Peer Review of Hudson River PCBs Reassessment RI/FS Phase 2 Reports

Data Evaluation and Interpretation Report
Low Resolution Sediment Coring Report

Premeeting Comments

Albany, New York
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Note: *Premeeting comment materials have been reproduced as received.*

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Charge for Peer Review 2

Members of this peer review will be tasked to determine whether the scientific analyses conducted for USEPA's Data Evaluation and Interpretation Report (DEIR) and the Low Resolution Sediment Coring Report (LRC) are credible, the conclusions valid, and whether the findings are appropriate to use to support the decision-making process for the Hudson River PCBs Site Reassessment study. The peer reviewers will base their assessment on the review of the DEIR and LRC, as well as additional information found in the Responsiveness Summary issued in December 1998 (responding to several documents including the DEIR) and the Responsiveness Summary for the LRC (which will be released in February 1999). The peer reviewers will also have available for their review the Hudson River Reassessment database, which contains all of the data used in the preparation of the above documents, along with other data.

The DEIR and LRC present the results of the geochemical analyses conducted on the water-column and sediment data collected for the Reassessment, as well as data collected by a number of other agencies and General Electric. It should be noted that there have been several changes in the available data since the time of the release of the DEIR in February 1997. These changes include a better estimate of flow for several reaches of the river, a recalculation of GE's PCB data due to an analytical bias, and the discovery of a sampling bias at the Thompson Island Dam monitoring station. These changes are discussed in the Responsiveness Summaries, and the analyses in the Responsiveness Summaries should supercede those conducted in the reports, as appropriate.

It is important to realize that the geochemical analysis conducted in the DEIR and LRC will be complemented by mass balance modeling and human health and ecological risk assessments to provide a thorough understanding of the fate and transport and impacts of PCBs in the Upper Hudson River. These other reports will address questions regarding the mechanisms that release PCBs from the sediment, toxicity, and bioavailability/biouptake. A peer review was previously conducted for the approach proposed to conduct the modeling for the Reassessment. After the modeling and the risk assessment reports are released, the Agency will also have those documents peer reviewed.

Specific Questions

Data Evaluation and Interpretation Report (DEIR)

1. Is the documented PCB load, which originated from the TI Pool, consistent with a source consisting of historically deposited PCB-contaminated sediments?

2. Are the two-phase and three-phase partitioning coefficients, derived in the DEIR, appropriate and do they properly address the physical parameters of the system (e.g., temperature).

3. Are the conceptual models based on the transect sampling consistent with the data?

4. Does the sampling at the TI Dam-West location impact EPA's conclusion that the sediments of the TI Pool are the major source of PCBs to the freshwater Hudson during low flow conditions considering the analytical corrections made to GE's PCB data? What are the other implications of finding higher concentrations along the shoreline than in the center channel?

5. Are the geostatistical techniques (polygonal declustering and kriging) correctly applied?

6. Are the methods applied in the DEIR (change in molecular weight (MW) and evaluating concentrations of BZ#s 1, 4, 8, 10 and 19 (MDPR)) appropriate standards for determining extent of dechlorination? Are there any significant problems with this approach, or more appropriate approaches?

7. The DEIR finds that the degree of anaerobic dechlorination is primarily a function of original concentration rather than time, and accordingly that there is not significant predictable dechlorination in sediments containing less than approximately 30 mg/kg PCB. Is this reasonable?

Low Resolution Sediment Coring Report (LRC)

1. In the LRC, EPA compared sediment data from cores taken in 1977, 1984 and 1994, which had the PCB analysis conducted by different laboratory methods. How valid are the methods used to establish a consistent basis for comparison?

2. In the upper Hudson River system, it has been well established that there is significant lateral heterogeneity in sediment concentrations. While it was attempted to reoccupy previous locations, some uncertainty is added with

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respect to the actual sampling location. While the statistical techniques help compensate for this, how does the sediment heterogeneity affect the comparison of cores from two different years? Given the spatial variability, is the finding that there is loss from most of the locations supported by the data?

3. What is the impact of the difference between replicate samples in the 1994 sampling effort (36 percent average variability) on the finding that there was a 40 percent loss of PCB inventory from the highly contaminated sediments in the TI Pool?

4. In the LRC, it was found that Hot Spot 28 contained much more mass than previous estimates. Is the conclusion that this "gain" is primarily due to incomplete characterization in 1977 valid?

5. Does the data set and its interpretation support the conclusion that significant losses have occurred from hot spots below TI Dam?

6. The LRC found that the historically contaminated sediments in the TI Pool were not universally being buried and sequestered from the environment. How much confidence would you place in the LRC evidence against widespread burial?

7. Is the interpretation of the sidescansonar data appropriate and supported by the analysis of the associated sediment properties?

General Questions

1. Is the data set utilized to prepare the DEIR, LRC and Responsiveness Summaries sufficient to understand the fate and transport of PCBs in the Upper Hudson?

2. Are there any additional analyses that should be done to verify certain findings of the DEIR and LRC?

Recommendations

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)

Dr. Reinhard Bierl

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Comments not available at time of print

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Dr. Per Larsson

Review of the "Data evaluation and interpretation report (DEIR) and low resolution sediment coring report (LRC).

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1. Introduction and major conclusions

The PCB problem in the Hudson River system is in my view a serious one, and the extent of the problem has several aspects that cover such areas as exposure and effect of aquatic biota; transport of the compounds from the source areas to the lower Hudson river and ultimately to the sea; volatilization from river water to the atmosphere (with a consequent exposure to terrestrial environments or further atmospheric transport); contamination of groundwater and river bed soils. The risk for human exposure of PCB in the area from e.g. fish and by lower extent by (drinking) water is obvious. The list of problem areas can, furthermore, be expanded substantially.

As I see it, a few simple and straightforward questions or objectives can be drawn from the two reports cited above, and if these are answered or fulfilled, I find that the reports can be considered as acceptable. It is then obvious that the studies answering the questions need to be carried out in a scientifically acceptable way and that the conclusions drawn are appropriate. The questions or objectives are:

*The major source areas (sediment) for PCB contamination can be identified.

*What is the extent of the PCB contamination in the source areas?

*Has the extent of the PCB contamination in the sediment (concentration, mass) changed over time?

*PCB in the sediment of the source areas affects concentration in the water (i.e. there is a PCB transport over the sediment/water interface).

*What is the extent of the sediment to water transport of PCB?

*PCB from the source areas are transported downstream.

*How does PCB in the river water speciate between the dissolved and particulate phase? The answer to this question is interesting in two ways;
      i.   the transport form of PCB in the river water (and possible resedimentation, readsorption, etc.)

ii.   for exposure to biota.

These are the major points that need to be evaluated, in order to establish a base for understanding of the fundamental behaviour of PCB in the upper Hudson River. Within the questions or objectives lie understanding of the potential variables of importance, like the effect of water discharge, water temperature, microbial activity etc. In addition to these points, other items of interest can be identified that cannot be considered to cover the main objectives, but may lead to understanding of the underlying mechanisms like:

*Is a potential change over time in PCB concentration in the sediment at one site due to transport to the water?

* Is a potential change over time in PCB concentration in the sediment at one site due to microbial, anaerobic dechlorination?

*Is a potential change over time in PCB concentration in the sediment at one site due to transport of contaminated sediment downstream?

* Is a potential change over time in PCB concentration in the surface sediment at one site due to burial by new, uncontaminated sediment?

The question of microbial, anaerobic dechlorination of PCB in the sediment is addressed thoroughly throughout the report, but for me this question has nothing to do with the main objectives of the studies. As anaerobic dechlorination as a process only dechlorinate congeners containing meta- and/or para positions and, consequently, reduce more chlorinated congeners to less chlorinated, it cannot be considered as a sink process for PCB. No ring cleavage or break-down of PCB occurs through this mechanism (e.g. Bedard et al. 1986). It will, however, have effects on the transport of PCB across the sediment/water interface (possibly increase the transport as low-chlorinated congeners have a higher transport-rate than high-chlorinated ones), and on toxicity and bioaccumulation.

In conclusion, I find that the important issues raised above have been addressed in the reports and in a majority of cases also have been satisfactory answered. I find that the two reports, DEIR and LRC, are acceptable. As no studies or reports are perfect, some minor revisions can be made as stated below, on parts of the material. My main negative comments are:

a) Multivariate data are best treated by multivariate statistics, as by Principal Component Analysis (PCA), Cluster analysis or Regression Tree. PCA would have been suitable for the data sets, resulting in a more comprehensive and objective analysis of the data (Zitko 1989, Bremle and Larsson 1997). The results are now concluded from individual regression or correlation analysis, similarities of curves, tests

of individual data sets, congener pattern etc. I do not conclude that these analysis are carried out in a erroneous way, they would probably be good instruments to combine with e.g a PCA approach. They do not, however, give a good overview in analysis of the whole data set. The PCA could have been especially useful for the congener "fingerprinting" in source identification, comparisons between matrixes, and indications of processes as anaerobic dechlorination as well as for determining variable importance (like discharge, water chemistry, etc. (Zitko 1989, Bremle and Larsson 1997, Bremle and Larsson 1998).

b) The sampling of river water for PCB is not as advanced as the sediment sampling program. It would have been better to have introduced more permanent sampling stations and pump up water from a defined water depth (10-20 cm below the surface in the centre of the river), and taken integrated, continuous water samples over time (Bremle and Larsson 1997). The water volumes taken in the sampling program, 17 L, is quite sufficient for PCB analysis, while 1 L is not (I L sampling will lead to substantial errors in the quantification process). The separation in dissolved and particulate phase PCB by filtering is a good approach, that facilitate later transport and exposure estimates of PCB.

c) Incomplete homogenisation of sediment samples, which could have been the case in the LRC program, may lead to errors in conclusions of PCB concentration and PCB mass in large sediment slices. It's tricky to homogenise a large amount of sediment containing low percentages of water. Note that I state may, it's hard to conclude from the reports that this was really the case.

2. Specific questions

2.1 DEIR

2.1.1. Historically deposited PCB contaminated sediment has been shown to contaminate the water of rivers (Brown et al 1985, Chevreuil and Granier 1991, Bremle and Larsson 1997). In principal, PCB transport from sediment to water of river systems is determined by i) water discharge, where high discharges (flooding) results in turbulence of the river sediment, and a consequent downstream transport of PCB contaminated particles (Chevreuil and Granier 1991). This transport does not change the PCB fingerprint in the water column (as stated in the report and Bremle and Larsson 1998) ii) temperature, where desorption (partitioning) from sediment is enhanced with increasing temperature and changing the PCB pattern to a low-chlorinated one (Larsson et al 1990). The process is enhanced by processes such as bioturbation by benthic invertebrates, and by microbial processes that mineralise organic matter in the sediment (Jeremiason et al. 1998, Larsson et al 1990). These processes are affected positively by concentration of PCB in the sediment (a higher sediment to water

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transport) and the latter three negatively to the organic carbon content in the sediment (e.g. Steen et al 1978, Lara and Ernst 1990).

The present study shows that the PCB load into Thompson Island pool (TI) is less than the transport out of the pool, than revealing an addition of PCB from within the pool, a PCB transport from sediment to water. Further, water parcels is followed downstream by simultaneous sampling revealing some dilution of PCB by increasing water discharge and some smaller addition to the PCB load (or constant PCB mass transport depending on sampling station). Fingerprinting of PCB congeners within the TI pool water and downstream show that the PCB originated from the pool. The results are convincing, and very similar to results obtained for a PCB contaminated river system in Sweden (Larsson et al. 1990, Anon 1998), where one single source (a small lake with PCB contaminated sediments within the river system, water residence time about 4 h for the lake) affected the whole river system downstream.

2.1.2. The two-phase and three-phase models are appropriate to use for predicting PCB partitioning between the dissolved and particulate phase in the water, and the models can be scrutinised in detail by using the extensive international literature on this subject (e.g. Horzempa and DiToro 1983, Baker et al. 1986). I find the approaches a bit out of focus for the objectives of this study. Instead, it would have been useful to include an empirical modelling work on, for instance, TI pool using variables as sediment surface (as determined by coring and side scan-sonar) and sediment concentration of PCB, water discharge and temperature to predict transport and mass-balances over time (Larsson et al. 1990, Bremle and Larssson 1997). In this way an empirical model for PCB in the upper Hudson River can be constructed and applied for different situations. For prediction on bioavailability of PCB the proposed models seem to be appropriate (dissolved versus particulate PCB).

2.1.3. The conceptual reasoning of PCB fate in the upper Hudson River is convincing and show that the authors of the report know the literature. The discussion on how the sources (PCB containing sediment) affect PCB in the water column, how concentrations of PCB decrease downstream as a result of volatilisation, and adsorption/settling, dilution by increasing water discharge in the river as the catchment area increases, are logic and can be understood by the reader. The figures underlying the reasoning could have been simplified, given a logic system of location numbering etc., but this is just a technical matter.

2.1.4. I don't find that the sampling location would affect the conclusion that TI pool is the major source of PCB to the upper Hudson River system. As far as I understand, corrections have to be made only under low flow conditions. As the PCB load follow water discharge, the major PCB loads occur under higher flow situations. As stated in my introduction, however, water sampling near the riverbanks (sides) or just upstream of large objects should be avoided, as there is a risk of sampling turbated, nearshore sediment or upwelling sediment. The

possible erroneous sampling can be detected in the results by studying filtered particle amounts in the water (too high amounts of particle dry mass), as stated by the report authors.

2.1.5. The applied techniques for evaluating sediment-coring analysis, and to calculate PCB masses for larger sediment areas (i.e. hot spots) using polygonal clustering and kriging seem correct to me. A further development suggested by the report authors to use results from side scan-sonar to identify primary accumulation areas containing small particles high in PCB and organic content, and combine that with polygonal clustering (clustering coring points within an accumulation area), seems even better.

2.1.6. In order to evaluate if microbial, anaerobic dechlorination of PCB has occurred in the sediment, the authors use enrichment in congener 1, 4, 8, 10 and 19 versus the total sum of all congeners as an index. The index is quite appropriate, and will reveal if dechlorination has occurred for the sample. There are other ways of constructing similar indexes, the important factor to consider is that the proportion of the dechlorination products (congener 1, 4, 8, 10 and 19) can be compared with the same congeners in a sample not subjected to dechlorination (or a standard) and the difference revealed. This is simple to perform for a limited data set of congeners but when a larger data set is to be evaluated, indexes have limitations. It is then more appropriate to evaluate the whole PCB pattern by a multivariate method, like principal component analysis (PCB, Bremle and Larsson 1997). If significant dechlorination has occurred in samples, this will be revealed by clustering of these data in a PCA plot.

2.1.7. I fully agree that the degree of anaerobic dechlorination is a function of the original PCB concentration in the sediment. The predictive model (figure) showing that the extent of dechlorination start to be significant at ca 30 ppm PCB is elegant, and show scientific skill. As stated in the introduction, I don't find that the subject of anaerobic dechlorination of PCB is a central objective of the study. The study by Williams and May (1997) suggesting that low-temperature microbial degradation was significant for di- and trichlorobiphenyls in laboratory model systems, and possibly connected to the reduction/oxidation of the iron cycle in the sediment surface seems to have higher relevance (although I find objections to parts of this study).

2.2. LRC

2.2.1. It is obvious that comparisons between concentrations of PCB in sediment cores, taken in similar areas from 1977, 1984, and 1994, will show variations due to i) the sampling methods used ii) the improvement of the analytical methods used, like capillary columns iii) the use of surrogate and internal standards. I do not, however, consider this a serious problem since you have to expect variation due to the analytical methods used in a time period >15 years. I find the quality control of the present study satisfactory, as well as the use of dual GC-columns,

and use of surrogate standards,(it is a bit confusing though, that the use of octochloronaphtalene (OCN), did not work out. We have used it extensively when analysing sediment for PCB at the ecotoxicology laboratory at Lund University), and confirmation on GC/MS for some of the samples.

To my experience, there is a much greater variation in the field sampling strategies between different studies and years, that lead to variability in the data and make comparisons hard to do. This kind of problems are hard to overcome, due to lack of information.

2.2.2. It is indeed so that the spatial heterogeneity is large for sediment in rivers, and thus concentration of PCB (e.g. Bremle and Larsson 1998 and references herein) in a 10-15 year period, accumulation areas within a river may change due to flow events and man-made measures upstream. It is possible that the core sampling locations in 1984 or earlier are not the same (i.e. that they don't show identical conditions) as in 1994. There are no statistical techniques that help to compensate for this (as stated in peer review questions). The techniques (statistical analysis) used by the authors generally seem to be adequate. It is, however, impossible for me to follow the statistical template used. The approach should be very simple; data on PCB concentration in the sediment (e.g. $\mu g/g$ dry weight) or PCB mass per surface area of sediment (ug/dm^2) from the defined area are compared in two populations, one from 1984 and the other from 1994. The comparison is limited by the number of cores taken at each sampling occasion, and nothing else. As the populations are log/normally distributed, PCB concentration data are log-transformed. A simple comparison test will now reveal if the populations differ significantly or not, and the direction the difference (PCB concentration 1984 > PCB concentration 1984). If significant (and only then), the possible decrease between years can be calculated, as carried out in the present report. I cannot elucidate if this was the case, as the statistical approach/calculation pattern is not transparent (I cannot follow it from step to step). A flow scheme of the statistical tests used would have been a great help. Further, high spatial variability (or any other high variability) can only be described properly by using a larger number of samples, reflecting the variability.

3. 2.3. The results from the "replicate" samples in 1994 from TI pool show a 36% average variability. At the same time, conclusions are reached that a 40% loss of PCB has occurred from the TI pool sediment from 1984 to 1994. I did a very simple simulation, using the average 10 g PCB m^{-2} in sediment for TI pool in 1984, a 40% decrease to 1994 and simulated all other data, obtaining a standard deviation around 36% for the two data sets (the variation thus defined by the standard deviation and n=19 for each data set). Understanding that this is a major simplification, the results revealed that the decrease in PCB concentration was significant (Student's t, p<0.001). So I cannot see any problems with the conclusion, assuming that the number of samples underlying the analysis is large enough (again I cannot follow the statistical testing).

Table 1. A simulated data set for changes of PCB concentrations in TI pool from 1984 to 1994 (N=19 for each sampling occasion in time).

Sample No	Sediment 1984 (g/m^{-2})	Sediment 1994 (g/m^{-2})
1	10	6
2	15	11
3	8	4
4	7	3
5	14	10
6	9	5
7	8	4
8	9	5
9	12	8
10	12	8
11	11	7
12	13	9
13	6	2
14	6	2
15	8	4
16	9	5
17	17	13
18	4	0
19	8	4
Average	**9.8**	**5.8**
Standard deviation	3.4	3.4*

*= higher than the 36% variation mention earlier

2.2.4. In the study of 1994, the calculated mass of PCB in the sediment of Hot Spot 28 was 20 metric tons. Previous estimations resulted in a mass of 2 – 7 metric tons. In the present study there was no evidence of overall burial of "old" sediment, <50% of the sediment core profiles. The only possible transport that would result in a transfer of >10 metric tons of PCB in a sediment in a river is a very large resuspension event in the upstream river system, transferring contaminated sediment downstream from one hot spot and depositing the sediment in Hot Spot 28 (with no similar transport to other areas). This is highly unlikely. Another unlikely explanation is a direct PCB discharge to Hot Spot 28. Ruling out these explanations the proposed one seems likely; the previous calculations underestimated PCB mass.

2.2.5. I agree to the conclusion that losses of PCB have occurred from TI pool to the river system downstream. Highly PCB contaminated sediment in rivers will have a major impact on PCB concentration in water and aquatic biota within the area of deposition and downstream (Brown et al 1985, Larsson et al. 1990). This impact is caused by a transport of PCB over the sediment/water interface, i.e. a loss of PCB from the contaminated area. The PCB loss from sediment need not to cause any significant decrease of PCB in the sediment (decrease in concentration), to cause substantial increase of PCB in water and biota. I do agree that that losses have occurred from the TI pool and from hot spots downstream. If the magnitude of these losses over a 10 year-period exceed 10% or more, this is caused by particle transport. Contaminated sediment particles are resuspeded and transferred downstream at high discharge events. These events are frequent in rivers. I do not conclude losses of this magnitude to be caused by desorption of PCB from sediment to water, bioturbation or anaerobic dechlorination.

