70257

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

FEB 26 1998

Mr. John Haggard
General Electric Company
1 Computer Drive South
Albany, New York 12205

Re: Hudson River PCBs Site - Memoranda on GE Sampling Data

Dear Mr. Haggard:

This letter conveys several memoranda prepared by Dr. Jon Butcher of Tetra Tech, Inc. I believe this information can serve as a basis for discussion regarding various issues that GE has raised over the past several months.

The memoranda enclosed are:

Preliminary Comments on GE Review of USGS Water Column Data
February 13, 1998

GE Bias Study
October 27, 1997

Revised GE Data and Load Across TIP
October 1, 1997

Note that these memoranda are still considered "draft" by the contractors, and as such certain conclusions may change based on additional information or further analysis. In addition, these memoranda do not necessarily reflect the position of the U.S. Environmental Protection Agency.

Once you and your contractors have had an opportunity to review this information, then I believe it would be worthwhile to set up a conference call to discuss our positions. At some point in the future, after GE submits the reports to EPA on its Thompson Island Pool monitoring, it may be appropriate to have a meeting regarding these issues.

If you have any questions, please contact me at 212-637-3956.

Sincerely yours,

Douglas J. Tomchuk

Douglas J. Tomchuk, Project Manager
Hudson River PCBs Reassessment

Enclosures

cc: John Connolly, QEA
Bill Ports, NYSDEC
Lisa Rosman, NOAA
Vic Bierman, LTI (w/o enclosures)
Al DiBernardo, TAMS (w/o enclosures)
Jon Butcher, Tetra Tech (w/o enclosures)

TETRA TECH, INC.
P.O. Box 14409
Research Triangle Park, NC 27709
Telephone: (919) 485-8278 Telefax: (919) 485-8280

MEMORANDUM
by Telefax

To: Doug Tomchuk (EPA R 2) **Date:** February 13, 1998

cc: Ed Garvey, Al DiBernardo (TAMS/NJ) [without attachments]
Vic Bierman (LTI) [without attachments]

From: J. B. Butcher **Project:** Hudson PCBs

Subject: Preliminary comments on GE review of USGS water column data **Pjn:** 1182-09

Pages: (2 + 10 pages of attachments, to EPA only; other recipients should already have these)

Attachments:
1. Memo of 4/18/97: Summary of PCB Data Issues for Modeling
2. Memo of 12/11/96: USGS Water Column Data: GE Splits

On February 10, 1998, GE submitted to EPA a memo entitled "Corrections to the U.S. GS Water Column Data." This memo is based on a preliminary reanalysis of USGS capillary column chromatograms for Hudson River water total PCB analyses between 1987 and 1992. In this memo, GE states "uncorrected U.S. GS data should not be used for model calibration." They further suggest that the USGS data should not be taken to represent a tri and higher-chlorinated congener sum, and, "because there is not a simple correction factor that fits all the data", thorough review and reanalysis of the chromatograms should be undertaken to correct the data before proceeding.

Because this suggested review has potentially significant implications for the schedule of model calibration, I am providing some quick-response comments on the contents and implications of this memo.

Our current recommendations for modeling are that historical model hindcasting use the sum of tri and higher-chlorinated congeners as the state variable, in all media. We have further contended that the USGS water column data can be taken as an approximate representation of the sum of tri and higher-chlorinated congeners. See copy of draft memo of 4/18/97 attached (particularly pp. 3-5 for USGS data). We did, however, have some unresolved questions regarding the interpretation of USGS capillary column data.

There are two separate, but related issues for the USGS capillary column data. One is whether the data can be used or corrected to represent a sum of tri and higher-chlorinated congeners. A second issue is what additional data might be extracted from the reanalysis of the chromatograms. For the model hindcasting, only the first issue needs to be resolved. The second item can yield valuable additional information relative to sources and dechlorination processes, but is not needed to proceed with the modeling. We fully expect that the USGS-reported totals will be biased low, because they will tend to omit the important contributions of BZ #1 (2-CB), BZ #4 (2,2'-CB), and BZ #10 (2,6-CB), either because these congeners are missed in the packed-column chromatograms, or because they are not quantitated in the analysis of capillary-column chromatograms in which the lightest standard used was Aroclor 1242. In this respect we are fully in agreement with GE. The important question for modeling is if, and how to use these data to provide a consistent basis for hindcasting.

