflects the contribution made by the sum of Aroclors 1254 and 1260, as was also seen previously.

The amount of variability explained by these two components increased to 54 percent but the amount explained by the first principal component increased substantially to 41 percent as compared to 32 percent in the first PCA analysis described above. This increase is attributed to a greater importance in the extent of dechlorination in differentiating among samples and to the exclusion of the unimportant congener patterns associated with the tributary sediments.

Examination of Principal Components Results for Sediments and Water: The revised PCA analysis yields nearly identical trends to those seen in the first analysis (compare Figure A-9 with Figure A-3). The main difference appears to be the relationship to Aroclor 1260, which appears further displaced from the sediment results. The main stem results are also slightly more scattered, which is to be expected with the removal of the tributaries from consideration.

An examination of the Upper Hudson sediments and suspended matter yields the same relationships as well, with TI Dam and Schuylerville suspended matter more closely matching the sediment patterns of the Upper Hudson (see Figure A-10). The other regions of the river yielded nearly identical relationships as well and are not repeated here. Again the results show the dominance of the GE-related PCB patterns in the freshwater Hudson as well as a substantive contribution to sediment contamination in the saline Lower Hudson.

Examination of 0-2 cm Sediments and Upper Hudson Suspended Matter: To further strengthen the assertion that sediment contamination in the freshwater Hudson originates from GE-related sources, the PCA results for the surficial sediment samples (0 - 2 cm) were examined alone. These samples should exhibit the least amount of dechlorination and thus most closely resemble the contaminant sources. Figure A-11 shows the results for these samples. In this instance, the samples of the Upper Hudson and freshwater Lower Hudson cluster relatively closely, just to the right of Aroclor 1242, suggesting minimal alteration. A few samples, representing relatively high concentration samples from the TI Pool, have already begun to dechlorinate and move toward the dechlorination end-member. In the saline Lower Hudson, surface sediment contamination is clearly a combination of the GE-related congener pattern and some heavier congener mixture, just as seen for the entire set of samples. Thus this analysis indicates that the characterization of the high resolution data set as a whole applies to the most recent sediments collected as well.

Examination of Relationships Between the Principal Components and Other Geochemical Measures: The second PCA was performed, as mentioned above to ensure that the relationships seen among the main stem samples were not obscured by the greater variability of the background and tributary samples included in the first PCA. The second PCA was run to also obtain principal components whose loadings were influenced only by the main stem samples. These principal components were then compared to the geochemically-derived variables used in the DEIR and LRC to confirm a tight correlation between the two approaches. Figures A-12 and A-13 compare principal component 1 with the MDPR and the total PCB concentration, respectively. As discussed previously, principal component 1 closely resembles the MDPR and thus the two variables are tightly correlated ($R^2 = 0.85$) for freshwater sediment samples. Saline Hudson samples have MDPR of approximately 0 and so there is no correlation between the MDPR and principal component 1 for these samples. In the DEIR, the log of the total PCB mass was shown to predict the degree of dechlorination relatively well. As shown in Figure A-13, the same holds true for the total PCB mass and principal component 1, confirming the relationship between the amount of PCB mass present in the sample and the degree of dechlorination.

Principal component 2, with its three distinct domains, is not as closely linked with molecular weight as principal component 1 is with the MDPR. Nonetheless, this component can be expected to vary with molecular weight as the extent dechlorination varies. Similarly, this component will vary as heavier congeners (e.g., Aroclor 1254) are added to the mixture. When this variable is compared with PCB molecular weight, a "V"-shaped pattern is noted (see Figure A-14). The lower portion of the "V" corresponds to the degree of dechlorination present in the samples and thus gives a simple linear relationship for the freshwater Hudson, both Upper and Lower, as might be expected. The upper portion of the "V" represents the change in molecular weight occurring almost exclusively in the saline Lower Hudson, as Upper Hudson PCBs are mixed with those of the harbor area. Taken together, the correlations among the principal components and the geochemically-derived parameters serve to supply statistical verification of the geochemical analyses presented in the DEIR. Notably, the relationships among the statistically-derived components are not as well defined (i.e., greater variability) as those among the geochemically derived parameters. Both have merit here and support the final DEIR conclusions.

Principal Components Analysis Using Main Stem High Resolution Cores, Low Resolution Cores, Ecological Sediment Samples (0-5 cm) and Upper Hudson Suspended Matter

Samples for Analysis Include All USEPA Sediment Samples and Suspended Matter Samples from Rogers Island, TI Dam and Schuylerville: The high resolution cores were used to establish the various relationships among the sampling locations and demonstrate the predominance of the GE-related PCB contamination in the Hudson. While these cores represent locations scattered throughout the Hudson typically 5 to 20 miles apart, the question of the representativeness of these samples may still be an issue. To further support the conclusions drawn from the high resolution cores, the other sediment sampling work performed by USEPA was examined in a PCA as well. This analysis included the main stem high resolution cores, the low resolution cores and the ecological sediment samples. The low resolution cores represented sediments collected up to 5 feet deep exclusively from the Upper Hudson while the ecological samples represented surface sediments (0-5 cm) from RM 25 to RM 197. The suspended solids samples used in the previous PCA were included as well.

Selected Congeners are the Same as in the Initial Analysis: The inclusion of the ecological and low resolution cores increased the total number of sediment samples to 760. No cesium-137 criterion was applied to the low resolution and ecological samples although this criterion was kept for the selection of the main stem high resolution cores. The same 51 congeners were utilized in this analysis.

Examination of Congener Composition of First Two Principal Components: The consistency of the congener relationships in the Hudson is demonstrated by the consistency of the congener loadings for the first two principal components (see Figure A-15). The two components are essentially identical to those derived for the high resolution cores alone, indicating the importance of the degree of dechlorination and the relative amounts of Aroclors 1242 and 1254 in distinguishing among contamination patterns. These components explain nearly the same amount of data set variability, 55 percent, with the first component responsible for 44 percent of this total, with 11 percent attributed to the second component.

Examination of Principal Components Results for Sediments and Water: The results of this principal components analysis yields a pattern nearly identical to that seen for the high resolution cores alone. This is illustrated in Figure A-16. The results create an arc with Aroclor 1242 at its apex, dechlorinated sediments to the left and higher molecular weight, saline Lower Hudson sediments to the right. An extension of the right side trend leads to Aroclor 1254. An expanded version of the results is presented in Figure A-17. In this figure, the low resolution cores extend from the apex to the left, as expected since the samples were collected exclusively in the Upper Hudson. These samples were only subject to GE-related contamination and dechlorination. The ecological samples fall along both arms of the arc since these samples were collected from the entire contaminated Hudson. Note that their distribution by river region matches that seen for the high resolution cores.

The importance of GE-related contamination to the entire set of samples is illustrated in the next sequence of diagrams. In Figure A-18, the results for the Upper Hudson alone are presented. This diagram shows the same trend noted in the previous PCA results, with dechlorinated sediments trending down and to the left of the suspended matter and relatively unaltered sediments. In the diagram, a box has been drawn around the upper end of the trend to represent the domain of sediments with relatively little dechlorination. This box characterizes the domain of GE-related congener patterns. Figure A-19 presents the results for the freshwater Lower Hudson, RM 154 to 88.9. Also shown in the diagram is the box derived from the Upper Hudson sediments. Notably nearly all samples in this region fall within the box. As discussed previously, the high resolution results which fall outside the box (away from the main cluster to the right) are attributed to a local release event in the early 1980s near Albany. Presumably the ecological samples which fall outside the box and down to the right represent similar local events. Note that these events and conditions are clearly in the minority in this region. It is also important to note how few samples fall outside the box to the left toward the dechlorination end-member. This is additional evidence for the lack of substantive dechlorination in the Lower Hudson. As discussed in the DEIR, if dechlorination does exist in the Lower Hudson, its rate is so slow as to not be important. The inventories and congener distributions of the Lower Hudson are essentially unaffected by this process.

Figure A-20 presents the results for both high resolution cores and ecological samples from the saline Lower Hudson. The trend to the lower right, indicative of higher molecular weight mixtures is clearly evident. Also evident is the origin of the trend that begins within the box derived from Upper Hudson sediments. The diagram clearly shows that the congener pattern of the PCBs at

the upper left of the trend closely matches that of Upper Hudson sediments and suspended matter. Given the absence of other patterns (*i.e.*, other sources) in the region upstream, this relationship to the Upper Hudson congener pattern is clear evidence of the presence and importance of GE-related contamination in the saline Lower Hudson. Notably, the secondary sample trend seen in Figure A-7 is much less pronounced here, suggesting that it is clearly of lesser importance relative to the GE and New York harbor-related contamination.

A last important observation that can be drawn from Figures A-16 to A-20 is the similarity of the congener patterns among the three sediment sampling programs (*i.e.*, high resolution coring, low resolution coring and ecological sediment sampling). This close agreement among the programs indicates a minimum of analytical differences and the applicability of conclusions regarding any of the individual programs to the other programs and to the Hudson itself.

Conclusions

Three related principal component analyses were completed for USEPA Phase 2 sediment samples to examine the PCB congener patterns throughout the Hudson. The initial PCA results served to clearly identify unrelated tributary congener patterns from those of the main stem Hudson, removing these tributaries from further consideration as possible PCB sources to the Hudson. The analysis also highlighted the importance of dechlorination in the Upper Hudson in terms of its effect on Upper Hudson congener patterns. The close similarity of Upper Hudson suspended matter, Upper Hudson undechlorinated sediments and Lower Hudson sediments clearly document the importance of GE-related contamination to the Lower Hudson. Only in the saline Lower Hudson could additional substantive sources of PCBs be identified, that is, sources whose effects extend over 10 river miles or more. This observation supports one of the main conclusions of the DEIR, that is, GE-related contamination is the dominant source of PCBs to the entire freshwater Hudson and a significant source to the saline region of the Hudson. Also evident in this analysis was the suggestion of an additional PCB source in the saline portion of the Hudson. While the evidence documenting this is somewhat thin, it is apparent that this source is relatively small as compared to the GE and New York harbor sources.

Further analysis restricted to the main stem sediments verified the results of the first PCA. Additionally, the principal components themselves were shown to be closely related to geochemically-derived parameters used in the DEIR. This provided statistical support for the approaches used in the DEIR. In particular, the first principal component was shown to be closely related to the molar dechlorination product ratio (MDPR). It was also shown to be correlated with total PCB mass, indicating that the degree of dechlorination is related to the amount of PCB mass present in the sediment as noted previously.

A final principal component analysis utilizing all Phase 2 main stem Hudson sediment samples also yielded results nearly identical to that found in the first two. Taken together, these results confirm the dominance of the GE-related PCB contamination in all freshwater areas of the Hudson, the absence of substantive dechlorination in the sediments of the Lower Hudson and the restriction of substantive additional PCB sources to the saline Lower Hudson. These analyses provide statistically-based support for the geochemical analyses and conclusions presented in the DEIR and thus serve to strengthen the conclusions overall.

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Table A-1
Congeners Selected in This Study, in BERA 1999 and by NOAA, 1997
for Principal Component Analysis

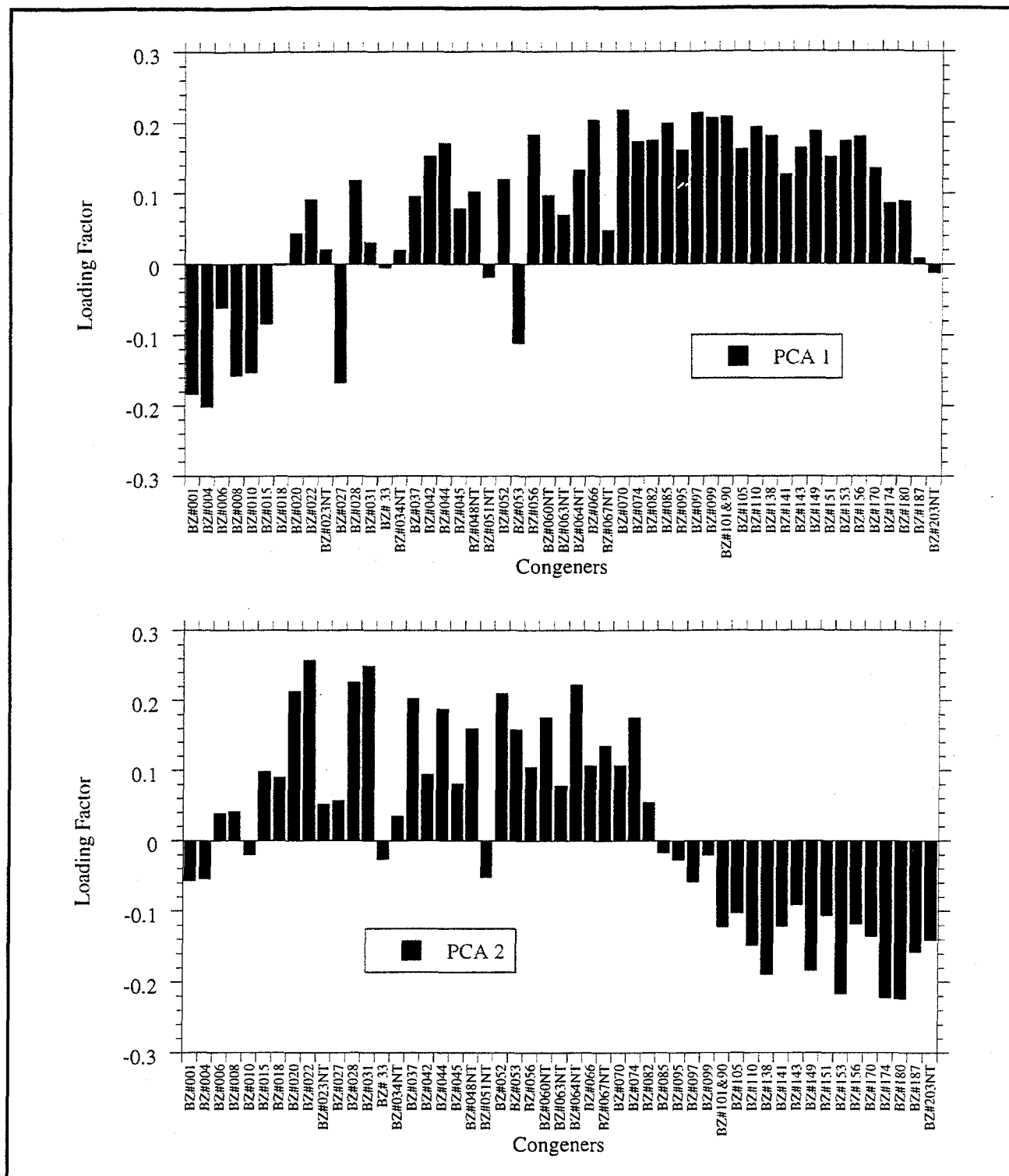
51 Congeners Used in This Study	Homologue Group	Congener Name
BZ#001	Mono	2-Chlorobiphenyl
BZ#004	Di	2,2'-Dichlorobiphenyl
BZ#006	Di	2,3'-Dichlorobiphenyl
BZ#008	Di	2,4'-Dichlorobiphenyl
BZ#010	Di	2,6-Dichlorobiphenyl
BZ#015	Di	4,4'-Dichlorobiphenyl
BZ#018	Tri	2,2',5-Trichlorobiphenyl
BZ#020	Tri	2,3,3'-Trichlorobiphenyl
BZ#022	Tri	2,3,4'-Trichlorobiphenyl
BZ#023NT	Tri	2,3,5-Trichlorobiphenyl
BZ#027	Tri	2,3',6-Trichlorobiphenyl
BZ#028	Tri	2,4,4'-Trichlorobiphenyl
BZ#031	Tri	2,4',5-Trichlorobiphenyl
BZ# 33NT	Tri	2',3,4-Trichlorobiphenyl
BZ#034NT	Tri	2',3,5-Trichlorobiphenyl
BZ#037	Tri	3,4,4'-Trichlorobiphenyl
BZ#042NT	Tetra	2,2',3,4'-Tetrachlorobiphenyl
BZ#044	Tetra	2,2',3,5'-Tetrachlorobiphenyl
BZ#045NT	Tetra	2,2',3,6-Tetrachlorobiphenyl
BZ#048NT	Tetra	2,2',4,5-Tetrachlorobiphenyl
BZ#051NT	Tetra	2,2',4,6'-Tetrachlorobiphenyl
BZ#052	Tetra	2,2',5,5'-Tetrachlorobiphenyl
BZ#053	Tetra	2,2',5,6'-Tetrachlorobiphenyl
BZ#056	Tetra	2,3,3',4'-Tetrachlorobiphenyl
BZ#060NT	Tetra	2,3,4,4'-Tetrachlorobiphenyl
BZ#063NT	Tetra	2,3,4',5-Tetrachlorobiphenyl
BZ#064NT	Tetra	2,3,4',6-Tetrachlorobiphenyl
BZ#066	Tetra	2,3',4,4'-Tetrachlorobiphenyl
BZ#067NT	Tetra	2,3',4,5-Tetrachlorobiphenyl
BZ#070	Tetra	2,3',4',5-Tetrachlorobiphenyl
BZ# 74NT	Tetra	2,4,4',5-Tetrachlorobiphenyl
BZ#082	Penta	2,2',3,3',4-Pentachlorobiphenyl
BZ#085	Penta	2,2',3,4,4'-Pentachlorobiphenyl
BZ#095	Penta	2,2',3,5',6-Pentachlorobiphenyl
BZ#097	Penta	2,2',3',4,5-Pentachlorobiphenyl
BZ#099	Penta	2,2',4,4',5-Pentachlorobiphenyl

Table A-1
Congeners Selected in This Study, in BERA 1999 and by NOAA, 1997
for Principal Component Analysis

51 Congeners Used in This Study	Homologue Group	Congener Name
BZ#101 with BZ#90	Penta	2,2',4,5,5'-Pentachlorobiphenyl
BZ#105	Penta	2,3,3',4,4'-Pentachlorobiphenyl
BZ#110NT	Penta	2,3,3',4,6-Pentachlorobiphenyl
BZ#138	Hexa	2,2',3,4,4',5'-Hexachlorobiphenyl
BZ#141	Hexa	2,2',3,4,5,5'-Hexachlorobiphenyl
BZ#143NT	Hexa	2,2',3,4,5,6-Hexachlorobiphenyl
BZ#149	Hexa	2,2',3,4',5',6-Hexachlorobiphenyl
BZ#151	Hexa	2,2',3,5,5',6-Hexachlorobiphenyl
BZ#153	Hexa	2,2',4,4',5,5'-Hexachlorobiphenyl
BZ#156NT	Hexa	2,3,3',4,4',5-Hexachlorobiphenyl
BZ#170	Hepta	2,2',3,3',4,4',5-Heptachlorobiphenyl
BZ#174NT	Hepta	2,2',3,3',4,5,6'-Heptachlorobiphenyl
BZ#180	Hepta	2,2',3,4,4',5,5'-Heptachlorobiphenyl
BZ#187	Hepta	2,2',3,4',5,5',6-Heptachlorobiphenyl
BZ#203NT	Octa	2,2',3,4,4',5,5',6-Octachlorobiphenyl

Note:

NT means non target



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Figure A-1
Congener Loadings for Principal Components 1 and 2
 (51 congeners, All HR Cores and Water Column Data from RI, TI Dam, and Schuylerville)

EPA REGION II
SCANNING TRACKING SHEET

DOC ID # 67423

DOC TITLE/SUBJECT:
HUDSON RIVER PCBS UPDATE #5
FIGURE A-2
MASS FRACTION OF AROCLOR 1242, 1254
AND 1260 (Page: 307328)

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Principal Component 2

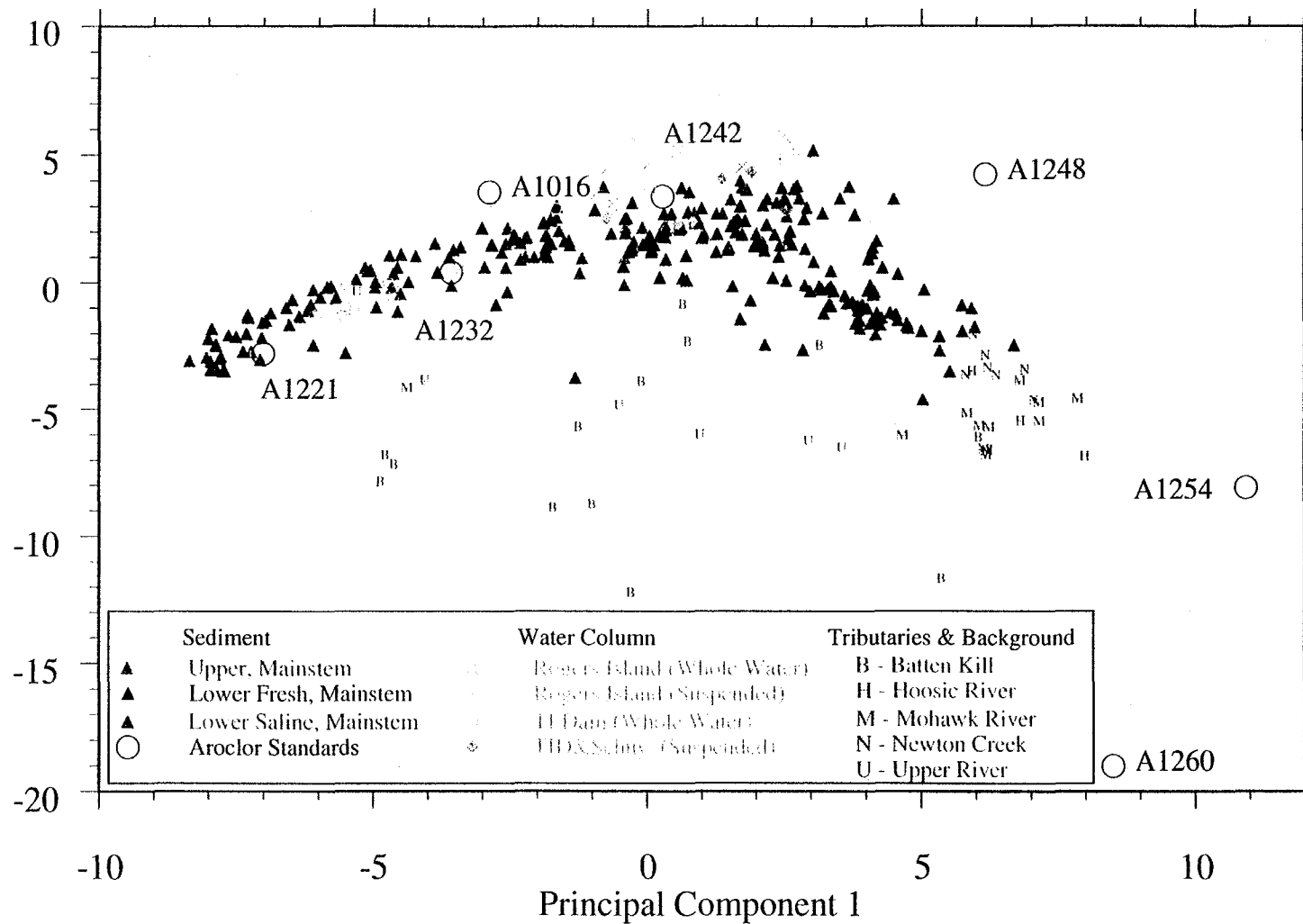


Figure A-3
Principal Component Results for Hudson River High Resolution
Core Sediments and Water-Column Samples

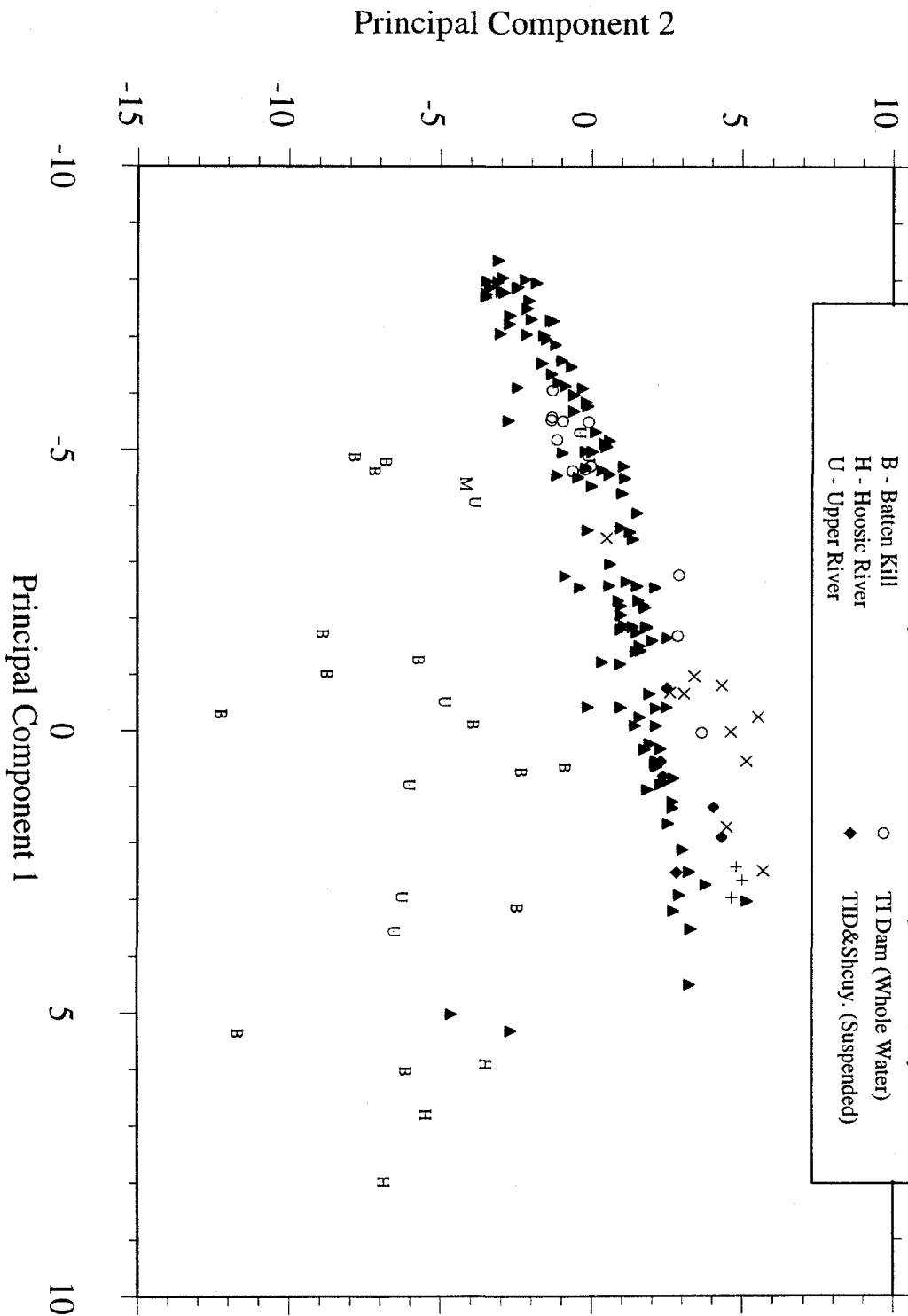
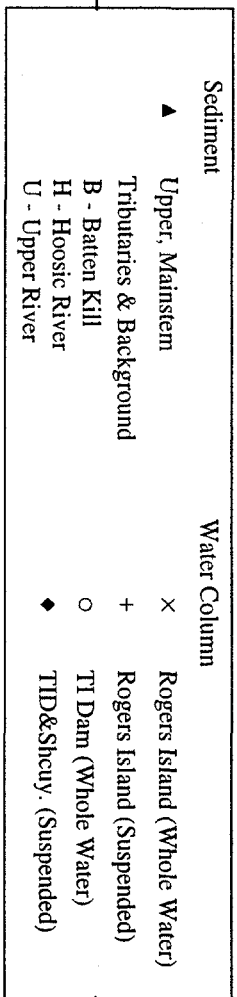