2.2.6. Within a river, sediment is subjected to resuspension, transport and resedimentation. As pointed out earlier, the extent of these processes depends on the water discharge. As discharge follow a seasonal cycle, sediment transport events are likely to occur during spring flooding. As the magnitude of flooding may vary greatly in a decade and even more in a longer time span, the transport/resuspension events occur irregularly. Being a dynamic system, there are no true sediment accumulation areas in a river, all sediment may be transported downstream. Therefore, any burial of contaminated sediment is just temporary. This is also shown in the LRC study.

2.2.7. I find the results from the side-scan sonar and the connection to particle size distribution very convincing. It's a good approach for determining the extent of temporary accumulation areas of organic sediment and thus areas with high PCB concentration.

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Dr. Keith Maruya

Specific Questions

Data Evaluation and Interpretation Report (DEIR)

1. Is the documented PCB load, which originated from the TI Pool, consistent with a source consisting of historically deposited PCB-contaminated sediments?

PCB contaminated sediments in the TI Pool were the most likely source of the water column loads described during summer low flow periods in the 1993 Phase 2 Transect study. A look at the corrected homolog distributions for the Transect study (Figs. 3-38, 3-40, 3-43 and 3-47 in Appendix C, LRC Responsiveness Summary) shows that for various flow conditions, total and dissolved PCBs greatly increase at the TI Dam relative to Rogers Island. In the absence of some undiscovered source, this sharp increase in dissolved PCBs strongly suggests a local source. Corrected estimates of PCB loading in the Upper Hudson are less consistent, with the bulk of the loading occurring above the TI Pool in the early transects of 1993 (Figs. C-6 and C-12 corresponding to Transects 1 and 4), switching clearly to the TI Pool during later, low flow transects (Figs. C-14 and C-16 corresponding to Transects 5 and 6). Both instantaneous ("transect") and 15d flow-averaged data reveal consistent patterns in loadings.

Load is the product of concentration and flow rate. Since it is assumed that flow rate increases with decreasing river mile (i.e. as one heads downstream), it follows that water column PCB concentrations in the river must decline after the TI Pool during summer low flow conditions. Conversely, PCB concentrations upstream of the TI Dam, and in particular in the TI Pool itself, must increase more rapidly than flow rate to sustain the consistent increase in loading observed. Plotting of total and dissolved PCB data for transect 6 illustrates this clearly (Fig. D1-1 below).

The origin of the PCBs within the TI Pool sediment inventory and what is meant by "historically-deposited" is less clear. From the LRC study, it is clear that "shallow" layers (<10 in depth) still contain a large PCB inventory at many TI Pool locations. Whether the water column PCBs originated from deeper, historically contaminated layers or recently deposited sediments cannot easily be determined. My own analysis of the LRC data indicates that sediment PCBs are split roughly 50:50 between shallow (0-8cm) and deep (>8 cm) layers (see also my comment on LRC Question 6). Each layer is dechlorinated, deeper layers probably being more so.

Another confounding factor that complicated interpretation of likely PCB sources, especially for the early 1993 transects (winter low flow and early spring high and transition flow), was the bulk release of Aroclor 1242-like PCBs from the Allen Mills source, reported to have ceased sometime during the middle of 1993. A major source of PCBs during this period was clearly the stretch above Rogers Island. Post 1993 water column data would have been extremely helpful, however, they were never put into a single, coherent presentation that this reviewer could comment on.

The only alternative explanation for these profiles is selective leaching of mono- and dichloro homologs from relatively immobile free product (oil droplets) upstream of the TI Pool. This would also require enhanced or accelerated "dispersion" of these homologs away from the source and a corresponding attenuation of trichloro- and higher homologs ("Tri+") in sediments upstream of the TI Pool. This scenario, however, would have been observed as a gradual shift in the homolog profile between the upstream Allen Mills source and the head of the TI Pool (Rogers Island). Since the sediments and water column samples collected at Rogers Island had a very different homolog pattern than that within the TI Pool (Figs. C-2 through C-4, and 3-38, 3-40, 3-43 and 3-47), this scenario is not a very likely one.
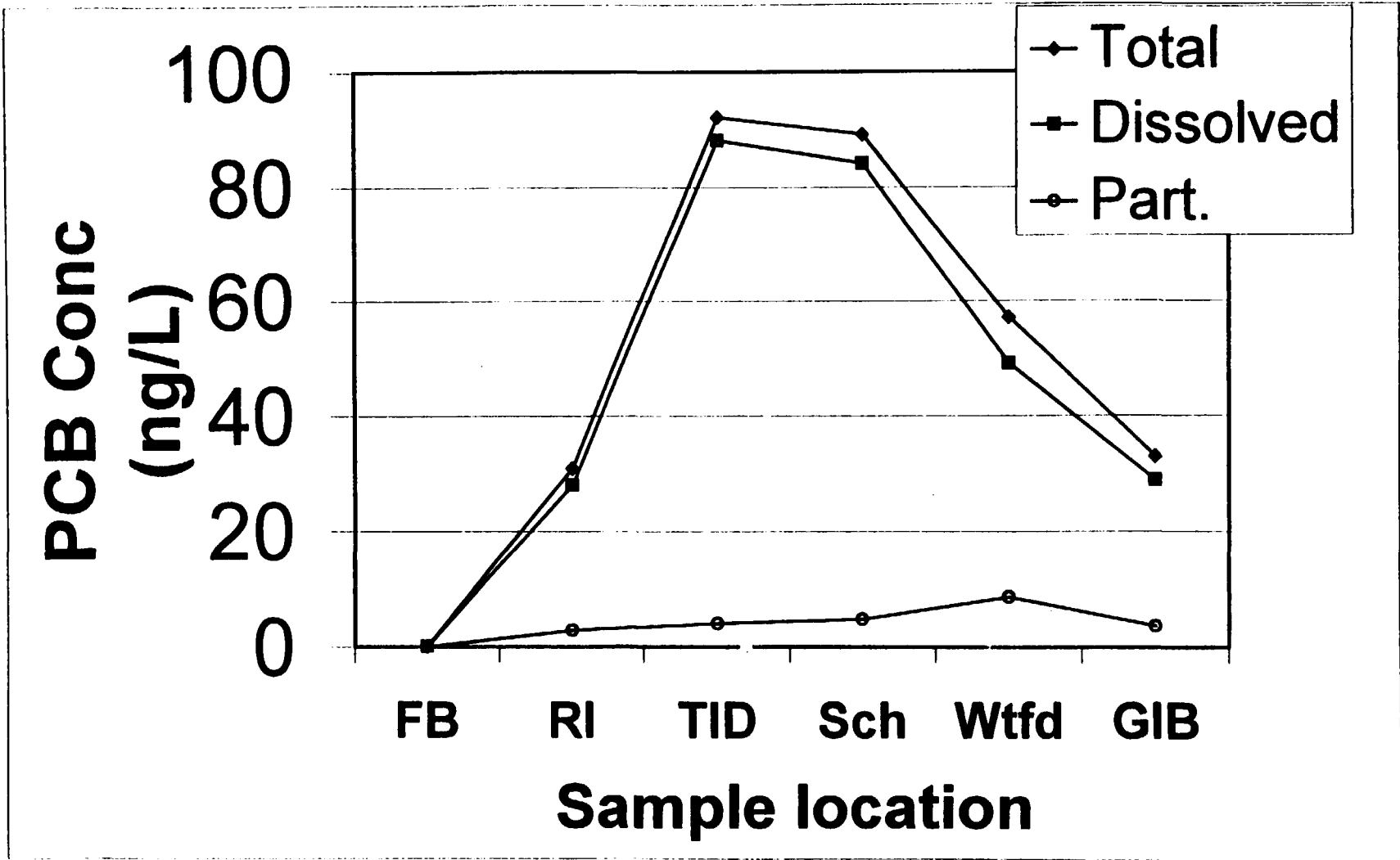
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Fig. D1-1. Water Column PCB Concentrations for Summer-Low Flow Conditions (Transect 6)

2. Are the two-phase and three-phase partitioning coefficients, derived in the DEIR, appropriate and do they properly address the physical parameters of the system (i.e. temperature)?

Based on its magnitude and trend relative to the octanol-water partition coefficient (K_{ow}), estimated values of the particulate organic carbon partition coefficient (K_{POC}) appear to be reasonable, but estimates of partitioning to dissolved organic carbon (K_{DOC}) should be viewed with skepticism and used with caution. The background discussion on two- and three-compartment partitioning theory and pertinent relationships/equations presented in section 3.1 of the DEIR are scientifically and mathematically sound. It is obvious, however, that *in situ* water column partitioning ratios reported in the Phase 2 study varied by orders of magnitude for the same congener, even when normalized to particulate organic carbon (POC) (see DEIR, Table 3-6a). A temperature correction was invoked to further help explain and account for this variability, the effect of which was consistent with experimental determinations (Warren et al. 1987). Estimates of K_{poc} and K_{doc} were thus made based on attempts to fit available *in situ* data into equilibrium, mass balance and temperature correction relationships.

These estimates are presented for partitioning in the water column in Table 3-8 of the DEIR, and appear again as corrected values for bedded sediments (i.e. sediment and porewater distributions) in Table 2-2 of Book 3 of the DEIR Responsiveness Summary. In Table 2-2, K values are given for coeluting congener combinations with $K_{POC} > K_{DOC}$ without exception. My own analysis of the data show that log K's are positively correlated with log K_{ow} ($p<0.01$; see Fig. D2-1 and Table D2-1 below). For New Bedford Harbor sediments, positive K_{POC}-K_{ow} associations were also noted by Burgess et al. (1996) and Brownawell and Farrington (1986). However, in Table 3-8, one curious exception is noted for BZ#8, where the estimated K_{POC} (5.19) is less than K_{DOC} (5.43). No explanation is given for this unique trend reversal, other than the fact that footnote "c" in Table 3-8 indicates some sort of blank problem. It is not clear if the congener specific results in Table 3-8 will be used in the future. If they are, I suggest that values for BZ#8 be revisited. If the data for BZ#8 turn out to be of questionable quality, interpolation or regressions based on aqueous solubility or K_{ow}, should be considered to estimate K values for this congener. For any future predictions of K, a quick check of the trend with increasing chlorines (or log K_{ow}) can be performed as a quick sanity check of the model.

On a more general note, it is not clear why all the effort was made to model the effects of DOC, especially since it was noted in the original version of the DEIR that DOC was fairly constant at ~5 mg/L in the water column. If these data were accurate, then one can conclude that DOC in the water column would exert a relatively constant and predictable influence in terms of partitioning. A case can be made that DOC in porewater of fine-grained sediment, although higher, would be relatively constant as well. In fact, in the example given in the DEIR Responsiveness Summary, Book 3, DOC was estimated @ 34 mg/L, ~10 times higher than that measured/assumed in the water column. The high degree of uncertainty in modeling the effects of DOC make it more of a mental exercise and less of a practical tool for modeling. The danger also exists that "over-manipulation" of model parameters such as partitioning constants can be abused to better fit in situ values.

I would thus recommend simplifying the partitioning model back to a 2-phase model instead of a 3-phase model. In the 2-phase model. DOC would be included as a more-or-less constant influence in the apparent or operationally defined dissolved phase.
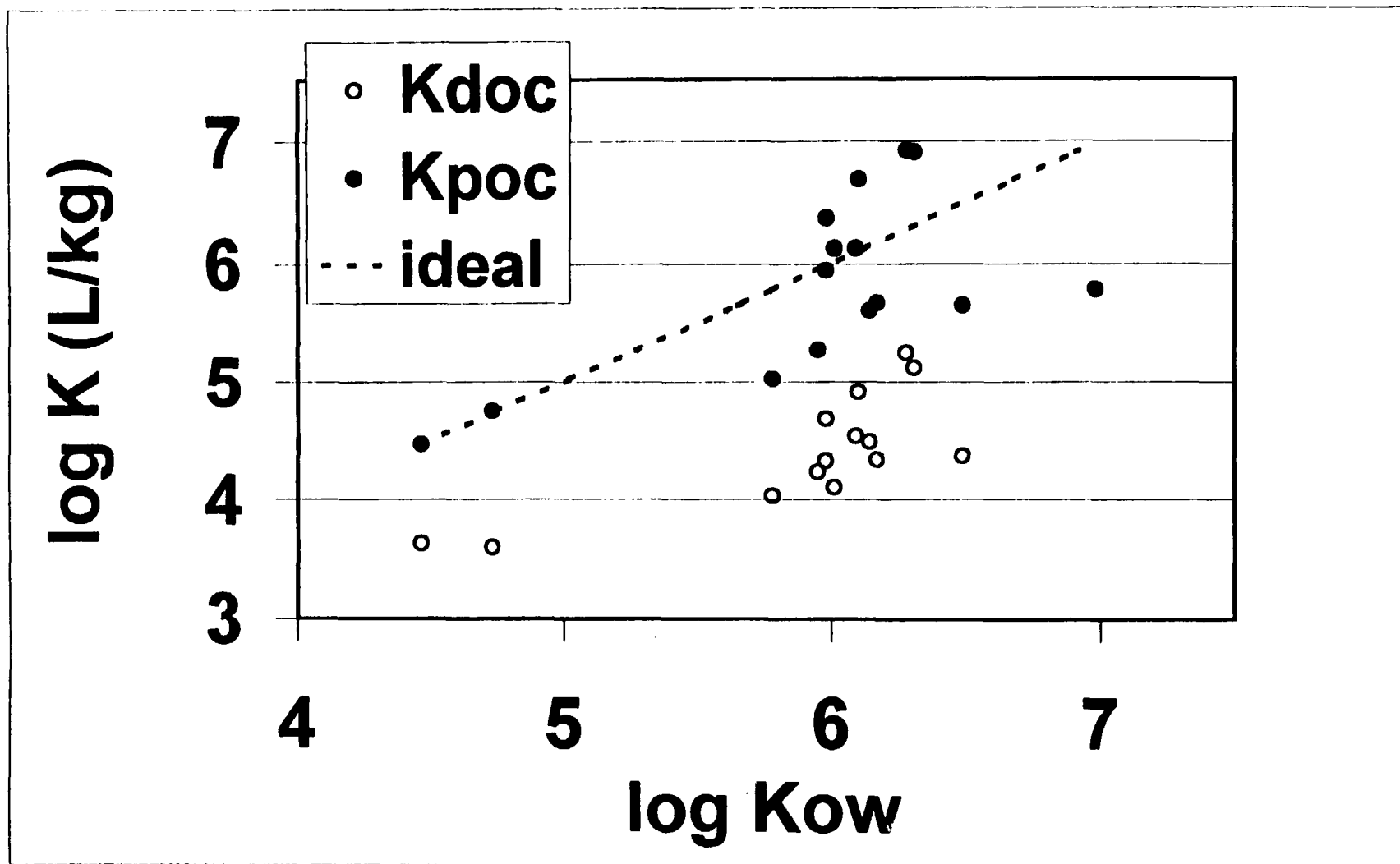
Fig. D2-1. Estimated Phase 2 log K's show increasing trend with log K_{ow} (Hawker and Connell 1988)

SUMMARY OUTPUT: log Koc vs. log Kow (H&C)

Regression Statistics	
Multiple R	0.653364
R Square	0.426885
Adjusted	0.382799
Standard	0.490518
Observatio	15

ANOVA

	df	SS	MS	F	gnificance F
Regressio	1	2.329824	2.329824	9.683055	0.008258
Residual	13	3.127909	0.240608		
Total	14	5.457733			

	Coefficient	andard Err	t Stat	P-value	ower 95%	pper 95%	ower 95.0	pper 95.0
Intercept	2.7C122	1.0368	2.663213	0.019515	0.52135	5.001091	0.52135	5.001091
X Variable	0.55038	0.176871	3.111761	0.008258	0.168274	0.932487	0.168274	0.932487

SUMMARY OUTPUT: log Kdoc vs. log Kow (H&C)

Regression Statistics	
Multiple R	0.733528
R Square	J.538063
Adjusted	0.50253
Standard	0.416725
Observatio	15

ANOVA

	df	SS	MS	F	gnificance F
Regressio	1	2.629623	2.629623	15.14239	0.001856
Residual	13	2.257577	0.17366		
Total	14	4.8872			

	Coefficient	andard Err	t Stat	P-value	ower 95%	pper 95%	ower 95.0	pper 95.0
Intercept	1.088098	0.880824	1.235317	0.238572	-0.81481	2.991003	-0.81481	2.991003
X Variable	0.58472	0.150263	3.891322	0.001856	0.260098	0.909343	0.260098	0.909343

Table D2-1. Linear regression indicates statistically significant ($p < 0.01$) positive correlations between log K and log K_{ow}

3.   Are the conceptual models based on the transect sampling consistent with the data?

The overall conceptual model invoked to explain the 1993 transect data is consistent with the corrected data/profiles contained in the LRC Responsiveness Summary, Book 1, Appendix C. This basic model, characterized by the reviewer in Fig. D3-1 below, translates the PCB load picked up in the upper reaches of the Upper Hudson via advection. Translation of PCBs into the water column of the TI Pool is expressed by a combination of sediment porewater exchange and advection/diffusion across the sediment-water interface, and exchange between resuspended sediment and the water column. This combination of processes is purported in the DEIR Responsiveness Summary, Book 3, to be consistent with the mono-, di- and trichloro homolog distribution observed for dissolved phase PCBs. Sediment porewater exchange was also found to be an important mechanism for PCB loading into the lower Hudson (Achman et al. 1996). Losses downstream of Rogers Island, and in particular downstream of the TI Dam, are suggested to be the result of gas exchange and/or aerobic degradation.

Because of their physicochemical properties including aqueous solubility and Henry's Law constants (see Fig. D3-2 below), mono- and diCBs will preferentially partition into the dissolved phase and into the atmosphere relative to heavier homologs. If air above the Hudson River is undersaturated, a constant flux of PCBs to the atmosphere can act to continually pull PCBs from the source (sediment) into the water column so that a concentration gradient is maintained.