I suggest that the USGS data can be used "as is" for hindcasting a tri and higher-chlorinated PCB sum, for the reasons noted below:

- The GE reanalysis applies ONLY to USGS capillary-column analyses, which commenced on the Hudson in November 1987 (information received from Ken Pearsall). All USGS results prior to this date were analyzed by packed-column methods, for which original chromatograms are not available—and reanalysis is thus impossible. We used GE split-sample analyses by capillary column and USGS packed-column protocol to show that these data do provide a good representation of the tri and higher-chlorinated sum (see attached memo of 12/11/96). GE's comments are thus not relevant to the bulk of the USGS data, from 1975 to summer 1986.

- USGS capillary column quantitations appear to omit BZ #1, 4, and 10, although they can apparently be detected in Peak 2 of the chromatogram. We believe Peak 2 was not used by USGS in quantitations, which appears to fit with GE's statement that the difference between USGS totals and recalculated totals is associated with BZ# 1, 4, and 10. We suspect that dichloros BZ #5, 6, 8, and 15 were within the quantitation peaks. Thus, what is measured by the USGS method is indeed not a pure tri and higher-chlorinated sum. It is, however, likely to be a close approximation because these congeners constitute only about 11% of the total mass of Aroclor 1242. When we note that most of the environmental observations are below 0.1 μg/l and reported to a resolution of 0.01 μg/l (i.e., > 10% of reported total), it is clear that this small bias is likely to be undetectable within the "noise" of the reported data.

- Potential bias in the 1987-92 USGS data will be greatest in the areas below Rogers Island, where a significant amount of dechlorination products are introduced into the water column. The bias should not present much of a problem above Rogers Island—and it is precisely the above-Rogers Island data which are needed as a boundary condition for the modeling.

- Given considerable uncertainty in the pre-1987 USGS data (due to frequent changes in calibration standards), a high degree of precision cannot be imputed to these data. Accordingly, it appears appropriate to treat the entire USGS time series as an approximate representation of the tri and higher-chlorinated sum. We should recognize that there is a high degree of uncertainty in this time series, and over-calibration to the water column data should be avoided. Ability to represent time trends in depositional sediment seen in high resolution cores is probably a stronger calibration target.

In sum, I suggest it is worthwhile for GE to go ahead, at their own initiative, with the re-read of the 1987-1992 USGS water column data. This may provide important information on congener/homologue patterns in the period leading up to the Allen mill event. It is not, however, necessary to delay model hindcasting to await this reanalysis, and the reanalysis is unlikely to have a substantive impact on the model. If there is sufficient concern regarding the potential findings of the GE study, one alternative would be to initially evaluate the hindcasting model on the 1984-87 (USGS) and 1991+ (EPA and GE) water column data only, while using the full time series at Rogers Island as the boundary condition. Readjusted 1987-91 data, when they become available, could then be used as a validation test of the model performance in predicting water column concentrations.

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MEMORANDUM
by Telefax

To: Ed Garvey, Al DiBernardo (TAMS/NJ)
~~Vic Bierman (LTI/IN)~~
~~Scott Hinz (LTI/DC)~~

Date: April 18, 1997

From: J. B. Butcher

Project: Hudson PCBs

Subject: Summary of PCB Data Issues for Modeling (DRAFT)

Pjn: 1182-09

During the past several months, Ed Garvey and myself have pursued a worthwhile series of discussions with LTI on data issues relevant to modeling. This memo summarizes our conclusions, and the status of ongoing issues regarding environmental PCB data for model hindcast runs. Most of the data issues have been resolved. Those data issues which I know to require further work are discussed below.

Hindcasting PCB State Variable

We are in general agreement that the state variable for use in hindcasting will be the sum of trichloro and higher-chlorinated PCB homologues. Congeners cannot be used for hindcasting, as congener data are not available in the historic record. On the other hand, neither individual Aroclors nor total PCBs are suitable state variables. Aroclor quantitations do not have a consistent meaning across different sampling campaigns, and most of the USGS water column data prior to WY 1990 does not provide a true, quantitative resolution of Aroclors in any case. Total PCBs are also not truly available in the historic record, because the historical packed-column GC quantitations will miss the monochloro and most or all of the dichloro homologues. The different historical measurement schemes, however, either give or can be converted to an estimate of trichloro and higher-chlorinated homologues. This sum (which I will abbreviate as "3° +" thus provides the common denominator which links the disparate historic PCB data. Use of the 3° + sum also has the advantage of eliminating congeners BZ#1 and BZ#4, which can show environmental behavior quite different from heavier, more hydrophobic congeners, from the bulk PCB representation.