Figure A-4

Principal Component Results for Upper River Only (RM 202.9 to RM 159)

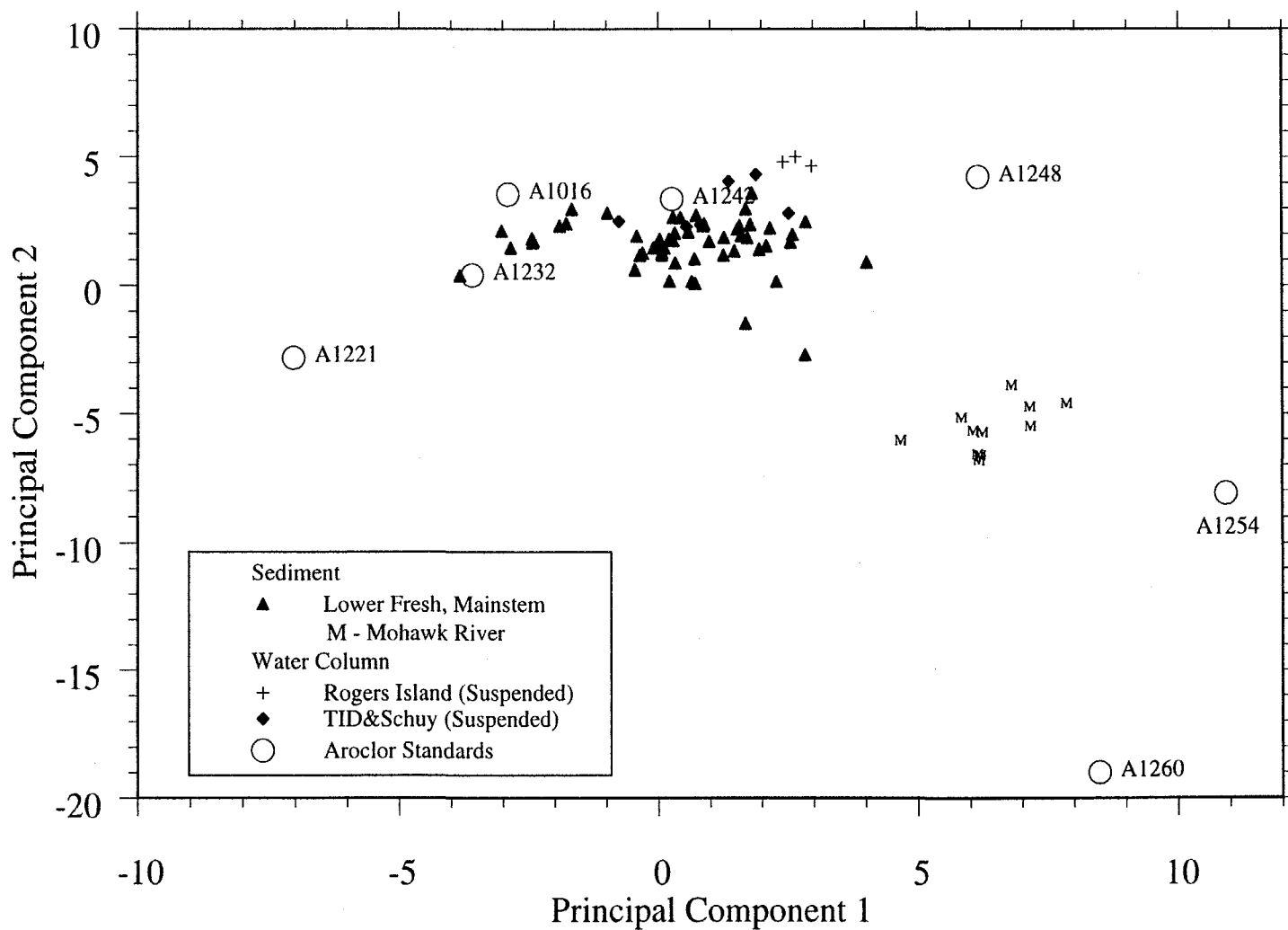


Figure A-5
Principal Component Results for the Freshwater Lower Hudson (RM 143.5 to RM 88.5)

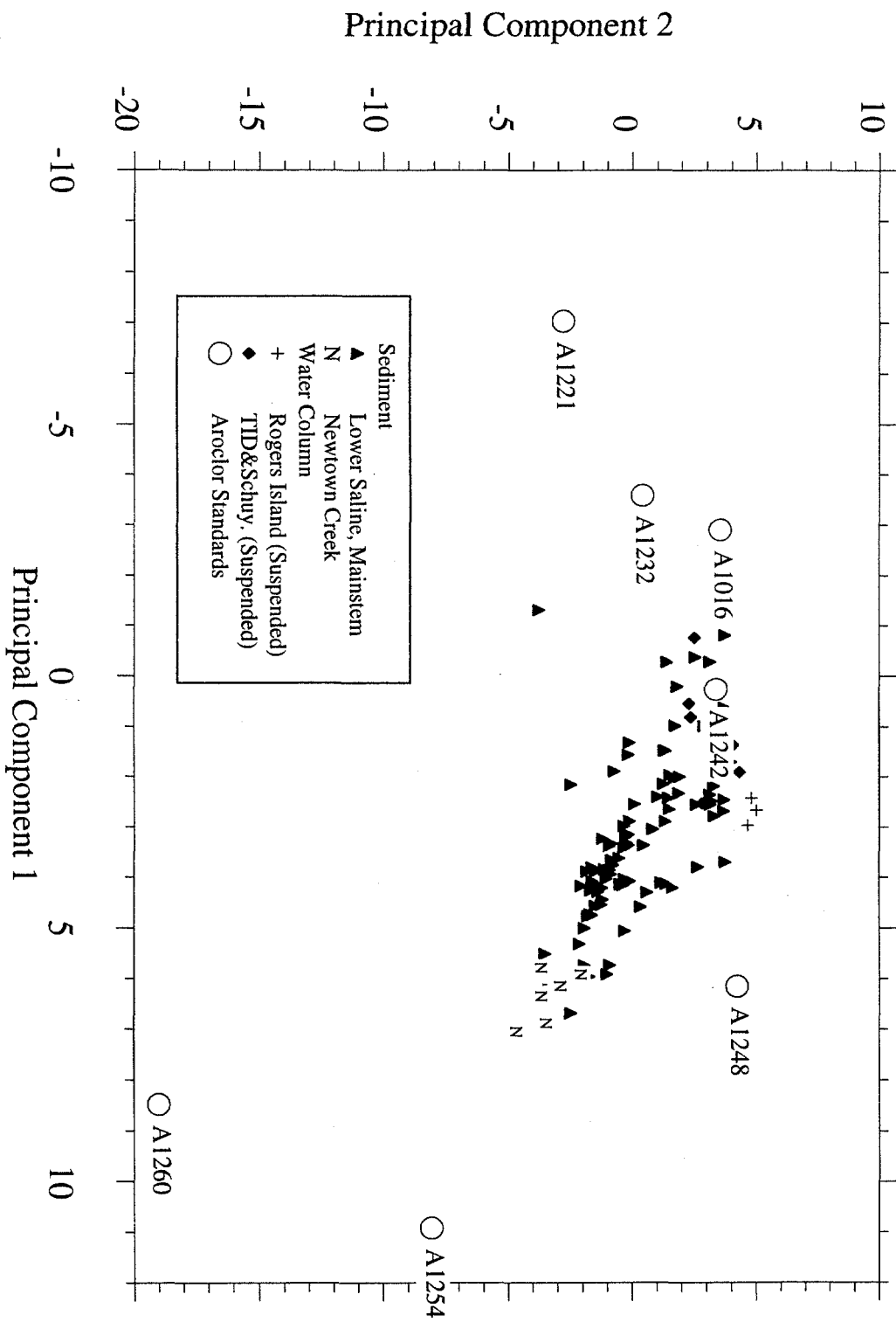


Figure A-6

Principal Component Results for the Saline Lower Hudson River (RM 59.6 to RM -2.2)

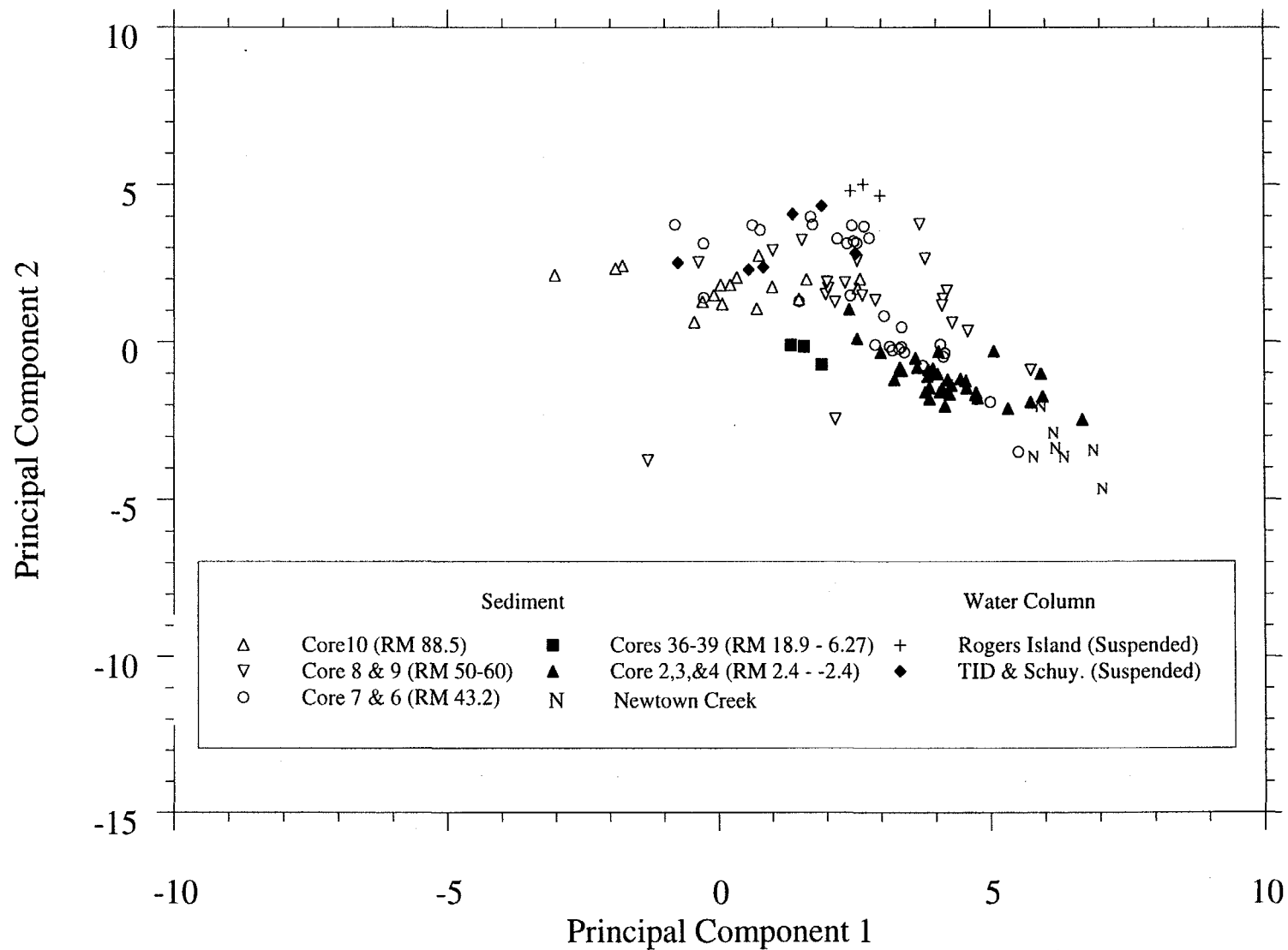


Figure A-7
Principal Component Results for the Saline Lower Hudson Labelled by River Mile

TAMS

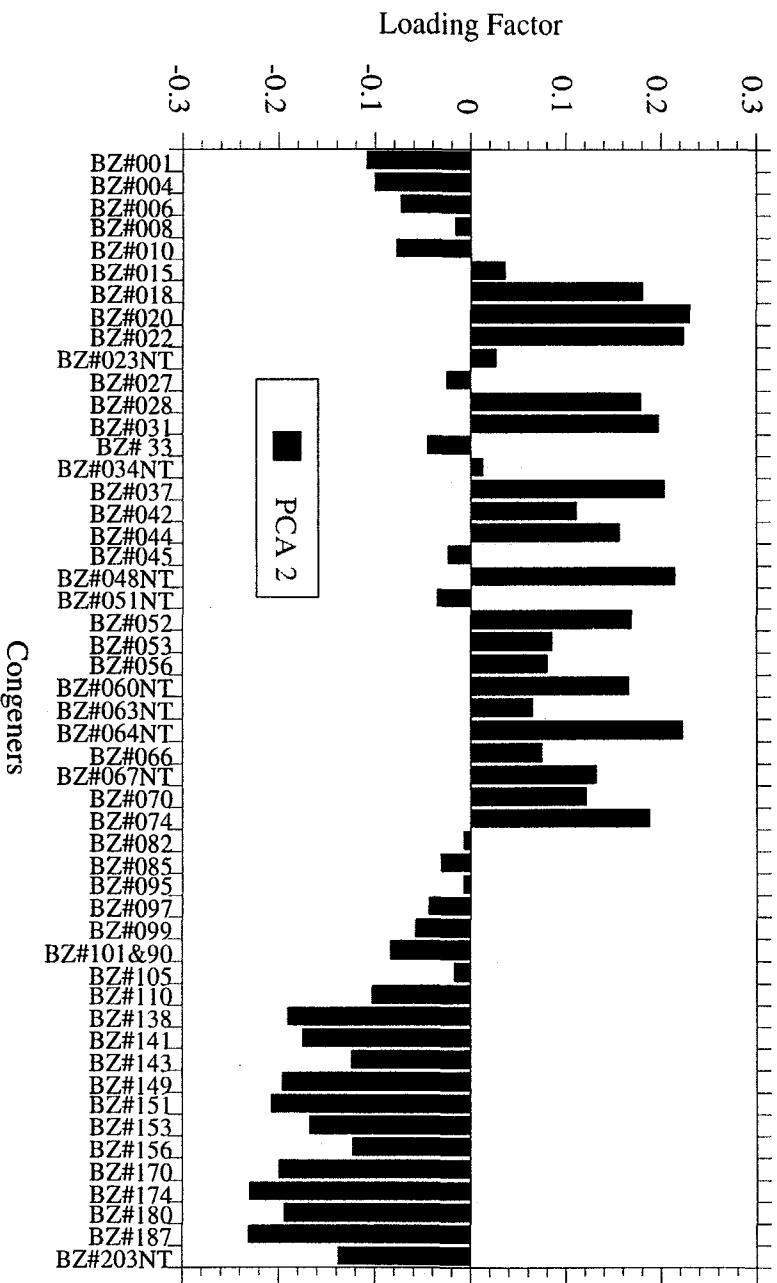
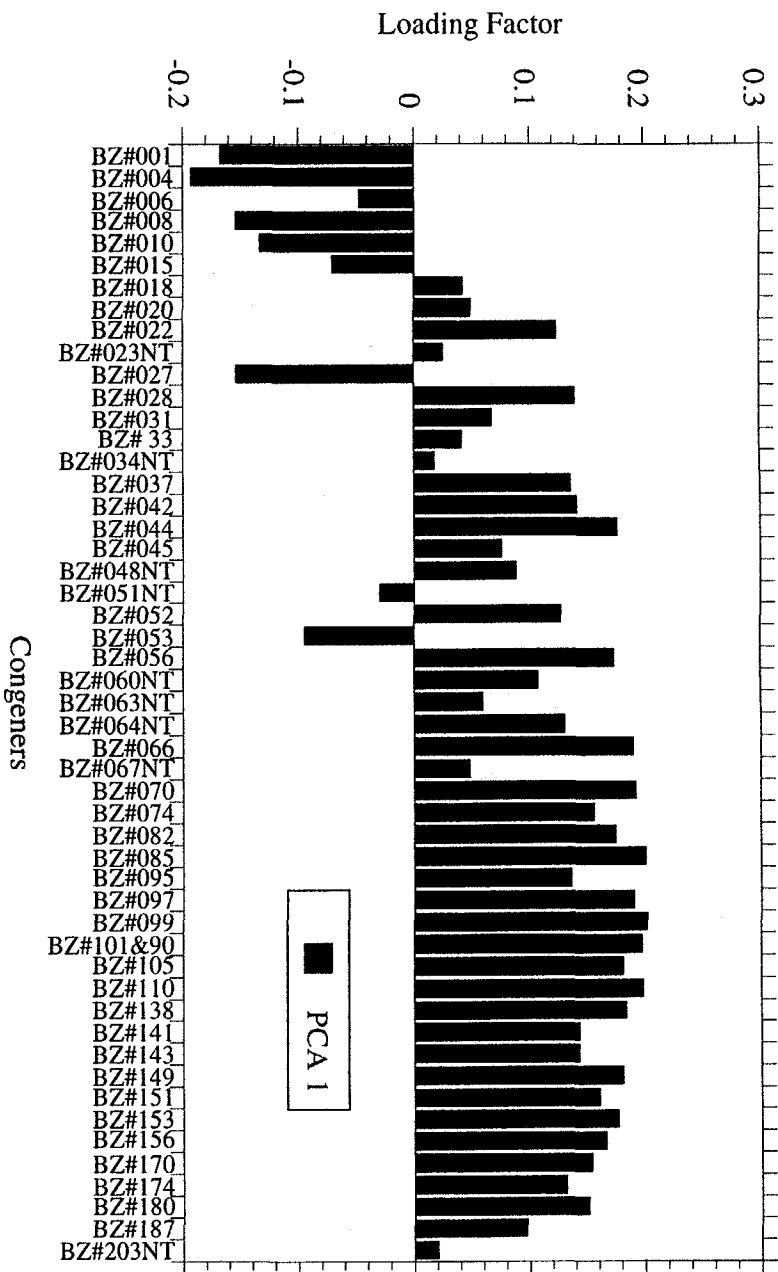


Figure A-8
Congener Loadings for Principal Components 1 and 2
(51 congeners, HR Cores Mainstem and Suspended Phase Data from RI, TI Dam, and Schuylerville)

TAMS

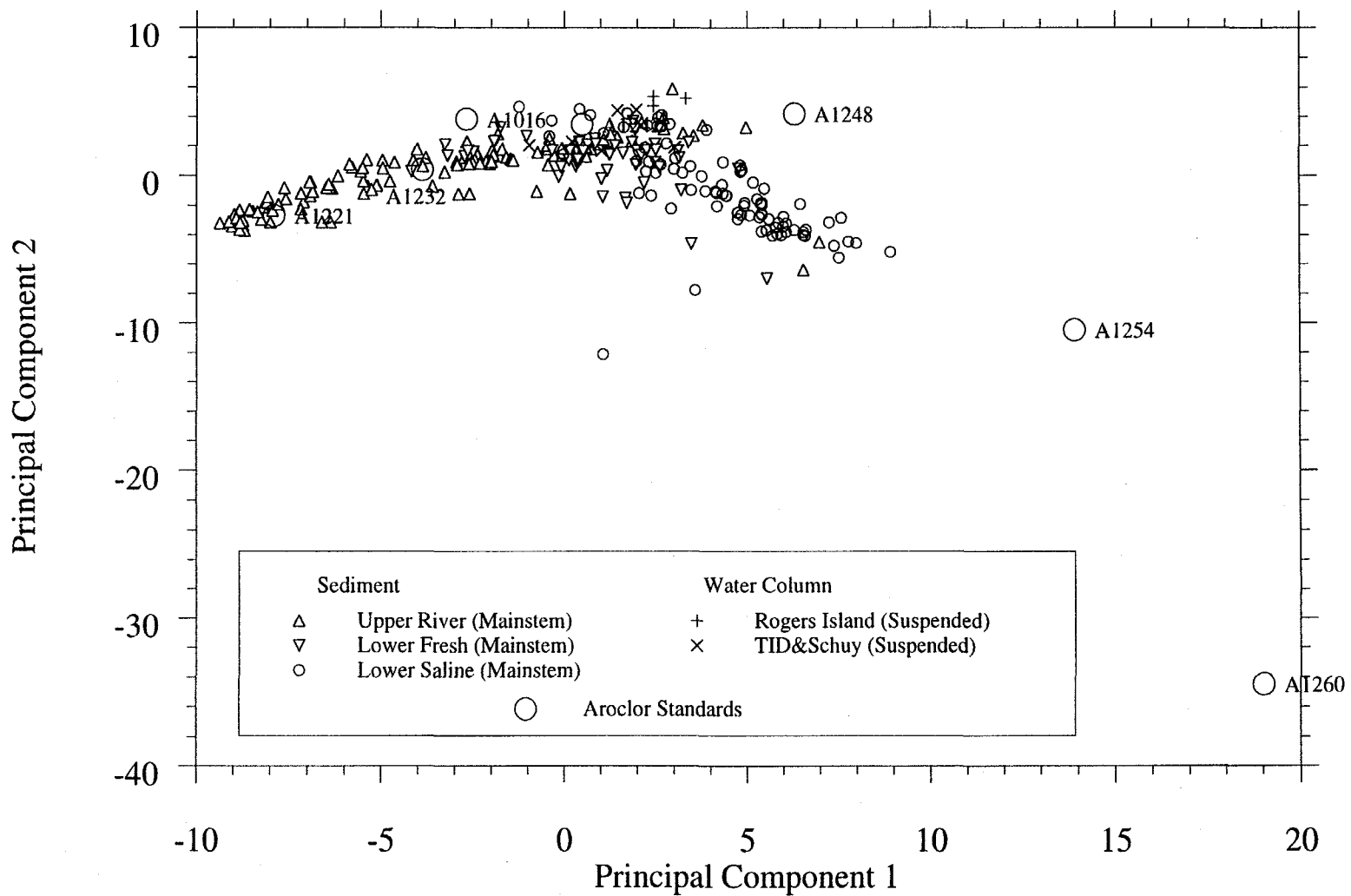
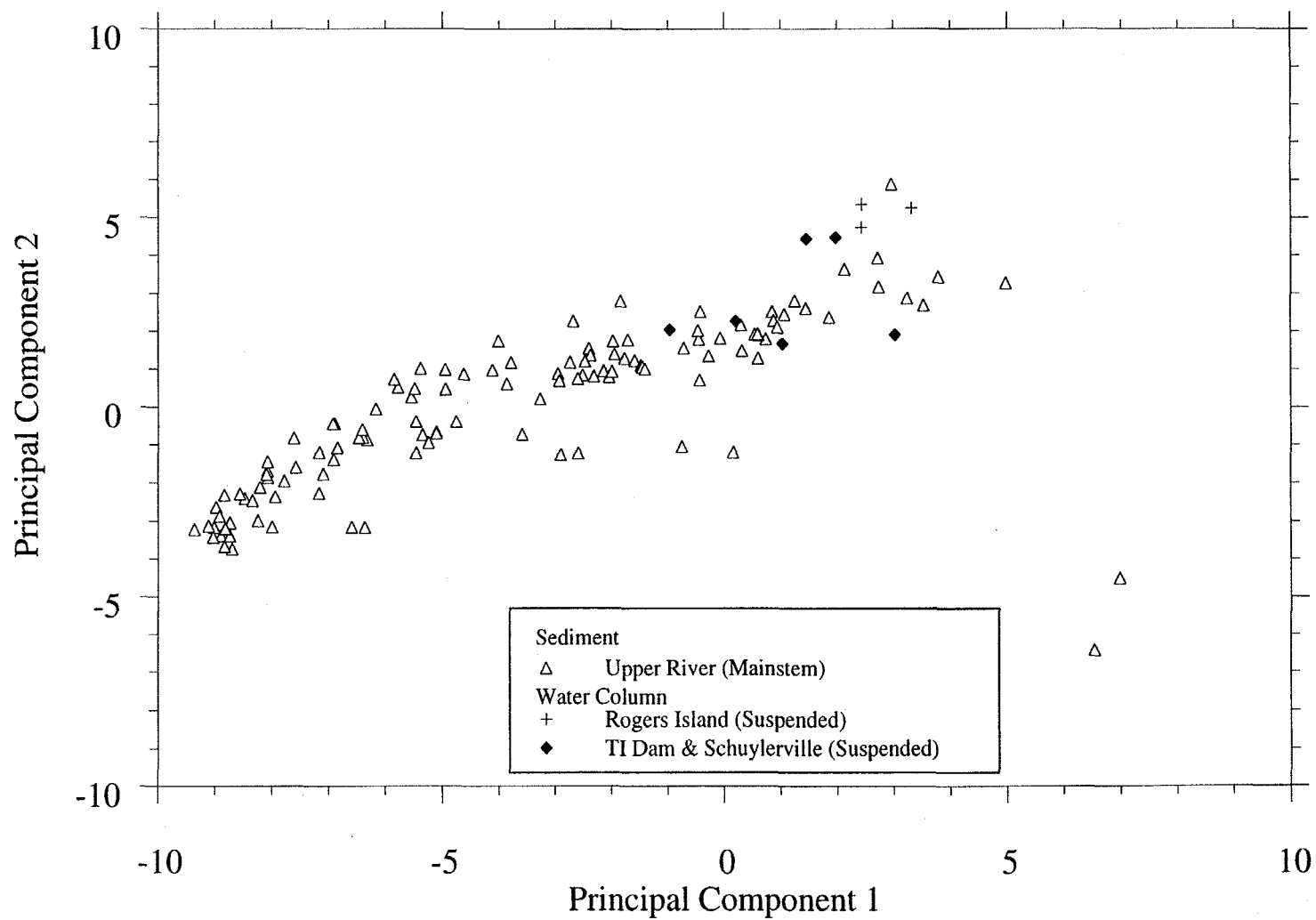