More limnological data (e.g. residence times; chlorophyll a, temperature gradients/stratification during summer low flow conditions) would likely improve our understanding of the processes at work in the TI Pool. For example, this stretch would seemingly act much more like a lake than upstream and/or narrower stretches of the Upper Hudson. As such, the processes acting on PCBs that are enhanced under lake-like conditions will be most important. The larger surface area to volume, increased residence time and quiescent flow regimes would likely result not only in greater fluxes of PCBs out of sediments and into the water column, but also into the air! Mass transport between phases is dependent both on the magnitude of the concentration gradient and surface area. The increased dissolved phase PCBs thus provide a larger driving force for transport out of the water column into the air. This flux would increase under summer, low-flow conditions when both air and water temperatures are at their annual maximum.
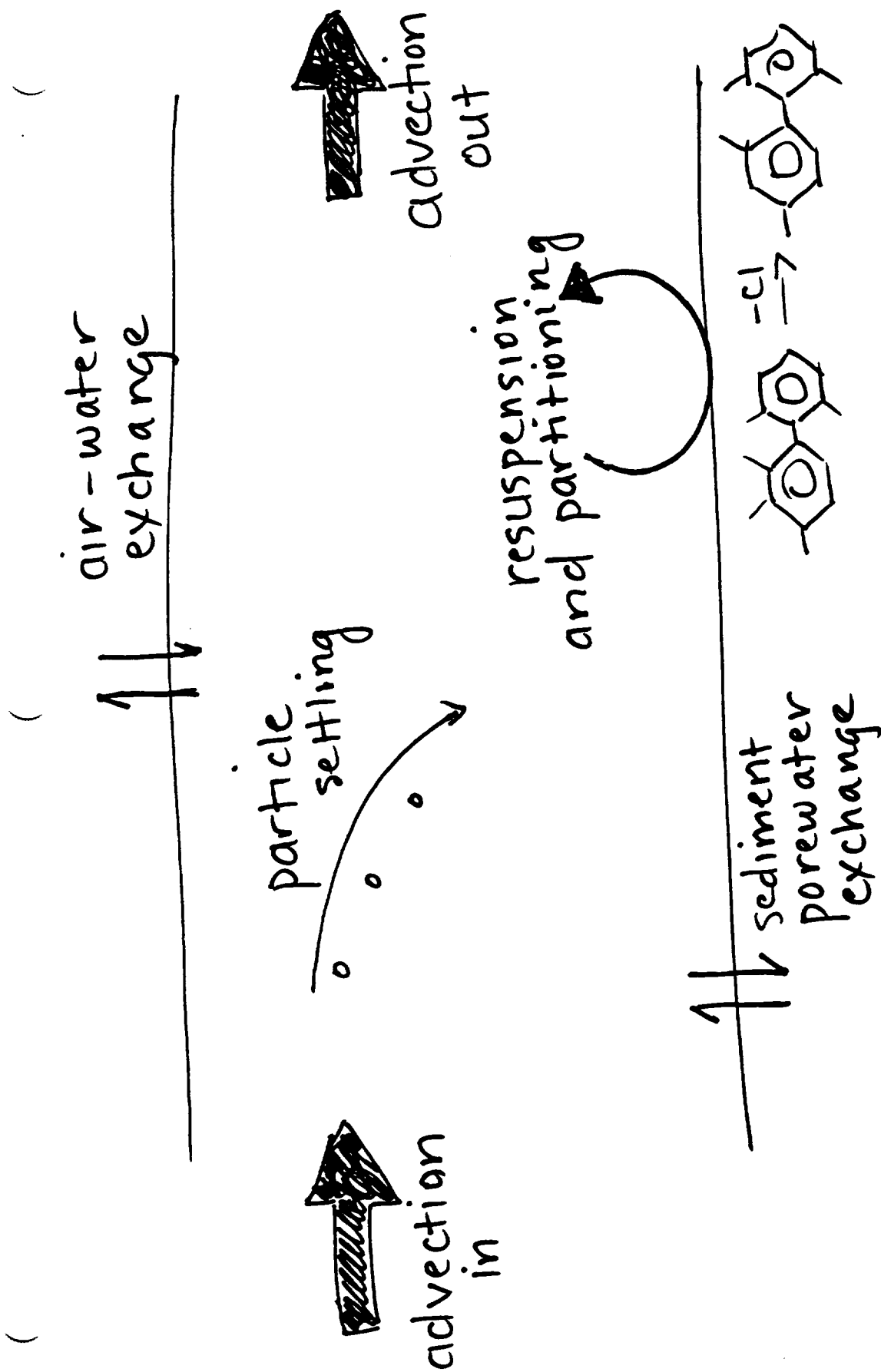
28

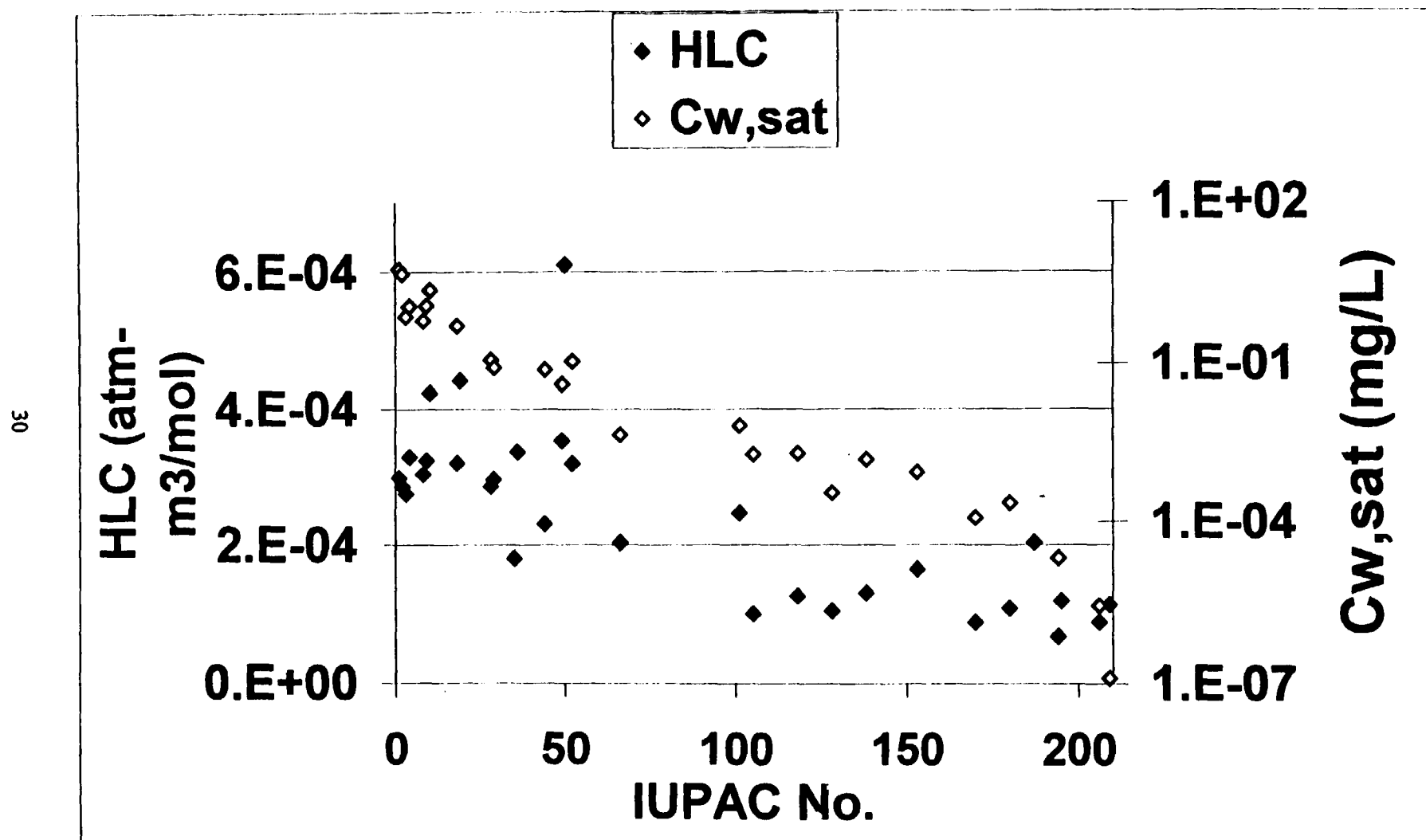Fig. D3-1. Model of PCB loading and downstream transport.

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Fig. D3-2. Aqueous solubilities and Henry's Law constants (from Dunnivant et al. 1992)

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4. *Does the sampling at the TI Dam-West location impact EPA's conclusion that the sediments of the TI Pool are the major source of PCBs to the freshwater Hudson during low flow conditions considering the analytical corrections made to GE's PCB data? What are the other implications of finding higher concentrations along the shoreline than in the center channel?*

Clearly, accurate estimation of PCB loads, and changes thereof, in the fashion adopted by EPA, relies on representative sampling of River conditions. Lateral and vertical heterogeneity in water column PCB concentrations result in estimations with greater uncertainties. If the sampling station at the TI Dam renders artificially high concentrations, loading will be exaggerated; conversely, if the station is isolated in a mainstream channel or at a depth where concentrations are artificially low, loadings will be underestimated.

As thoroughly stated in Book 3 of the Responsiveness Summary for the DEIR, **any sampling bias imparted due to systematically high PCB concentrations measured at TI Dam West location were more than offset by the underestimation of water column PCB concentrations.** The analytical bias was deemed to be 40% on average whereas the sampling bias was 40% maximum (low-flow, low concentration @ Rogers Island), a condition that was deemed to exist in 2 of the 7 years that data was collected (1991-97). **These biases appear to be mostly a wash, and loadings stated in the original DEIR report appear to be correct in relative, if not absolute magnitude.**

If water column (and sediment) PCB concentrations are higher in nearshore areas, several implications to both modeling and monitoring efforts can be envisioned. First, spatial coverage and resolution criteria for estimating PCB mass inventory need to be revisited. Specifically, are "hot spot" near shore areas represented with sufficient spatial resolution? If the higher nearshore PCB concentrations were not accounted for in the Phase 2 kriging analysis, an underestimate of total PCB inventory may have resulted. Second, what is the degree of mixing between shallow and center-channel regimes of the TI Pool? Third, what are the airborne losses associated with shallow vs. deep portions of the Pool? Fourth, what is the net suspended sediment deposition rate in these areas? Are these fine grained near shore deposits/sediments subsequently scoured and/or resuspended during "first flush" Spring melt flow events?

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5. Are the geostatistical techniques (polygonal declustering and kriging) correctly applied?

I am not qualified to give a detailed critique of these methods; however, I will offer the following general comments.

The polygonal declustering method described in section 4.2.3 of the DEIR resulted in the creation of Thiessen polygons of vastly unequal area (Plates 4-5 through 4-9 in the DEIR). Also, spatial correlation between adjacent sampling points is complicated by the high degree of heterogeneity in PCB levels, presumably also coupled to profound differences in sediment texture. Total mass inventory estimates from the LRC based on this first order method was 19.6 MT (DEIR, p.4-34), 16% less than the original 1984 assessment.

To better account for uncertainty associated with large unsampled areas, a geostatistical method known as kriging was applied. A semi-variogram function is used to represent the degree of "continuity" between PCB concentrations of adjacent sampling points. This approach was not successful for the full dataset but was deemed successful for various sub-reaches ("chopped up segments") of the TI Pool using a "block kriging" approach. An estimate of 14.5 MT resulted from this analysis, 38% less than the original 1984 estimate.

Clearly, estimates based on polygonal declustering are considered "conservative" (i.e. upper bound) whereas the lower estimates based on the kriging analysis are probably more accurate. However, the importance of nearshore areas with higher than expected PCB concentrations is unclear. Perhaps, a detailed assessment should be made on a short, spatial scale in two or three different reaches with (a) varying sediment texture and (b) significant nearshore PCB inventories, to "verify" the results of the kriging analysis (see also comments to DEIR Question 4 and General Question 2).

6. Are the methods applied in the DEIR (change in molecular weight (MW) and evaluating concentrations of BZ#s 1, 4, 8, 10 and 19 (MDPR) appropriate standards for determining extent of dechlorination? Are there any significant problems with this approach, or more appropriate approaches?

The change in MW (ΔMW) and molar dechlorination product ratio (MDPR) appear to be appropriate quantities for tracking the extent of dechlorination in Upper Hudson River sediment samples. The accumulation of *ortho*-substituted mono- and dichloro congeners (i.e. BZ#1, 4, 10, and 19) is consistent with the pattern of (reductive) dechlorination observed in this environment as reported in several papers (e.g. Bedard et al. 1996) and summarized in Bedard and Quensen III (1995). For example, it was noted that dechlorination patterns B, B' and C in Hudson River sediments were enriched in 2-chlorobiphenyl (BZ#1), 2,2'- and 2,6-dichlorobiphenyl (BZ#4 and #10), and 2,2',6- and 2,3',6-trichlorobiphenyl (BZ#19 and #27). BZ#8 is not a strictly *ortho* substituted congener so its inclusion in this ratio may be superfluous. That ΔMW and MDPR track well together is an additional indication that their representation of dechlorination is consistent.

There appear to be no significant problems associated with this approach for Upper Hudson River sediments. There are, however, alternate approaches as outlined in Quensen III & Tiedje (1997) that also give measures of the extent of *meta*- and *para* dechlorination. These methods require congener specific data which for the most part are available for the Phase 2 study. The first of these plots the average number of *meta* and *para* chlorines vs. *ortho* chlorines. This is compared to the unaltered source material (in this case e.g. 90-95% A1242; 5-10% A1254) and the vertical distance between the altered and unaltered source data point is a direct indication of the extent of dechlorination. The second method is the creation of "+/-" charts, subtracting mole fractions of individual congeners in a dechlorinated sample from the original or starting mixture. Individual molar increases and decreases should balance if dechlorination is the only transformation process involved.

It is worth noting that although EPA/TAMS justified in detail the use of ΔMW and MDPR these parameters as overall good indicators of dechlorination, they chose to disregard a large portion of the LRC data where these parameters appeared to indicate "widespread" dechlorination in samples with lower total PCBs that were primarily from deeper core segments. (see also comments on DEIR Question 7).

7. *The DEIR finds that the degree of anaerobic dechlorination is primarily a function of original concentration rather than time, and accordingly that there is not significant predictable dechlorination in sediments containing less that approximately 30 mg/kg PCB. Is this reasonable?*

Based on academic investigations into PCB dechlorination, and the selectivity with which a good deal of Phase 2 data was discarded from dechlorination analysis, I do not agree with this conclusion. The DEIR and LRC both show evidence that suggests that rates and extents of anaerobic reductive dechlorination in Upper Hudson River sediments are a function of PCB concentration. However, data from deeper sediments with lower concentrations that also appeared to show evidence of dechlorination were thrown out of the analysis. The reason given for excluding these data (constituting ~40% of all core data) was cross-contamination resulting from the core slicing procedure. **Inspection of the entire LRC core data (see Figs. 3-2 and 3-3 of the LRC), however, suggests that there is no relationship between MDPR or ΔMW and total PCBs.**

Abramowicz et al. (1993) showed that measurable dechlorination occurred in Upper Hudson River sediments collected near Ft. Edward (RM 194) that contained total PCB concentrations as low as 20 mg/kg. Although most laboratory investigations into PCB dechlorination utilize relatively high concentrations due to time constraints, there is no clear scientific basis for a single threshold.

In fact, there are many chemical and biological factors which are thought to impact rates and extents of in situ dechlorination. These include absence of oxygen, nutrient, carbon and electron donor availability and quality, PCB availability, organic carbon content and quality, and the presence of the appropriate microbes (Mohn & Tiedje 1992). Temperature has also been shown to affect not only rates and extents, but also patterns resulting from PCB transformation under anaerobic conditions (Wu et al. 1997). Whereas there is no doubt that higher PCB concentrations will increase the likelihood of PCB availability through porewater, given equal TOC, the order of magnitude heterogeneity observed for in situ partition coefficients reported in the DEIR (see also comments for DEIR Question 2) suggests that this generalization cannot be made with a high degree of confidence.

Low Resolution Sediment Coring Report (LRC)

1. In the LRC, EPA compared sediment data from cores taken in 1977, 1984 and 1994, which had the PCB analysis conducted by different laboratory methods. How valid are the methods used to establish a consistent basis for comparison?

The method described to correlate 1984 "total Aroclor" PCB concentrations with 1994 Phase 2 "congener specific" data appears to be valid. However, this is true only for ΣTri+ homologs. No satisfactory method was given to correlate 1977 data with other years or to estimate mono- and dichlorohomologs for earlier periods. Clear biases exist among data sets arrived at using different PCB analytical methods. The 1976-78 and 1984 data sets tracked the response of a limited number (3) of packed column peaks in Aroclor standards, which ignored mono- and diCBs and thus underestimated their contribution. The 1994 LRC was based on congener specific analysis, the preferred and most accurate method to date. In Appendix E of the LRC, a linear correlation method was described to estimate "tri+" values from 1984 total Aroclor concentrations. For the "as if" analysis of 1994 Phase 2 high resolution core data using the Aroclor method, Fig. 2 of Appendix E shows that a strong correlation exists for ΣTri+ concentrations (r^2 = 0.983).

If PCB congener profiles had changed drastically between the 1984 and 1994 sampling, this correlational method would probably not yield adequate results. Since the composition of the major PCB contaminant, Aroclor 1242 in this case, is dominated by lower to mid-range congeners in term of chlorines per biphenyl molecule, the resultant degraded mixtures are potentially less complex and/or variable than would be for heavier Aroclor sources (e.g. 1254 and 1260). Another indication that this estimation scheme did not impart a significant bias is the fact that both PCB mass inventory losses and gains were determined.

Concerning 1976-78 data for hot spots below the TI Pool, it was stated on p.27 of Book 3 of the DEIR Responsiveness Summary that "The 1977 (USGS) sediment data are also suspected to approximate a sum of tri- and higher-chlorinated congeners, but may have a small upward bias relative to the 1984 results due to the use of Aroclor 1016 standard rather than an Aroclor 1242 standard. Unfortunately, surviving documentation of this analytical effort does not appear to be sufficient to definitively establish exactly what was measured in 1977." However, on p.4-27 of the DEIR, it was stated "The three peaks used were the same ones used by O'Brien and Gere for Aroclor 1016 in the 1978 analysis." **Based on this discrepancy and the general lack of information/analysis, I cannot comment on the comparability of 1977 data.**

Clearly, a major limitation of earlier PCB datasets is the absence of mono- and dichlorobiphenyl homolog data. Based on Table A-7 in the Responsiveness Summary for the LRC, these homologs account for ~ half of the entire inventory on a molar basis. In terms of assessing changes in PCB inventory, it is presumed that mono- and diCBs would be most mobile and losses to compartments not accounted for in Phase 2 DEIR measurements would be potentially the greatest. Then there is the impact of dechlorination which over a 16-18 year period might be expected to be significant. If a substantial fraction of the 1976-78 ΣTri+ PCB mass was subsequently dechlorinated (and not desorbed), the "non-change" would be reflected only in the 1994 total PCB estimates, and not the ΣTri+. This no-change in truth would would be detected as a loss based on comparison of ΣTri+. Losses between 1976-78 and 1994 were in fact reported in the LRC general conclusions. (see also comments to LRC Question 3). As repeatedly asserted throughout Phase 2 reports, this dechlorination change would be limited to 25% of the total PCb mass for Aroclor 1242; however this is still a significant fraction that could be unaccounted for.

2. *In the upper Hudson River system, it has been well established that there is significant lateral heterogeneity in sediment concentrations. How does sediment heterogeneity affect the comparsion of cores from two different years? Given the spatial variability, is the finding that there is loss from most of the locations supported by the data?*

Based on the general agreement between the loss amounts stated in the original LRC analysis ("point-to-point comparison") and the Reassessment analysis ("cluster area"), the losses appear to be supported by the data. The original LRC point-to-point comparison resulted in a 39% mass loss for sediments with higher PCB inventories ($>10g$ PCB/m^2). The Reassessment included regression and ratio-based analyses to estimate mass loss using the mass per area (MPA) parameter for PCB inventory. The regression analysis resulted in a mean mass loss of 59 ± 19 percent; the ratio-based analysis resulted in a mean mass loss of 45 percent (95% confidence range: -59 to -4 percent). A small correction (~5%) was also made for dechlorination.

Although spatial and temporal variability in sediment PCB concentrations are of concern, it is prudent to utilize as much of the collected data set as possible when making conclusions. Sediment texture (grain size) and total organic carbon (TOC) data are two classic examples of parameters that are typically correlated with the concentrations of particle reactive, hydrophobic contaminants like PCBs (LRC, Figs 3-20 and 3-21). The grouping of core data into 14 cluster areas served to eliminate sampling location bias caused by short scale spatial heterogeneity that could lead to very large errors when comparing data on a "point-to-point" basis, as was done in the original LRC analysis. In fact, 11 of the 14 cluster areas analyzed in the Reassessment were determined to be largely fine-grained sediments (LRC Reassessment, Book 1, Appendix A, p.A-5).

Thus, in all likelihood, the effect of spatial heterogeneity of PCBs is associated with differences in sediment types as measured by these parameters. In other words, as long as the basic sedimentological parameters were similar in cores collected from the same location, I would not expect sediment heterogeneity to impart significant comparative errors, as supported by the general agreement of mass change estimates from point-to-point and cluster area estimates.

3. *What is the impact of the difference between replicate samples in the 1994 sampling effort (36 percent average variability) on the finding that there was a 40 percent loss of PCB inventory from the highly contaminated sediment in the TI Pool?*

The LRC (p.2-18) reports an average relative percent difference (RPD) of 36 for total PCBs in core field splits. The formula for calculating RPD is also given on p.2-18. Total PCB concentrations in a given core segment are then used to calculate mass per unit area (MPA) estimates and length weighted averages (LWA) (LSR, eqs.4.1-1 and 4.1-2, p.4-3). Thus any error in the concentration term (C_i) are directly translated into these estimates. In fact, EPA/TAMS found that absolute changes could not be assessed because of this uncertainty. As a result, they switched to relative measures of mass change. The relative percent change in PCB inventory (Δ) is calculated according to Eq. 4.1-4 (p.4-6):

$$\Delta = [(MPA_{94} - MPA_{84})/MPA_{84}] * 100\%$$

In this representation, uncertainties in MPA estimates are now applied in both the numerator and denominator.

A problem with accepting a 40 percent decrease in sediment-associated PCB mass (actually 39%, p.4-17) would arise if one believed that the 36% uncertaintly reported were primarily of a systematic nature. In other words, if the 36 percent uncertainty was consistently applied as an underestimation of 1994 data relative to the 1984 estimates, then little or no change in PCB inventory could be concluded. However, there appeared to be little/no evidence of extreme systematic bias in the 1994 data and so it can be assumed/concluded that these uncertainties would be expected to be somewhat random (i.e. an equal chance for underestimation and overestimation). This is supported in this case by inspecting the regression slopes for field split pairs for BZ#52 shown in Fig. 2-6 of the LRC where 11 slopes were less than unity and 10 were greater than unity. This suggests that on average field duplicates were biased high with the same frequency that they were biased low. As such, the tendency for mass losses to be real is not compromised.