In general, the 3° + sum approximately represents packed column peaks with retention time relative to p,p'-DDE of 0.28 or greater. Peak .28 has frequently been used to quantitate either Aroclor 1016 or 1242. One complication arises because peak .28 contains, in addition to trichlorinated congeners BZ#17 and 18, the dichlorinated congener BZ#15. Nevertheless, a reasonable approximation of the 3° + sum can apparently be obtained for all the historic data sets by appropriate manipulation.

Note that BZ#15 constitutes an average of 3.6 % of total PCBs (particulate plus dissolved on a volumetric basis) in the water column of the upper Hudson, although the percentage ranges up to 68% in individual samples. It may, in theory, be preferable to use the sum of all congeners from BZ#15 up (that is, the

3° +sum plus BZ#15). This would require considerable reanalysis on my part, and could not be finalized until Hydroqual/NEA completes the planned reanalysis and correction of reported results for NEA Peak 14 (BZ#15+BZ#18). ***We need to make a decision as to whether this refinement to the method should be implemented.***

Data Sources and Conversions

The next sections summarize methods and outstanding issues for converting the various PCB data to a 3° + sum basis. Status of the analysis for the various sources of PCB data is summarized in Table 1, then discussed below.

Table 1. Status of Efforts to Convert PCB Data to Consistent Basis for Modeling

Data Source	Do not use!	Tentative method: Further analysis required by TAMS team.	Tentative method: Awaiting additional documentation or database changes.	Final method proposed.
Phase 2 Data				✓
GE/NEA Water Column Data			✓	
GE/NEA Sediment Data			✓	
USGS 1977-87				✓
USGS 1988-95			✓	
1984 Sediment				✓
1977-78 Sediment		✓		
1983 NUS Sedt.	✓			
1989 GE Sedt.	✓			
1990 GE Sedt.			✓	

Phase 2 Data: Use sum of 3° + homologues, available from the database.

GE/NEA Water Column Data: These data can also be directly converted by summing the 3° + mass percentage (not the mole percentage) and applying this fraction to the reported capillary column total PCBs. (Beware of a few evident errors in reported units, which vary from ppm to ppt). Three notes regarding use of the GE water column data:

- The trichloro BZ#18 and dichloro BZ#15 co-eluted at NEA (Peak 14), and our database key assigns Peak 14 to the dichloro homologue group. (Therefore, do not recalculate homologue sums directly from the peak lookup table key.) The database contains homologue weight percentages calculated by NEA. According to Jim Rhea, NEA calculated these percentages by partitioning the Peak 14 concentration and assigning 75% of the concentration to the trichloro homologue sum and 25% to the dichloro homologue sum, based on approximate percentages of these congeners in Aroclor 1242. An analysis of whole water concentrations in the Phase 2 data indicates that, on average, BZ#15 constitutes 31% of the BZ#15+BZ#18 sum. There is considerable variability among samples, however, and the observed fraction of BZ#15 ranges from 1% to 99%. Thus, NEA's partitioning of Peak 14 to homologues is not exact, but should not introduce a major systematic bias in terms of the 3°+ sum. Therefore, no additional manipulation of the NEA reported trichloro homologue sum is needed - except that the effects of the data reanalysis described in the next bullet will need to be incorporated.

- Peak 14 (along with Peak 5 and Peak 18) is one of three capillary column peaks selected by GE/Hydroqual/NEA for reanalysis and requantification (personal communication from Jim Rhea, 4/17/97). GE has not yet provided us with the results of the reanalysis, although a general discussion is included in Appendix A of GE's comments on the DEIR. Apparently, the GE water column data for Peak 14 are biased low for 1993, but the exact range of dates affected is not yet clearly known to us. Page A-7 of GE's comments contains a regression equation to correct the affected data. The bias correction apparently will not provide an analytical separation of BZ#15. After adjustment of these peaks, it will be necessary to repartition Peak 14 concentrations among dichloro and trichloro fractions to correct the homologue percentages as well. I presume Hydroqual will make this correction in the database, but can't say for sure if or when this will be done and made available to us.