Figure A-9
Principal Component Results for Mainstem High Resolution
Cores and Upper Hudson Suspended Matter



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TAMS

Figure A-10
Principal Component Results for Mainstem High Resolution Cores
(RM 197 to 159) and Upper Hudson Suspended Matter

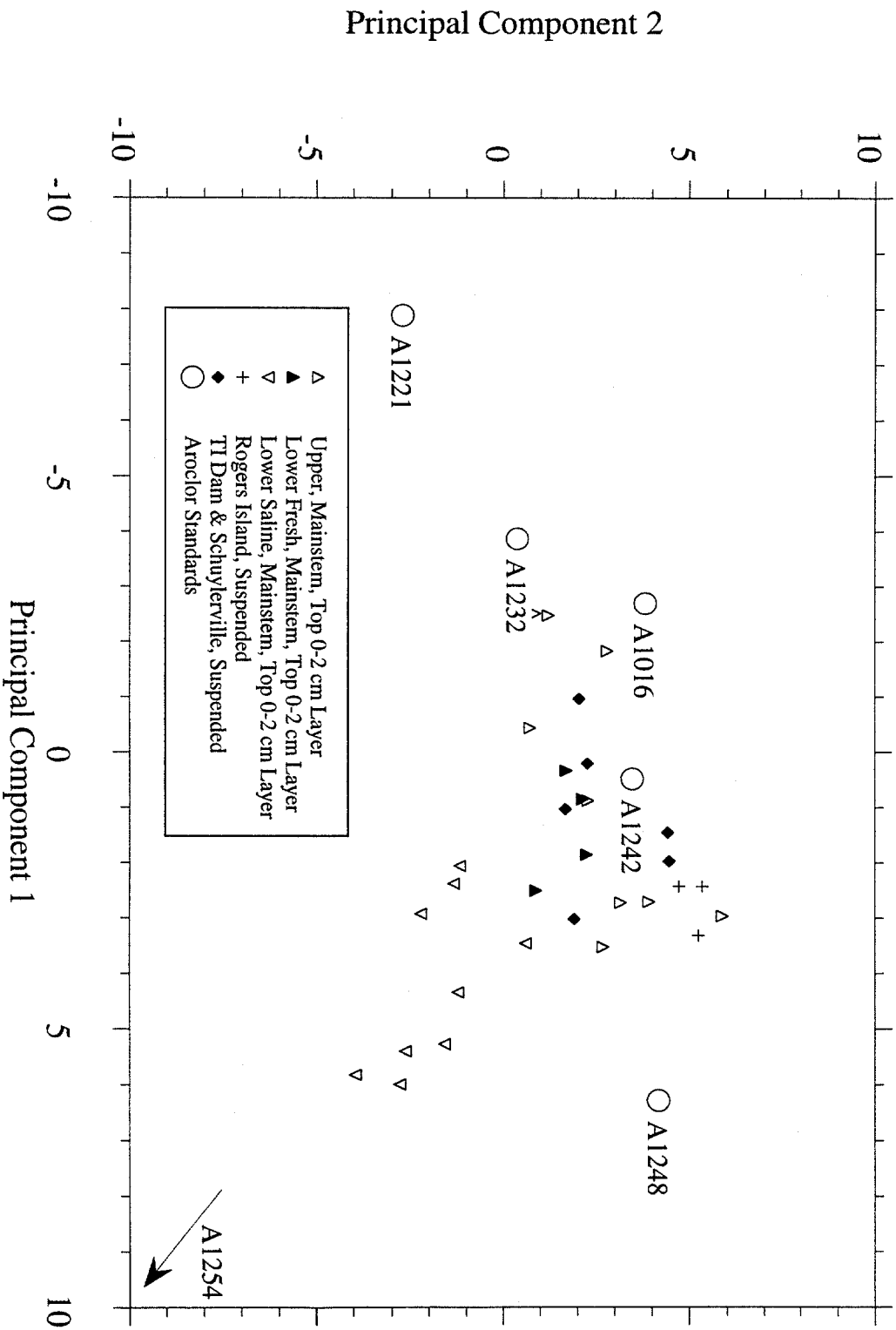
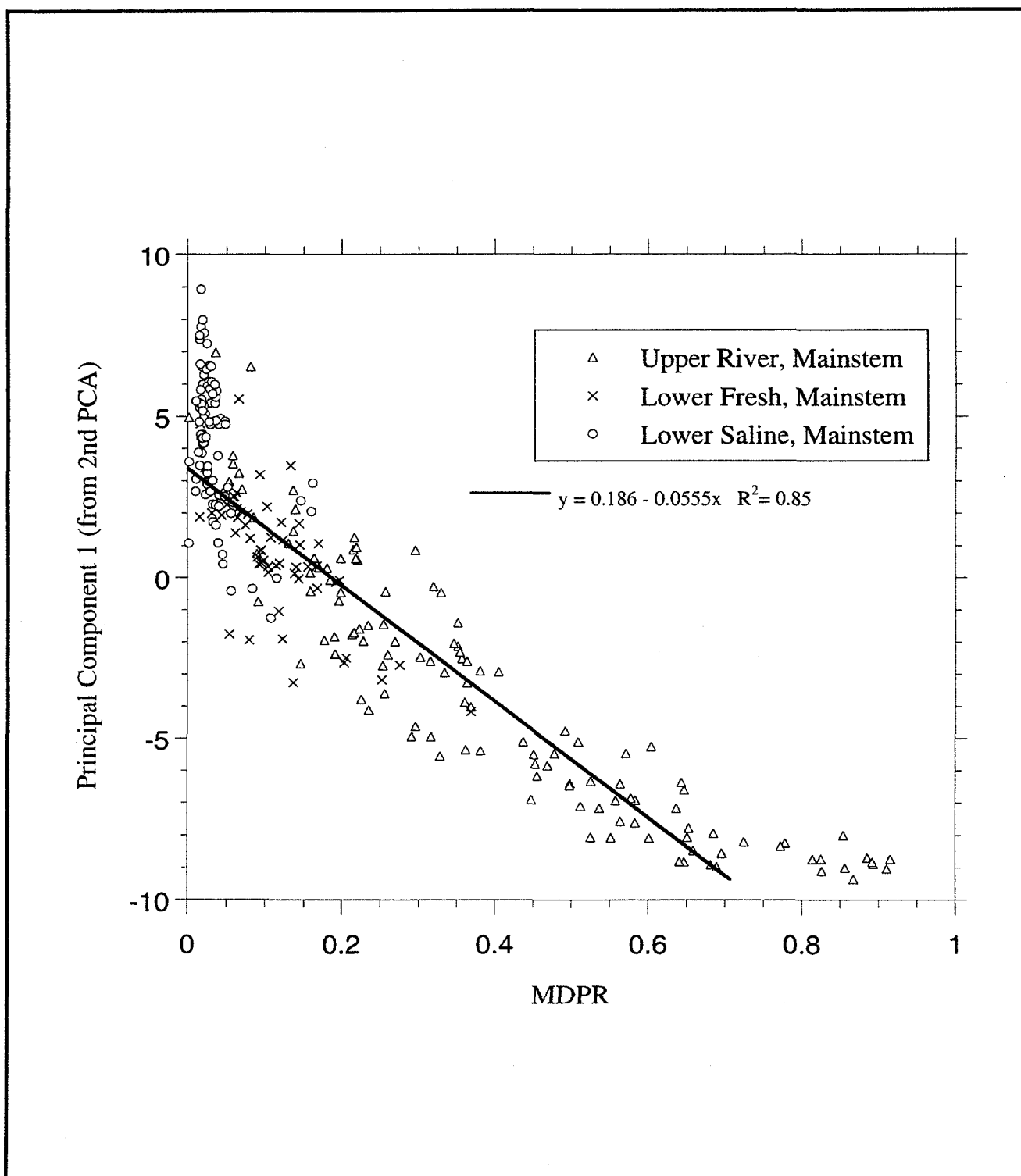


Figure A-11

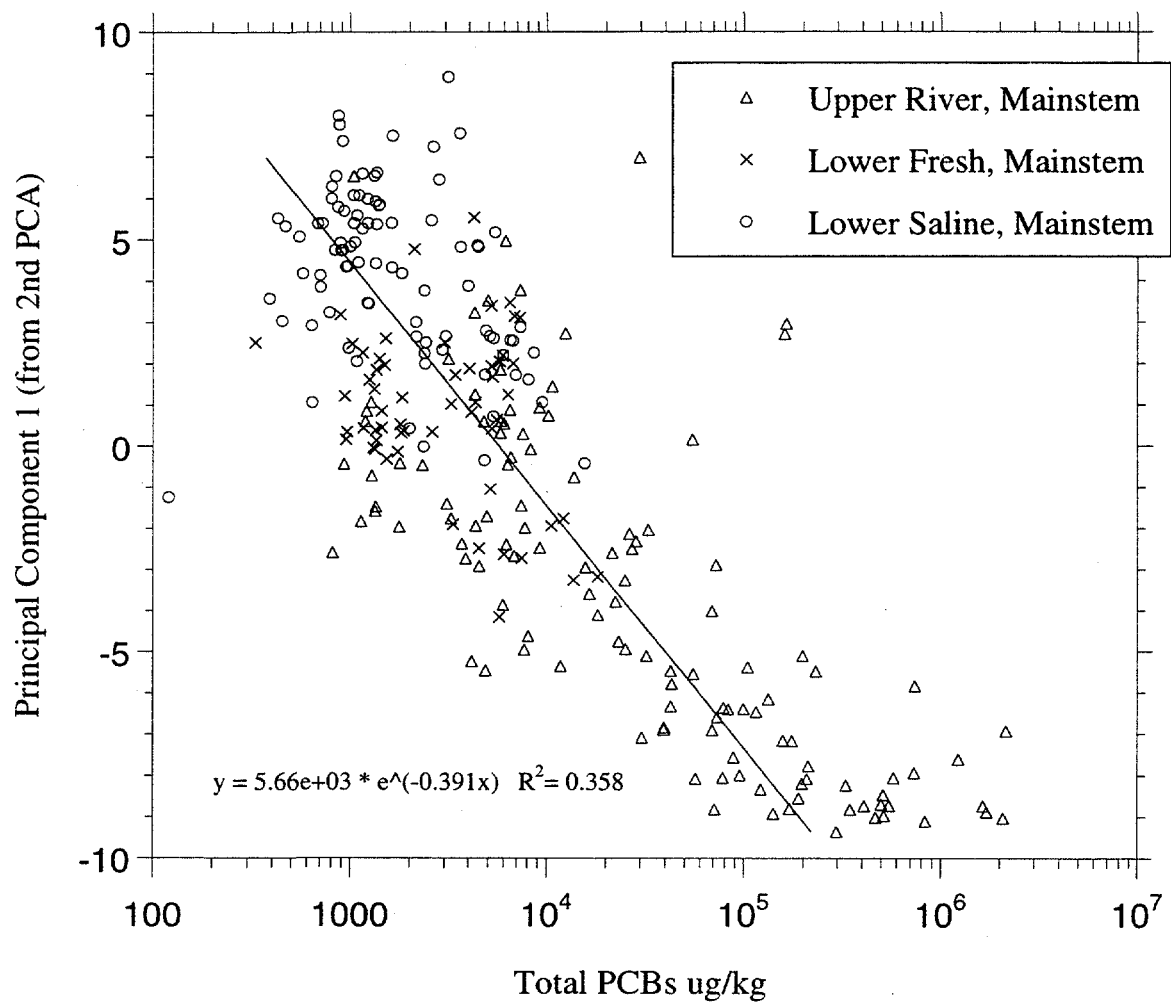
Principal Component Results for Mainstem High Resolution Cores
(RM 197 to 159, Top 0-2 cm Layer Only) and Upper Hudson Suspended Matter



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TAMS

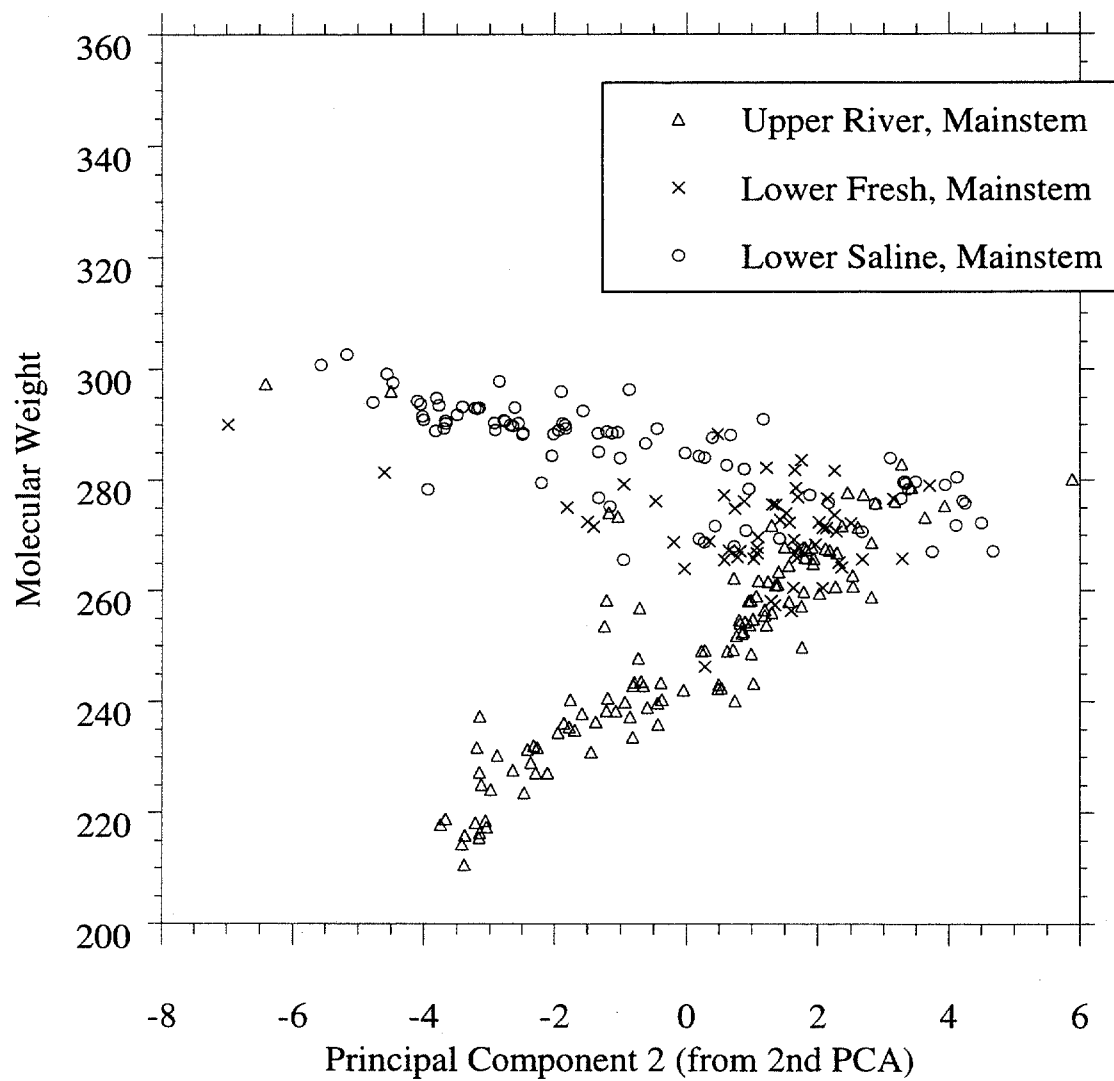
Figure A-12
Principal Component 1 versus MDPR for High Resolution Cores
from the Mainstem Hudson River



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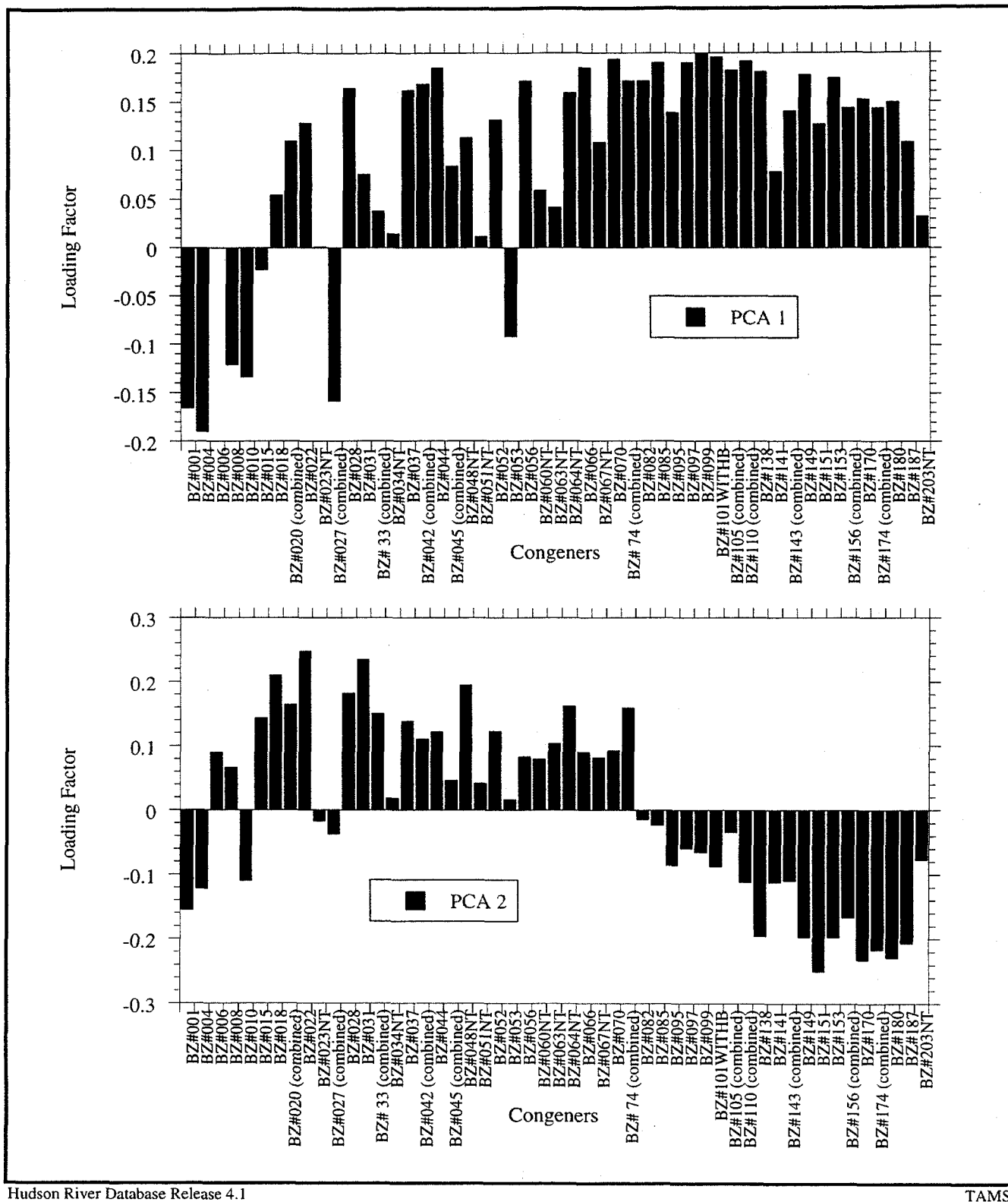
Figure A-13
Principal Component 1 versus TPCB for High Resolution Cores
from the Mainstem Hudson River



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Figure A-14
Principal Component 2 versus Molecular Weight for
High Resolution Cores from the Mainstem Hudson



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Figure A-15
Congener Loadings for Principal Components 1 and 2
 (High Resolution Mainstem Cores, Low Resolution Cores,
 Ecological Sediment and Upper Hudson Suspended Matter)

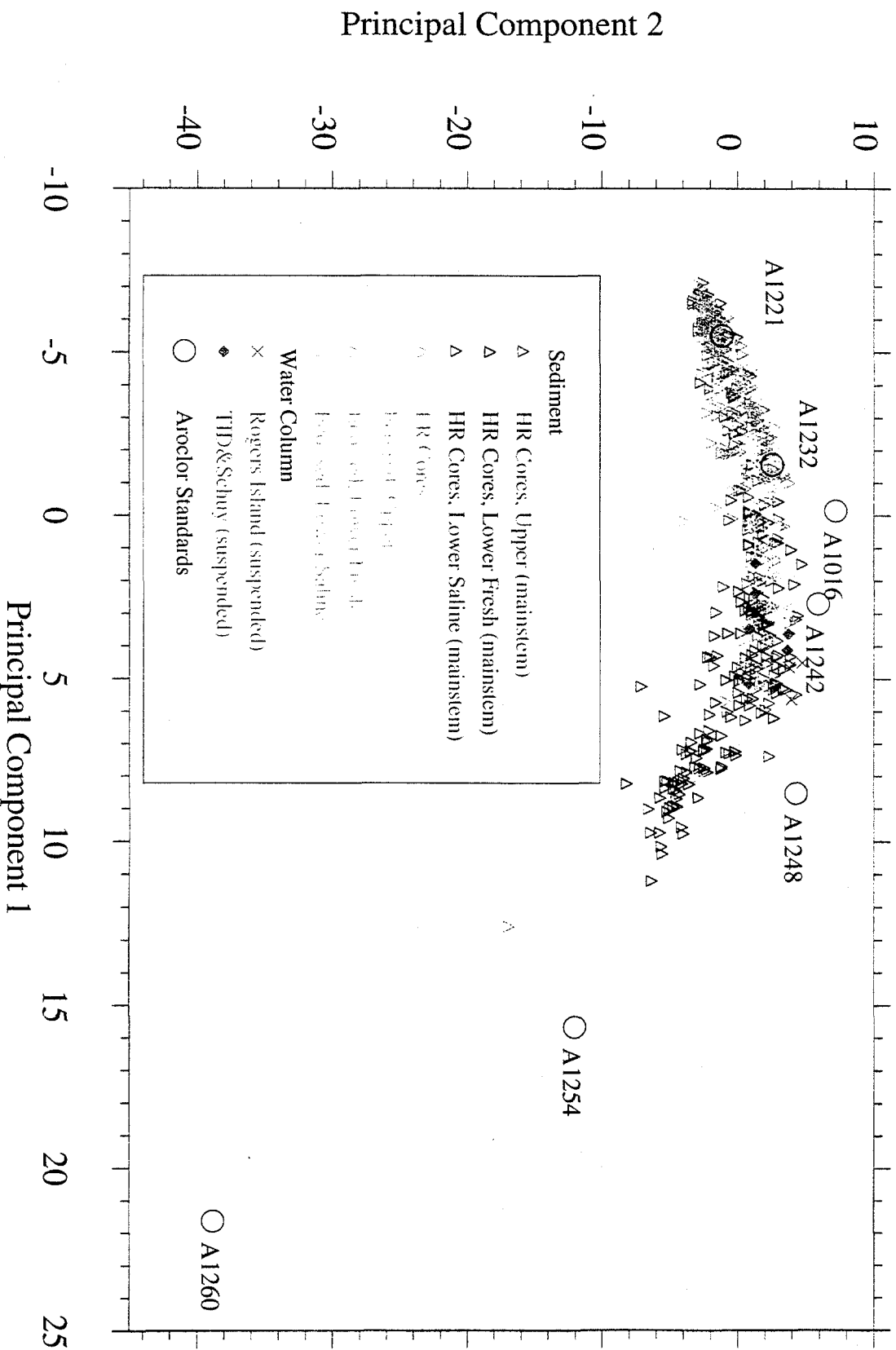
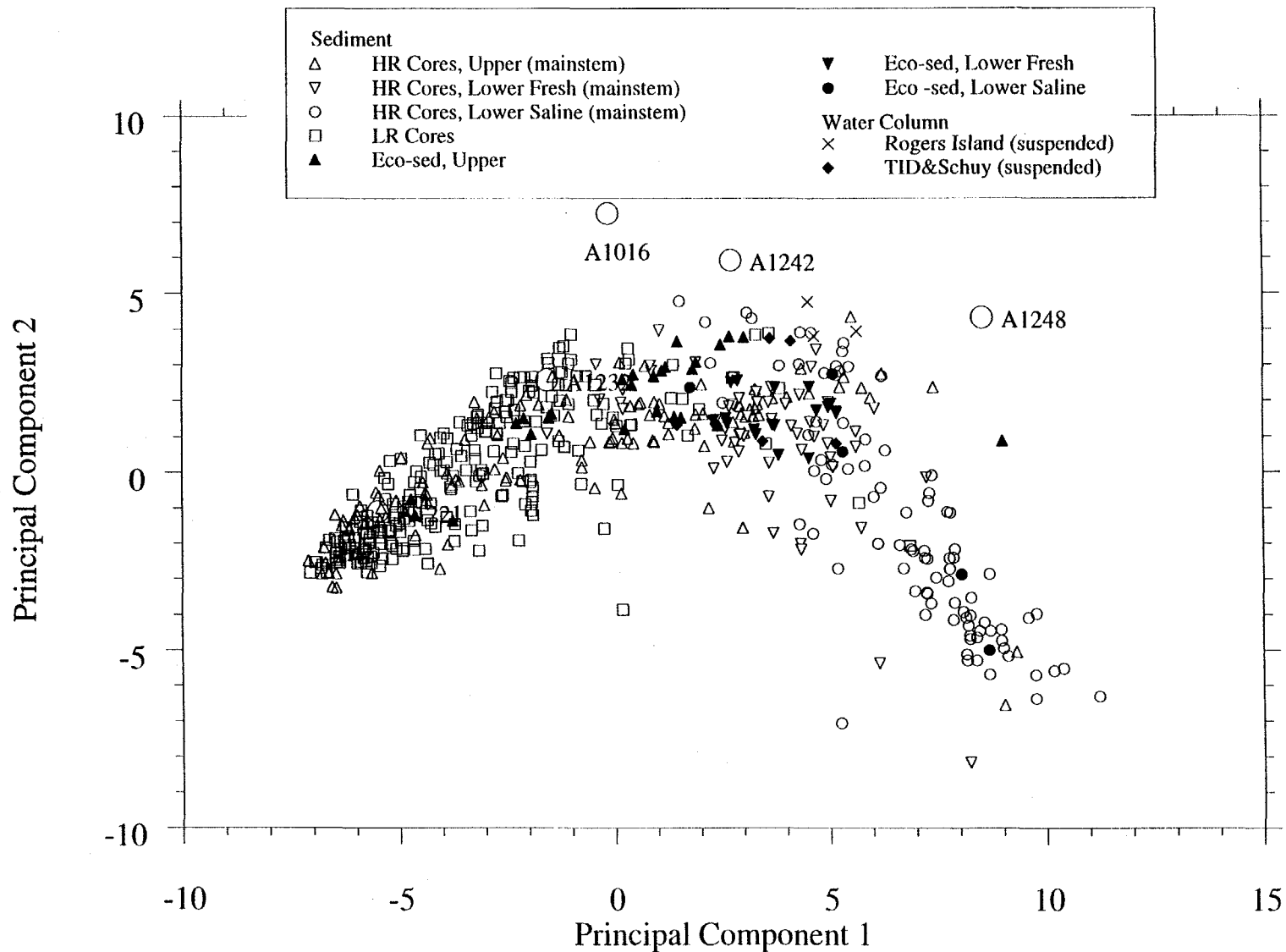