I would like to point out that the confidence intervals around the reported 40-50 percent mass losses are substantial and reflect the uncertainty in the mean estimates. Reporting single values without mention of their rather large uncertainties in this case is misleading and should be avoided. **Thus, I do not feel that the 36 percent variability between replicates invalidates the conclusions of mass losses; however, the predictions of mass losses should be represented as ranges instead of single "mean" values to avoid misrepresentation/misinterpretation.**

4. In the LRC, it was found that Hot Spot 28 contained much more mass than previous
estimates. Is the conclusion that this gain is primarily due to incomplete characterization in
1977 valid?

This conclusion appears to be the only plausible explanation for the substantial inventory
increase and is supported by at least 2 pieces of evidence. First, there were widely divergent
PCB concentrations for co-located cores (LRC, Plate 4-22). For example, the 1994 core
exhibiting a length weighted average (LWA) PCB concentration of 1184 mg/kg was co-located
next to the NYSDEC 1976-78 sediment grab sample whose reported mean PCB concentration
was 176 mg/kg, almost one order of magnitude less. Second, several 1994 cores with significant
PCB levels were collected in areas apparently not sampled in the 1976-78 survey. Two examples
of this are the cores with LWA PCB concentrations of 680 and 267 mg/kg near the center of the
large area of fine-grained sediments. It is also possible that accretion over the past 15 years has
greatly increased the mass inventory at this location, or that inventories have shifted within the
Hot Spot itself. These scenarios are not likely to have occurred based on the "stability" of
location of most other major hot spots (see core profiles in the LRC, Appendix D).

5. Does the data set and its interpretation support the conclusion that significant losses have occurred from hot spots below TI Dam?

Based on the significant inventories in shallow sediments and the potential difference/bias in PCB quantification, I am more inclined to believe the "losses" reported from these hot spots more than I would "gains". PCB inventory losses were reported for Hot Spots 31, 34 and 37; gains were reported for Hot Spots 28 and 39 (LRC, Table 4-10). Based on the PCB concentration profiles in Appendix D, I created a simple spreadsheet to estimated relative PCB inventories in up to 3 core horizons, i.e. the "shallow" (roughly 0-10in); "second" (8-20in) and "third" (>20in) core segments (see also LRC, Fig. 2-2). Based on my calculations, which simply sum the product of average core segment concentrations and the corresponding core length, 48% of the PCB inventory in sediments from these Hot Spots resides in the surface (0-10in) layer (Table L5-1). Thus it can be concluded that a large fraction of the PCB inventory associated with bedded sediment is not buried "deeply" and is available for resuspension and advection downstream, resulting in a net mass loss if replenishement from upstream sources did not keep up with losses to the water column (and beyond).

However, many of the cores collected were incomplete, particularly for Hot Spots 34, 37 and 39. In the LRC, it is acknowledged "PCB estimates derived from these incomplete cores probably underestimate the actual sediment inventory in the affected cores by less than 50 percent" (LRC, p.2-17). The other factor to consider for all PCB mass change estimates (between 1984 and 1994) is the presumed underestimation of PCB sediment inventory in the 1976-78 NYSDEC study. This underestimation is due to the use of packed column GC analysis and quantitation based on total Aroclors and would serve to increase confidence in mass loss estimates relative to those that concluded a mass increase.

Review of Phase 2 LRC   **Maruya**

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HS#	25	28	31	34	35	37	39	41	42	43	44	sum	%
a	64		108	179	4225	359	430	5	10430	194	198		
b	186	270	3840	46	1100	120	8	919	4620	84	22		
c	64	14050		41	532	212	116	36	444	345	20		
d	51	183	45	50	264	200	1000		276				
e	1500	17500	1430	392	4	150	1080						
f	40	9500	44	7		20	3905						
g	950	1250	693	40			604						
h	5900	15960	20	57			2665						
I	860	12380	290	290			2355						
j	2700	2655	130	3520		1650	2396						
k		3890		556		168	1070						
l		1032		672		56	2160						
m		16660		51			418						
n		9830				63	251						
o						9770	16						
sum	12315	105160	6600	5901	6125	12768	18474	960	15770	623	240	184936	
mean	1232	8089	733	454	1225	1161	1232	320	3943	208	80	1698	
0-10	9772	51656	3936	2134	5317	9831	3555	887	1472	377	82	89016	48
10-20	2503	42796	2324	3277	716	2582	9280	73	13014	218	84	76868	41
>20	13	10683	1373	446	88	354	5639		1285	28	72	19981	11
check sum	12288	105134	7633	5857	6121	12767	18474	960	15770	622	238	185865	100
												sum	%
%top	80	49	52	36	87	77	19	92	9	61	34		
%interm	20	41	30	56	12	20	50	8	83	35	35		
%bottom	0	10	18	8	1	3	31	0	8	4	30		

Table L5-1. Spreadsheet summary of PCB inventory in low resolution cores from downstream Hot Spots.

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6. *The LRC found that the historically contaminated sediments in the TI Pool were not universally being buried and sequestered from the environment. How much confidence would place in the LRC evidence against widespread burial?*

Since I don't know what is meant by "historically contaminated sediments", I chose to answer instead **"Are significant concentrations/inventories of PCBs available in the shallow layers of sediments in the TI Pool?"** And my answer to this question based on the data provided in the LRC is yes. Based on the PCB concentration profiles in Appendix C, I created a simple spreadsheet to estimate relative PCB inventories in up to 3 core horizons, i.e. the "shallow" (roughly 0-10in); "second" (8-20in) and "third" (>20in) core segments (see also LRC, Fig. 2-2). Based on my calculations, which simply sum the product of average core segment concentrations and the corresponding core length, 58% of the PCB inventory in TI Pool sediments resides in the surface (0-10in) layer (Table L6-1). Thus I conclude that a large fraction of the PCB inventory associated with bedded sediment is not buried "deeply".

Review of Phase 2 LRC   Maruya

Core zon	1	2	3	4	5	6	7	8	9	10	11
a	400	320	0	800	2400	450	240	130	611	3400	6840
b	200	1040	1120	5500	1100	4000	324	264	0	2200	2160
c	1360		0	8800	3860	0	1280	1050	1060	2430	1800
d	1120			3500	9200		108	90	200	1530	
e					12500			252	450		
f									290		
sum	3080	1360	1120	18600	29060	4450	1952	1786	2611	9560	10800
mean	770	680	373	4650	5812	1483	488	357	435	2390	3600
0-10	1400	320	370	15200	9209	2450	672	45	740	6365	2750
10-20	1700	1040	370	3400	17892	2000	1280	1741	1871	3195	594
>20	0	0	370	0	1959	0	0	0	0	0	7434
check su	3100	1360	1109	18600	29060	4450	1952	1786	2611	9560	10778

Core zon	10	11	12	13	14	15	16	17	18	sum	%
a	3400	6840	207	330	72	290	243	1400	960		
b	2200	2160	138	80	60	25	490	360	6200		
c	2430	1800	90	90	244	200	70	176	1125		
d	1530		660		220	710	476	1360	7200		
e			182					259	0	2820	
f											
sum	9560	10800	1277	500	596	1225	1538	3296	18305	111116	
mean	2390	3600	255	167	149	306	308	659	3661		
0-10	6365	2750	538	386	474	1014	1538	2596	17743	63809	58
10-20	3195	594	668	56	122	104	0	700	563	37295	34
>20	0	7434	68	56	0	104	0	0	0	9991	9
check su	9560	10778	1274	498	596	1222	1538	3296	18305	109873	101

Table L6-1. Spreadsheet summary of PCB inventory in low resolution cores from the TI Pool.

General Questions

1. Is the data set utilized to prepare the DEIR, LRC and Responsiveness Summaries sufficient to understand the fate and transport of PCBs in the Upper Hudson?

The simple answer to this ambitious question is no. Understanding the "fate and transport" of PCBs in the Upper Hudson requires an extensive multimedia investigation. An potentially important medium that has been ignored (i.e. no data collected or presented) is the gas phase. I would suspect airborne measurements of the lighter, more volatile PCBs might help with closure of the mass balance (see also comments to DEIR Question 3). Because these homologs are expected to be "more mobile" as the Phase 2 reports repeatedly point out, they are also more prone to partition into the gas phase, and leave the aquatic system entirely. This would be especially pertinent during warmer (low-flow) months, and possibly in slower-moving, larger surface area to volume quiescent pools such as the TI Pool. Evidence supporting the importance of this mechanism are the revised water column loads in Appendix C of the LRC Responsiveness Summary ("However, both of these events show a marked decline in the fraction of monochloro-homologue(s) between the two stations, representing about a 50 percent loss", p. C-11). The 2 events referred to are transects 2 (May) and 3 (June) and the 2 stations are the TI Dam and Waterford. **Loss of PCBs to the air is never estimated or quantified.**

Another problem with Phase 2 comparisons of PCB mass inventory is the lack of mono- and dichloro homolog data for earlier years. According to McNulty (1997) as reported in the LRC Responsiveness Summary (Table A-7), roughly 40-50 percent (molar or mass basis) of PCBs in fine-grained TI Pool sediments are mono- and diCBs. However, for analytical reasons, comparisons could only be made for "Tri+" homologs. There are obviously competing processes that would determined the net shift, if any, in congener patterns over several years. Among these are dechlorination (shift toward lighter PCBs) and degradation (shift toward heavier PCBs), selective "weathering" (dissolution, diffusion/advection away from sediments; shift toward heavier PCBs), air-water partitioning (mentioned above; shift toward heavier PCBs?) and particulate-mediated transport (resuspension, scouring; no shift). These competing mechanisms are consistent with the advertised loss of PCBs from the sediment inventory, and also the maintenance of a relatively stable or declining water column load, if that is indeed what has happened since 1993.

Another limitation of this study was the collection and analysis of water column loading data for a single year (1993), a year that unfortunately was subject to transient upstream inputs. Clearly, loadings resulting from the Allen Mills source influenced PCB loading prior to June of 1993, and probably for at least several months thereafter assuming a stepwise transport downriver. Thus, it was difficult to assess the nature and degree of loading in the TI Pool, at least during the early months (winter low flow and spring flood conditions). Thus, water column monitoring data from post 1993 years would clearly be helpful (see also comments for General Question 2).

These limitations aside, I do believe that the data presented in the Phase 2 DEIR and LRC reports are adequate to (I) identify stretches of the Upper Hudson where major PCB loading to the water column occurred under summer low flow conditions, including as an example the TI Pool; and (2) suggest mass losses from many of the Upper Hudson hot spots, including the TI Pool. The major questions are thus shifted from "Where are water column PCBs coming from?" to "How long will these Hot Spots persist?" and "What is the ultimate fate of the PCBs introduced into the water column from these locations?"

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2.   *Are there any additional analyses that should be done to verify certain findings of the DEIR and LRC?*

Several additional analyses may help verify the general conclusions of the DEIR and LRC. The first has to do with "validating" the 1993 water column/PCB loading study. Reference was made throughout parts of the Phase 2 reports and the Reassessment Summaries concerning post 1993 water quality monitoring data, mostly compiled by GE. However, no coherent analysis and/or summary of this data was included. If enough data exist, it would be extremely useful to see if the same general water column PCB concentration and loading trends, particularly during winter low flow conditions, are observed for years where transient upstream inputs of PCBs (e.g. the Allen Mills source of the early 1990s) were absent/minimized.

The second analysis has to do with assessing the significance of elevated "neashore" PCB contamination. It was not clear to me whether these areas were considered in the DEIR geostatistical analyses. They certainly were underrepresented in sheer numbers of coring locations (roughly 20 of 200 or $\leq$ 10%). The concern here would be whether PCB inventories were underestimated because these areas were "ignored" or incorrectly weighted in the analysis.

The third analysis would combine the major conclusions of the Phase 2 analysis to see if sediment PCB inventory losses are consistent with annual water column loadings and estimates of downstream transport. The difference between the two could then be investigated as losses via evaporation and/or in situ degradation in future monitoring and/or modeling exercises. This mass balance check was mentioned somewhere in the Reassessment Summary, but should be elevated into the summary of major Phase 2 conclusions.

A final analysis would reassess the compatibility of 1976-78 and Phase 2 PCB data. In my experience, total PCB estimates based on Aroclor or congener-specific data are generally strongly correlated, unless major congener/homolog shifts are present. This was done convincingly for the 1984 NYSDEC and Phase 2 data in Appendix E of the LRC. Statements made concerning Aroclor standards used for the 1976-78 data set were not consistent throughout the Phase 2 documentation, but if a consensus could be reached on what approach was used, a correlational analysis would help determine if these data were compatible.

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Dr. Ronald Mitchum

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February 26, 1999

This peer review is provided in response to the "Charge for Peer Review 2" given to the review panel on January 11 and 12, 1999. The following addresses the specific questions before the panel.

I.   Data Evaluation and Interpretation Report (DEIR)

1.   "Is the documented PCB load, which originated from the TI Pool, consistent with a source consisting of historically deposited PCB-contaminated sediments?"

The TI sedimentary material was the result of several events, which deposited PCB. The first known event would have been associated with Federal Dam structure which was removed in 1973 and the sediment resulting from more recent and continuing releases associated with the GE Baker Falls Plant.

Response:

The determination of the source of PCB originating from the TI inlet pool can be formulated by comparing the congener distribution of the aroclor 1242 and that of biodegraded 1242 found in the sediment. The use of congener patterns will provide the most information where the use of homolog patterns will provide the least.

Figure 3-53 distinctly shows the redistribution of sediments caused by the destruction of the Federal Dam up river from the TI pool which occurred about 1973. This establishes that the sediment contained in the pool predominantly occurred via redistribution caused by that event.

The data has been treated using both congener and homolog patterns. The homolog data in figure 4-34 indicates that at normal to low flow conditions the load is consistent with the TI pool load. At high flow conditions where equilibrium was not established in the TI pool the down river load approximates the new material being released at Baker Falls.

A comparison of congener data in the same way the homolog data was compared in 4.34 can not be readily done. The use of multivariate statistical technique would have allowed a similar comparison.

In conclusion the data supports the thesis that the PCB load originates from the TI pool. Deviations from the model may occur during high flow upsets.

2.   "Are the two-phase and three-phase partitioning coefficients, derived in the DEIR, appropriate and do they properly address the physical parameters of the system (e.g. temperature)?"

To define the porewater derived equilibrium concentration, the partitioning coefficients must contain the most important physical parameters. The equilibrium may be described as the ratio of the absorption and the desorption rate constants. The rate constants have a fundamental temperature term, which must be included. The discussion on page 3-15 and the derivation of the temperature term appears to be correct. The three-phase system would seem more appropriate, however, there was not enough data to apply the model consistently.

In addition to the three phases used in the model some PCB was lost to aerosol formation in the falls (dams), ripples, edge eddy currents and surface evaporation. This source may be minor, however, significant pesticide transport has been observed in fog water in the San Joaquin Valley located in California. The use of Henrys Law to explain away the importance of the process may not be warranted. PCB present at the surface may not behave as an ideal gas. If the mechanism is via aerosol formation, Henrys Law can not be invoked except to explain how PCB may be lost from the particle. Dechlorination by photolysis is a significant chemical degradation process (see Erickson pp. 37). This factor may be significant in the near surface water of a stagnate system, such as, the TI pool and the river flow.

The adequate representation by the two or three phase models is supported by the data. The comparison of the data with the model may suffer due to non-equilibrium events such as temperature currents, gradients and stratification within the system.

3.   "Are the conceptual models based on the transect sampling consistent with the data?"

The conceptual models suggest that the TI pool is the source of the PCB down river either through resuspension of fine sediments or porewater equilibrium. The data is consistent with the above. The transect sampling events support the conceptual model.

4.   "Does the sampling at the TI-West location impact EPA's conclusion that the sediments of the TI-Pool are the major source of PCBs to the

freshwater Hudson during low flow conditions considering the analytical corrections made to GE's PCB data? What are the other implications of finding higher concentrations along the shoreline than in the center channel?"

The total net load resulting from the TI pool was calculated as the net increase observed from a sample point up river at mile 194.6 and at the dam at mile 188.5. The GE data as adjusted by EPA does show a gain across the pool, see figure 3-83. The EPA data set should be recalculated based upon the GE target sampling and the estimates revised. The GE data consisted of enough data points to fully characterize the gain due to the TI-Pool.

The flow through a system such as the TI pool is not uniform across the pool. The flow will be slower near the edge of the pool and faster near the center. A current will be established during high flow conditions, which will influence the concentration of PCBs in the water column. A concentration gradient across the dam should exist if equilibrium dynamics are used as the mechanism for developing the TI pool contribution to the down river PCB load. However, during low flow conditions the influence will be minimal and the over the dam   · concentration of PCB may reflect the equilibrium concentration in the pool.

5.   No Comment – This is out of my area of expertise. The discussion presented a logical argument for the use of each.

6.   "Are the methods applied in the DEIR (change in molecular weight (MW) and evaluating concentrations of BZ#s 1,4,8,10 and 19 (MDPR)) appropriate standards for determining extent of dechlorination? Are there any significant problems with this approach, or more appropriate approaches?"

The approach provides a quantifiable method to represent the dechlorination on a per sample basis and to compare it to other samples in the set. This appears to be a brut force method and the linearity of the plot in figure 4-21 simply represents the derivation of the equation 4-13, which is the equation for a straight line. The difference in the intercept between the regression line and the theoretical line may be due to the initial assumptions regarding the concentration of the total PCB rather than the PCB containing only ortho chlorines.

The MDPR approach looses the information, which may be present if each congener were treated. Use of a technique such as SIMCA or other

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multivariate statistical packages may provide fine detail information regarding the dechlorination of the PCBs found in the Hudson River system. In addition information regarding possible changes to the dechlorination pattern due to further dechlorination or changes due to further sediment equilibration may be observed.

7. "The DEIR finds that the degree of anaerobic dechlorination is primarily a function of the original concentration rather than time, and accordingly that there is not significant predictable dechlorination in the sediments containing less than approximately 30 mg/kg PCB. Is this reasonable?"

    The rate of anaerobic dechlorination contains both a concentration term and a time term according to:

    d[dechlorination product concentration]/dt = k [original concentration]

    Therefore, the dependence upon the original concentration would be expected. No experiment was performed which would determine the time dependence. The time dependence may be on the order of days, weeks or months rather than years.

    The 30 mg/kg was deduced from a plot of fractional dechlorination vs log total PCB. The basis for the plot comes from rearrangement of equation 4-13 to:

    (.86/.14)*ΔM = MDPR * 6.43 -.223

    This equation predicts the intercept will be -.223 and if .86/.14 ΔM were plotted against MDPR the resultant slope of the line would be 6.43. There are no provisions for the log relationship. The use of a log relationship simply allows what would be a discontinuous relationship observed in figure 4-21 to now appear continuous.

    The meaning of the data is as follows: The points which lie below the aroclor 1242 in 4-21 and those which are referred to as being below 30 ppm in figure 4-22 belong mostly to the class referred to as being derived from the fresh water lower Hudson River and a few representatives of the upper Hudson. This represents a change in congener pattern (ratio) in the lower Hudson. A multivariate analysis may have indicated that this group of samples belongs to a separate congener composition representing the lower fresh water Hudson.

II.   Low Resolution Sediment Coring Report (LRC)

1.   "In the LRC, EPA compared sediment data from cores taken in 1977, 1984 and 1994, which had the PCB analysis conducted by different laboratory methods. How valid are the methods used to establish a consistent basis for comparison?"

Some assumptions were made based upon the various methods used during these eras. In 1977 PCB analysis consisted mainly of packed column ECD analysis following drinking water methods developed by EPA or FDA. Only the significant homolog groups were separated. Typically the data was reported as the closest matching aroclor and reported as a total. Access to the data could not have resulted in the deciphering of homolog groups. The samples may or may not have been preserved and quality assurance programs were not in place to assure the integrity of the data.

In 1984 data were generated again using packed column technology and followed the NYSDEC program methodology. The data would have been reported as totals or homologs. The aroclor would have been identified. The data was most likely useable. There was no indication that the data had been validated. In 1994 the data collected consisted of congener specific data collected using capillary chromatography. The quality assurance protocols reflected a mature QA program. The data should be useable.