- The homologue percentages shown in the existing database will also be affected to some extent by "correction" of the other two peaks. I suspect the effect will be minor in terms of the 3°+ sum, but the data won't be final until these corrections are also incorporated.

GE/NEA Sediment Data: The GE capillary column sediment data is similar to the NEA water column data, and can be used fairly directly to obtain a 3°+ sum. We have verbal assurance (I believe) that only a small fraction of the capillary column sediment data will be affected by the peak reanalysis - but, again, we are not certain of exactly which data at this time.

USGS Packed Column Water Data (1977-87): Note first that it is essential to use the corrected USGS data set distributed this week. In addition, there has been some confusion regarding date of USGS switch from packed to capillary column. GE/Hydroqual (DEIR comments, Appendix A) reports that the USGS analyses are packed column through 1989. Our information, however, is that the USGS lab began some use of capillary column analyses in November 1987 (personal communication from Ken Pearsall, USGS/Troy, based on letter received from Brooke Connor in USGS Denver laboratory).

The USGS capillary column methodology is described in general in Wershaw *et al.*(1983). A clearer description of exactly what was done is given in Schroeder and Barnes (1983). The analysis was a two-step procedure:

1. Determine an appropriate Aroclor standard, based on requirements that at least 60 percent

of the peaks in the standard are present in the sample and "both relative peak ratios and column detention time must match." If a single Aroclor standard cannot be found which matches these criteria, use a standard containing a mixture of two or more Aroclors.

2. Calculate concentrations "by dividing the area of a sample's identified PCB peaks by the area of all peaks for an Aroclor standard, then multiplying this ratio by the concentration of the Aroclor standard."

Step 2 indicates that this is not a Webb and McCall procedure with peak-by-peak quantitation. Instead, the observed peaks in a sample are scaled-up to estimate a complete Aroclor concentration. No compensation is made for differing response factors, only the sum of peak areas is used. We are not certain exactly which packed-column peaks were observed by USGS, although it appears certain that the mono-chlorinated homologue was not represented. The first peak used is thought to be either RRT .21 or RRT .28. For quantitations against an Aroclor 1221 or 1232 standard (where there is substantial unobserved concentration in peaks below RRT .21) this approach is equivalent to assuming that the early-eluting (unobserved) congeners in the sample are present in the same fraction as in the Aroclor standard. In reality, concentrations of these congeners (*e.g.*, BZ#4) are likely to be higher in the environment due to dechlorination. Further, the number reported by USGS is dependent on choice of standard, which is only incompletely documented.

In addition, USGS used a dual column method, and always selected the lower of the two values obtained. Finally, no corrections were made for incomplete extraction. Extraction efficiency, it is estimated, "probably exceeds 80 percent in nearly all samples".

Because of all these factors, it is difficult to predict exactly what was measured in USGS packed column analyses. NEA conducted split sample experiments to compare the USGS packed column method (based on the description in Schroeder and Barnes) to capillary column analyses, using individual or mixed standards composed of Aroclor 1242, 1254, and 1221. Hydroqual agrees with us (DEIR comments, Appendix A) that the best means of converting these data to a basis consistent with Phase 2 and NEA capillary column results is a regression relating USGS total PCBs to the 3°+ sum. I analyzed the NEA split samples in a memo of 12/11/96 and found that a regression of USGS-method total PCBs on the capillary column 3°+ sum gave a good linear fit, with an intercept not significantly different from zero and a slope not significantly different from one. Thus, the USGS packed-column data can be used as a direct measure of the 3°+ sum. This is further supported by noting that the USGS-method results are consistently biased low relative to NEA's Webb and McCall results (which do quantitate much of the dichlorobiphenyl fraction).

USGS Capillary Column Water Data (1988-95): As with the earlier USGS data, these are whole water estimates. The revised USGS database release should be used, although there may be an update for 1990 data if the original lab reports are located by Ken Pearsall.