Figure A-16

Principal Component Results for Mainstem High Resolution Cores,
Low Resolution Cores, Ecological Sediment and Upper Hudson Suspended Matter



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TAMS

Figure A-17
Principal Component Results for Mainstem High Resolution Cores,
Low Resolution Cores, Ecological Sediment and Upper Hudson Suspended Matter
(Expanded Scale)

307343

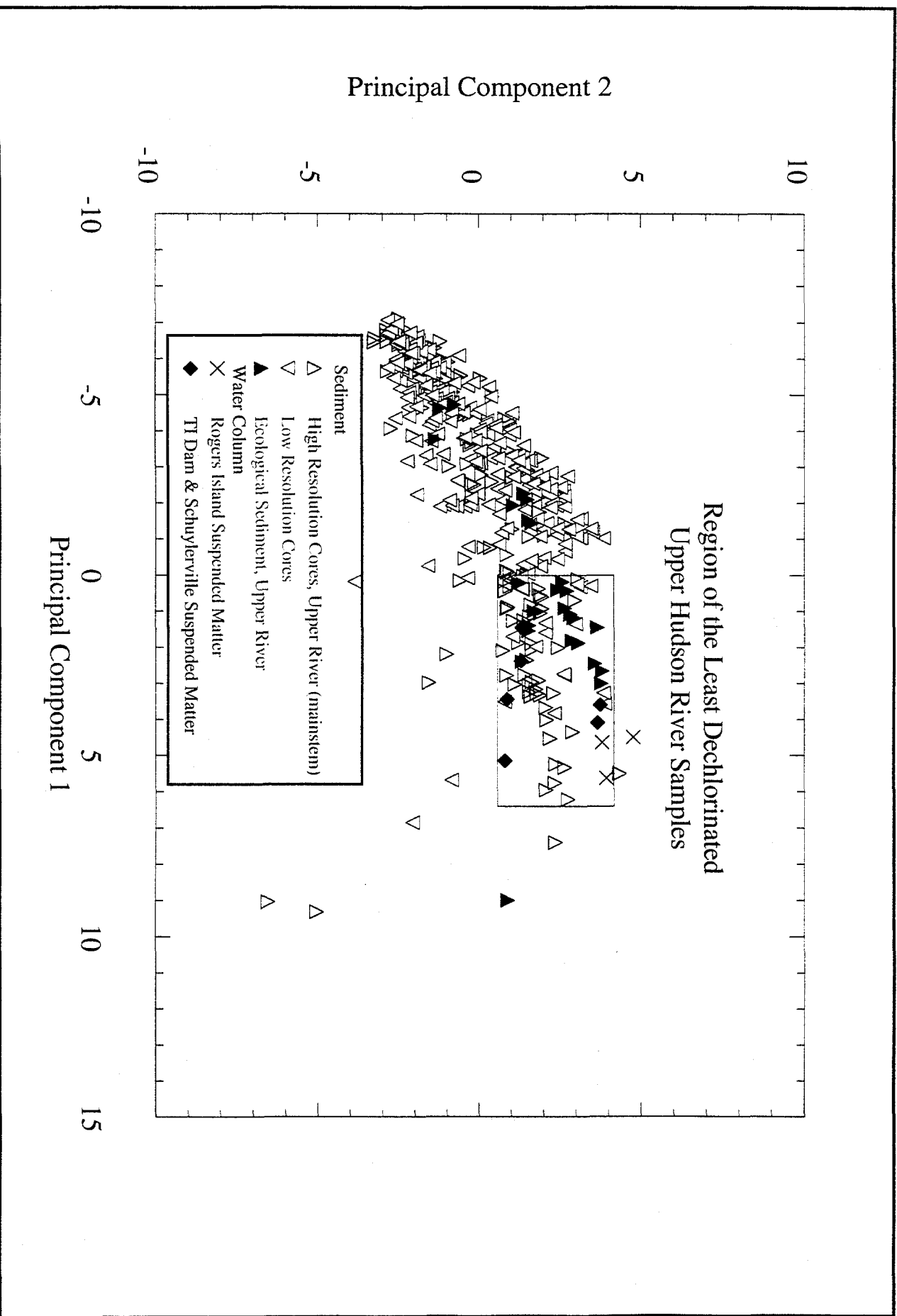


Figure A-18
Principal Component Results for Lower Freshwater Mainstem
High Resolution Cores, Ecological Sediment and Upper Hudson Suspended Matter

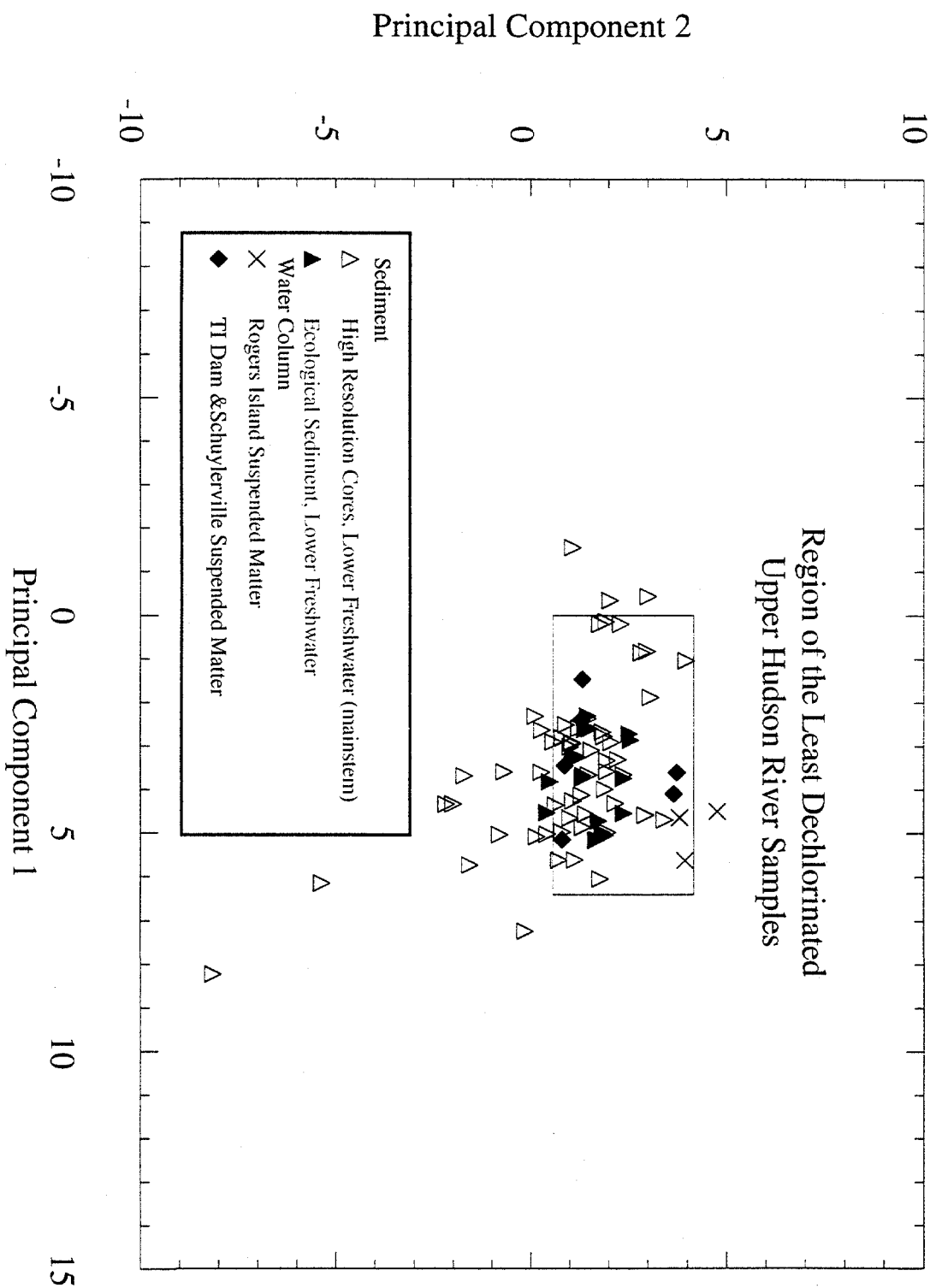


Figure A-19

Principal Component Results for Lower Freshwater Mainstem
High Resolution Cores, Ecological Sediment and Upper Hudson Suspended Matter

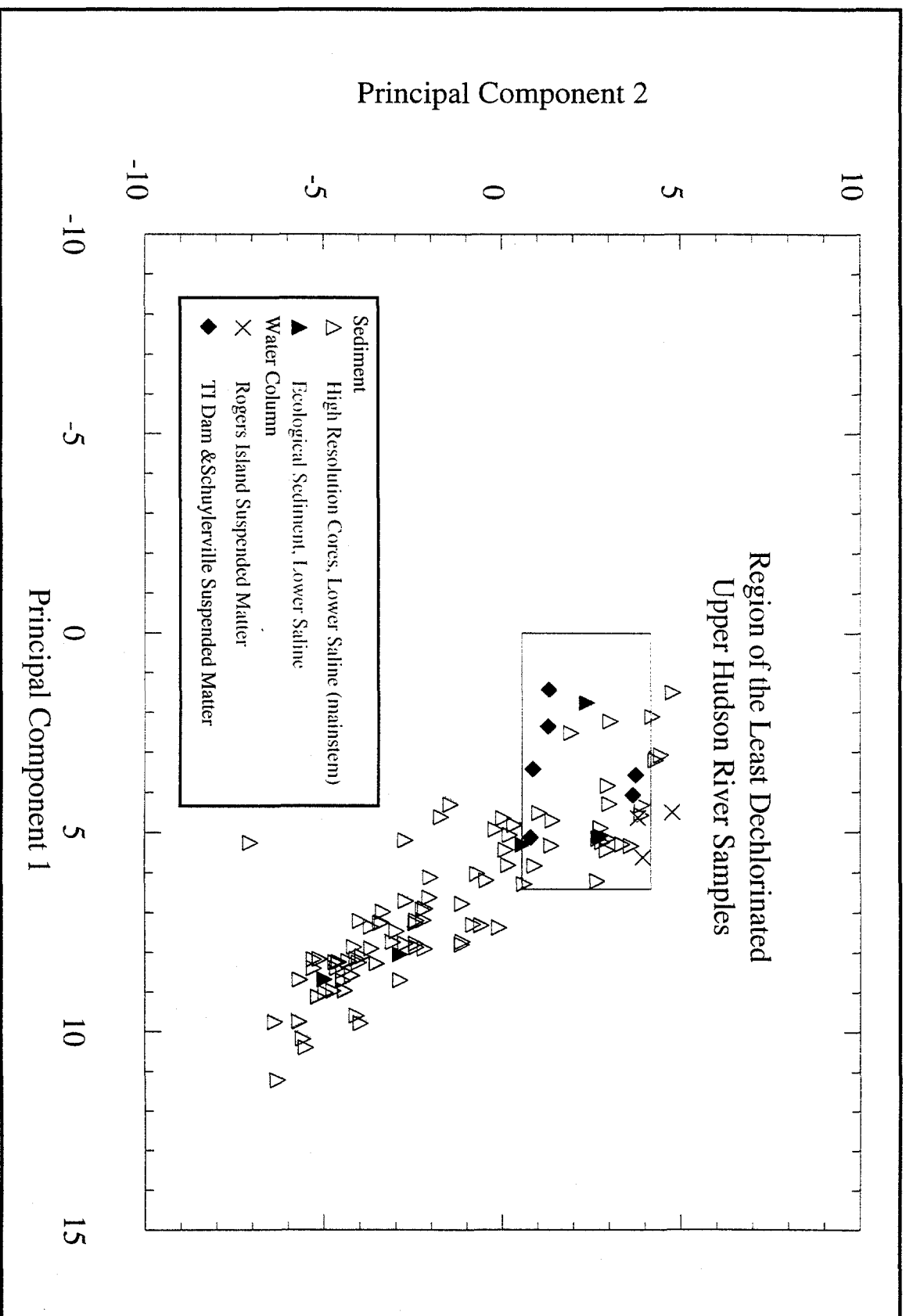


Figure A-20

Principal Component Results for Lower Saline Mainstem High Resolution Cores,
Ecological Sediment and Upper Hudson Suspended Matter

Attachment B

Hudson River PCBs Site Reassessment RI/FS Revised Executive Summary for the Data Evaluation and Interpretation Report and the Low Resolution Sediment Coring Report November 2000

Hudson River PCBs Site Reassessment RI/FS
Revised Executive Summary for the
Data Evaluation and Interpretation Report
and The Low Resolution Sediment Coring Report
November 2000

The U.S. Environmental Protection Agency is conducting a Reassessment Remedial Investigation and Feasibility Study (Reassessment) of the Hudson River PCBs Superfund site, reassessing the Agency's interim 1984 No Action decision for PCB-contaminated sediments in the Upper Hudson River. The goal of the Reassessment study is to determine an appropriate course of action for the PCB-contaminated sediments in the Upper Hudson River in order to protect human health and the environment.

During the first phase of the Reassessment, EPA compiled existing data on the site, and conducted preliminary analyses of the data. As part of the second phase, EPA conducted field investigations to characterize the nature and extent of the PCB loads in the Upper Hudson and the importance of those loads to the Lower Hudson. EPA also conducted analyses of data collected by the New York State Department of Environmental Conservation (NYSDEC), the U.S. Geological Survey, and General Electric Company (GE), as well as other private and public agencies.

Two large-scale sediment investigations were previously conducted by NYSDEC to characterize the extent and magnitude of PCB contamination in the sediments--one from 1976 to 1978 (denoted 1977), and one in 1984. On the basis of data gained from these investigations, approximately forty zones of highly contaminated sediments, designated as *hot spots*, were identified. These data were used to estimate total PCB inventory in Hudson River sediments at the time of the completion of both the 1977 and 1984 studies.

The Data Evaluation and Interpretation Report provides detailed descriptions and in-depth interpretations of the water column and dated sediment core data collected as part of the Reassessment. The report helps to provide an improved understanding of the geochemistry of PCBs in the Hudson River. The Low Resolution Sediment Coring Report is a companion to the Data Evaluation and Interpretation Report. The low resolution sediment coring program was designed to evaluate changes in sediment PCB inventory over time and the degree of burial of PCB-contaminated sediments. The conclusions from these studies are based primarily on direct geochemical analyses of the Phase 2 and historical data, using conceptual models of PCB transport and environmental chemistry.

Program Objectives

- Determine the nature and size of the PCB load originating in the Thompson Island Pool;
- Determine the likely source of the load;
- Determine the other sources of PCBs which are important to the Hudson;

- Determine the likely fate of PCBs within the Hudson;
- Determine the basic mechanisms which govern PCB transport in the Hudson;
- Determine the major factors affecting the long term recovery of the Hudson;
- Obtain new estimates of sediment PCB inventories at selected locations in the Thompson Island Pool to compare against the existing PCB sediment database constructed from the 1984 NYSDEC survey; and
- Refine the PCB mass estimates for a limited number of historical *hot spot* locations defined by the 1977 NYSDEC survey in the Upper Hudson below the Thompson Island Dam.

Major Findings

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 Ft. Edward facilities, the Remnant Deposit area and the sediments of the Thompson Island Pool.
2. The PCB load from the Thompson Island Pool has a readily identifiable homologue pattern which dominates the water column load from the Thompson Island Dam to Troy.
3. The PCB load from the Thompson Island Pool originates from the sediments within the Thompson Island Pool.
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.
5. There was little evidence found of widespread burial of PCB-contaminated sediment by clean sediment in the Thompson Island Pool. Burial is seen at some locations, but more core sites showed loss of PCB inventory than showed PCB gain or burial.
6. From 1984 to 1994, there has been a statistically significant loss of PCB inventory from highly contaminated sediments in the Thompson Island Pool. This loss is between 4 and 59 percent, with a best estimate of 45 percent.
7. From 1977 to 1994, between the Thompson Island Dam and the Federal Dam at Troy, there has been a net loss of PCB inventory in *hot spot* sediments sampled in the low resolution coring program.
8. The PCB inventory for *Hot Spot* 28 calculated from the low resolution coring data is considerably greater than previous estimates. This apparent "gain" in inventory is attributed to significant underestimates in previous studies rather than actual deposition of PCBs in *Hot Spot* 28.

One of the recommendations of the peer reviewers for the Data Evaluation and Interpretation Report (DEIR) and the Low Resolution Sediment Coring Report (LRC) was to provide a concise summary of the information provided within those reports as well as the Responsiveness Summaries to those reports. The following is a revised Executive Summary for the DEIR and LRC that has been updated to reflect the changes based on the Responsiveness Summaries as well as the peer review on those reports. This Executive Summary does not integrate the findings of the modeling efforts conducted for the site. A summary of the current state of knowledge of the geochemistry, fate and transport, bioaccumulation, and the associated risks from PCBs in the Hudson River will be available in the Feasibility Study, to be released in December 2000.

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The importance of this load downstream of the Thompson Island Dam is demonstrated by the Phase 2 water samples collected downstream of the Dam. These samples indicate the occurrence of quasi-conservative transport of water column trichloro and higher homologues (*i.e.*, no apparent net losses or gains) throughout the Upper Hudson to Troy during much of the Phase 2 sampling period. This finding is based on the consistency of homologue patterns and individual homologue loads among the downstream stations relative to the Thompson Island Dam load. Thus, the region above the Thompson Island Dam is responsible for setting water column concentrations and loads downstream of the Dam to Troy. During the low flow conditions seen in the Phase 2 sampling period, as well as in most of the post-June 1993 monitoring data collected by GE, the Thompson Island Pool was responsible for the majority of the load at the Dam. Thus, the Thompson Island Pool load represents the largest fraction of the water column PCB load below the Dam during at least 10 months of the year, corresponding to low flow conditions.

The importance of this load for the freshwater Lower Hudson is derived from a combination of the water column and the sediment core results discussed above. Specifically, the water column results show the Thompson Island Pool to represent the majority of the water column load during much of the year throughout the Upper Hudson to Troy. The dated sediment core results show the Upper Hudson to represent the dominant load to the sediments of the Lower Hudson and, by inference, to the water column of the Lower Hudson. Since the majority of the Upper Hudson load is derived from the Thompson Island Pool, the Thompson Island Pool load represents the majority of the PCB loading to the entire freshwater Hudson as well.

3. The PCB load from the Thompson Island Pool originates from the sediments within the Thompson Island Pool. The PCB homologue pattern present in the water column at the Thompson Island Dam is distinctly different from that which enters the Thompson Island Pool at Rogers Island. This change in pattern was nearly always accompanied by a doubling or tripling of the water column PCB load during the Phase 2 sampling period and subsequent monitoring by GE. This pattern change and load gain occurred as a result of passage through the Thompson Island Pool. With no known substantive external loads to the Thompson Island Pool, the sediments of the Thompson Island Pool were considered the most likely source of these changes. Upon examination of the PCB homologue and congener patterns present in the sediment cores collected from the Thompson Island Pool and elsewhere, it became clear that the sediment PCB characteristics closely matched those found in the water column at the Thompson Island Dam and sampling locations downstream during most of the Phase 2 sampling period. On the basis of this PCB "fingerprint" it was concluded that the Thompson Island Pool sediments represented the major source to the water column throughout much of the year as discussed above.

Two possible mechanisms for transfer of PCBs to the water column from the sediment were explored and found to be consistent with the measured water column load changes. The first mechanism involved porewater exchange, *i.e.*, the transport of PCB to the water column via the interstitial water found within the river sediments. This mechanism was examined using sediment-to-water partition coefficients developed from the Phase 2 water column samples. These coefficients were used to estimate the homologue patterns found in porewater from the Thompson Island Pool sediments. These patterns were then compared with the measured water column patterns at the Thompson Island Dam. On this basis it was demonstrated that this mechanism is generally capable of yielding the water column homologue patterns seen. This analysis suggested that if porewater

exchange is the primary exchange mechanism, then sediments with relatively low levels of dechlorination are the likely candidates for the Thompson Island Pool source.

The alternate mechanism, resuspension of Thompson Island Pool sediments, was also shown to be capable of yielding the water column patterns seen. Since this mechanism works by directly adding sediments to the water column, sediment homologue patterns were directly compared to those of the water column at the Thompson Island Pool. The close agreement seen between the sediment and water column homologue patterns demonstrated the viability of this mechanism. If resuspension is the primary sediment-to-water exchange mechanism, then the responsible sediments must have comparatively high levels of dechlorination, since the water column homologue pattern at the Thompson Island Dam contains a relatively large fraction of the least chlorinated congeners.

As part of the investigation of Hudson River sediments, a relationship between the degree of dechlorination and the sediment concentration was found such that sediments with higher PCB concentrations were found to be more dechlorinated than those with lower concentrations, regardless of age. This relationship had important implications for the nature of the sediments involved in the sediment-water exchange mechanisms. For porewater exchange, which indicated a low level of dechlorination in the responsible sediments, the sediment concentrations had to be relatively low, although no absolute concentration could be established. For resuspension, the sediment concentrations had to be relatively high (*i.e.*, greater than 120,000 µg/kg (120 ppm)) in order to attain the level of dechlorination necessary to drive the Thompson Island Pool load. This in turn suggested that older sediments, particularly the relatively concentrated ones found in the previously identified *hot spots*, are the likely source for the Pool load via the resuspension mechanism. Given the complexities of sediment-water column exchange, it is probable that the current Thompson Island Pool load is the result of some combination of both mechanisms.

Large releases from the Bakers Falls area in the early 1990's may have also yielded sediments with sufficient concentration so as to undergo substantive alteration and potentially yield some portion of the measured load via resuspension. However, the mechanism for rapid burial and subsequent resuspension is unknown. It is also conceivable that these materials could be responsible for a portion of the load if porewater exchange is the driving mechanism. However, the presence of such deposits is undemonstrated and must still be viewed in light of the prior, demonstrably large PCB inventory.

In the DEIR, neither porewater exchange nor resuspension was evaluated in terms of the scale of the flux required to yield the measured Thompson Island Pool load. The mechanisms that may cause the PCB load increase across the Thompson Island Pool have been evaluated as part of the Revised Baseline Modeling Report.

4. Sediment inventories will not be naturally "remediated" via dechlorination. The extent of dechlorination is limited, resulting in probably less than 10 percent mass loss from the original concentrations. Evidence for this conclusion is principally derived from the dated sediment core data obtained during the Phase 2 investigation. These data show that dechlorination of PCBs within the sediments of the Hudson River is theoretically limited to a net total mass loss of 26 percent of the original PCB mass deposited in the sediment. This is because the dechlorination mechanisms which occur within the sediment are limited in the way they can affect the PCB molecule, thus limiting the effectiveness of the dechlorination process. In fact, although theoretically limited to 26

percent, the actual estimated mass loss is much less. The mean mass loss for the high resolution sediment core results was eight percent. Dechlorination mass loss of greater than 10% was limited to sediments having greater than 30,000 µg/kg of total PCBs and for the sediments with the concentration lower than 30,000 µg/kg, dechlorination mass loss did not occur predictably and was frequently 0%.