There are a couple of problems with the old data using packed column technology. First, one may want to interpret the groupings in packed column data as pure homolog groups, such as, Cl-3, Cl-4, Cl-5 etc. Although distinct peaks are seen in the chromatogram these are not pure homolog groups. Therefore, time travel of the data to 1994 was not possible. Using the data presented in the LRC, E-4, for the congener distribution within the individual quantification peaks for the various aroclors, reverse extrapolation to packed column data was made. The data is shown to be self-consistent when the tri + congeners are used in the extrapolation.

There are several assumptions, which have been made which detract from the use of the estimate. First, the data set has been corrected by NYSDEC to reflect an apparent oversight by Versar in the calculation of PCB concentration for aroclor 1242. Second, the work of Gauthier-TAMS may not have reproduced the column or conditions used for the NYSDEC study. Third, the data is not of known defensible quality. That is, the same quality standards were not in place in 1984 both in the laboratory or the field sampling.

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The 1984 data at best should be used for estimation purposes only. In addition, since the old data does not reflect the lower homologues which play an important part in the assessment of the PCB containing sediments, its use may detract from conclusions regarding fate and transport.

2.   "In the upper Hudson River system, it has been well established that there is significant lateral heterogeneity in sediment concentrations. While it was attempted to reoccupy previous locations, some uncertainty is added with respect to the actual sampling location. While the statistical techniques help compensate for this, how does the sediment heterogeneity affect the comparison of cores from two different years? Given the spatial variability, is the finding that there is loss from most of the locations supported by the data?"

Sampling errors associated with homogeneity, sample transects, and sample numbers and the statistical design associated with the sampling plan represent the single largest error associated with assessments of this nature. Comparison of sampling events provides the opportunity to propagate these errors. If the sampling plan covers an area with 300 ft transects, then the error associated with comparison of core samples 10 years apart may be large if the sediment has significant lateral heterogeneity. If the sampling plan included more samples with smaller transects than the error would be smaller.

The sampling used a grouping around the 1984 sample site. This will tend to average out sampling error associated with position.

Question 2.

Given that the data set for 1984 is internally consistent and that the data set for 1994 is internally consistent but that there is no common ground between the methods makes it likely that some bias may be introduced. Given the estimates of PCB concentration in the 1984 study and the error associated with sampling, an error estimate should be established which will define the likelyhood of the data supporting loss of PCB from most locations.

3.   "What is the impact of the difference between replicate samples in the 1994 sampling effort (36% average variability) on the finding that there was a 40 percent loss of PCB inventory from the highly contaminated sediments in the TI Pool?"

The variability of the 1994 and the 1984 data must be considered together. If the deviation, change from the mean is ±18%, this is the only data available and the 1984 data is considered to have the same variability, then

an observed 40%, in 1994 may not be significantly different from the 1984 data.

4.   "In the LRC, it was found that HOT Spot 28 contained much more mass than previous estimates. Is the conclusion that this "gain" is primarily due to incomplete characterization in 1977 valid?"

      The insufficient characterization in 1977 could have resulted in the discrepancy observed. More likely the analytical and sampling methodology contributed to the apparent underestimate. Since the 1977 data is not of known quality.

5.   "Does the data set and its interpretation support the conclusion that significant losses have occurred from hot spots below the TI dam?"

      The comparison of the 1984 and the 1994 data sets indicate that most of the hot spots lost mass during the 10 years. The sampling design is robust enough to have located the 1984 sediment sampling sites. The chemistry comparison may produce a bias due to uncertainties in the 1984 data set.

6.   "The LRC found that the historically contaminated sediments in the TI pool were not universally being buried and sequestered from the environment. How much confidence would you place in the LRC evidence against widespread burial?"

      There is a preponderance of evidence in the DEIR and the LRC, which suggest the sediment borne PCB, are being redistributed to the water column. High-resolution cores supported the low-resolution core data. If the data under penning the conclusions are sound, widespread burial does not appear to be occurring.

7.   "Is the interpretation of the sidescan sonar data appropriate and supported by the analysis of the associated sediment properties?"

      I can not draw a conclusion due to my lack of knowledge of SSS.

General Questions

1.   The data set has addressed many of the variables necessary to assess the fate and transport of PCB in the Upper Hudson.
2.   New deposition from the GE Bakers Falls plant site appears to be occurring. Due to the high loading of PCB in the sediment, NAPL, may be of concern. Although none was reported in the LRC, sampling methods to determine NAPL were not used. The equilibration of the water column appears to be associated with the dissolution of NAPL from

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the GE plant site. The loss of PCB either photochemically or by aerosol formation resulting from the stripping occurring below each dam on the Hudson may be factors, which influence the PCB load. Recalculation of the water column PCB load resulting from the apparent overestimate introduced due to sample inhomogenity near the TID in the DEIR data needs to be performed.

Development of a multivariate statistical treatment of the data needs to be performed. Much of the information has been lost due to the data treatment using bivariate statistics.

Reviewer: Ronald K. Mitchum, Ph.D.
Review of the DEIR
March 4, 1999

Recommendation: Acceptable with minor revision

Review of the DEIR and associated Responsiveness reports indicate that the objective of the reassessment has been accomplished. Inclusion of the fate compartments consisting of air transport, resulting from the dams along the Upper Hudson, and photochemical degradation complete the overall conclusions. Perhaps of more concern is the bivariate statistical treatment of the data. It is understood that this may stem from a historical approach in which continuity of presentation was desired. The use of multivariate statistics will express obscured trends in the data. The congener specific analysis offers a rich data base from which to reassess and expand upon the conclusions drawn to date.

The plot representing the fractional dechlorination vs. the log of the dechlorination ratio appears to have no theoretical basis. The log transform removes the skewness in the data set and has led to an inadequate conclusion regarding the apparent 30 ppb dechlorination limit.

A recalculation of the PCB load leaving the TIP requires using the new GE data from the transect sampling across the dam. Inclusion of a model, which addresses the edge effects, may serve to explain the apparent sampling discrepancies observed.

Reviewer: Ronald K. Mitchum, Ph.D.
Review of the LRC
March 4, 1999

Recommendation: Acceptable with major revision

The LRC provides a current 5-year-old update to the 1984 sediment study
performed by NYSDEC. The sampling design was adequate to assess the
1984 sampling points. The underlying data variability must be assessed to
determine if the conclusions, which were drawn, are valid. The joint
variability of the 1984 and the 1994 analysis events along with the
sampling variability due to spatial variations need to be addressed. The
conclusions then need to be reassessed. Although the data trend is present
which suggests there has been a los⌐ of hot spot PCB load below the TID
are the measurements precise enoug⌐ to define the loss.

The inclusion of data, which was derived from 1977, or earlier events has
so much analytical uncertainty as to be unusable. Any conclusions drawn
from these comparisons should be qualified or removed from the
document.

The use of a bivariate data treatment rather than a multivariate statistical
treatment may have obscured trends in the data. The congener specific
analysis offers a rich data base from which to reassess and expand upon
the conclusions drawn to date.

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Dr. Ken Reimer

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Hudson River PCBs Site Reassessment (RI/FS)

Date Evaluation and Interpretation Report (DEIR) and

Low Resolution Sediment Coring Report (LRC)

Peer Review 2: Pre-meeting Comments

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March 1, 1999

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Hudson River PCBs Site Reassessment (RI/FS)

Date Evaluation and Interpretation Report (DEIR) and

Low Resolution Sediment Coring Report (LRC)

Peer Review 2: Pre-meeting Comments

A.   Introduction

The comments that follow are based on an evaluation of the DEiR and LRC reports as well as the corresponding Responsiveness Summaries. As noted in the charge for the peer review, the analyses in the responsiveness documents were considered to supersede those in the original reports. The Hudson River Reassessment Database (Release 4.1) was also used in preparing the following remarks. Reference was also made to the scientific literature as found in refereed reports, but not to other documents or reports dealing with this Hudson River issue.

Comments are divided into:

- Responses to the specific charge questions for the DEIR – Part B.
- Responses to the charge questions for the LRC – Part C.
- General question responses – Part D.
- Recommendations – Part E.

B.   Response to DEIR Questions

1.   Is the documented PCB load, which originated from the TI Pool, consistent with a source consisting of historically deposited PCB- contaminated sediments?

There seems to be little disagreement that the combined TI Dam (TID) load – i.e. the PCB load originating above the TI Dam and including Hudson Falls, the Remnant Deposit area and the Thompson Island Pool (TIP) – is the major source of PCBs to the freshwater Hudson. It further

seems reasonable that the PCBs in the water column at the TID originate from the sediments of the TIP. The question remains – 'what portion of the sediments?'

In order to assess if it is historically contaminated sediments or some other source it is necessary to examine several lines of evidence – foremost among these is a change in homologue pattern across the TIP (DEIR, page 3-171).

Section 3.4.2 of the DEIR examines the nature of the PCB loading to the TIP. The results of the March 1993 Phase 2 and GE monitoring programs show similar homologue patterns at the Rogers Island station. Both analyses demonstrate (Figure 3-102) that the load largely consists of tri- and tetra-chlorinated congeners – suggestive of an Aroclor 1242-like source. It is suggested that this similarity, together with the highly variable loading, is due to the GE Hudson Falls releases. [It is interesting that the loading is higher at Rogers Island relative to the station at RM 195.5 near the Remnants Deposit although the congener patterns at the two stations are frequently the same. This raises the question of a PCB source from the Remnants Deposits, although GE has apparently concluded that they are only important as a source of secondary mobilization of PCBs from the Bakers Falls source (page 2-20).]

Section 3.4.3 indicates that the homologue patterns of the net TI Pool loading during two Transects (3 and 6) are characterized by a higher loading from the Pool with a homologue pattern dominated by dichlorobiphenyls. The data seems reasonable (compare Figures 3-102 with 3-103) but the case for temporal variations (Figure 3-103 March versus August) at the TI Dam is less persuasive as the reader has no knowledge of the analytical variability of the individual congeners. Indeed the lack of information regarding analytical precision is a major problem in reading the DEIR. Much is made about trends and visual comparisons but the reader cannot independently evaluate their significance.

Book 3 of the Responsiveness Summary provides additional evidence of a change in the homologue pattern. An argument is made (page 18) that, at a time of low load (summer 1997) and low flow, the data show "the usual strong shift to mono-, di- and tri-chlorobiphenyl dominated pattern" for the TID relative to Rogers Island. Unfortunately, this is difficult to see from the provided Figure (2-1). Figure 2-2 is more illustrative in that it shows, at a time of low upstream load (summer 1997), a shift to a pattern enriched in the mono- and di-chlorinated congeners relative to Aroclor 1242. It is noted that these data are similar regardless of whether the TID-West or center station data are used. This reviewer cannot, however, see that this plot makes the case for enrichment of the trichlorinated

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congeners; the only apparently significant changes are in BZ#1 (mono) and BZ#4+10 (di). It is unfortunate that there is no comparison to the Rogers Island data in this instance as a direct comparison of the two patterns would have strengthened the argument. Nevertheless, as will be shown later in this document (Part B.3), an alternative analysis of the Transect 6 data by the reviewer confirms the difference in congener fingerprint between Rogers Island and the TI Dam.

Given that there is a distinctive change in the congener pattern, it remains to determine if this is derived from the sediments of the TIP. Section 3.2 of the DEIR makes the case that the "load at the TI Dam is derived almost entirely from the sediment given the consistency of the total TI Dam load and its homologue pattern." The Responsiveness Summary provides the most direct evidence by making a comparison between Aroclor 1242 and the composition of the surface sediments from the TIP. The sediment patterns (Figure 2-3, page 22) appear to be significantly dechlorinated relative to unweathered Aroclor 1242 – less obvious are the suggested differences between the cores within a reasonable limit of analytical variability.

The enrichment in the lightly chlorinated PCBs in the water column could be a result of resuspension of dechlorinated sediment. An alternative mechanism is diffusion and pore water advection – which could move the more soluble congeners (dissolved and DOC-bound) into the surface sediments. The Responsiveness Summary makes the case (Sections 2.3.1 and 2.3.2) that the congener patterns can only result from a mix of pore water and direct exchange of sediment with the water column. It further argues (Section 2.3.3) that the less strongly sorbed lightest congeners will be more easily mobilized from depth relative to the more strongly sorbing congeners.

Section 5.4 of the Responsiveness Summary examines the potential effect of the Bakers Falls area releases on six sediment cores. Comparison of the Aroclor 1242 equivalent concentrations in the surface sections, 0-2 and 2-4 cm, suggests that surface layer PCB concentrations had been increased by recent upstream loadings. The evidence is not strong as many of the changes must be close to analytical variability (no comment is made as to what is significant or not). It is unfortunate that congener fingerprints were not used. In a reanalysis of some of the data by this reviewer (described later in this report), the Rogers Island East Core (core 26) appears to have a different composition than the other cores. It would be interesting to know if this is due to a greater proportion of recent input.

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In conclusion, the PCB load can be reasonably associated with historically contaminated sediments but the contribution of recent inputs must also be considered. It would appear that USEPA has reached a similar conclusion, at least according to a statement in the DEIR Responsiveness Summary (Book 1, page DEIR-47) - "it is highly unlikely that either PCB type (i.e. old or recently-contaminated sediments) is solely responsible for the water column load generated by the sediments. Most likely, the PCB load is a combination of both recently deposited and older PCBs." I concur with this statement.

2. *Are the two-phase and three-phase partitioning coefficients, derived in the DEIR, appropriate and do they properly address the physical parameters of the system (e.g. temperature)?*

The calculation of the constants appears to have been conducted according to normal procedure but rigorous analysis is left to those more expert in this area. Comments are, therefore, restricted to concerns regarding the degree to which one can accept the conclusions drawn from these constants.

It is presumed that 126 vice 130 congeners were used in the analysis.

Figures 3-13, -14 and -15 plot K_{Pa} for various congeners with River Mile for different Transects. Various conclusions are drawn – such as partitioning at Waterford (RM 156.6) is very similar to that in the freshwater portion of the lower Hudson (at least for Transects 1 and 6). Given at least the variability of the constants (not obvious and not shown on the plots), one must question the conclusions as well as the common sense in attempting an interpretation of any kind.

3. *Are the conceptual models based on the transect sampling consistent with the data?*

In general, the conceptual models are consistent with the data obtained from the transect sampling. The discussion put forth in Appendix C, Book 1 of the Responsiveness Summary for Volume 2C-A Low Resolution Sediment Coring Report is, for the most part, much more convincing than that in the DEIR itself.

Concurrence with several aspects of the general construct of the conceptual model for water column PCB transport (section 3.2.4, pages 3-59,60 of the DEIR) is straightforward and it is useful to briefly summarize these:

- It is clear from the data that there is no significant PCB load generated above Bakers Falls although it is optimistic to conclude that background = 0. It is unlikely that there is any region of the earth, including the poles, where there are zero PCBs.

- The principal source of PCBs to the freshwater Hudson is undoubtedly the GE facilities as there are no other apparent sources such as tributaries and atmospheric input is expected to be small. Direct input and re-release via sediment suspension and/or porewater exchange are the only remaining pathways.

- The congener patterns are consistent with a mixture of Aroclors with 1242 dominating.

- As noted in response to an earlier question, the TI Pool is a substantive source of PCBs, consistent with the framework for the conceptual model.

The conclusions of the "Revised Estimates of PCB and Suspended Solids Loads in the Upper Hudson River" (LRC Responsiveness Summary, Appendix C, Book 1, pages C-14, 15) indicate that the revisions do not require a major modification to the main conclusions of the DEIR. It is noted that concept of year-round conservative transport has been abandoned and that (page C-13) "Low flow/low temperature or high flow conditions yield near conservative transport. During late spring and summer conditions, the total PCB load is not conservative and declines downstream of the TI Dam." This seems reasonable in light of the revised load data.

I have less confidence in the congener specific arguments even though the presentation in the Low Resolution Coring Responsiveness Summary is much improved over that found in the DEIR. Visual comparison of homologue patterns (e.g. Figures 3-36 to 3-49, DEIR) is not very convincing – especially as it is not obvious as to how analytical variability would impact on the conclusions. Indeed, analytical variability is not mentioned –at least often – and the reader must ask whether it was forgotten. It is noted that several sections of the Responsiveness Summaries address this point and this is a distinct improvement. Nevertheless, it is very difficult *for the reader to determine* what is statistically significant or not.

Amongst Figures C-6 through C-31 (LRC Responsiveness Summary, Appendix C, Book 1) are plots showing the PCB load for mono-, di-, tri- and tetra-chlorinated congeners with River Mile. Considerable interpretation is made of the changes in these plots but it is not apparent what the

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variation is about each point. In one instance (page C-11) a comment is made about a 50% loss in monochlorinated congeners and that this change is beyond the analytical uncertainty. This begs the question of what analytical uncertainty was considered when interpreting *any* of the plots. One can make some assumptions based on the comments regarding Figure C-31 (which shows a downward slope for all congeners from the TI Dam to Waterford) as it is stated (page C-9) that there is a "similarity of the homologue pattern between the TI Dam and Waterford" thereby suggesting that the slope is not significant. This raises questions about the interpretation of other plots, particularly those representing low PCB loads (lower concentrations near detection limit may be less reliable) from just the Figures. Statements (page C-11) such as "these changes are quite substantial...and are well beyond any analytical variability" are a distinct improvement over the DEIR but it should be stressed that there is no way that the reader can independently verify such conclusions with the information provided.

More worrisome is the use of homologue patterns in this section and throughout the report. In view of the rigor of the analytical program (i.e. 126 congeners in most cases) it is surprising that a more rigorous statistical approach was not used – such a principal components analysis (PCA) to interpret congener specific data.

In order to examine the conclusions made in the DEIR, three of the Transects (1, 4 and 6) were examined using PCA. Data were obtained from the Hudson River Reassessment Database (Release 4.1). Plots are appended as Annex A to this report. It should be stressed that this was a cursory attempt to see if the DEIR conclusions could be confirmed by another approach. Some interesting points can be noted and these are summarised for each of the Transects examined. Comparisons are made to the conclusions found in the DEIR and associated Responsiveness Summary.

Transect 4

Plot 1 presents the preliminary PCA for dissolved and particulate phases of the water column samples collected during this Transect (April; spring flood). Samples are labelled with d and p prefixes indicating dissolved and particulate phases. The first number denotes the sampling station number and the second the transect; e.g. the dissolved fraction collected at Rogers Island during Transect 1 is labelled d4-1. As time only permitted a cursory examination of the data, this discussion and those that follow will be similarly restricted. In simplest terms, samples that project in the same region of a PCA plot may be assumed to have similar compositions.

It can be noted that the dissolved and particulate samples generally project differently. The samples collected from Glens Falls and the Fenimore Bridge (stations 1 and 2 respectively) appear at the right side of the plot; tributaries are widely scattered throughout suggesting different and variable inputs of PCBs. These observations are consistent with the argument that the tributaries do not contribute to the congener composition of the Upper Hudson. Most pertinent is the behaviour of samples associated with stations at the Remnant Deposits (stn 3), Rogers Island (stn 4) and the series of samples from the Thompson Island Dam (stn 5), Schuylerville (stn 6), Stillwater (stn 7) and Waterford (stn 8). All samples from the Remnant Deposits to Waterford cluster tightly together. *This observation is consistent with the conclusion (page C-8, Book 1) that total PCBs are transported to Waterford in a conservative manner.*

Transect 1

Plot 2 displays the results of the sampling for this Transect (Jan/Feb). Fenimore Bridge and some tributaries project to the right side. The dissolved samples for the TI Dam, Schuylerville and Waterford cluster tightly – indicating similar composition – but are very different from the Remnant Deposits. The corresponding particulate samples are not as tightly grouped but appear to the left side of the plot. It was noted in the DEIR that the Rogers Island sample was suspect and this is confirmed by the PCA – both the dissolved and particulate samples project tightly and to the right side. *These observations are reasonably consistent with the conclusion that the water column load originating above the TI Dam is transported in a near-conservative manner, for all homologues.*

Transect 6

Plot 3 presents the results of the PCA for this transect (August). Once again, background samples (Glens Falls, Fenimore Bridge), both particulate and dissolved, project to the right side of the plot and the tributaries are widely scattered. The dissolved samples for the TI Dam, Schuylerville and Waterford are clustered as are the particulate samples (although these project to the left of the dissolved samples). The dissolved samples for the station at the Remnant Deposits and Rogers Island are tightly grouped but this is not the case for the particulates. This plot would suggest that the congener composition is maintained from the TI Dam to Waterford, not showing a loss in mono- and di-chlorinated congeners as discussed in the Responsiveness Summary. This difference may be due to the insensitivity of the PCA to the loss of the lightly chlorinated congeners (the PCA was run using all congeners) but it does raise questions.