A second finding was obtained from the core data which supports this conclusion as well. In core layers whose approximate year of deposition could be established, no correlation was seen between the degree of dechlorination and the age of the sediment. If dechlorination were to continue indefinitely, such a correlation would be expected, with the oldest sediments showing the greatest degree of dechlorination, while sediment as old as 35 years were found where little or no dechlorination was present. Instead, a relationship was found between the degree of the dechlorination and the log of the total PCB concentration in the sediment, such that the most concentrated samples had the greatest degree of dechlorination. Also, sediments below 30,000 µg/kg (30 ppm) showed no predictable degree of dechlorination. Some low level samples exhibited substantive levels of dechlorination but these were typically found in the Upper Hudson in regions of high contamination. Most low level samples and nearly all sediment samples from the Lower Hudson exhibited little substantive dechlorination suggesting that PCBs in sediments with less than 30 ppm are largely left unaffected by the dechlorination process. These findings also indicate that the dechlorination process occurs relatively rapidly, within perhaps five to ten years of deposition but then effectively ceases, leaving the remaining PCB inventory intact. These results also indicate that the dechlorination process is generally limited to the areas of the Upper Hudson where concentrations are sufficient to yield some level of dechlorination. For those areas characterized by concentrations less than 30 ppm, dechlorination is expected to have little if any effect at all. Thus, dechlorination cannot be expected to yield further substantive reductions of the Hudson River PCB inventory beyond the roughly ten percent reduction already achieved.

5. There was little evidence found of widespread burial of PCB-contaminated sediment by clean sediment in the Thompson Island Pool. Burial is seen at some locations, but more core sites showed loss of PCB inventory than showed PCB gain or burial. Thirty percent of coring sites do not exhibit burial, or may exhibit erosion, based on the absence of beryllium-7 in core tops. Comparisons of sediment core profiles between the 1984 and 1994 data indicate that burial is not occurring at more than half of the locations investigated. Burial does occur at some *hot spot* areas, but there is also evidence of sediment PCB loss occurring, often within the same *hot spots*. Again, there is more evidence for sediment PCB loss rather than burial.

Beryllium-7 is a naturally-occurring isotope whose presence in sediments indicates recent deposition or interaction with surface waters within the six months prior to sample collection. The absence of beryllium-7 was shown to be a statistically significant indicator of inventory loss. Absence of beryllium-7 is attributed to a core collected in a non-depositional area or an area that has undergone scour (erosion) of river sediment. Thus, this radionuclide was used to test a core top (0 to 1-inch) for the presence of recently deposited sediment. Surficial sediments in which beryllium-7 was not detected (no burial) had lower PCB inventories than cores in which beryllium-7 was detected, indicating that burial of PCB mass by less contaminated sediments is not occurring at these locations. Although this analysis does not offer proof of sediment scour, it does show that burial of contaminated sediments is not occurring in at least 30 percent of the coring sites.

The core profiles, or core results presented by depth, show an important finding. PCB maxima are principally found in the top-most core layer in approximately 60 percent of the samples, which represent shallow sediment (median core segment depth of 9 inches). These results indicate that burial of PCB-bearing sediments is not occurring on an extensive basis and that high concentrations of PCBs remain relatively close to the sediment/water interface. In addition, in areas where burial does occur, the newly deposited sediments commonly contain PCBs.

In addition, the average depth to the maximum total-PCB concentration (taken as the bottom of the core section in which the PCB maximum was found) varied considerably according to whether the area showed a gain or loss of PCB inventory. In the *hot spots*, for cores exhibiting a PCB inventory increase, the average depth to the maximum total-PCB concentration was 18.7- inches (46.8-cm), contrasted to 10.6 inches (26.5-cm) in the cores exhibiting a loss of PCB inventory. The difference in mean depth between areas of PCB loss and gain is statistically significant. This finding confirms that the PCB-maximum moves downward in areas of PCB (and accordingly, sediment) gain, and does not exhibit such burial in areas where PCB loss is occurring.

6. From 1984 to 1994, there has been a statistically significant loss of PCB inventory from highly contaminated sediments in the Thompson Island Pool. This loss is between 4 and 59 percent, with a best estimate of 45 percent. Fine-grained sediments in the Thompson Island Pool have been demonstrated with statistical certainty to have shown a loss of trichloro- and higher PCB homologues between 1984 and 1994. The degree of loss is estimated to be 45 percent with an uncertainty of 4 to 59 percent. The loss of PCB inventory is not due to dechlorination, as other investigators have found evidence that dechlorination losses were approximately five percent over the period 1984 to 1994. The PCB mass that is lost from the highly contaminated sediment is interpreted to have been released into the water column. Following its release, some of this PCB mass would be transported downstream while some would be redeposited in other areas of the Thompson Island Pool.

7. From 1977 to 1994, between the Thompson Island Dam and the Federal Dam at Troy, there has been a net loss of PCB inventory in *hot spot* sediments sampled in the low resolution coring program. When the 1994 total PCB inventory is compared to the 1977 inventory, a statistically significant loss is seen for *Hot Spots* 31, 34 and 37. The scale of loss was estimated to be 50 to 80 percent of 1977 PCB inventory, but the actual magnitude of loss is considered to be poorly known (particularly due to uncertainties associated with the 1977 estimates). As calculated, this represents a potential loss of approximately 3 metric tons into the water column, although some loss may be due to dechlorination. However, the more important conclusion is that *hot spots* in general cannot be assumed to be stable, long-term storage areas for PCB contamination. The other *hot spots* evaluated either appear unchanged or have not experienced significant gains in PCB inventory, with the exception of *Hot Spot* 28, as noted in Major Finding 8, below.

Several locations in *Hot Spot* 39 exhibit burial. Total PCB concentrations are at greater depths than previous sediment surveys. Because of the inability to obtain "complete" cores in this *hot spot* in 1994, there is uncertainty in our current estimate as well as the previous estimates, making it difficult to determine whether there is inventory loss or gain. Given this uncertainty, *Hot Spot* 39 is considered to not have experienced a significant change in inventory.

A weight-of-evidence approach provides the support for these conclusions, with several different lines of investigation typically supporting each conclusion. The subordinate conclusions and findings supporting each of these major findings are discussed below.

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 Ft. Edward facilities, the Remnant Deposit area and the sediments of the Thompson Island Pool. Analysis of the water column data showed no substantive water column load increases (*i.e.*, load changes were nearly always negative) from the Thompson Island Dam to the Federal Dam at Troy during ten out of twelve monitoring events. These results indicate the absence of substantive external (*e.g.*, tributary) loads downstream of the Thompson Island Dam as well as minimal losses from the water column in this portion of the Upper Hudson. Some PCB load gains were noted during spring runoff and summer conditions, which were readily attributed to Hudson River sediment resuspension or exchange by the nature of their homologue patterns. These load gains were notable in that they represent sediment-derived loads which originate outside the Thompson Island Pool, indicating the presence of substantive sediment inventories outside the Pool. Based on the review of more recent GE data from TI Dam and Schuylerville, the sediments between these two stations also appear to contribute to water column loads although to a lesser degree than the TI Pool sediments. This result was not surprising given that an additional 15 hot spots lie between the two monitoring points.

The Mohawk and Hoosic Rivers were each found to contribute to the total PCB load measured at Troy. The loading from the Mohawk during the 1993 spring runoff event could be calculated to be as high as 20 percent of the total load at Troy. However, this load represents an unusually large sediment transport event on the Mohawk since the river was near or at 100-year flood conditions. The contribution by the Hoosic River appeared to be the result of resuspension of Hudson River sediments based on the close agreement of congener patterns between the increased transport and that of the Hudson sediments themselves. This event was particularly noteworthy because of its scale (20 kg/day) and because the scale of the associated Hoosic River flow was consistent with a one-in-three to one-in-five-year event, meaning that events of this magnitude can be expected on a regular basis.

A second line of support for the above conclusion comes from the congener-specific analyses of the water column samples which show conformity among the main stem Hudson samples downstream of the Thompson Island Dam and distinctly different patterns in the water samples from the tributaries. These results indicate that the tributary loads cannot be large relative to the main stem load since no change in congener pattern is found downstream of the tributary confluences. An additional examination of the water column results by homologue and congener showed that downstream variations were typically associated with the lightest congeners, which exhibited substantial losses from the water column during summer conditions. The heavier congeners, trichlorohomologues and higher, yielded nearly constant load rates downstream of Thompson Island Dam. This provides further support to the absence of additional loads and demonstrates the importance of the region above Thompson Island Dam in controlling loading to all locations downstream. Most of all, it documents that the region above Thompson Island Dam is the major source for the heavier PCB congeners, which are the most important to fish body burdens, ecological impacts and human health risks.

The conclusion concerning the loads at Thompson Island Dam is also supported by the results of the sediment core analyses which showed the PCBs found in the sediments of the tributaries to be distinctly different from those of the main stem Hudson. As part of this analysis, two measurement variables related to sample molecular weight and dechlorination product content were shown to be sufficient to clearly separate the PCB patterns found in the sediments of the freshwater Hudson from those of the tributaries, indicating that the tributaries were not major contributors to the PCBs found in the freshwater Hudson sediments and by inference, to the freshwater Hudson as a whole. This result was also confirmed by a principal components analysis of sediment and water congener patterns throughout the Hudson.

When dated sediment core results from the freshwater Hudson were examined on a congener basis, sediment layers of comparable age obtained from downstream cores were shown to contain similar congener patterns to those found in a core obtained at Stillwater, just 10 miles downstream of the Thompson Island Dam. Based on calculations combining the homologue patterns found at Stillwater with those of other potential sources (*e.g.*, the Mohawk River) it was found that no less than 75 percent of the congener content in downstream cores was attributable to the Stillwater core. This suggests that the Upper Hudson is responsible for at least 75 percent of the sediment burden, and by inference, responsible for 75 percent of the water column load at the downstream coring locations. Only in the cores from the New York/New Jersey Harbor was substantive evidence found for the occurrence of additional PCB loads to the Hudson. Even in these areas, however, the Upper Hudson load represented approximately half of the total PCB load recorded by the sediments.

The last line of evidence for this conclusion was obtained from the dated sediment cores wherein the total PCB to cesium-137 (^{137}Cs) ratio was examined in dated sediment layers. Comparing sediment layers of comparable age from Stillwater (10 miles downstream of the Thompson Island Dam) to Kingston (100 miles downstream of the Thompson Island Dam), the data showed the sediment PCB to ^{137}Cs ratios at downstream cores to be readily predicted by those at Stillwater, implying the same PCB sources (*i.e.*, GE release and the sediments of TI Pool are the primary sources and the sediment downstream TI Dam is the secondary source) and quasi-conservative transport between Stillwater and locations downstream. These calculations showed downstream ratios to agree with those predicted from Stillwater to within the limitations of the analysis (± 25 percent).

2. The PCB load from the Thompson Island Pool has a readily identifiable homologue pattern which dominates the water column load from the Thompson Island Dam to Troy 10 months of the year. Evidence for the first part of this conclusion stems largely from the Phase 2 water column sampling program which provided samples above and below the Thompson Island Pool. In nearly every water column sampling event, the homologue pattern of the water column at the Thompson Island Dam was distinctly different from that entering the Thompson Island Pool at Rogers Island. In addition, the Phase 2 and GE monitoring data both showed increased water column PCB loads at the downstream station, relative to the upstream station, particularly under low flow conditions. Based on the monitoring data collected from June 1993 to the present, water column concentrations and loads typically doubled and sometimes tripled during the passage of the river through the Pool. Thus, a relatively large PCB load originating within the Thompson Island Pool is clearly in evidence in much of the Phase 2 and GE data. This load was readily identified as a mixture of less chlorinated congeners relative to those entering the Pool.

The sediment inventories of three other areas appear unchanged (*Hot Spots* 25, 35 and dredge location 182), but only one (*Hot Spot* 25) had a sufficient number of samples to statistically confirm the lack of change.

8. The PCB inventory for *Hot Spot* 28 calculated from the low resolution coring data is considerably greater than previous estimates. This apparent "gain" in inventory is attributed to significant underestimates in previous studies rather than actual deposition of PCBs in *Hot Spot* 28. An evaluation of the 1994 data collected for the low resolution coring program found that the PCB inventory in *Hot Spot* 28 was substantially greater than had been estimated in previous studies. The Low Resolution Sediment Coring Report estimates the mass of PCBs in *Hot Spot* 28 to be 20 metric tons. Previous estimates varied between two to seven metric tons. Therefore, based on a comparison of these estimates there would appear to be a large gain in PCB inventory. However, further examination of the core profiles for *Hot Spot* 28 shows that less than 50 percent of the sample locations have evidence of deposition (burial). The remaining sites are either unchanged or have undergone scour based on the presence of the maximum total-PCB concentration in the shallow sediment. The deposition history recorded by the nearby high resolution cores indicates that this type of profile can only be caused by scour. Only two to five percent of PCB mass was deposited between 1977 and 1991 for two nearby high resolution cores, thus making such a large gain in inventory unlikely. Therefore, an apparent "gain" of PCBs in *Hot Spot* 28 based on a comparison of historical estimates to the current estimate is not real. There have been losses of PCBs from several locations within the *hot spot* but, overall, the evidence suggests no significant change in inventory in the *hot spot*. The previous mischaracterization of the inventory probably results from an initial inaccurate assessment of *Hot Spot* 28 by the 1977 sediment survey caused by too many shallow cores and grabs (*i.e.*, "incomplete" cores). EPA's current estimate is based on cores that have been found to be "complete" based on radionuclide analysis.

It should be noted that the PCB inventory for *Hot Spot* 28 is estimated to be 20 metric tons. This is greater than the inventory of the entire Thompson Island Pool, which was estimated to be between 14.5 and 19.6 metric tons in the Data Evaluation and Interpretation Report, based on the 1984 NYSDEC data.

Additional Findings

In addition to the conclusions described above there are several additional findings which have important implications for the understanding of PCB transport in the Hudson River. These are discussed briefly below.

- The geophysical survey (side scan sonar) showed a general correlation between areas of fine-grained sediment and the *hot spot* areas previously defined by NYSDEC. Since PCBs have a general affinity for fine-grained sediments, it can be assumed that the fine-grained sediment areas mapped by the geophysical survey represent the same PCB-contaminated zones mapped by NYSDEC. This indicates that the *hot spot* areas previously mapped by NYSDEC are largely still intact and have not been completely redistributed by high river flows.

- Erratic releases of apparently unaltered PCBs above Rogers Island, probably from the GE Hudson Falls facility, dominated the load from the Upper Hudson River during the period September 1991 to May 1993. Interim remedial measures at the GE Hudson Falls plant have reduced this load substantially. The load at Rogers Island now represents less than one fifth of the total load at the Thompson Island Dam.
- The unaltered PCB load originating above Rogers Island is predominantly Aroclor 1242 with approximately 4% Aroclor 1254 and 1% Aroclor 1260.
- The annual net Thompson Island Pool load ranged from 0.36 to 0.82 kg/day over the period April 1991 to October 1995, representing between 20 to 70% of the total load at the Thompson Island Dam based on data obtained by GE. During the period of June 1993 to October 1995, the net Thompson Island Pool load varied between 50 to 70% of the total load at the Thompson Island Dam. The net load from the TI Pool (kg/day) in 1999 represents about 80% of the total PCB load at the TI Dam.
- The Upper Hudson area above the Thompson Island Dam, *i.e.*, the Hudson Falls and Fort Edward facilities, the Remnant Deposit area and the Thompson Island Pool, has represented the largest single source of PCBs to the entire freshwater Hudson for the past 19 years, representing approximately 77 to 91% of the PCB load at Albany in 1992 - 1993 based on water column measurements.
- While the homologue pattern in the freshwater Hudson is dominated by the homologue pattern from the Thompson Island Pool, minor changes in the PCB pattern downstream of the Thompson Island Dam have been observed. The resulting water column patterns resemble those seen in downstream sediments and associated porewater. However, it is unclear whether this change is the result of subsequent downstream sediment-water exchange or *in situ* water column processes (*e.g.*, aerobic degradation or gas transfer), given the temporal dependence. In particular, the congener pattern seen at the Thompson Island Dam is preserved throughout the Upper Hudson during winter and spring but appears to undergo modification during summer conditions when biological activity is high but energy for sediment-water exchange is low. In particular, loads of the lightest congeners substantially decrease with distance downstream while heavier congener loads (trichlorohomologues and higher) remain constant or occasionally increase.
- Water-column PCB transport occurs largely in the dissolved phase, in the Upper Hudson, representing 80% of the water-column PCB inventory during 10 to 11 months of the year.
- GE sampling in the vicinity of the Thompson Island Dam suggests that some Thompson Island Dam samples collected at low flow conditions in the absence of loadings above Rogers Island may overestimate the water column load at the dam. For the five-year period of GE data collection prior to 1996, the results suggest the values may be too high by 20 percent. During 1996 and 1997, the low-flow estimates may be 36 percent too high. No corrections are required for flows higher than 4000 cfs prior to 1996 (which covers most of the USEPA Phase 2 work). These corrections account for both flow and Rogers Island load which are shown to affect the sampling bias. (See the discussion in Section 1 of the USEPA

review of the GE/QEA model in Book 3 of the Responsiveness Summary for Volume 2A: Database Report, Volume 2B: Preliminary Model Calibration Report, Volume 2C: Data Evaluation and Interpretation Report.)

- The loads at Thompson Island Dam, Schuylerville, Stillwater and Waterford were revised to account for corrections to Thompson Island Dam concentrations and USGS flow estimates in Appendix C of the Responsiveness Summary for the Low Resolution Sediment Coring Report. The net result of the revisions is lower overall loads (approximately 20% lower) in the Upper Hudson under low flow conditions, with high flow conditions largely unmodified from those estimated in the DEIR. The revisions did yield a more distinct and consistent decline in less chlorinated homologues under the condition of low flow and warm water, suggesting loss of these homologues via a process such as gas exchange or aerobic degradation.
- Dissolved-phase and suspended-matter PCB water-column concentrations at the Thompson Island Dam and downstream appear to be at equilibrium as defined by a two-phase model dependent on temperature and the particulate organic carbon content.
- Evidence suggests that the Upper Hudson River PCB load can be seen as far downstream as RM -1.9. The contribution is estimated to represent about half of the total PCB loading to the New York/New Jersey Harbor.
- Three estimates were made of the PCB inventory sequestered in the sediments of the Thompson Island Pool, based on the 1984 NYSDEC data. The first estimate, based on a technique called polygonal declustering, yielded an estimate of 19.6 metric tons (the original NYSDEC estimate was 23.2 metric tons by M. Brown et al., 1988). The second, based on a geostatistical technique called kriging, yielded an estimate of 14.5 metric tons. The third estimate incorporates sediment texture by forming Thiessen polygons around the samples in cohesive and noncohesive areas to determine separate inventory estimates for these areas. This last estimate yields an estimate of 15.4 metric tons which is in close agreement with the results of the kriging estimate.
- An analysis of the side-scan sonar 500 kHz signal and the 1984 NYSDEC sediment PCB survey indicated that the acoustic signal could be used to predict the level of sediment PCB contamination. Acoustic data can be used to separate areas of cohesive or fine-grained sediment from areas with non-cohesive coarse-grained sediments. These areas correspond with sediments with high PCB contamination (mean concentration of 49.5 mg/kg) and relatively low PCB levels (mean concentration of 11.4 mg/kg). Based on this correlation and corresponding changes in river cross-sectional area, maps were created delineating the likely distribution of contaminated sediments within the region of the river surveyed.
- Some sediments, particularly those in the freshwater Lower Hudson, show substantively higher molecular weights and lower fractions of BZ#1, 4, 8, 10 and 19. These conditions may be the result of aerobic degradation or gas exchange during transport from the Upper Hudson.

- Regardless of the sediment type or mechanism, the sediments of the Thompson Island Pool have historically contributed to the water column PCB load and will continue to do so for the foreseeable future. It is unlikely that the current loading levels will decline rapidly in light of their relatively constant annual loading rates between 1993 and 1999.
- The interpretation of the low resolution coring data is consistent with the findings of the Data Evaluation and Interpretation Report. The analysis in the Low Resolution Sediment Coring Report supports the conclusions from the Data Evaluation and Interpretation Report that the extent of dechlorination is proportional to sediment concentration, and that the water-column PCB load originates primarily from the sediments of the Upper Hudson River.
- Historical estimates of PCB mass in *hot spots* below the Thompson Island Dam assumed a solid specific weight of 1 g/cc . Based on the low resolution core relationship between solid specific weight and total PCB concentration, more appropriate values of solid specific weight ranged from 0.5 to 0.79 g/cc for the majority of the 1977 *hot spot* sample locations. Applying a solid specific weight based on length-weighted average concentrations yielded about a 20 to 30 percent decrease in the original PCB inventory estimates. In other words, the previous calculations of PCB inventories were somewhat overestimated.
- Sediments in the near shore environment, which was defined as within 50 feet of the shoreline, had higher PCB concentrations than estimated in the Phase 1 Report. The Phase 1 Report estimated an exposure point concentration of 66 mg/kg (parts per million) for the 95 percent confidence interval of the arithmetic mean of the shallow sediment concentration based on the 1984 data, whereas the current estimate would be within the range of 135 to 264 mg/kg. The implications of higher PCB concentrations in the near-shore sediments are addressed in the Revised Human Health Risk Assessment (USEPA, 2000).
- A principal components analysis of the sediment and water column data of the Hudson provided statistical support for the geochemical conclusions of the Phase 2 investigation. Specifically, conclusions regarding the dominance of the GE- related sources throughout the Hudson, the use of the molar dechlorination product ratio (MDPR) and change in molecular weight as measures of the degree of dechlorination, the absence of substantive dechlorination in Lower Hudson sediments, and the correlation of the degree of dechlorination with the sediment PCB mass were all borne-out by the statistical analysis.

Summation

The findings of the DEIR and LRC provide valuable information regarding the geochemistry of PCBs in the Upper Hudson River. The analyses conducted within these reports have led to a number of important findings, including; the sediments of the Thompson Island Pool are the largest source of PCBs to the freshwater Hudson River; large sediment PCB inventories are still present in the Upper Hudson River; anaerobic dechlorination will not substantially deplete the PCB mass in the Upper Hudson; burial is not preventing PCBs from entering the water column; and, there is redistribution of PCBs within the river system. Simply stated, the PCBs in the sediments of the Upper Hudson are still a source of PCBs to the water column and biota in the river, and are likely to be so for some time. The information from these reports will be used in conjunction with the computer modeling, risk assessments and feasibility study in order to select an appropriate remedy for the PCB-contaminated sediments of the Upper Hudson River.

Attachment C

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Attachment C

**Examination of the Gas Exchange Flux for PCBs from the Upper
Hudson
Schuylerville to Waterford**

Examination of the Gas Exchange Flux for PCBs from the Upper Hudson Schuylerville to Waterford

Introduction

The recent examination of PCB transport in the Upper Hudson performed by the USEPA (see Appendix C of the Responsiveness Summary for the Low Resolution Sediment Coring Report, 1999) noted a consistent decline in the less chlorinated congener loads. Specifically, the lightest congeners declined substantially relative to the remainder of the PCB load as the river traveled from Thompson Island (TI) Dam and Schuylerville to Waterford during the summer months. The cause of the loss is unknown but may result from several processes including gas exchange, photodegradation and aerobic degradation. Among these possibilities, gas exchange is perhaps best characterized and so was examined for the purpose of comparison with the actual load declines. Essentially, this exercise was intended to determine whether the pattern and scale of observed congener loss were consistent with that predicted from an estimate of gas exchange from the water column. To the extent that the losses are not consistent with gas exchange, the differences may suggest the nature of additional fluxes affecting PCB fate and transport.

General Approach

Two estimates were made of gas exchange loss of PCBs from the Upper Hudson River in the region between Schuylerville and Waterford. The region between TI Dam and Schuylerville was not directly examined for this purpose due to the greater uncertainty (sampling bias) associated with the data collected at Phase 2 shoreline sampling location at the TI Dam. The estimates developed in this attachment focused on individual congeners representing the most massive constituents in the dissolved phase of the water column. Additionally, the congeners were selected to represent a broad range of geochemical properties as well as apparently different load variations between Schuylerville and Waterford. Estimates were obtained from the literature pertaining to geochemical constants such as molecular diffusivity and Henry's Law constants. Additionally, models for estimating the water film and gas film resistance for exchange were obtained from the literature and integrated into the estimating equations. Two different models were used to develop the estimate for the liquid film resistance while a single model was applied to estimate the gas film resistance. The first model used to estimate the liquid film resistance to gas exchange was developed from Wanninkhof *et al.* (1991) and is based on wind-driven gas exchange in lakes. The alternative model was developed by O'Connor and Dobbins (1954) and is based on gas exchange in flowing rivers. The gas film resistance model was obtained from Achman *et al.*, (1993) based on studies on Lake Michigan.

This work was intended to both estimate the magnitude of the gas exchange losses as well as the congener pattern of that loss. In this fashion, the estimate could provide a basis to suggest the occurrence of other processes whose magnitudes and effects on congener pattern are unknown.

Theoretical Considerations

The basic equation to estimate the instantaneous rate of transfer of a trace constituent across the air-water boundary is given as (from Whitman, 1923):

$$F = K_{OL} (C_D - C^*) \quad (1)$$

where: F = flux in $\text{g/m}^2\text{-day}$
 K_{OL} = gas transfer coefficient or piston velocity in m/day
 C_D = concentration of the dissolved constituent in the bulk water phase in g/m^3
 C^* = concentration of the constituent in air expressed as the water concentration in equilibrium with the air.
= C_A/H
where: H = Henry's Law constant
 C_A = concentration of the constituent in air (g/m^3)

For the purposes of this exercise, the concentration of the individual congener in Hudson River water (C_w) is assumed to be much larger than the air concentration term C^* and so the latter can be ignored. Thus this equation reduces to:

$$F = K_{OL} (C_D) \quad (2)$$

Equation 2 can then be applied to each congener in question so long as the geochemical parameters are known or can be estimated. Estimates for K_{OL} were developed from the following relationship:

$$1 / K_{OL} = 1/k_w + RT / Hk_A \quad (3)$$

where: k_w = the water side gas transfer velocity in m/day
 k_A = the air side gas transfer velocity in m/day
 R = the universal gas constant ($8.2057 \times 10^{-5} \text{ atm-m}^3/\text{mol K}$)
 H = the Henry's Law constant in $\text{atm-m}^3/\text{mol}$, and
 T = the absolute temperature in K .

In the above equations, k_w and k_A are estimated from models and studies of gas exchange utilizing wind speed and water flow.

Gas Film Transfer Coefficient

The expression for k_A was taken from Achman *et al.* (1993) and is based on the transfer of water vapor from a lake surface. For water, k_A is given by:

$$k_{A(H_2O)} = 0.2 * u_{10} + 0.3 \quad (4)$$

where: u_{10} = the wind speed at a reference height of 10 m in m/s
 $k_{A(H_2O)}$ = the gas film transfer coefficient for water in air in cm/hr

Wind speeds were obtained from the National Weather Service long term records for the Albany Airport for the months corresponding to the transect events. The coefficient $k_{A(H_2O)}$ is related to the k_A for the constituent of interest by the expression also given by Achman *et al.* (1993):

$$k_{A(\text{organic})} = k_{A(H_2O)} * [D_{A(\text{organic})} / D_{A(H_2O)}]^{0.61} \quad (5)$$

where: $k_{A(\text{organic})}$ = the gas film transfer coefficient for the constituent in cm/hr
 $D_{A(\text{organic})}$ = the molecular diffusivity of the constituent in air in cm^2/s
 $D_{A(H_2O)}$ = the molecular diffusivity of water in air in cm^2/s

Molecular diffusivities for PCBs in air were developed by Bopp (1983) from the Fuller, Schettler and Giddings correlation (Reid *et al.*, 1977, as cited in Bopp, 1983) for 10 and 25 C and were interpolated to the *in situ* temperatures of the transects. Molecular diffusivity of water in air was estimated from Perry (1976).

Henry's Law constants were reported by Brunner *et al.* (1990) and then corrected for temperature as reported by Achman *et al.* (1993) as follows:

$$\log H_T / \log H_{298} = (7.91 - 3414 / T) / (7.91 - 3414 / 298) \quad (6)$$

where: H_T = Henry's Law constant at the temperature T in atm-mol/ m^3
 T = the absolute temperature in K.

Henry's Law coefficients were not available for BZ#1 in Brunner *et al.* (1990) and instead were obtained from Bopp (1983) based on his reported monochlorohomologue result.

Liquid Film Transfer Coefficient

The liquid film gas transfer velocity was estimated in two ways. The first was based on a series of direct measurements of gas exchange using dual tracer techniques involving sulfur hexafluoride and helium-3 by Wanninkhof *et al.* (1991) and others. These studies utilize tracers with extremely high Henry's Law constants so that the gas film resistance becomes negligible and a true measure of the liquid film resistance is obtained.

The main advantage of this approach is that the model is based on direct measurements of the gas exchange rate in several lake and pond settings, conditions close to those of the Upper Hudson. The river reaches in the Upper Hudson can be best characterized as a series of slowly flowing ponds. In systems such as this, it is expected that much of the energy for gas exchange will be derived from wind shear at the water-air interface.

The majority of vertical displacement in the Upper Hudson takes place at the seven dams between Rogers Island and the Federal Dam at Troy, NY. However, for constituents such as PCBs with low Henry's Law coefficients, Cirpka *et al.* (1993) report little enhancement of gas exchange at falls or cascades. This is principally due to the limited effect of air bubbles on compounds with low Henry's Law constants. Thus in the Upper Hudson, the principal areas for gas exchange are the long, smooth regions of the river where wind-driven shear stress serves to stir the water surface. This approach will be compared with the method of O'Connor and Dobbins which is based on water velocity (gravity-driven shear stress). It can be reasonably argued here that a wind-driven approach based on lakes should represent a minimum estimate for gas exchange in the Upper Hudson. The movement of water through the reaches should only serve to enhance the gas exchange rate calculated for a stagnant surface such as that of a lake.

Wanninkhof *et al.* (1991) gives the relationship between the gas transfer coefficient and the wind speed as follows:

$$k_w = 0.45 * u_{10}^{1.64} * [Sc_{PCB} / 600]^{-0.5} \quad (7)$$

where: k_w = the water side gas transfer velocity in cm/hr
 u_{10} = the wind speed at a reference height of 10 m in m/s
 Sc_{PCB} = the Schmidt number for the PCB congener given as:

$$Sc_{PCB} = \mu / D_{L(PCB)}$$

where: $D_{L(PCB)}$ = the diffusivity of the PCB congener in water in cm^2/s
 μ = the kinematic viscosity of water (cm^2/s)
= viscosity of water (cp) / density of water (g/cc) * 0.01

For this calculation, wind speeds were obtained for the National Weather Service, as described above. Molecular diffusivities were obtained from Bopp (1983) and interpolated to the *in situ* temperatures. Properties of water were obtained from CRC (1977).

An alternative estimate of the gas transfer coefficient was developed from O'Connor and Dobbins (1954). This model was principally intended for estimates of re-aeration of flowing streams. Given the low velocities of the Upper Hudson reaches, its applicability here may be limited but it is included here for comparison. The gas transfer coefficient is given by the following:

$$k_w = [D_w * u / d]^{0.5} \times 8.64 \times 10^4$$

where: k_w = gas transfer coefficient in m/day
 u = mean water velocity in m/s
 d = mean water depth in m
 D_w = molecular diffusivity of constituent in water in m^2/s
= $22.0 \times 10^{-9} / (MW)^{2/3}$
 MW = molecular weight in g/mole

Values for flow were obtained from USGS measurements corresponding to USEPA's Phase 2 transect events. Water velocity and depth were calculated based on LTI *et al.* (January 2000). These values were length-weighted into two segments corresponding to the river segment between Schuylerville and Stillwater and the segment between Stillwater and Waterford to simplify the calculation.

Integration of the Model

The gas exchange rate given in Equation 2 represents the instantaneous rate of loss from the water column which varies as the water column concentration of the congener varies. For each of the transect events examined, the water column concentrations for nearly all congeners varied substantively with time and thus, so did the gas exchange coefficient. For this reason, it was necessary to integrate the instantaneous losses so that the total gas exchange for the reach for the transect could be compared with the observed changes in inventory.

For these calculations, PCB fluxes from or to the water column other than gas exchange and volumetric transport have been ignored. The purpose behind this was to calculate the relative and absolute changes in the congener concentrations and ratios solely as a result of gas exchange. If the congener conditions calculated for Waterford could be shown to match those measured at Waterford, the potential ability of gas exchange to produce the changes noted would be verified. While there are certainly other sources and sinks in this region, the ability to constrain them over the short sampling periods examined here was limited. The Revised Baseline Modeling Report discussed these sinks and sources in detail but did not examine them in the same manner since the focus is on longer time scales than this analysis considers. Of particular concern to this analysis is the fact that the lightest congeners are not particularly subject to losses to the sediments as a result of particle settling (*i.e.*, low K_{oc}). Thus sediment-related sinks for the lighter congeners are unimportant here and were ignored. Sediment sources of these congeners only serve to increase lighter congener loads. Thus the dramatic load decreases documented in Appendix C of the Responsiveness Summary for the LRC (USEPA, 1999) must represent a process which acts on and reduces the water column concentration itself, such as gas exchange. The purpose of this exercise was to simply examine the possibility that gas exchange can accomplish the reductions seen while leaving the heavier congener loads largely unaffected.

As noted previously, the dissolved phase PCB concentration must be known or estimated to estimate the gas exchange flux. Additionally, dissolution of particle-bound PCBs must be accounted for since the particle-bound fraction may be large for the heavier congeners and thus serve to "buffer" the dissolved phase concentration. Due to the additional uncertainties regarding the TI Dam sampling location, the detailed analysis of gas exchange was restricted to those sampling events

where Schuylerville samples were collected. Flow-averaged events did not include Schuylerville and so were not analyzed in detail but are discussed later in this attachment.

The derivation of the integrated gas exchange flux assuming a constant flow rate is given in Figure C-1. This derivation yields the following formula:

$$\frac{C_{wx}}{C_{w0}} = e^{-\frac{K_{OL} \cdot W \cdot x}{Q}} \cdot \frac{1}{[1 + TSS \cdot K_{oc} \cdot f_{oc} + DOC \cdot K_{DOC}]}$$

where: $C_w(x)$ = the total concentration of the congener in the water column at a distance x downstream in g/m^3
 C_{w0} = the concentration of the congener in the water column at the upstream boundary condition (Schuylerville) in g/m^3
 W = width of the river in m
 Q = volumetric flow rate in m^3/s
 K_{OL} = gas transfer coefficient in m/s
 x = Distance downstream in m
 K_{OC} = Organic carbon partition coefficient estimated from the actual dissolved and suspended matter data in L/kg
 f_{OC} = fraction of organic carbon on the suspended matter (unitless)
 TSS = suspended solids concentration in kg/L

The reaches from Schuylerville to Waterford were chosen for this exercise for several reasons, including one related to the derivation above. First, water flow in these reaches primarily increases in discrete steps at known locations and thus can be well constrained. In particular, the flow rates can be taken as essentially constant from Schuylerville to Stillwater during most conditions. Additionally, the flow from just below Stillwater (at the confluence of the Hoosic River) can be considered constant to Waterford. Thus, the reach between Schuylerville and Waterford can be represented by two model segments at constant flow with a single flow adjustment between the segments. Second, the stations at Schuylerville and Waterford were collected from bridges via a horizontal compositing procedure and so should represent accurate estimates of the entire PCB load at the location. Third, these areas are sufficiently downstream of the majority of sediment contamination so that the changes in PCB load are more gradual than that seen upstream. Lastly, PCB data from these stations had few quality assurance issues for the transects in question.

Application

The model derived above was specifically intended to address the gas exchange losses in the reach between Schuylerville and Waterford. Unlike the regions upstream which frequently show large PCB water column load increases, this region is characterized by relatively constant PCB loads within sampling events (*i.e.*, Schuylerville loads are equal to Waterford loads for most of the heavier congeners). This region is also characterized by large losses of the lightest congeners (*e.g.*, BZ#1,

4 and 8), again unlike upstream reaches where these congeners frequently increase with distance downstream. In particular, the Phase 2 water column sampling events from May 1993 to September 1993 all exhibit the characteristics described above between the two locations. (The flow-averaged events show these characteristics between TI Dam and Waterford). Among the seven sampling events examined, five were flow average events and two were transect events. The transect events provide greater detail on the load changes in this region. In this section, the model derived above is applied to the two Phase 2 summer transects (transects 5 and 6) and is also used to examine relative gas exchange rates during one cool weather (spring) transect.

Congener Selection

Before beginning the examination, it was necessary to select a subset of congeners for which all of the parameters described above could be estimated. Additionally, these congeners had to be present at sufficiently high levels so as to be measurable at both stations, preferably in both dissolved and suspended matter phases. The congeners that showed dramatic losses in these reaches (*i.e.*, BZ#1, 4, 8, 10 and 19) were included since they were the main focus of this analysis. The losses of these congeners were particularly noteworthy since loss of these congeners due to sedimentation from the water column is greatly limited relative to heavier congeners due to their low partition coefficients. Therefore, sediment settling can be ruled out as an important loss mechanism for these congeners. These congeners are principally (greater than 80 percent) carried by the river in the dissolved phase.

The congener selection was also designed to represent a broad range of properties so that the effects on the entire congener spectrum could be examined. Thus four congeners were selected from each of the trichloro to pentachloro homologue groups in addition to those listed above. No hexachloro or higher congeners were selected due to their low concentrations and strong preference for the suspended matter phase. The table below presents the list of congeners examined in this analysis.

Homologue Group	Congeners Selected
Monochlorobiphenyl	BZ#1
Dichlorobiphenyl	BZ#4, 8, 10
Trichlorobiphenyl	BZ#18, 19, 26, 28, 31
Tetrachlorobiphenyl	BZ#44, 52, 66, 70
Pentachlorobiphenyl	BZ#87, 101(+90), 110, 118

Flow Considerations

As noted above, the model derivation leading to an analytical solution is dependent on a constant flow condition over the integral. This requirement could be met because of the following conditions. First, the Schuylerville station is situated just below the confluence with the Batten Kill. Between this location and Stillwater, there is only one substantive tributary (Fish Creek) which does not contribute significantly during summer. Thus, for Schuylerville to Stillwater, flow could be assumed to be constant. The actual increase was less than 8 percent for both transect 5 and 6. Below Stillwater, the largest contributor is the Hoosic River whose confluence is just about a mile below

the Stillwater sampling station at RM 168.3. Because of its proximity to the Stillwater station, the model flow at Stillwater was set equal to the Waterford flow (*i.e.*, Stillwater + Hoosic flows) and held constant for the model calculation. The actual flow increase in addition to the Hoosic contribution was estimated to be less than 1 percent for transect 5 and less than 12 percent for transect 6.

The final calculations involved calculating the load changes to Stillwater for the first river segment using the flow conditions at Schuylerville, then correcting the output for dilution to the Waterford flow and using the result as input to the second model segment at Stillwater and calculating the results at Waterford.

Initial Conditions

For each transect calculation, the initial conditions were set equal to the conditions measured at Schuylerville. Congener concentrations, f_{OC} , and TSS were used as reported for the reach from Schuylerville to Stillwater. Partition coefficients were calculated from the Phase 2 samples at Schuylerville and applied to this reach as well. Notably, TSS and f_{OC} did not remain constant, as might be expected due to the additional flow and TSS load from the Hoosic. For this reason, the second reach was calculated using f_{OC} and TSS from the Waterford station, effectively assuming that the observed changes between Schuylerville and Waterford occurred at the confluence with the Hoosic. Partition coefficients developed from the Waterford samples were also used in the second reach. For congeners where partition coefficients were not available for a given reach, the results from the other transect for the same reach were utilized when possible. This selection was based on the closer agreement between partition coefficients for the same reach on different transects than for different reaches on the same transect. When this was not possible, then an estimate from the same transect was used.

Ultimately, the calculations could be described as setting the initial conditions at Schuylerville and calculating the results at Stillwater. Concentrations at Stillwater were then adjusted for flow and then used to calculate the concentrations at Waterford using the Waterford partition coefficients, TSS and f_{OC} .

Tables C-1 and C-2 contain the parameters used for each transect calculation.

Results

Using the formulations described above, gas exchange losses were estimated for all 17 congeners for the two transect events. Two estimates of gas exchange were made for each transect, one based on the wind-driven liquid film transfer coefficient (k_L) developed by Wanninkhof *et al.*, (1991) and one based on the gravity-driven (flow-driven) liquid film transfer coefficient developed by O'Connor and Dobbins (1954). The same gas film transfer coefficient was used in both cases. These results were then compared to the measured differences between Schuylerville and Waterford. Figures C-2 and C-3 present the calculated and observed load differences for transect 5 and transect 6, respectively as the absolute difference in mg/s between Schuylerville and Waterford. Notable in each diagram is the relatively close match of the two gas exchange models. Also notable is the relatively close agreement between the model-predicted losses and those observed for transect 5.

Many congener load changes are bracketed by the two model results. Several congeners stand out as exceptions, BZ#1, BZ# 8 and BZ#66 and heavier congeners. The losses of these congeners are greater than that predicted by the model. As discussed above the additional losses of the lighter congeners are not likely to occur due to particle settling, and so are likely to result from an *in situ* degradative process. Losses of the heavier congeners are less constrained by the partition coefficient argument.

Transect 6 exhibits some of the same properties. Mass losses for BZ#4, 10 and 19 are well matched by the models. Additionally, losses of BZ#1 and BZ#8 cannot be explained by gas exchange. However, for congeners BZ#18, and BZ#26 through 118, the water column load exhibits little or no change. As discussed in Appendix C of the Responsiveness Summary for the LRC, total load estimates are expected to have an uncertainty of ± 20 percent but congener proportions are not subject to such a large uncertainty. It is likely that these results are indicative of real changes in the water column loads (*i.e.*, there likely were additions of the heavier congeners similar in scale to their calculated gas exchange losses.).

The results were also examined on a relative basis, normalizing to the total load at Schuylerville so that values represent the percentage of the load at Schuylerville that was lost or gained while traveling to Waterford. These results are shown in Figures C-4 and C-5 for the two transects. These diagrams provide a better perspective of the effect of gas exchange on the individual congeners. In transect 5 (Figure C-4), the model estimates fall substantially short for BZ#1 and BZ#8 as well as for BZ#66 and higher, as noted above. However, expressed in this fashion, the results illustrate that fairly large portions of the total water column loads for the individual congeners are lost to gas exchange between Schuylerville and Waterford. This is especially true for the lighter congeners where losses were calculated to be on the scale of 40 percent of the total inventory.

This becomes even more clear for transect 6 when examined in this manner (see Figure C-5). Gas exchange losses are unable to explain the losses of BZ#1 and 8 in this transect while providing a fairly good match for the other three dechlorination products. Estimated gas exchange mass loss as a percentage of the water column load is not trivial for the heavier congeners, indicating an additional process is probably supplying additional PCB mass to the water column in this region of the Hudson. However, its scale is clearly smaller than that which occurs in the reaches upstream of Schuylerville.

While the nature of the source term is unknown, it is clear that the load it supplies has little in the way of dechlorination products. This conclusion is based on the close agreement of the gas exchange loss and actual losses for congeners BZ#4,10 and 19, the larger, unexplained losses of BZ#1 and 8 and the relative increase in the proportions of the heavier trichloro and higher congeners. That is, the results suggest a source consistent with the suite of congeners exhibiting gains.

Figure C-6 presents the congener pattern of several surface (0-2 cm) high resolution sediment core samples from the Schuylerville to Waterford region of the river. Two of the four samples contain little of the dechlorination congeners (only BZ#8 was present), suggesting that sediments such as these may be responsible for the load gain. The remaining samples have substantial fractions of the lighter congeners. Addition of these sediments would serve to raise the lighter congener portions of the water column inventory which is not consistent with the observations.

Discussion

The changes in the measured and modeled congener concentrations suggest the occurrence of several fluxes in this region which can be fairly well constrained by the examination of the congener patterns. Losses of BZ#1 and BZ#8 are clearly larger than can be explained by gas exchange and do not follow the trends seen for other congeners of similar molecular weight (*i.e.*, BZ#4, 10, and 19). The losses of the latter congeners is well explained by a simple gas exchange model. Notably, the losses of BZ#4, the most massive congener in the water column inventory, were well explained by the gas exchange model in both transects. In one of the two events (transect 5), gas exchange losses were comparable in scale (although typically higher) to the observed differences in load between Schuylerville and Waterford for the heavier congeners examined. In the second event (transect 6), the gas exchange losses were clearly incongruent with the observed mass gains observed for these congeners, suggesting the presence of a source with relatively little dechlorination product content.

The poor agreement between calculated gas exchange congener losses and those seen for BZ#1 and 8 is a strong indicator that gas exchange is not the only mechanism responsible for the pronounced losses of these congeners. Although it is possible that the observed congener loss patterns are the result of a balance of sediment additions and gas exchange losses, this does not appear likely in view of the gas exchange loss pattern and the available sediment patterns. Instead, the results suggest a mechanism that is specific to these congeners, such as aerobic degradation or photodegradation, perhaps related to the single orthochlorine structure common to these molecules. This mechanism would be responsible for at least half of the loss of these congeners and possibly more.

The load gains seen for the heavier congeners in transect 6 appear to be consistent with a sediment-based source, similar in nature to the sediments collected from high resolution cores 21 and 22 near Stillwater at RM 177.8.

While this examination has only dealt with two transects exhibiting the preferential loss of the lighter congeners, in fact there are seven Phase 2 events which exhibit such behavior, spanning the period May to September, 1993. These events are shown sequentially in Figures C-7 to C-13. Each of these figures present four diagrams, representing the individual congener fluxes grouped by homologue. Monochloro and dichloro homologues have been grouped together. The figures present a sequence of conditions in the Hudson wherein the fluxes of the orthochlorine congeners steadily decrease downstream and over time. Loads of heavier congeners typically remain constant within events, although absolute magnitudes of some fluxes decrease over the summer. The decreasing loads of lightest congeners is a consistent summer phenomenon in all seven events. Inferring from the analysis above, losses of three of the lighter congeners would be expected to match that predicted from gas exchange. Notably BZ#1 and BZ#8 decrease markedly in several summer sampling events, similar to the declines noted above. This suggests that the mechanisms responsible for the enhanced losses noted above apply throughout the summer period.

Also evident in the diagram is the tendency for loads of heavier congeners to remain constant or increase slightly downstream relative to the TI Dam and Schuylerville loads. These results are consistent with the two events examined above and suggest that the region below Schuylerville

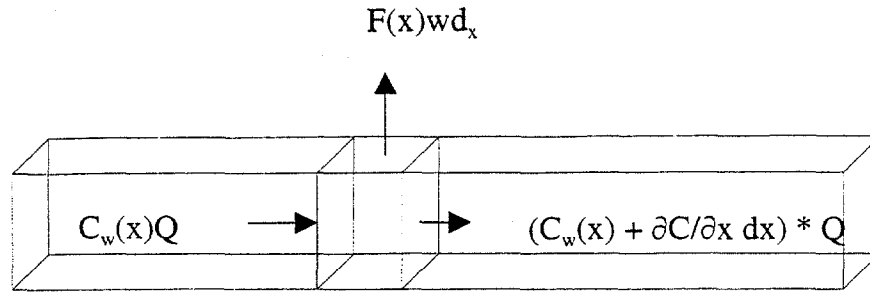
(most likely the sediments in this region) continue to be a source of PCBs to the water column throughout this period of monitoring and presumably into the future.

Notably, Phase 2 events earlier in 1993 did not exhibit such losses of lighter relative to heavier congeners (for example, see Figure C-14). In this spring runoff event and the other events of the spring and winter (Transect 2 was excluded due to QA/QC issues.) congener load variations typically track one-another, suggesting the reduced importance of gas exchange and the degradative process(es) affecting BZ#1 and BZ#8.

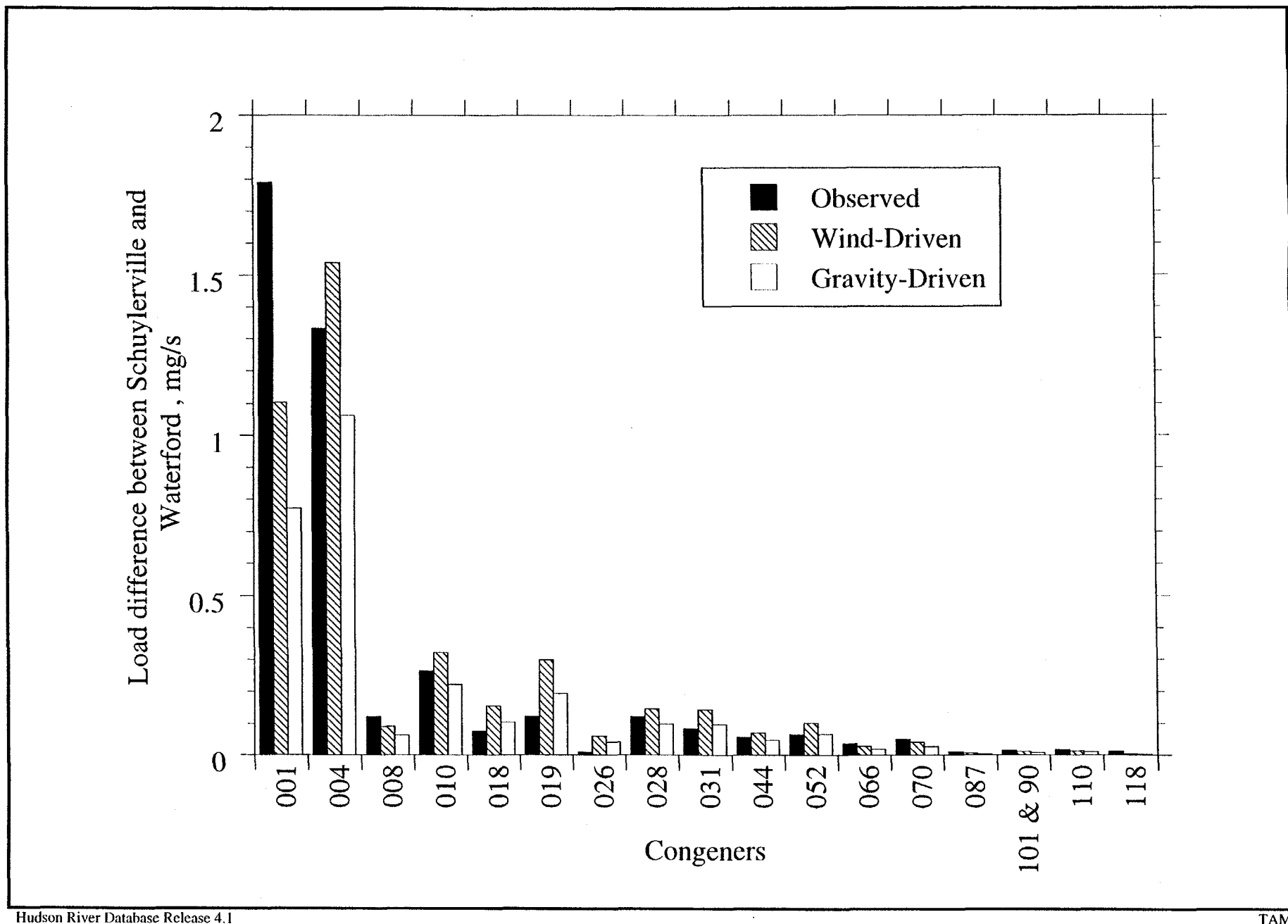
Without a complete mass balance, it is difficult to estimate the exact magnitude of the apparent degradative losses seen in the summer sampling events. However, because the affected congeners would not be expected to partition to particles and subsequently settle out of the water column, the observed mass losses, beyond that of the gas exchange loss estimates, provide a minimum measure of the scale of these losses. Noting that the losses are limited to the lightest congeners and do not affect the congeners typically found in fish, the observations suggest the following. Losses of BZ#1 and BZ#8 are typically 50 percent of peak values obtained at TI Dam and are sometimes reduced to between 80 and 100 percent of the peak upstream loads. Based on the gas exchange estimates for these congeners, non-gas exchange loss is at least half of the total loss and possibly more. Losses of BZ#4, BZ#10 and BZ#19 are less but still substantial with maximum losses close to 50 percent of the TI Dam peak value. These losses are large when viewed in the context of the 10 to 20 percent variability typically seen for the other congeners and suggest that gas exchange represents a significant sink for all water-borne congeners, even those whose loads do not decrease downstream. Finally, load gains for heavier congeners are apparent despite the occurrence of gas exchange losses indicating the reach from Schuylerville to Waterford contributes to the water column PCB load albeit to a much lesser degree than the reaches upstream.