The PCA plots do indicate that at low flow, sources above the Thompson Island Pool do not significantly influence the congener profile at the TI Dam through to Waterford. This provides additional verification of the importance of the TI Pool.

The surface sediments from the high resolution coring study were also examined by PCA (Plot 4). In general, background (s27 = core 27 at RM 202.9) projects to the right of the plot and tributaries and lower Hudson River samples are widely scattered. Most of the remaining samples project to the lower left with the exception of core 26 from Rogers Island East which is displayed to middle lower section of the plot.

It is recommended that the significance of the congener profile changes from the TI Dam to Waterford be discussed at the Peer Review.

4.   *Does the sampling at bias of samples collected at the TI Dam-West sampling location impact EPA's conclusion that the sediments of the TI Pool are the major source of PCBs to the freshwater Hudson during low flow conditions considering the analytical corrections made to GE's PCB data? What are the other implications of finding higher concentrations along the shoreline than in the center channel?*

The arguments put forward in Section 1.0, Book 3 of the DEIR Responsiveness Summary as well as Appendix C, Book 1 of the Responsiveness Summary for Volume 2C-A Low Resolution Sediment Coring Report appear reasonable. Evidence for the bias is persuasive but much of the effect appears to be mitigated by the analytical corrections.

The ratio between center channel and TID-West appears to approach unity as either flow or upstream concentration increases and this is consistent with the explanation provided – i.e. that increased flow creates greater lateral mixing and that as the upstream concentration increases it will overwhelm the effect from the nearshore areas. An intriguing argument is made (section 1.4, Book 3) that the actual daily load transported downstream may be an average of the TID-West and TIP-18C observations.

The correction factors and the revised load calculations are consistent with EPA's conclusion that the sediments of the TI Pool are the major source of PCB to the freshwater Hudson during low flow conditions. The conclusion (Appendix C, Book 1) that the net result of the revisions (including flow

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corrections) is ≈20% lower overall loads in the Upper Hudson under low flow conditions appears warranted.

Furthermore, the presence of a bias is consistent with the argument that hot spots within the TI Pool are a source of PCBs to the water column. The point made in the Responsiveness Summary (page 43) – "Elevated concentrations in near shore low velocity areas are consistent with a pore water flux loading mechanism, which would result in higher concentrations where dilution flow is lowest" – is quite reasonable.

5.   *Are the geostatistical techniques (polygonal clustering and kriging) correctly applied/*

The techniques appear to have been correctly applied. I would prefer to see a range of estimates for the PCB inventory. Reporting the calculated inventory to a decimal place strikes me as overly optimistic and potentially misleading to the public – considering the variability in the results (not stated) and the two estimates – 19.6 and 14.5 - that have been determined.

6.   *Are the methods applied in the DEIR (change in molecular weight (MW) and evaluating concentrations of BZ#s 1, 4, 8, 10 and 19 (MDPR) appropriate standards for determining extent of dechlorination? Are there any significant problems with this approach, or more appropriate approaches?*

The molar dechlorination product ratio (MDPR) relies on the measurement of five specific congeners in order assess the degree of dechlorination in sediments. The congeners used (BZ# 1, 4, 8, 10 and 19) all possess chlorines in the ortho positions on the assumption that anaerobic dechlorination processes only remove meta and para chlorines.

The DEIR notes, correctly, that the less chlorinated congeners are more soluble and more susceptible to aerobic degradation processes and may be lost from the sediments more readily, in which case the MDPR will underestimate the actual degree of dechlorination. It might also be expected that the less chlorinated congeners could be lost, by similar mechanisms, from the sediments prior to the establishment of the anaerobic conditions that are essential to dechlorination – in such a case the MDPR would be reduced.

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The MDPR will also underestimate the degree of dechlorination if ortho-substituted chlorines were removed. There is evidence in the literature of ortho-dechlorination [Van Dort and Bedard, Appl Environ Microbiol, May 1991, 1576-1578; Berkaw, Sowers and May, Appl Environ Microbiol, July 1996, 2534-2539 (marine sediments)]; if this is significant in the Hudson River sediments, the reliability of the MDPR will be compromised.

The change in mean molecular weight, ΔMW, is less susceptible to the points noted above. However, loss of the lighter congeners – a likely possibility – would increase the molecular weight of the mixture and reduce ΔMW.

Low values of MDPR and ΔMW found for the sediment samples from the Lower Hudson River are interpreted (DEIR, page 4-63; Figures 4-19.20) to be representative of lower levels of dechlorination with only some loss of lighter congeners. The linear relationship between MDPR and ΔMW (DEIR, Figure 4-21) is the most convincing evidence that contributions from the above-mentioned processes are minimal and that the approach is appropriate.

Both the DEIR and the LRC normalize data to BZ#52 (2,2'-5, 5'-tetrachlorobipheny). Considering the dechlorination argument, it is surprising that this congener does not undergo removal of the meta-chlorines.

7.   *The DEIR finds that the degree of anaerobic dechlorination is primarily a function of original concentration rather than time, and accordingly that there is not significant predictable dechlorination in sediments containing less than approximately 30 mg/kg PCB. Is this reasonable?*

No. I do not agree with the conclusion as originally suggested in the DEIR (page 4-68) in discussing Figure 4-22; namely, that "the distribution of the data strongly suggests that virtually all samples with PCB concentrations greater than 30ppm are measurably altered with respect to Aroclor 1242. More convincing are the conclusions stated in the Responsiveness Summary (Book 1, page DEIR-62 and elsewhere): "Below 30ppm, the occurrence of dechlorination is not predictable using ΔMW as a measure, because data fall above and below the initial ΔMW of Aroclor 1242. It is possible that samples with ΔMW values less than that of an Aroclor 1242 have undergone dechlorination and preferentially lost the mono- and di-chlorobiphenyls."

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In our own work (unpublished) we have found no such threshold for dechlorination of even the more recalcitrant Aroclors (such as 1260). Experiments with concentration ranges from 5 to 500ppm gave essentially the same percent dechlorination (e.g. 80% removal of hexa-chlorinated biphenyls). Rates were low at low PCB concentrations but there was no threshold concentration in the range tested. Inhibition was noted above 500ppm for Aroclor 1260.

Although not part of this charge, the argument for lack of correlation of dechlorination with age is not totally convincing. Figure 4-23 in the DEIR appears to suggest this but the results could be overwhelmed by the relationship to total PCB concentration. Figure 4-24 could be interpreted as a correlation with age when analytical variability about each data point is included.

C.   Response to LRC Questions

Note: The Responsiveness Summary for the LRC is quite extensive and includes numerous corrections as well as an alternative calculation for the comparison of sediment inventories in the Thompson Island Pool. The Summary was received later than expected and it was not possible to conduct a detailed review prior to the submission of pre-meeting comments. Accordingly, the following comments are intentionally brief. A more detailed examination will be completed prior to the peer review meeting.

1.   *In the LRC, EPA compared sediment data from cores taken in 1977, 1984 and 1994, which had the PCB analysis conducted by different laboratory methods. How valid are the methods used to establish a consistent basis for comparison?*

The correction factor developed in Appendix E of the LRC and the arguments supporting it seem quite reasonable. Using the Σ trichloro to decachloro homologues puts both sets of data on an equal footing. It is interesting to note (Responsiveness Summary, page LRC-41) that this approach is being reviewed – presumably this information will be made available before the LRC is considered complete.

Given the effort to make meaningful comparisons between the 1994 and 1984 data, it is surprising that there is little discussion of the potential problems associated with the 1977 information. It is noted (page 4-21, LRC) that "the simple sum of the reported Aroclor values yields an estimate for

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total PCB concentration, which is probably the best that can be done to create a value for comparison to the low resolution coring results." It is agreed that this is probably the best that can be done but it does suggest that any trends derived from comparison of these data should be qualified.

2.   *In the Upper Hudson River system, it has been well established that there is significant lateral heterogeneity in sediment concentrations. While it was attempted to reoccupy previous locations, some uncertainty is added with respect to the actual sampling location. While the statistical techniques help compensate for this, how does the sample heterogeneity affect the comparison of cores from two different years? Given the spatial variability, is the finding that there is a loss from most locations supported by the data?*

Sample heterogeneity is always a concern in such an investigation. The Responsiveness Summary appears to provide a more convincing argument in favour of the validity of comparing the 1984 and 1994 data than does the LRC.

The sampling locations were reoccupied with quite good accuracy (Responsiveness Summary page LRC-5). Equally important is the fact that, within the clusters, the sampling density matched that of the NYSDEC study – thereby strengthening the ability to make comparisons. It is stressed that the intention of the study was to assess the direction and approximate magnitude of change of the PCB inventory over the intervening period. The reanalysis of the data – presented in Appendix A, does suggest that there has been a general loss; it further emphasizes the difficulty in assigning an absolute value to this loss. This seems more reasonable than the impression one might get from the LRC even though the word *approximately* is used in the discussion.

3.   *What is the impact of the difference between replicate samples in the 1994 sampling effort (36 percent average variability) on the finding that there was a 40 percent loss of PCB inventory from the highly contaminated sediments in the TI Pool?*

The point made in the preceding response is emphasized by this question. There is a tendency once a number – i.e. 40% - is cited to forget the 'approximately' qualifier.

A quick read of the Responsiveness Summary (Appendix A) suggests that the estimated loss has been revised but that the value is in agreement with that presented in the LRC. A case is also made (LRC-11 to 19) that the low-resolution cores have uncertainties closer to 20% vice the 37% originally

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proposed. No mention is made in either report as to the uncertainty associated with the 1984 data, but one could assume that it is about the same – i.e. approximately 20-30%. The point (LRC-71) that dividing by the 1984 concentration has the effect of normalizing the 1994 and 1984 data to account for analytical uncertainty is a good one. Again, the data appear to be consistent with a loss of PCB inventory from the highly contaminated sediments of the TI Pool; a comment on the magnitude of this change is left to those who can more adequately review Appendix A.

4. *In the LRC, it was found that Hot Spot 28 contained much more mass than previous estimates. Is the conclusion that this "gain" is primarily due to incomplete characterization in 1977 valid?*

Yes. The argument that the 1977 samples underestimated the amount of PCBs whereas a more complete characterization was achieved in the recent program is reasonable. Several lines of evidence seem particularly persuasive. These include the ^{137}Cs data (Figure 4-25) which show that in 1994 the bottom of the core represented true background as well as the argument that there would be insufficient quantity of PCBs to so dramatically raise the sediment inventory between 1977 and 1994. The general statement that the earlier studies probably underestimated the PCB inventory provides additional support.

5. *Does the data set and its interpretation support the conclusion that significant losses have occurred from hot spots below the TI Dam?*

The data set is consistent with a statistically significant loss of 50 to 80% for hot spots 31, 34 and 37 whereas hot spots 35 and probably 25 are unchanged. It is presumed that the term "significant" in this question relates to statistical significance. Caution should be used in calculating overall mass changes given the challenges in comparing the analytical data from the two eras.

6. *The LRC found that the historically contaminated sediments in the TI Pool were not universally being buried and sequestered from the environment. How much confidence would you place in the LRC evidence against widespread burial?*

The evidence provided in the LRC - in particular the loss of sediment inventory and that the depth of contamination has decreased or remained the same – is consistent with the water column information

described in the DEIR. Accordingly, the weight of evidence argues against widespread burial – at least deep burial.

7.   *Is the interpretation of the sidescan sonar data appropriate and supported by the analysis of the associated sediment properties?*

The comparison of the sonar images with the 1976-1978 NYSDEC sediment survey seems reasonable.

D.   General Questions

1.   *Is the data set utilized to prepare the DEIR, LRC and Responsiveness Summaries sufficient to understand the fate and transport of PCBs in the Upper Hudson?*

It would appear that the data set lays out the overall understanding of the fate of PCBs in the Upper Hudson. The debate that appears in the Responsiveness Summaries – namely the relative influence of the TIP and releases from the Hudson Falls facility – could, however, be dealt with by direct comparison of current data showing the relative loads at Rogers Island and the Thompson Island Dam. Several points allude to this comparison but I could find no direct evidence.

2.   *Are there any additional analyses that should be done to verify certain findings of the DEIR and LRC?*

I would have liked to see more discussion of the effect of analytical variability in the DEIR documents and the application of techniques such as principal components analysis.

E.   Recommendations

I will finalize my opinion at the Peer Review when I have heard the comments of the other reviewers but my preliminary opinion is that the DEIR and the LRC are acceptable.

The question of revisions hinges less on the need to make a more substantive argument than on what the reports will be used for next. If they are to be used as a basis for the next report and the new

conclusions and statements that appear in the Responsiveness Summaries are to be incorporated at that point, there is little use in making revisions to the DEIR and LRC. If these conclusions are to be publicly accessible, however, a succinct summary document would be very useful.
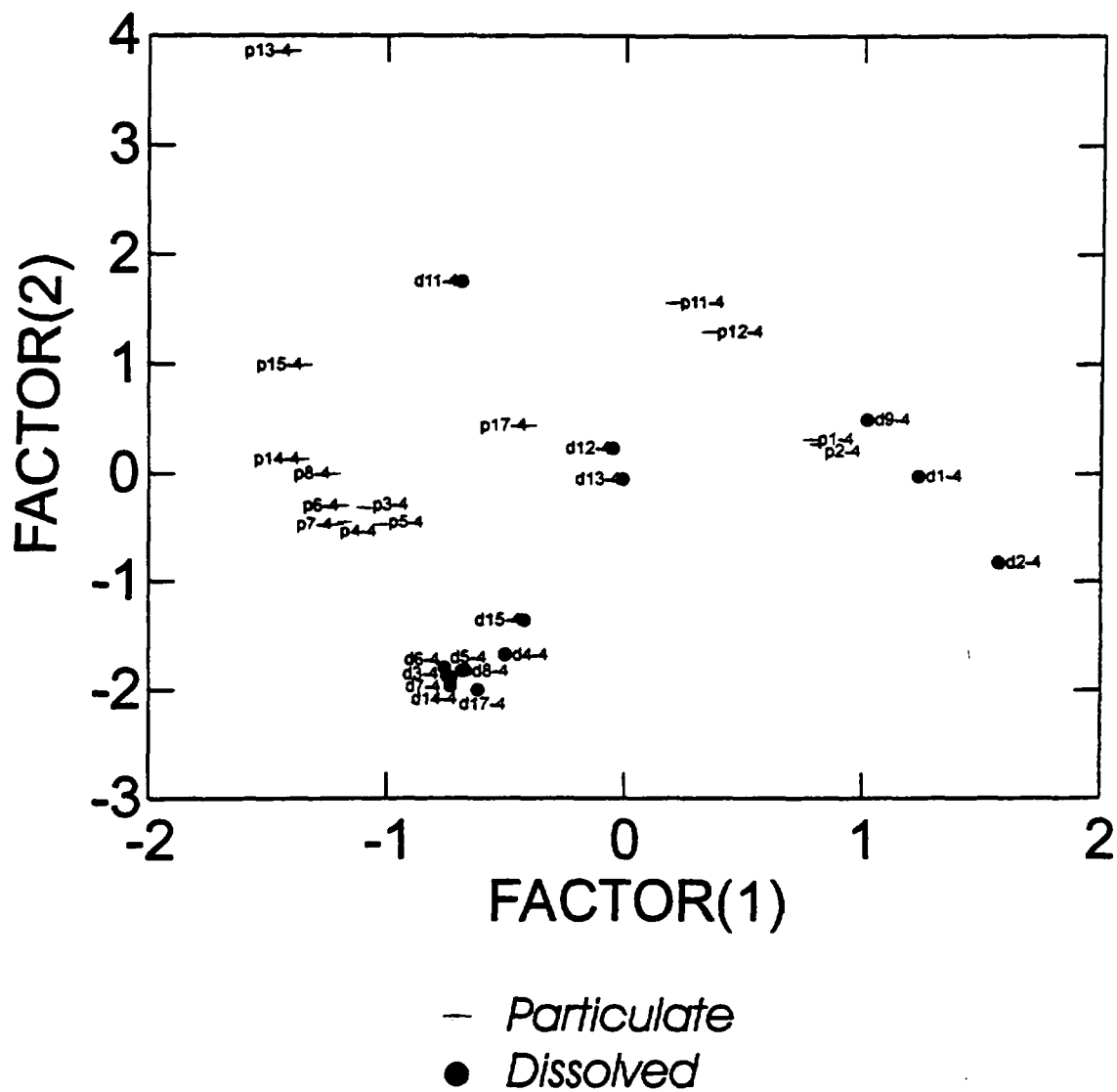
ANNEX A

Principle component analysis (PCA) was carried out to explore patterns in the PCB congener data. In this indirect gradient analysis, all of the variables (in this case congeners) are considered simultaneously; variance in the congener data is explained by fitting a straight line through a multidimensional normal curve, using a converging iterative ordination algorithm, such that the residual sum of squares is minimized. This line is the first ordination axis, or first principal component. Further axes are constructed in the same way, with the constraint that they are uncorrelated. This technique is thus a convenient way to summarize multivariate data in two dimensional space.

PCA was carried out using the statistical program SYSTAT (version 6.0.1). Twenty-eight surface sediments, and 83 water samples (separated into dissolved and particulate phases) were normalized using standard techniques and then ordinated according to their congener profiles (based on 126 congeners). PC axes 1 and 2 explained 44.3% and 7.0% of the total variance in the data indicating that PCB congeners explain the bulk of variation in the samples collected.
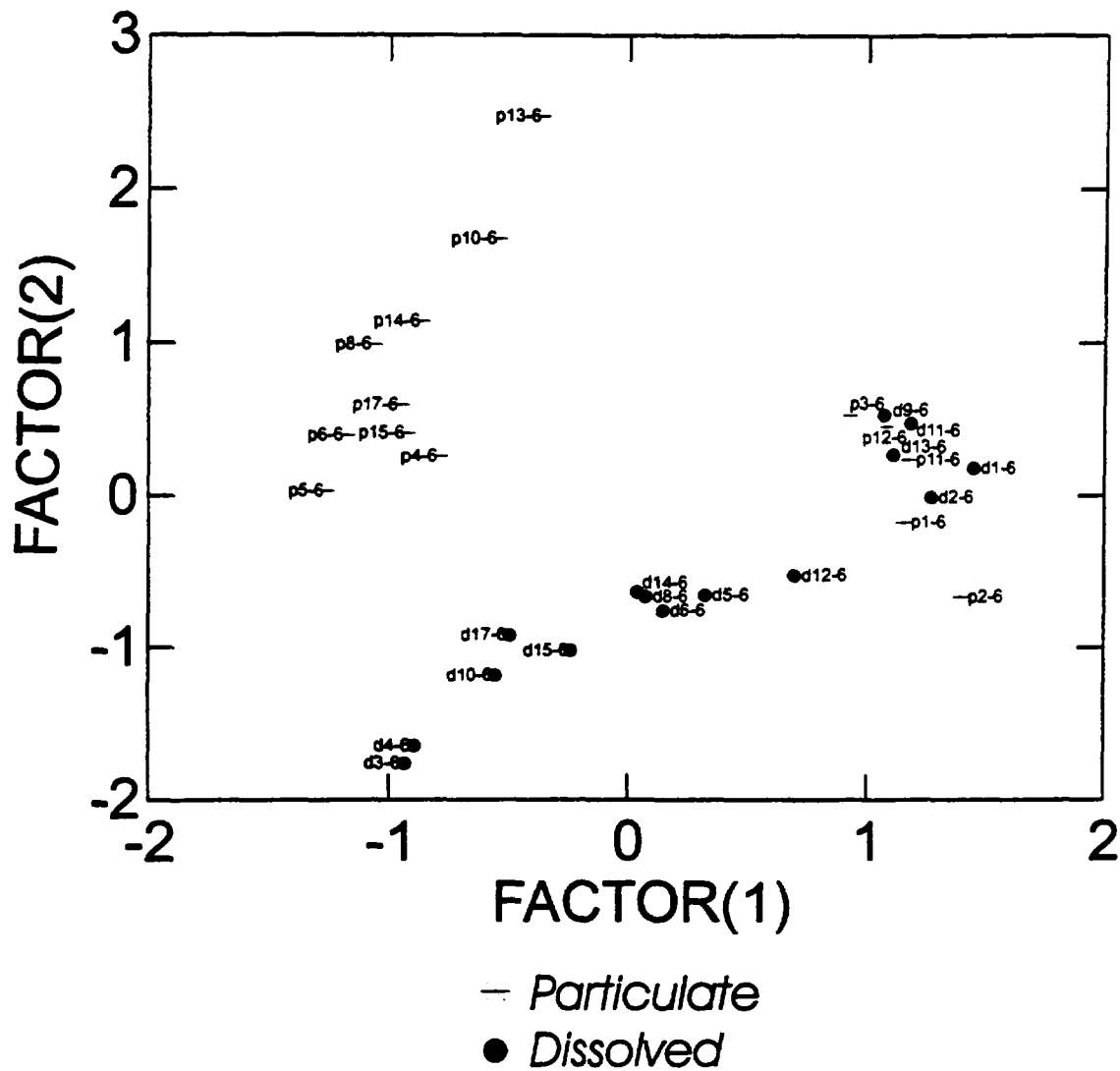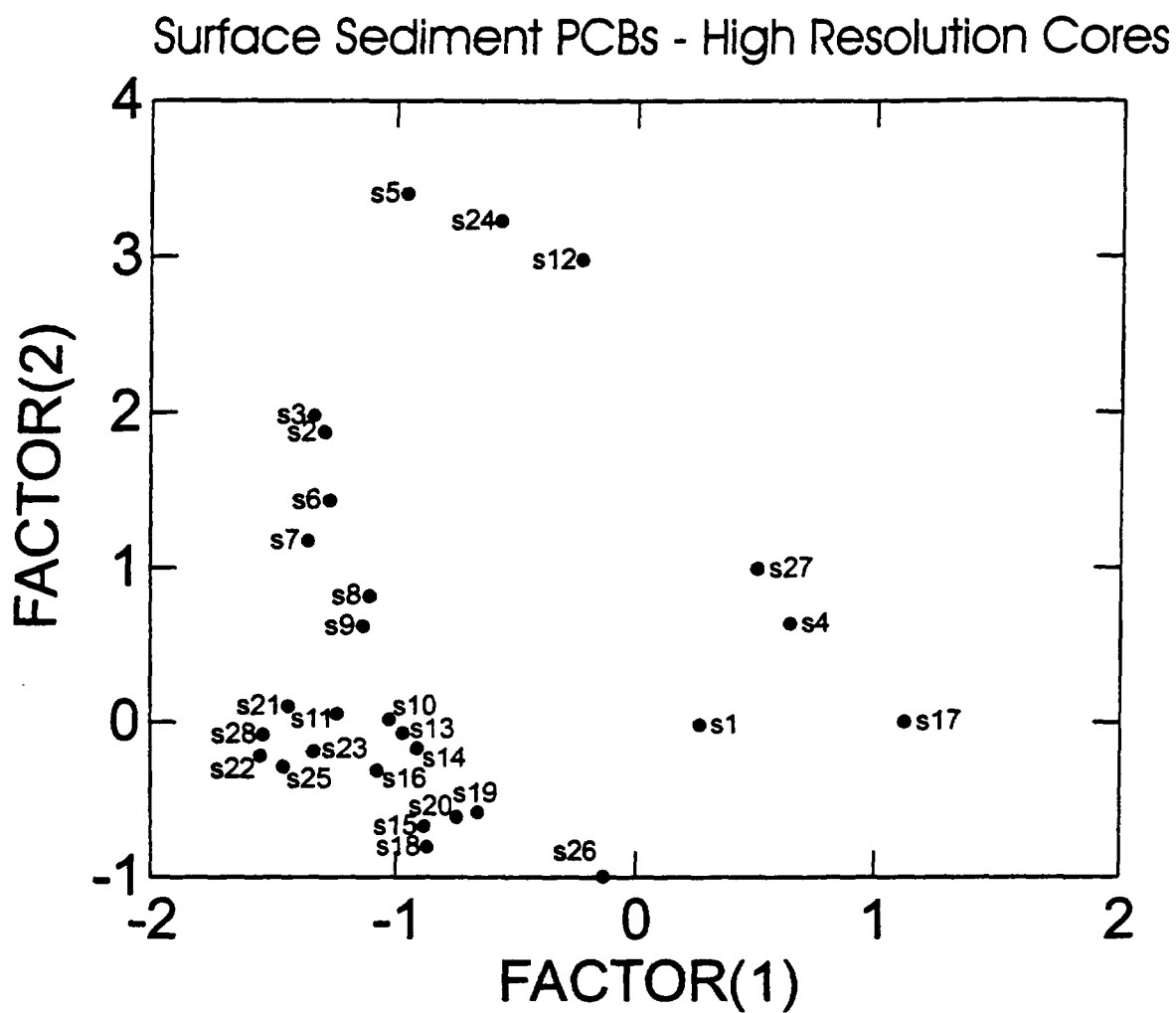
Transect 4 - Particulate and Dissolved PCBs

— Particulate
● Dissolved

Transect 1 - Particulate and Dissolved PCBs

Figure legend:
— Particulate
● Dissolved

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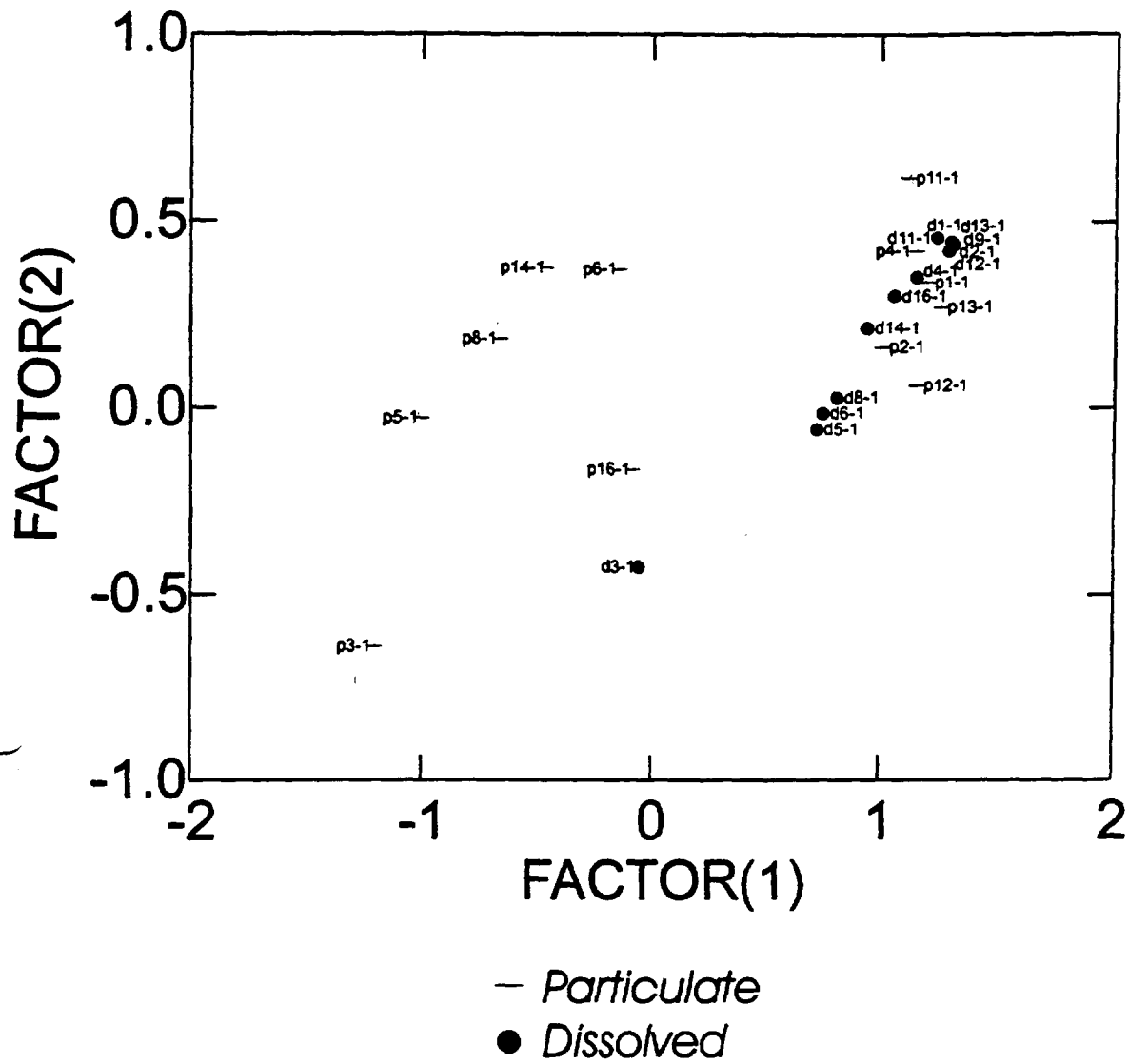
Transect 6 - Particulate and Dissolved PCBs

- — Particulate
- ● Dissolved

Surface Sediment PCBs - High Resolution Cores

Dr. James Risatti

Dechlorination Index.

The dechlorination index,used in this report (MDPR), is based on a ratio derived from the sum of the molar concentrations of congeners BZ-1,4,8,10,and 19 found in the sample, divided by the sum of 126 congeners identified in the study (V:2C,bk1,pg 4-56). The degree of *in situ* dechlorination is determined relative to Aroclor 1242 by calculating a similar ratio from Aroclor 1242 and using the Aroclor 1242 index as a base value. This value (0.14) is subtracted from the sample ratio to give the degree of *in situ* dechlorination.

Harkness et al.(1993), characterized the extent of *in situ* dechlorination in a Hudson River sample by noting the amount of mono- and dichlorobiphenyls present relative to the predominant Aroclor originally released. The product of complete PCB dechlorination is an unchlorinated biphenyl molecule but in Hudson River sediments the dechlorination scheme favors removal of chlorines at the *meta* and *para* positions which leaves congeners containing *ortho* chlorines such as BZ 1,4, 8, 10, and 19 to accumulate as ultimate or penultimate products. For Hudson River samples the suite of congeners selected for the MDPR would appear to reasonable but there are other issues inherent with the MDPR which reduce its effectiveness as an indicator of dechlorination.

The major problem associated with a using a PCB dechlorination index based on final product accumulation is diminished confidence that the measured product is a true representation of the original compound mixture. In addition to lower ECD response (particularly BZ 1), the less chlorinated PCB congeners are subject to aerobic degradation and to physical-chemical movement out of the sample environment. Aerobic degradation has been recognized and has been well studied for some time (Ahmed and Focht,1973, Furakawa, et al. 1978 and Beddard et al., 1986, among others); although some isolated cultures can degrade specific highly chlorinated biphenyls, most aerobic PCB degrading bacteria favor the less chlorinated mono-, di- and tr- chlorinated congeners as substrates. Furakawa, et al. (1978) also found that in addition to more rapid degradation of the lower chlorinated congeners,the non-chlorinated ring was preferentially degraded. A screening study by Beddard et al., (1986) indicated that BZ 4 and BZ 8,both of which are used for the MDPR, were rapidly degraded by the environmental isolates used in the study.

The mono-, di- and tri- chlorinated congeners are also more readily lost from the sample pool by sorbtion and partitioning into the sediment pore water and into the water column than are the more chlorinated congeners. In the report (pg 3-31), it has been recognized that the movement of BZ 1,4,and 8 out of the Thompson Island pool sediments "may be facilitated by binding to dissolved organic carbon" and that PCBs in general "may move from the porewater to the water column by diffusion and groundwater advection of dissolved and DOC-sorbed phases."(pg 3-31). Lastly, the report notes that because of their lower partitioning coefficients, the " concentration of mono- and dichlorobiphenys is enhanced in porewater relative to more highly chlorinated congeners, which may facilitate loading of these congeners from the sediment to the water column " (pg3-39) and that the sediments of the TI Pool

released less-chlorinated congeners typical of dechlorinated sediments found in the Pool (pg. 3-2). Under ideal conditions (temperature, pH, DOX), biological and partitioning processes may become strongly interactive as biodegradation of the less chlorinated congeners maintains a disequilibrium in the sediment porewater and near the sediment surface.

Loss of the lighter congeners (BZ 1,4, 8, 10, and 19) directly affects the sensitivity of the MDPR by underestimating the amount of dechlorination. The underestimated difference depends on the MDPR estimate and the amount of BZ 1, 4, 8, 10, and 19 lost from the sample. Underestimates can range from about 2 percent in samples with a MDPR of 0.2 and 10 percent loss of the index suite to as much as 17 percent in samples with a MDPR of 0.6 but which has had 50 percent of the index congeners lost from the dechlorinated sample.

As an index to compare dechlorination or other PCB changes, it is better to use a ratio indicating decrease in concentration of two or more peaks selected from chromatograms of the PCBs in the system being studied. Murphy (1989) correlated changes in sediment PCBs from within Waukegan Harbor and with Lake Calumet by changes in the BZ18 / BZ17 ratio. Ideally, however, ratios of more chlorinated congeners having similar chemical characteristics should be used as they are less susceptible to aerobic biodegradation and partitioning into the aqueous phase and at lower concentrations still give a measurable ECD response (see Brown and Wagner ,1990 for ratios used in a study of the Acushnet Estuary sediments).

Also, for both MDPR and MW, Aroclor 1242 is considered as the as the only commercial PCB mixture in the sediments but in some areas, as much as 19 percent Arolor 1254 was found (pg. 2-19) and Brown et al., (1988) indicate that in the area of RM 194.8, their "hot spot " analysis indicates an average of 94 % Aroclor 1242, 5 % Aroclor 1254 and 1% Aroclor 1260/1268. Both of the indices should be weighted if they are to be used.

Limits of Dechlorination

The suggestion that dechlorination of PCBs is limited by PCB concentration has been suggested by laboratory dechlorination experiments with natural sediments (Quensen et al. 1988, Risatti,1992, Rhee et al. 1993 and Fish,1996) and discussed by Brown and Wagner (1990) in reference to field observations. Brown and Wagner (1990), state that there are no examples of PCB dechlorination at *isolated* low level (1-3 ppm) sites but that they have seen dechlorination in low concentration PCB samples collected near sites of active dechlorination. Quensen et al. (1988), working with Hudson River sediments found active dechlorination at PCB levels of 700 ppm, less active at 140 ppm and none at 14 ppm. In experiments with Waukegan Harbor sediment cultures (no PCBs added),that there was very little, if any, dechlorination at PCB concentrations of 150 ppm, some dechlorination at 1,500 ppm and very rapid dechlorination at 17,000 ppm (Risatti,1990 and unpublished data). Fish (1996) observed

rapid dechlorination rates in Hudson River sediments spiked with approximately 248 ppm to 25 ppm Aroclor 1242 and slow dechlorination rates at concentrations of about 9.9 ppm. A wide range of dechlorination limits observed have been observed in laboratory cultures and in field studies.

The authors state (page 4-68) that "the distribution of the data strongly suggests that virtually all samples with PCB concentrations greater than 30 ppm are measurably altered with respect to Aroclor 1242.". That is, dechlorination is limited at about 30 ppm PCB concentrations. The trend in Figure 4-22 suggestss a trend of increasing dechlorination with increased PCB concentration but from the figure the dechlorination threshold limit could be anywhere from 20 ppm to 40+ppm. Also, Figure 4-23 doesn't support the 30 ppm statement. Sub-sample 10 has approximately 55 ppm PCB but has undergone only 3 percent dechlorination. On the other hand, at horizons 1 and 2, 9 ppm and 6 ppm respectively, dechlorination is 16 percent and 21 percent. The middle horizons seem to be relatively consistent with extensive dechlorination and high PCB levels. The trend in Figure 4-24, indicates, for the most part, dechlorination increasing with both PCB concentration and depth (age), and that sample 1(approx. 26 ppm PCB) has been dechlorinated by about 21 percent.

Although there is evidence indicating that PCB concentration levels limit the degree of PCB dechlorination in sediments, the threshold concentration seems to vary with the sites examined as well as within the stations sampled including the ones investigated for this report. There does not appear to be a universal PCB dechlorination threshold limit. Given slight changes in conditions (which are as yet unknown), dechlorination may occur rapidly and at lower PCB concentrations; Beddard (1996) has managed to "prime" dechlorination in Housatonic River sediments which had lain dormant for years. However, the factors that induced 98%-99% dechlorination of specific congeners within 30 days from unammended, 15 year old Waukegan Harbor sediment cultures are still unknown. What is interesting about Figure 4-27 is not that it illustrates the contention of poor correlation between time and the dechlorination ratio but that most of the dechlorination in the Upper Hudson occurs within the envelope bounded by approximately 20 percent to 80 percent dechlorination and about 5 cm to 45 cm depth levels. This suggests there is a common factor in the system which influences dechlorination rates. It may be available organic carbon, reducing potential, or flushing of inhibitors or nutrients into or out of the system.

Most of the data presented in the report supporting PCB dechlorination limits is based on the molar dechlorination product ratio (MDPR). This index, as stated above, is not a useful measure of dechlorination and must be calibrated with another set of ratios determined from chromatograms of the samples and which avoid the problems inherent with the MDPR as derived in the report. Consequently, until the degree of error associated with the MDPR data are determined the usefulness of data derived from the MDPR are limited.

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It is much better to use ratios involving the more chlorinated congeners

The less chlorinated congeners used in the MDPR are more subject to aerobic degradation than the

Anaerobic degradation may occur but I'm not convinced that degradation rates are significant *in situ*.

Anaerobic degradation (alteration of the molecule by ring cleavage)   here has been some is products is valid but the major problem

ortho-substituted chlorines are more resistant to dechlorination (Brown, 1987, Abramowisz..) and congeners containing ortho-chlorines, such as the suite chosen for the MDPR also can be final products. associated with using mono-, di- and tri-chlorinated congeners is loss into the water column from the sediments or by aerobic degradation. The loss of "light" congeners from the sediment pool of congeners will give a MDPR that underestimates the degree of dechlorination.

Figure 1. Changes in the MDPR at specific dechlorination indices with postulated losses from the sediment of the "lighter" congeners used to determine the index.

Additional comments forthcoming

COMMENTS

Chpt. 1)

P1-2, Sect 1-2: The format should have been organized according to work plan tasks.

Should have a diagram showing tasks in the report and an outline for each chapter.

This chapter should also have for the report a tasks accomplished plot similar to a Gant plot.

1.4.4 - Analytical ChemProgram:

How about a flow sheet showing which samples were analyzed and methods for analyses.

How many congeners were actually identified as occuring in the study ? Particularly in the sediments ? - chromatograms would have been useful .

Chpt. 2.

P2-3: Air Monitoring for VOCs--were any PCBs detected ?

P2-5: Purchases by GE from 1955-1971 were 97.4% Aroclor 1242, (50.6.106kg) and 2.6% Aroclor 1254 (1.4.106kg)
(Brown et al., 1988--Science, V240,p. 1675)

Chpt.3:

P3-7: Samples should be specified as water samples - grab samples most often imply solid samples and it's hard to visualize grabbing "dissolved PCBs and ...

This paragraph is confusing - if these samples are not "appropriate" (does this mean not useful or not unbiased) why are they discussed and then how can they be "important to reveal possible non-equilibrium... "?

p3-8: Same paragraph as above. State the number of samples used (10 of 18 collected) and refer to the table (Table 1-1). I think the samples from tributaries since they were collected and analysed for PCBs could also have been used. Last paragraph. "Appear to represent" or are they a representative set ?

Figure 3-2.: A line graph showing change may have been better for POC

P3-10: Perhaps because theoretical values assumed equilibrium conditions - deviations from theoretical should be discussed

P3-12: Last paragraph. "Dissolved concentration (DOC) should be dissolved organic carbon

Figures 3-7 to 3-10: Do these represent single water samples taken at a point in the river at the RM given? Also, it would be helpful to have dates of collection below transect numbers -particularly since figure represents seasonal data

P3-17: Samples were held for four days- were they kept at 4° C ? Were measures taken to inhibit biological activity ?

P3-18: Maybe it should be assumed that disequilibrium in nature is the norm-regarding PCBs: if dechlorination, as an example, is occurring the PCBload is changing-generally from more chlorinated to less chlorinated congeners which in turn would alter the pore water concentration, etc. The process is probably not a slow, continuous reaction throughout the year, but probably goes in spurts as favorable conditions occur.

Figure 3-13: Why is BZ 52 on this figure?