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Figure C-1
Derivation of Simple Gas Exchange Model



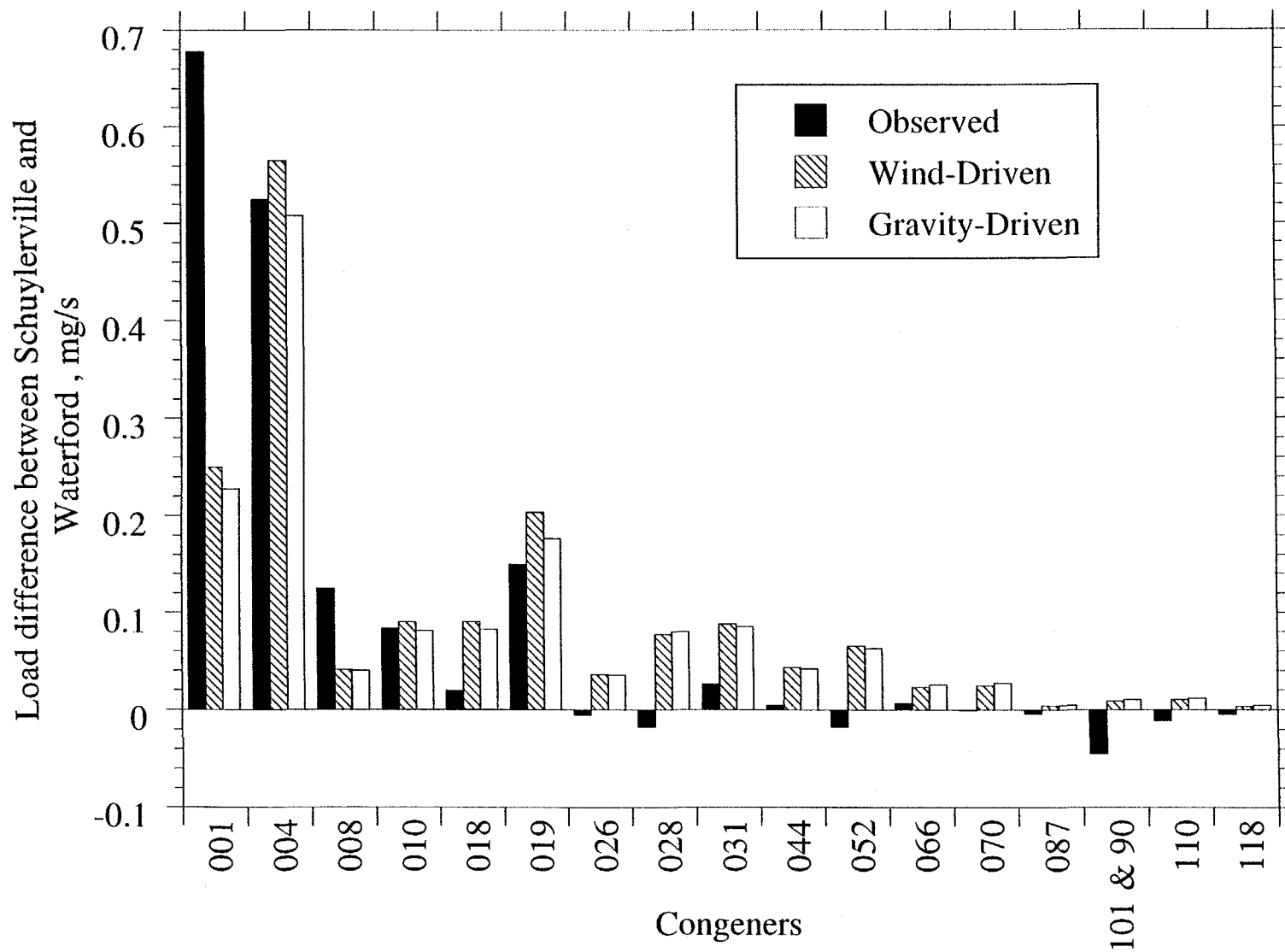
1. $(C_w(x) + \frac{\partial C_w(x)}{\partial x} dx) * Q + F(x) * Wdx = C_w(x) * Q$
2. $\frac{\partial C_w(x)}{\partial x} dx * Q + F(x) * Wdx = 0$
3. $\frac{\partial C_w(x)}{\partial x} * Q = -F(x) * W$
4. $F(x) = K_{OL} * C_D(x)$
5. $C_w = C_D + C_{ss} * TSS$
6. $C_{ss} = C_{oc} * f_{oc}$
7. $C_w = C_D + C_{oc} f_{oc} * TSS$
8. $\frac{C_{oc}}{C_D} = K_{oc} \therefore$
9. $C_w = C_D + C_D K_{oc} f_{oc} TSS$
10. $C_D = \frac{C_w}{(L + K_{oc} f_{oc} TSS)}$
11. $F(x) = K_{OL} * \frac{C_w}{(l + K_{oc} f_{oc} TSS)}$
12. $\frac{\partial C_w}{\partial x} = \frac{W}{Q} * \frac{K_{OL} * C_{wx}}{[1 + TSS * K_{oc} * f_{oc} + DOC * K_{DOC}]}$
13. $\int_{C_{wo}}^C w \frac{\partial C_{wx}}{C_{wx}} = \int_0^x \frac{K_{OL} * W}{Q [1 + TSS * K_{oc} * f_{oc} + DOC * K_{DOC}]}$
14. $\ln \frac{C_{wx}}{C_{wo}} = -\frac{K_{OL} * W * x}{Q} * \frac{1}{[1 + TSS * K_{oc} * f_{oc} + DOC * K_{DOC}]}$
15. $\frac{C_{wx}}{C_{wo}} = e^{-\frac{K_{OL} * W * x}{Q}} * \frac{1}{[1 + TSS * K_{oc} * f_{oc} + DOC * K_{DOC}]}$



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Figure C-2
Comparison of Absolute Congener Load Difference Between Schuylerville and Waterford
Transect 5, June 1993



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Figure C-3
Comparison of Absolute Congener Load Difference Between Schuylerville and Waterford
Transect 6, August 1993

Load difference between Schuylerville and
Waterford relative to the load at Schuylerville

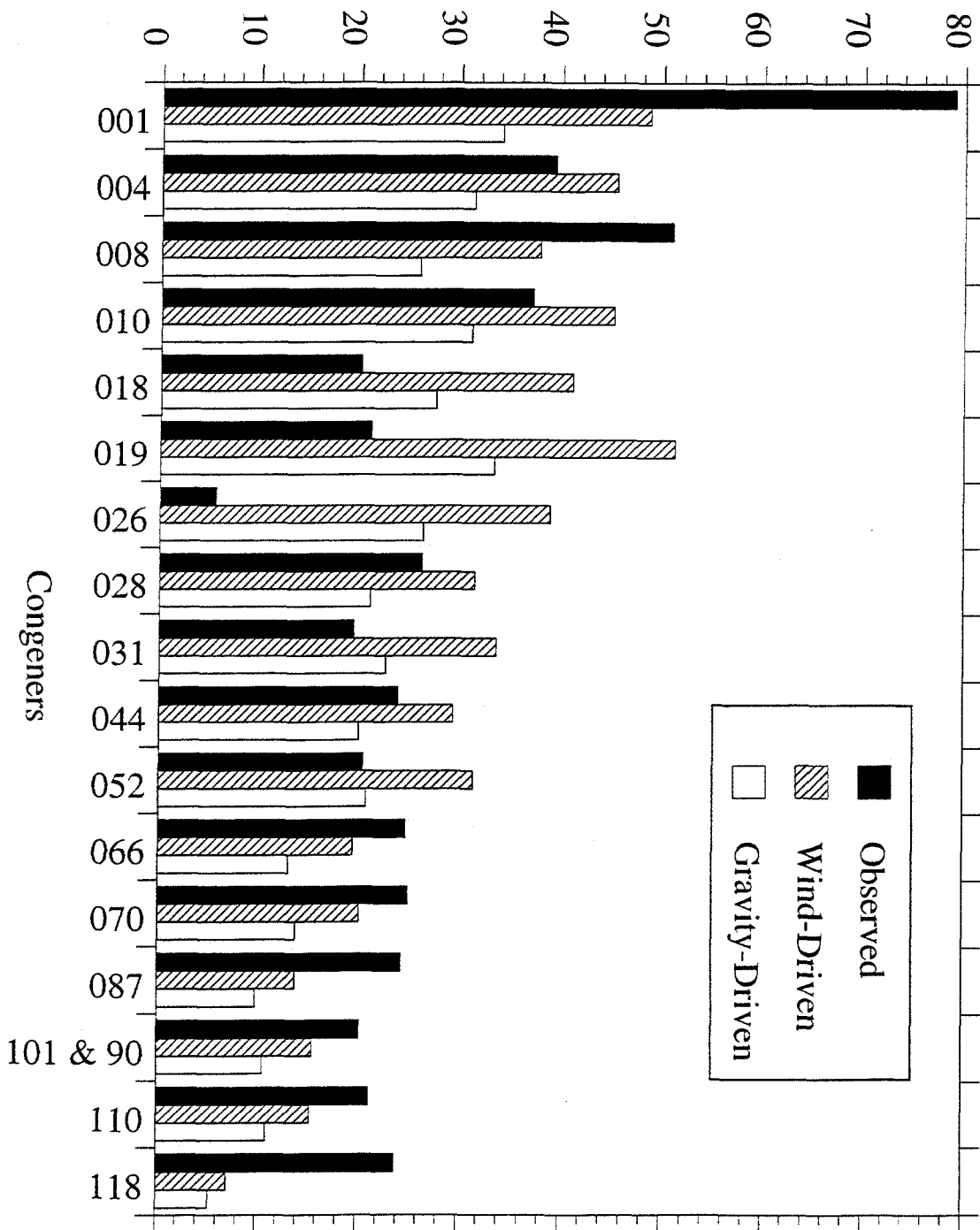
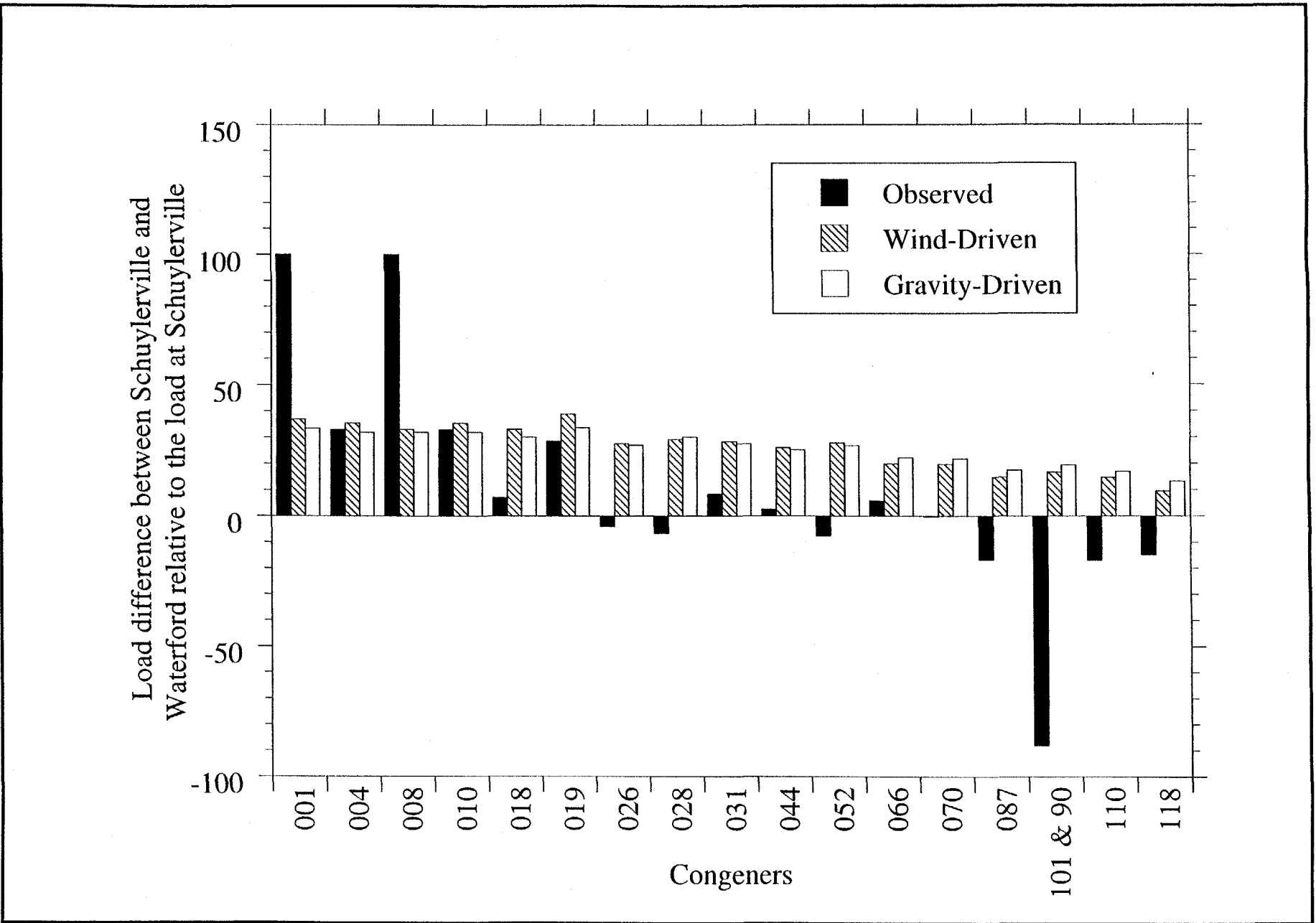


Figure C-4

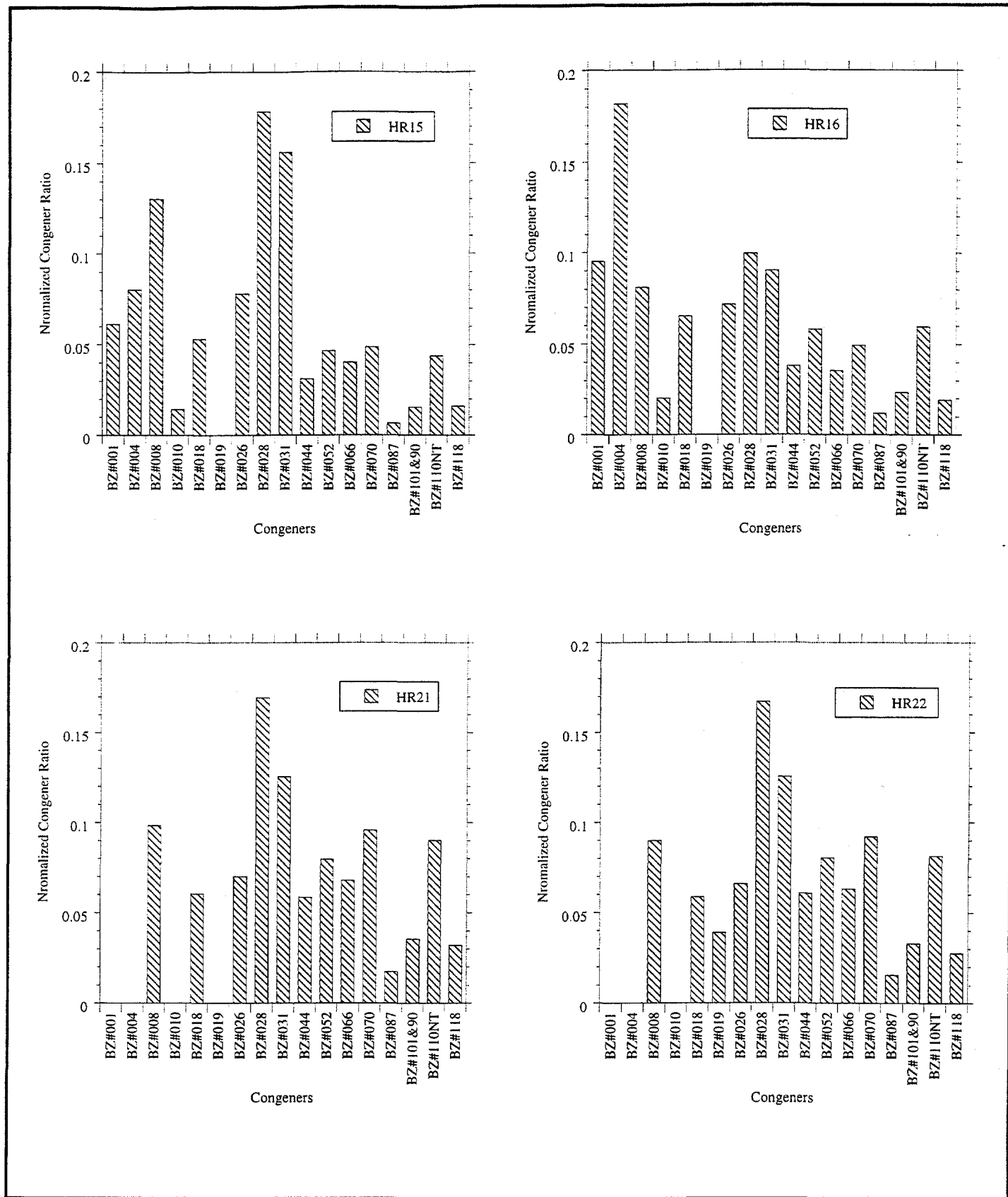
Comparison of Relative Congener Load Difference Between Schuylerville and Waterford
Transect 5, June 1993



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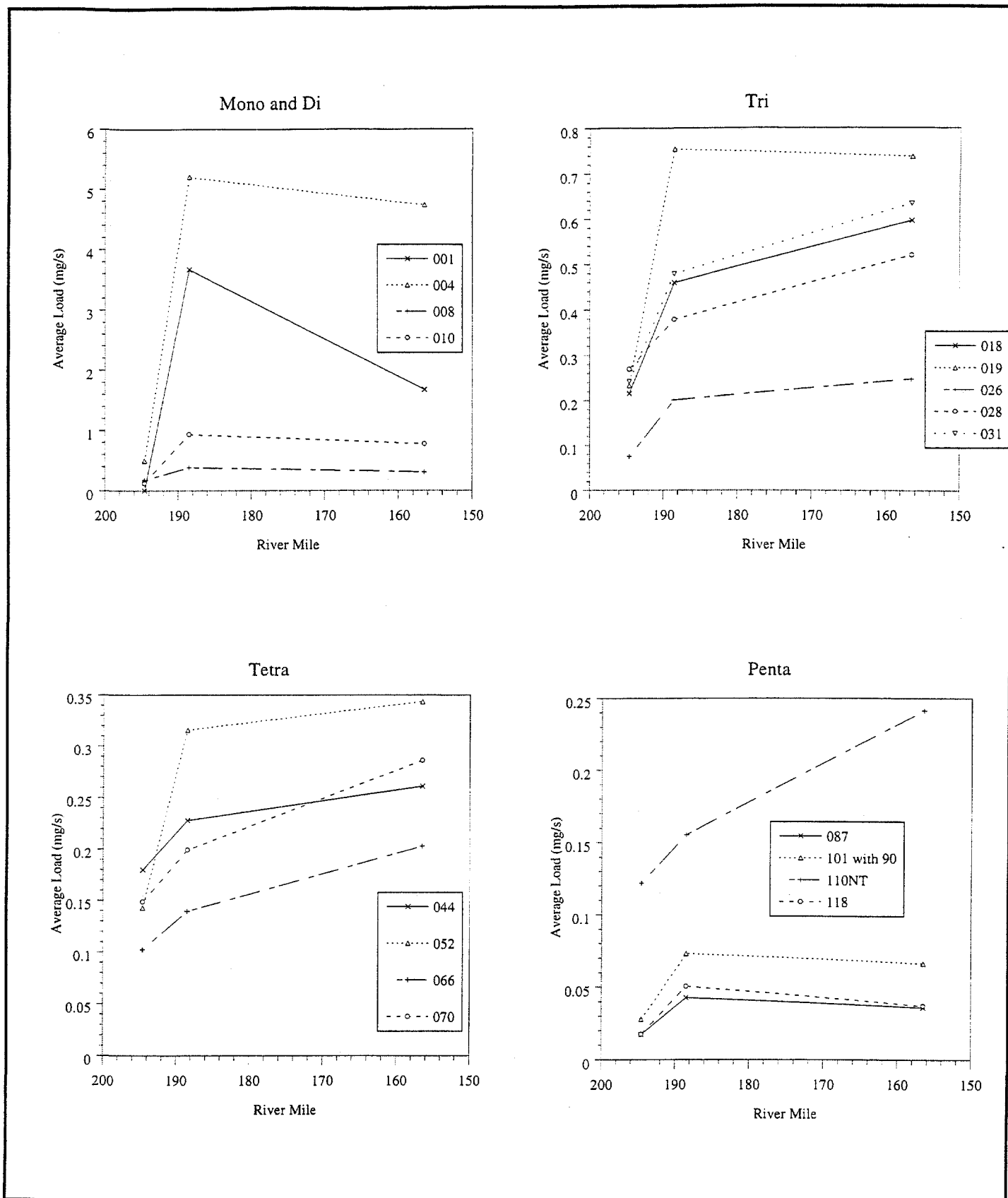
Figure C-5
Comparison of Relative Congener Load Difference Between Schuylerville and Waterford
Transect 6, August 1993



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Figure C-6
Relative Congener Patterns in Upper Hudson Surface Sediment
Schuylerville to Waterford



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Figure C-7
Congener Loads as a Function of River Mile
Flow - Average Event 2 (May 12 - May 27, 1993)

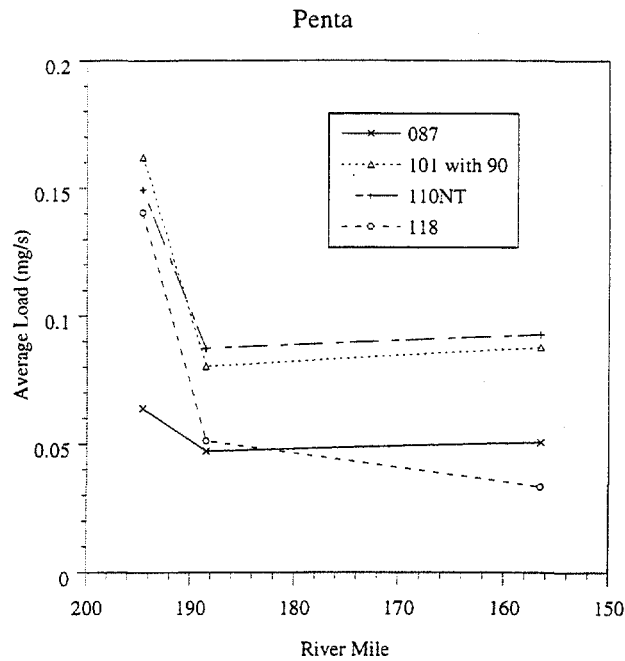
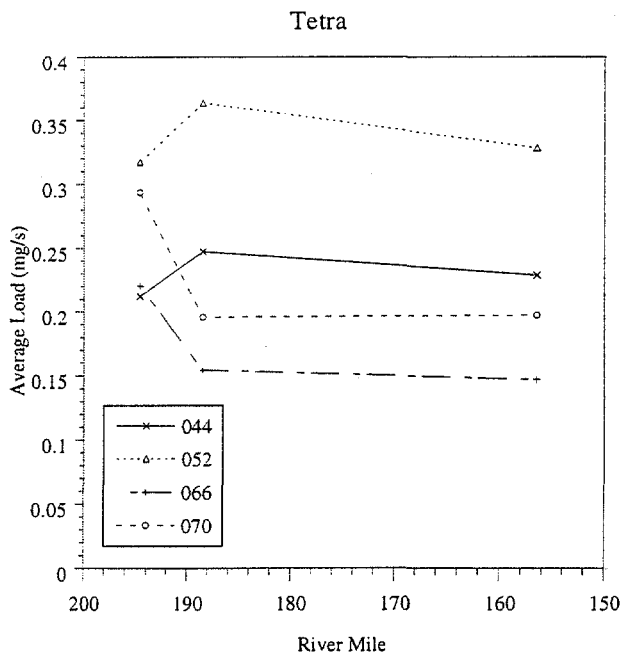
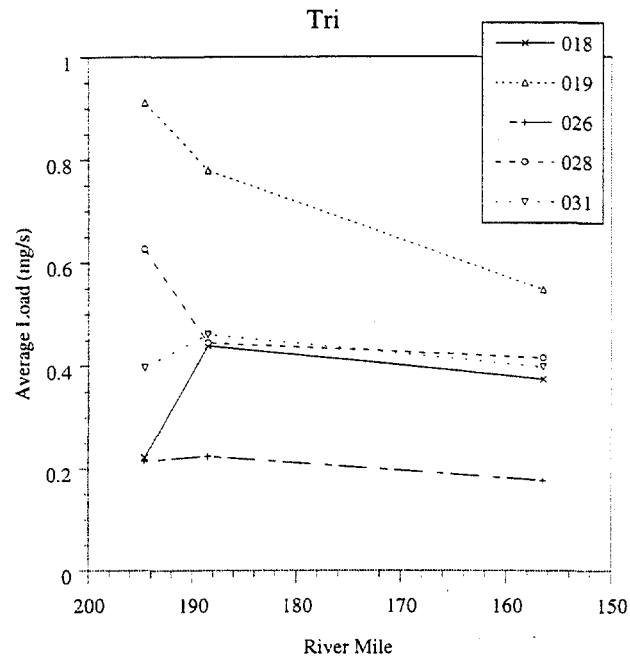
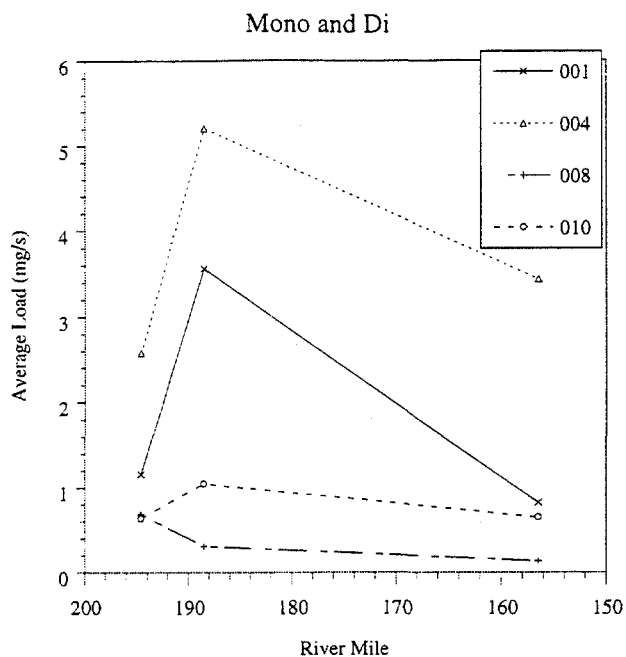


Figure C-8
Congener Loads as a Function of River Mile
Flow - Average Event 3 (June 6 - June 19, 1993)

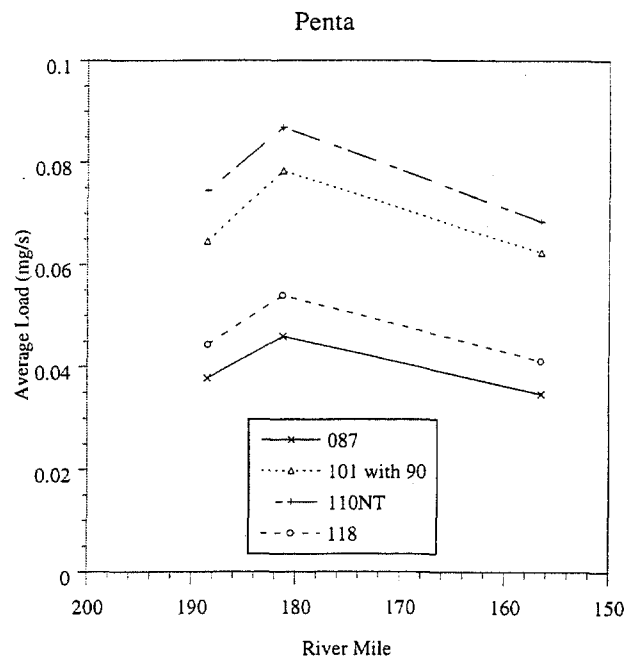
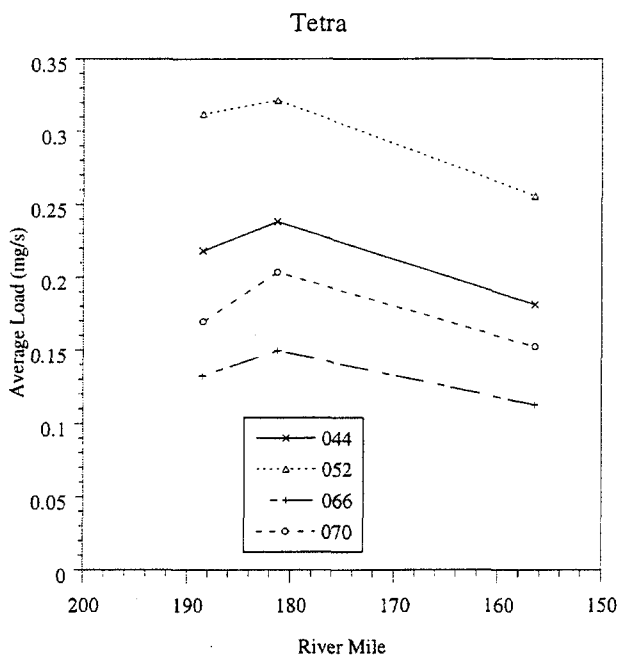
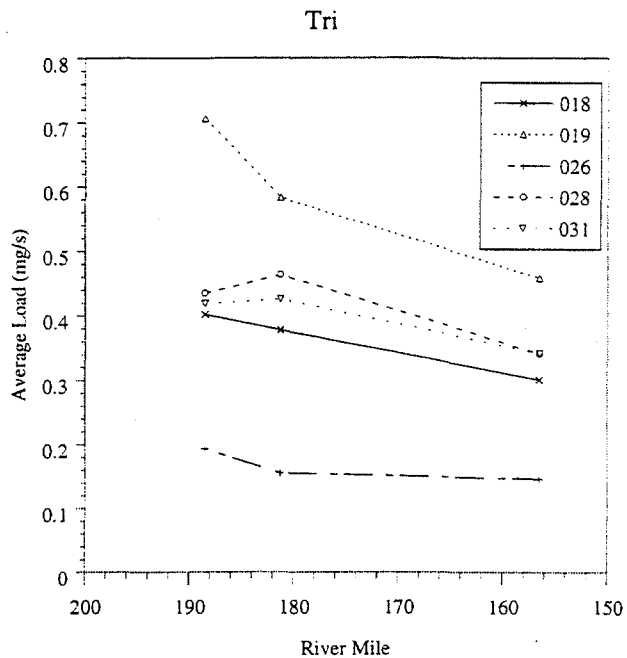
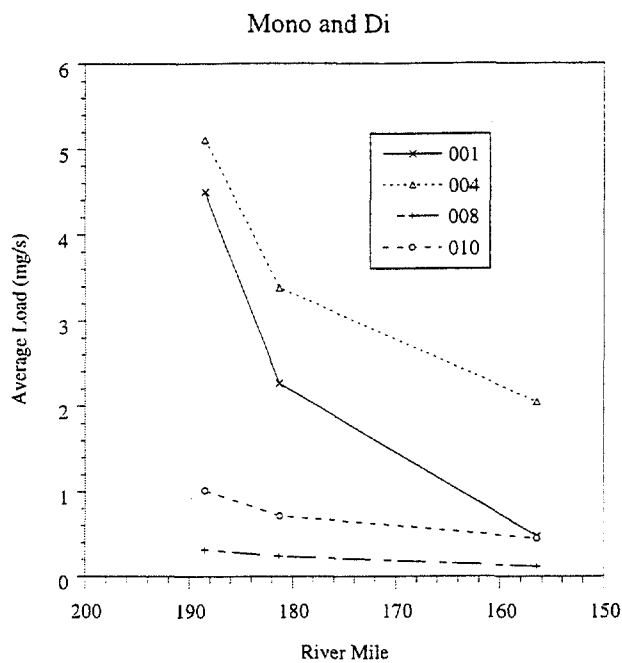
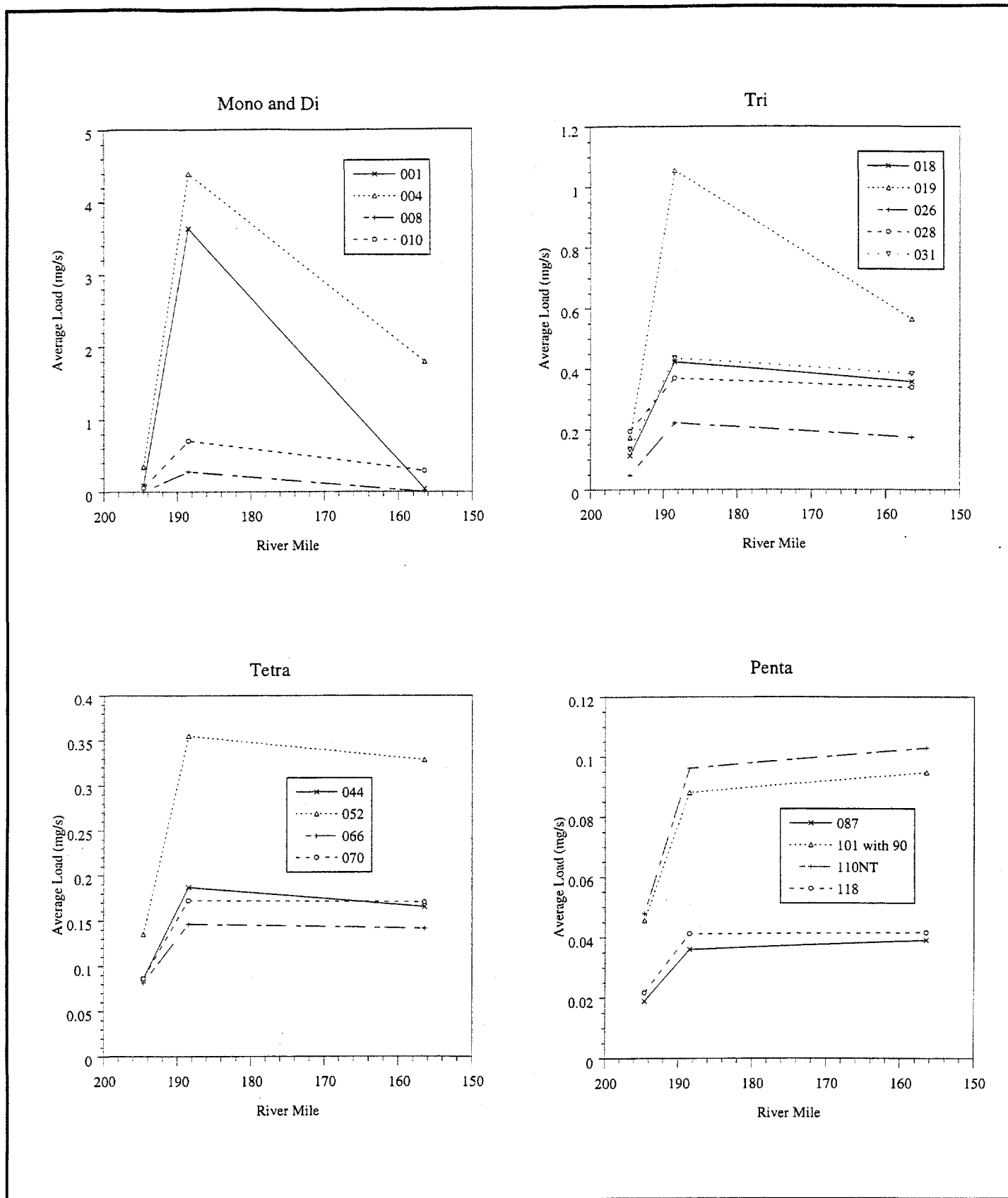


Figure C-9
Congener Loads as a Function of River Mile
Transect Event 5 (June 24 - June 30, 1993)

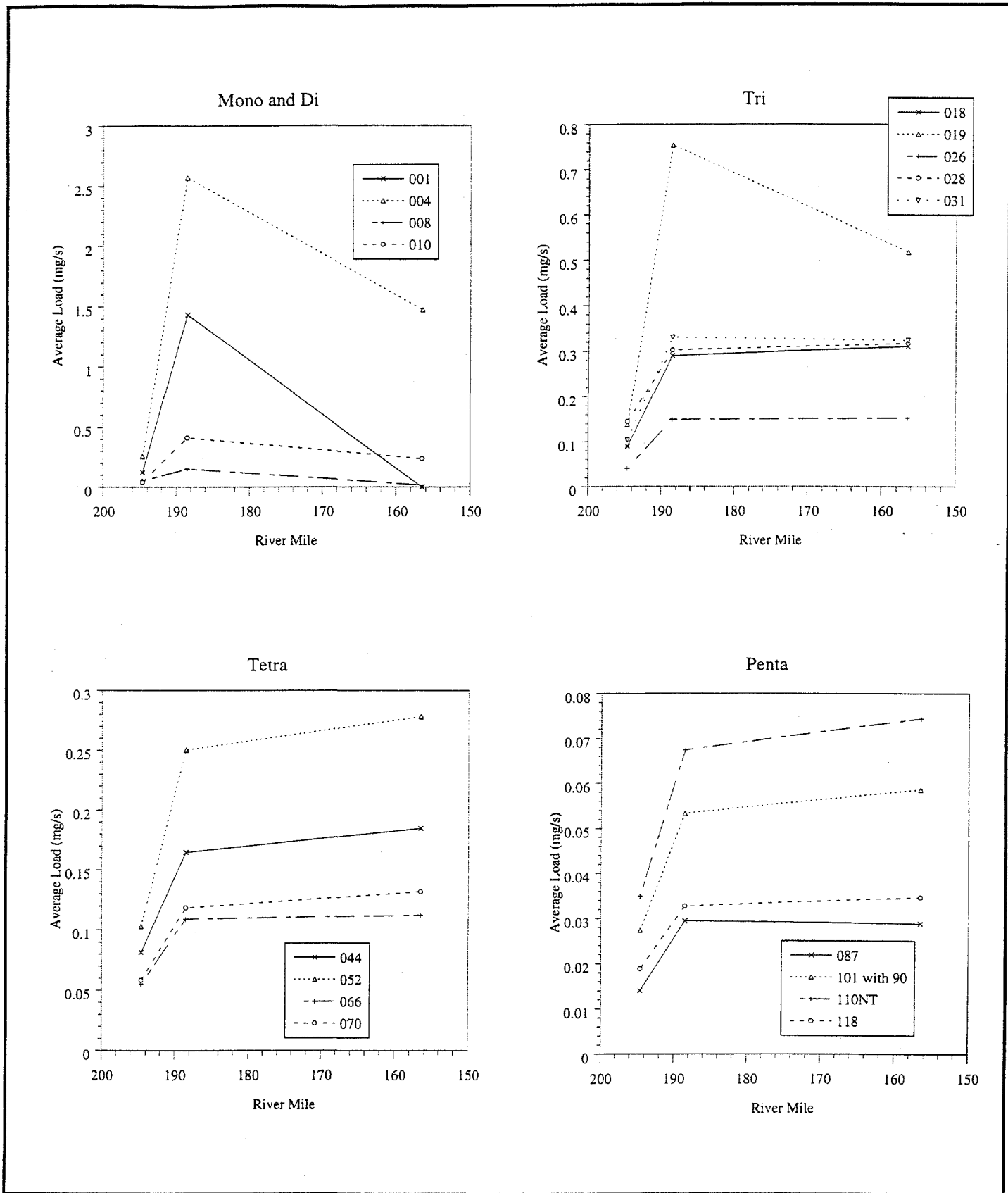


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Figure C-10
Congener Loads as a Function of River Mile Flow-Average
Event 5 (July 5 - July 20, 1993)

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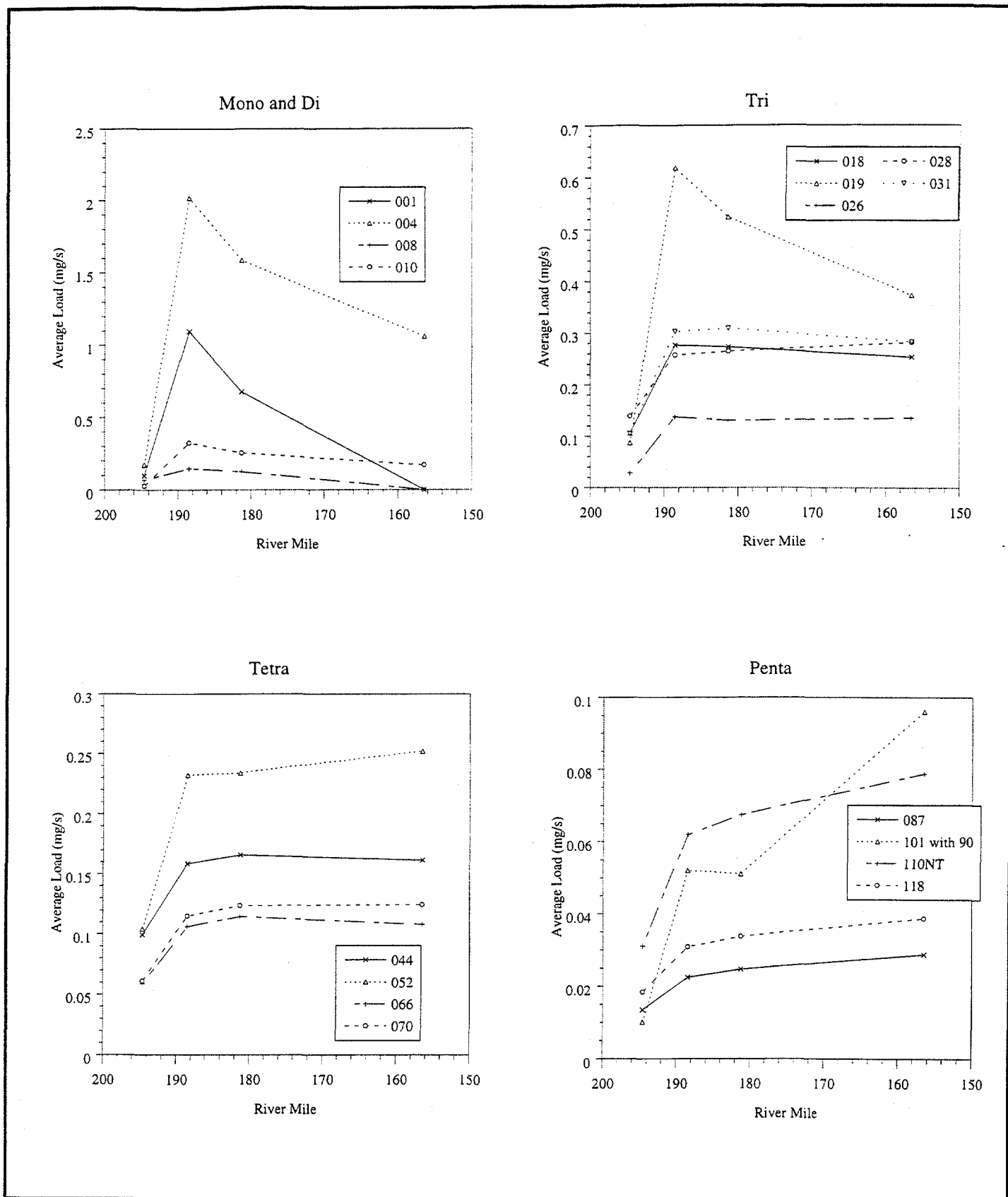


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Figure C-11
Congener Loads as a Function of River Mile
Flow - Average Event 5 (August 2 - August 17, 1993)

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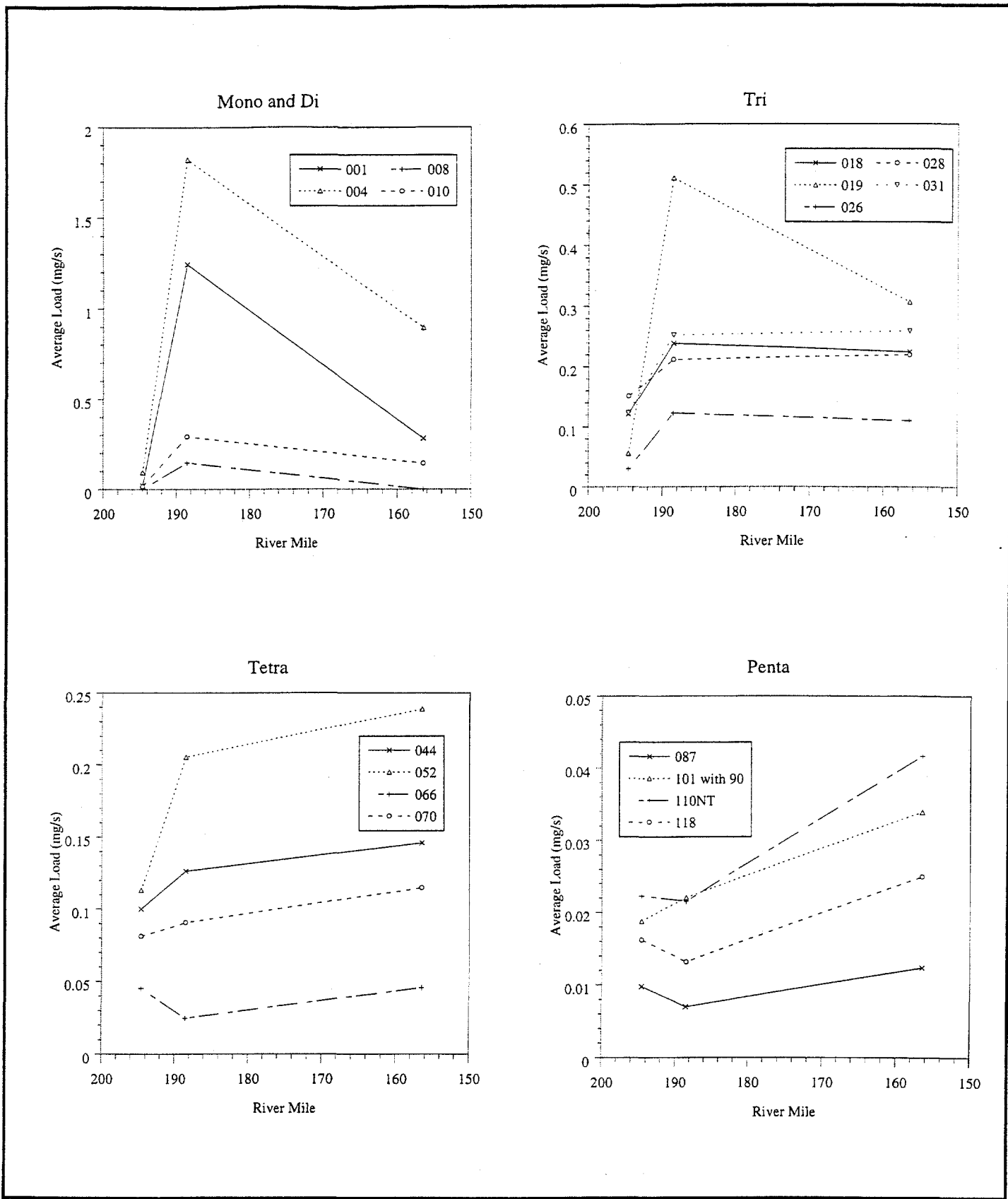


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Figure C-12
Congener Loads as a Function of River Mile
Transect Event 6 (August 19 - September 1, 1993)

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Figure C-13
Congener Loads as a Function of River Mile
Flow - Average Event 6 (September 9 - September 23, 1993)

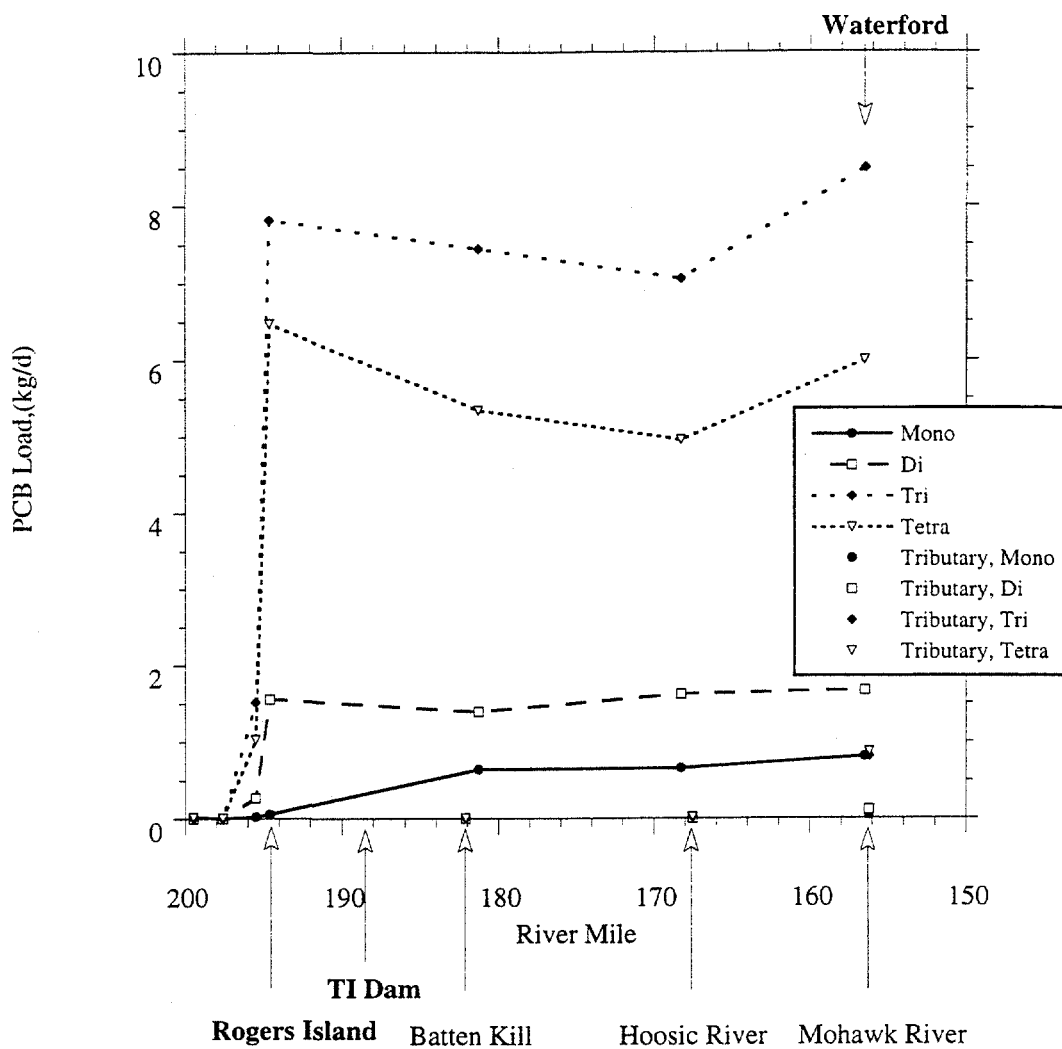


Figure C-14
Water-Column Instantaneous Total PCB Loads for Transect 4