Figure 3-16: At approximately RM196.8--does this suggest that more Mono, Di and Tri-s are being put into the water column from sediments? Could this be related to biological activity in the sediments?

Is this due to input of sediments from Rogers Island?

P3-24: Was this information regarding DOC (4 mg/l) etc. obtained during this study? I don't recall a prior discussion.

P3-27: What is the relationship of Hudson River [POC] and[DOC] to fitting data at Green Bay ?

P3-28: Why was BZ 151 used? It occurs in Aroclor 1254 but not at all in A 1242- Yet the emphasis particularly with MDPR and MW is put on Aroclor 1242.

P3-31 Sect 3.1.3: Makes case for flux of PCBs out of sediments from porewater to H_2O column by diffusion and groundwater advection of DOC and dissolved phases.

P3-35: What specific analytical differences were used by GE and could some of the Congener analyses from the GE study be used?

P3-38: Could reasons for non-equilibrium be due to addition of PCBs from (a) other than sediments and (b) movement of specific congener from the sediments to water column.

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P3-39: Lower partition coefficients (Koc and Kpoc) mono/di CBs concentration is enhanced in porewaters relative to higher Cl-congeners facilitating loading to water column from sediments.

P3-40: Were water samples kept on ice or biological activity inhibited in some way?

P3-53: Regarding suspension of fine grained cohesive sediments--could these sediments or a fraction of them, go into suspension (before flows reach the necessary shear stress levels) by impacts and scouring from saltating and suspended particles?

P3-59: Also, Aroclors 1260 and 1268 approximately 1%; Aroclor 1254 approximately 5% (Brown et al 1988)

P3-124: Were water and sediment samples examined by GE or just water samples?

P3-125: Report needs chromatograms.

P3-125: Coelution of BZ 4/10 common with DB-1 and DB-5- but why not group this peak and use in a ratio with other peaks in the chromatogram to measure change?

Figure 3-83: Follow text (p3-128) and put total PCB's on y axis label.

Figure 3-84 to 3-87: I think the y axis labels need to be corrected to fit the figure's legends.

P3-128: From these plots (Fig. 3-83 to 3-87) it would be interesting to determine rates of change between Roger's Island and TI Dam.

Why is there an increase through the winter months. It seems that the curve would flatten out as biological activity decreased as a result of lower temperatures. Also, eventually the curve must become asymptotic - could this possibly be used to get an estimate of the dechlorination rate.

P3-119: Why not use ratios of these congeners (BZ 56, 60, 70 and 74) as a measurement of dechlorination?

Chpt. 4)

P4-9/4-13: The occurrence (persistence) of wood and wood chips at surface and to 30cm depth is interesting--does the wood show any signs of degradation and have PCBs been extracted and analysed from any of the wood debris ?

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P4-5: 8. Should this read finer-grained sediments with and without higher total PCB inventories...?

Figure 4-7: Higher PCB levels do correlate with lower DN values, but there is a lot of scatter- In reality, DN values correspond to sediment type and not to PCBs - PCBs are more likely to be associated with finer grained sediments - it is a good approximation tool to help increase the probability of finding sediments with higher PCB levels.

P4-21: Last two lines: "finer sediments tend to be more easily eroded...". Would this also be true with clays or clay rich sediments?

Table 4-3: Check the natural log values.

Table 4-9: Notes: b. Refers to Eq 4-7 and 4-8 for definition of terms. These are not the correct equations (see pg 4-14).

P4-50: 4-3.1: Last line. Dechlorination "reduces" PCB to biphenyl-not "destroys" it because molecule is still intact -although it's nbo longer a PCB.

P4-51: Last paragraph-J. Brown, 1993 is not in reference list.

P4-54: J. Brown, 1987 reports the occurrence of BZ 54 in Hudson River sediments, probably a dechlorination product as according to it doesn't occur in Aroclors 1016, 1242, 1254, 1260, or in Clophen A30, A40, A50, and A60 (Schulz et al 1989).

P4-56: Underestimation could be greater than 5% depending on the amount of light congeners lost and the MDPR ratio.

P4-57: Aroclor 1242 is not primarily a tri-chlorinated biphenyl mixture but instead a tetra- and penta-chlorinated mixture. Tetra-CBs comprise about 31% and penta-CB about 29% of the congeners found in Aroclor 1242 by Frame et al.,(1996) See attached Table I . Table II indicates the Aroclor 1242 congeners listed in the report- (Table 4-8) the differences in the congeners found in the same commercial mixture (Aroclor 1242) Particularly the larger number of Hexa- and hepta chlorinatedbiphenyls.

P4-57-P4-65: See discussion of MDPR.

Figures 4-23. 4-24: the RMs in the text differ from those on in the figures.

P4-71: Brown and Wagner (1990) have found dechlorination in marine sediments of the Acushnet Estuary.

A.5.2.6: Why was OCN used as a recovery standard? Hexachlorobenzene (HCB), among others, would have been a good choice. It gives a good ECD response, and with an HP-5 or Rtx-5 column shouldn't co-elute with any congener. OCN would have better served as an internal standard. This would have facilitated gc peak identifications by enabling comparisons relative retention times determined by Mullin et al.(1984) for all 209 congeners on a similar column. It seems strange that OCN would breakdown during extraction. Was the OCN standard chromatographed to   determine if it was pure ?

Holding times: Were sediment and water samples maintained at 4°C after collection and prior to extraction ?

Pg.A-10; B-11: Why was BZ18 used to differentitate Aroclor 1016 from Aroclor 1242? Why not a ratio of BZ 56 Aroclor 1242 to BZ 56 sample? There is about 30X more BZ 56 in A1242 than in A1016.-   Even with extensive dechlorination (90%) the ratio would still work and could be used to measure dechlorination.

Table I. Congeners in Arochlor 1242 (wt.% ≥ 0.05). Compiled
             from Frame et al. (1996).

nCl	IUPAC NUMBER
1	1, 3
2	4, 5, 6, 7, 8, 9, 10, 12, 13,15
3	16, 17, 18, 19, 20, 22, 24, 25 26, 27, 28, 29, 31, 32, 33, 35, 37
4	40, 41, 42, 43, 44, 45,46, 47,48, 49, 51, 52, 53, 55, 56, 59, 60, 63, 64, 66, 70, 71, 74, 76, 77
5	82, 83, 84, 85, 86, 87, 89, 91, 92, 95, 97, 99, 101, 102, 105, 109, 110, 114, 115, 118, 119
6	138, 149, 153

Table II. Congeners (wt.% ≥ 0.05) in Arochlor 1242 from Report Table 4-8

nCl	IUPAC NUMBER
1	1, 3
2	4, 6, 8, 9, 10, 12, 15
3	16, 17, 18, 19, 20, 22, 23, 25 26, 27, 28, 29, 31, 32, 33, 37
4	41, 42, 44, 45, 47, 48, 49, 51, 52 53, 56, 60, 63, 64, 67, 70, 74, 75, 77
5	82, 83, 84, 85, 91, 92, 95, 96, 97, 99, 101 105, 107 110, 114, 115, 118, 119, 122, 123
6	128, 129, 136, 137, 138, 141, 149, 153, 156, 157, 158, 167
7	170, 178

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Premeeting Comments Submitted by Reinhard Bierl

Review of the Data Evaluation and Interpretation Report (DEIR) and Low Resolution Coring Report (LCR) - Hudson River Reassessment Study

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1. Specific Questions (DEIR)

(1) *Is the documented PCB load, which originated from the TI Pool, consistent with a source consisting of historically deposited PCB-contaminated sediments?*

I think the data support the assumption that the whole Thompson Island Pool which includes the upper areas are the main source to the water column load during low flow periods. It is not clear which parts of the sediments deliver most of the PCBs, what is the difference between „historically" deposited PCBs and recent loadings and what happens during high flow events. Additionally we have rise the question whether one year of sampling is representative for the hydrological and geochemical situations in the Hudson River system.

(2) *Are two-phase and three-phase partitioning coefficients, derived in the DEIR, appropriate and do they properly address the physical parameters of the system (e.g. temperature)?*

The theoretical background represented in the report expresses mainly the state-of-the-art in the scientific literature. The estimated particulate organic carbon partition coefficients seem to be reasonable. It would have been necessary to see the variability of the constants to comment some of the conclusions

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which have been made.

Applying three-phase partitioning coefficients would require a much more detailed analysis of the dissolved organic carbon and colloid contents and properties of pore and surface water. I think this is far beyond the task of this study and should be avoided.

(3) Are the conceptual models based on the transect sampling consistent with the data?

The conceptual models applied to explain the transect data of the 1993 sampling campaign are mainly supported by the data of the Responsiveness Summary. As in some other parts the discussion in the Responsiveness Summary is much more detailed and convincing as in the original DEIR report.

Inspite of the quite detailed analysis there remains a kind of unsatisfactory feeling. First most of the corrections concerning flow has to believed. A detailed analysis of the flow data would require much more time. Second much effort has been spent to present and discuss the transect results but no hint is given towards the variability of the data. Third due to the tremendous variety of data a multivariate approach would have been a useful approach to interpret congener specific data.

(4) Does the sampling at bias of samples collected at the TI Dam-West sampling location impact EPA's conclusion that the sediments of the TI Pool are the major source of PCBs to the freshwater Hudson during low flow conditions considering the analytical corrections made to GE's PCB data? What are the other implications of finding higher concentrations along the shoreline than in the center channel?

As stated in the DEIR Responsiveness Summary, „the net result of combining

and assessing the interpretations of QEA and the phase 2 team is an improved understanding of the TIP sediment PCB source", the arguments put forward in the report appear reasonable. The problem of the sampling bias seems to be compensated by the analytical corrections. Therefore the loadings reported in the DEIR appear to be in the right order.

The implications of higher concentrations along the shoreline would stress different areas: the PCB inventory needs probably be revisited. That means a more detailed geostatistical analysis of the present data emphasizing the shoreline in a more detailed way. Sampling in the future should also consider these areas with a more detailed resolution.

Concerning the transport and the exchange mechanisms it would be necessary to answer a few more questions:

- how are the differences in deposition and resuspension rates between shoreline and center channel,
- is the biological activity very high,
- will you find forms of biofilms during the months with higher temperatures with an influence on sorption processes and sediment stability,
- what are the volatilization losses in the shallow parts of the pool.

(5) Are the geostatistical techniques (polygonal clustering and kriging) correctly applied?

I do not feel as a real expert on geostatistical techniques to say the methods were not correctly applied. Anyway I have a few comments. Fact is that we have data of unequal quality, with a spatial variance of the variograms and with spatial and temporal unfavorable distributed data. In that case it would be useful to use more advanced geostatistical methods, that means unlinear methods. The program GeoEAS which has been used for the analysis does not offer such options. It would be necessary to quantitate the uncertainty of the estimated values. The variograms which are represented have mostly the

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character of white noise which reinforces the need for analysis of the estimation uncertainty. I think it would be useful, to express the parameters of the variograms as a function of the spatial coordinates. As far as I understood are the kriging results not only a matter of estimating the PCB-amount in the TI Pool but are also intended to support a redevelopment in the future. Therefore some additional effort would be quite helpful.

(6) Are the methods applied in the DEIR (change in molecular weight (MW) and evaluating concentrations of BZ#1,4,8,10 and 19 (MDPR) appropriate standards for determining extent of dechlorination? Are there any significant problems with this approach, or more appropriate approaches?

The approach to take the change in molecular weight (MW) and molar dechlorination product ratio (MDPR) appears to be reasonable. It gives similar results concerning the accumulation of ortho-substituted mono- and dichloro - congeners as has been reported in several papers working with samples of the Hudson River.

A major restriction to the use of this kind of index is that it depends on the knowledge of the pure original Aroclor-mixture. I'm not sure if this point is completely addressed. A second restriction is that the different mobility of the congeners is neglected that means in reality you will have a chromatographic effect in sediments.

(7) The DEIR finds that the degree of anaerobic dechlorination is primarly a function of original concentration rather than time, and accordingly that there is not significant predictable dechlorination in sediments containing less than approximately 30 mg/kg PCB. Is this reasonable?

Even when it is reasonable that the adaptation of microorganisms is connected to certain amounts of PCBs ((1) how comes the PCB-molecule to the miroorganism or vice versa; 2) selectivity advantage), there is no indication in the literature that there exists a single threshold. The factors which control the dechlorination process are numerous.

A second point which has influenced my opinion is that I could not proof why quite a huge amount of data have been excluded from this analysis.

2. Specific Questions (LCR)

(1) In the LRC, EPA compared sediment data from cores taken in 1977, 1984 and 1994, which had the PCB analysis conducted by different laboratory methods. How valid are the methods used to establish a consistent basis for comparison?

Analysis of environmental samples over a period of nearly 20 years will cause differences. This is hardly avoidable due to development of analytical techniques but also due to different sampling techniques and different teams doing the work. There has been much effort to establish a comparable basis especially between the 1984 and 1994 data. Despite the quite detailed work of Butcher (1997) to get a comparison of the non-resolved PCBs I'm not completely convinced about the correctness of the analytical data. I can imagine that much of the variance in the analytical data could be a result of different quantitation methods (e.g. how to draw the baseline in chromatograms which are a result of different matrix of samples etc.) and of problems with the use of the surrogate and internal standards. In the Final Phase Working Plan (1992) it was planned to do some comparable analysis of the older sediment

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and water extracts. I haven't seen results to that. When samples (extracts or original sediment material) had been stored in a suitable way (that means at a minimum of -20°C, better -40° to -80°C) I would suggest to do this comparison at least for some of the samples. It would be very interesting to get at least an impression of the lower chlorinated congeners in the 1984 samples. Concerning the internal standards I'm aware that for reasons of keeping methods comparable and perhaps for reasons of cost, OCN and TCMX has been used but why are not at least some samples analysed by using ^{13}C-standards to validate the results.

(2) In the upper Hudson River system, it has been well established that there is significant lateral heterogeneity in sediment concentrations. While it was attempted to reoccupy previous locations, some uncertainty is added with respect to the actual sampling location. While the statistical techniques help compensate for this, how does the sample heterogeneity affect the comparison of cores from two different years? Given the spatial variability, is the finding that there is a loss from most locations supported by the data?

There has been much effort to reoccupy previous sampling locations which indeed has worked out in many locations. But we have to keep in mind the governing factors which are responsible for lateral heterogeneity. Depends it merely on „historical" deposition, dynamic exchange or predominately on sediment parameters like texture (grain size) and total organic carbon content (TOC). Based on the data in the report and of literature it is obvious that PCB are mostly connected to fine grained sediments especially in the silt fractions with second maxima in coarse fractions. This is due to differences in the properties of the organic matter. The data on organic carbon and nitrogen are neither complete nor are they precise enough but a careful look on the C/N-ratio shows at least a trend that low ratios are followed by high contents of Bs and high ratios by low contents. Low C/N-ratio expresses organic matter

with less polar hydroxyl and phenolic groups and a more hydrophobic microenvironent which in fact has consequences on partitioning of hydrophobic micropollutants like PCBs.

In the LRC Reassessment analysis most of the cluster areas were determined to be fine-grained sediments. Therefore some of the uncertainty of comparing data on a „point-to-point" basis was ruled out. Based on the agreement of the mass change estimates between the two methods the data seem to support the general loss of PCBs. But I do not believe that a certain amount of loss can be stated.

(3) What is the impact of the difference between replicate samples in the 1994 sampling effort (36 percent average variability) on the finding that there was a 40 percent loss of PCB inventory from the highly contaminated sediments in the TI Pool?

The relative measures of mass change as calculated by the equation 4.1.4

$$\Delta = [(MPA_{94} - MPA_{84})/ MPA_{84}] * 100\%$$

in the LRC is an accectable means to compensate for some of the uncertainty.

As stated before the uncertainty of the estimated mean values does not allow to represent mass losses as single values. It's definitely a range and should be presented as a range.

(4) In the LRC, it was found that Hot Spot 28 contained much more mass than previous estimates. Is the conclusion that this „gain" is primarly due to incomplete characterization in 1977 valid?

I think no other explanation is plausible enough. Comparison of the data from the NYSDEC 1976-78 sediment samples and the TAMS 1994 samples show considerable differences even at near located sampling points. A shift in the hot spot itself is certainly possible. A mass loss at other „hot spots" of the pool and a mass gain exactly at this location below the dam is not very likely. These would be fundamental events which are not supported by the data of most of the other hot spots.

(5) Does the data set and its interpretation support the conclusion that significant losses have occured from hot spots below the TI Dam?

I do agree with this conclusion that significant losses have occured from hot spots below the dam. Again I think it is not possible to calculate overall mass changes but it is sufficient to estimate trends. A more rigorous (geo)statistical analysis of the data would be perhaps more persuasive. The question however what mechanism has caused this losses has still to be answered. Losses of more than 10% in my opinion can only occur due to resuspension and advective transport during the major runoff events.

(6) The LRC found that the historically contaminated sediments in the TI Pool were not universally being buried and sequestered from the environment. How much confidence would you place in the LRC evidence against widespread burial?

The aspect of burial depends to a certain part on the values for deposition and resuspension rates which are not known exactly in the different zones. Depending on the PCB concentration profiles given in the reports there is no indication that large fractions of the PCB inventory are buried very deeply. This is supported by the high-resolution cores, by the loss of PCB inventory and by

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the fact that a redistribution of sediment-bound PCBs is consistent with the water-column data.

(7) ***Is the interpretation of the sidescan sonar data appropriate and supported by the analysis of the associated sediment properties?***

I have no personal experience with sidescan sonar data but the results are very convincing and the comparison of the SSS-data and the other grain-size data show that valuable spatial data could be gained.

3. General Questions

(1) Is the data set utilized to prepare the DEIR, LRC and Responsiveness Summaries sufficient to understand the fate and transport of PCBs in the Upper Hudson?

The data set is very comprehensive and I think it is enough to get a quite good impres-sion of the transport behavior of PCBs in the Upper Hudson. Nevertheless some points - already discussed in the Responsiveness Summary - concerning for example the exact influence of the Thompson Island Pool to the overlying water still remain. It would be interesting to see how good the transport models are working.

Concerning the fate of PCBs I would state the data set it is **not** sufficient. USEPA/TAMS suggest some additional work in the modeling and (eco)toxicology part of the Hudson Reassessment study but these data are not the basis for this review. There are some compartments which seem to be addressed only theoretically in the DEIR. To determine exact volatilization rates of PCBs is certainly a very difficult task but some measurements of atmospheric PCB contents along the Hudson River would be very helpful. Due to the frequent situations with pools (very low flow velocity) and dams (spray) volatilization could be an essential process of PCB removal. Photochemical destruction of PCBs (both in the surface water and in the atmosphere) is an important fate mechanism but the overall rate limiting steps are diffusion from sediments and the transfer at the water/atmosphere boundary.

Another point of concern is the fate of the coplanar congeners. In respect of the enourmous amounts of PCBs in the Hudson River system the toxicological importance of the coplanar PCBs can not be ignored. Are there any data on these congeners and perhaps some recent data on dioxins and furans besides

the data given in Brown et al. (1988)?

Nevertheless I have the feeling that the important issues have been addressed and mostly answered. Combining all the available and most recently data from USEPA/TAMS, GE, USGS and the other involved organizations the database should serve as a qualified basis for the further reassessment study. So to my opinion the DEIR and LRC are acceptable.

(2) Are there any additional analyses that should be done to verify certain findings of the DEIR and LRC?

Some of the points have already been addressed in the preceding questions. I would have liked some additional work on the geostatistical techniques and the statistics as a whole. In certain parts a multivariate approach would have been the better choice to come to qualified results. Particularly it could have been useful to trace sources of the PCBs by a multivariate fingerprinting approach as well as to analyze the dechlorination patterns.

In general it's a pity that the study didn't use a more multivariate approach determining for example the main nutrients and metals which could serve as additional indicators of the system behavior.

I would suggest to do some additional analysis in the estimation of the sampling and analytical error. The described sampling program for river water rises some questions. How are the 17 L water results comparable to the 1 L results taken by GE? How big are the deviations concerning the filtering of water samples in a dissolved and particulate phase? Is the colloidal phase of minor importance to transport and is it adequately addressed by the DOC-content?

As stated earlier I would also suggest, if the storage of the extracts and samples has been done in an adequate manner, to do some re-analysis of the old extracts or samples. It could be (or not) a confirmation of the results done by estimation of the packed column analysis and it could give some indication of the low-chlorinated congeners in the 1984 samples.