During the period 1988 to Sept. 1991 USGS continued the approach of selecting a single or mixed Aroclor standard for quantitation. In contrast to earlier years, however, only Aroclors 1242, 1248 and 1254 are reported as identified Aroclors; Aroclor 1221, 1232 and 1016 standards were not used. From October 1991 on, USGS consistently reported quantitations against Aroclor 1242 and 1254 standards, presumably based on a specified rule for peak separation. {Ed: any further info here?}. Ed Garvey states that it is clear that BZ#1, BZ#3, BZ#4, and BZ #10 were not seen in the USGS chromatograms for this period, but it is not clear if the dichloros BZ#5 through 15 were quantitated. USGS data for this period should give the 3°+ sum, but perhaps also some dichloros as well. Because Aroclor 1242 was the lightest standard used, the potential problem is not severe: BZ#5, 6, 8, and 15 constitute 10.5% of the mass of Aroclor 1242 according to the Aquatec analysis, so about 11% of the reported Aroclor 1242 value could be dichlorinated homologue. A correction could be applied (pending further analysis); however, for most observations a 10% correction is within the noise of quantitation (*i.e.*, most observations are below 0.1 μg/l and reported to a resolution of 0.01 μg/l). My tentative recommendation is to use the total PCB amount in the revised USGS database as a direct surrogate for the 3°+ sum in this period as well.

1984 Sediment Data: Analysis of these data should be based on the reported "Total PCBs". The Aroclor 1242 data contained in the database are the rejected Versar values, and should not be used, while Total PCBs was formed using NYSDEC's recalculated Aroclor 1242 estimate.

"Translation" of the 1984 sediment data was summarized most recently in my memo of 12/5/96. Based on this memo, I recommend correcting the 1984 sediment data using the zero-intercept regression

3°+ sum = 0.934 • 1984 reported total PCBs

1977-1978 Sediment Data: The 1977-78 data are expected to include biases similar to those found in the 1984 data; however, a full quantitative analysis of the discrepancies is not possible because (1) O'Brien and Gere used a complicated decision tree to decide which peaks to quantitate in a given sample which cannot readily be backed out of the reported results, and (2) quantitation peaks are identified only by absolute retention time, not RRT, and we have not been able to firmly identify which peaks were used for Aroclor 1254 quantitation.

The 1977-78 sediment data contain quantitations for Aroclor 1221, 1016, and 1254. Aroclor 1221 was usually quantitated based on a single peak, probably RRT .21 (Brown *et al.*, 1988), containing dichloros BZ#5 and BZ#8 (I believe Tom Gauthier's attribution of RRT .11 is incorrect). Aroclor 1016 base quantitation peaks were RRT .28, .47 and .58. These are the same peaks used by NYSDEC to recalculate Aroclor 1242 in 1984. Eight peaks are specified for Aroclor 1254. These appear to include the peaks used by NYSDEC in 1984 for Aroclor 1254, as well as additional peaks, probably through RRT 2.32, used by NYSDEC for Aroclor 1260.

The calculation method for the 1977-78 data is Gauthier Approach 2: Multiple packed column peaks are selected and each peak is used to generate a separate estimate of the Aroclor concentration. The average of these separate estimates is then reported as the Aroclor concentration. This introduces bias into the calculation, as the spectrum of congeners in the environment is altered relative to the Aroclor standard. Given uncertainties regarding method, we do not have a direct basis for correcting the 1977-78 data to a consistent measure of the 3°+ sum, but some inferences can be made based on comparison to the 1984 results.

Aroclor 1016 in 1977-78 uses the same peaks, and the same quantitation method as used for Aroclor 1242 in 1984. The only difference should be in the weight percent of congeners in the two standards. For peaks .28, .47 and .58, the average of the packed column peak ratio of weight percent in 1016 vs. 1242 is 1.22. Thus, multiplying 1977-78 Aroclor 1016 results by 1.22 should give an estimate of Aroclor 1242 as quantitated by the 1984 method.

For Aroclor 1254, methods differ between 1977-78 and 1984. The 1984 method for Aroclor 1254 and 1260 was a Webb and McCall approach, which should give an actual estimate of the concentration of congeners contained in the selected peaks. For 1977-78, Aroclor 1260 was not analyzed, while Aroclor 1254 concentration was estimated using an averaging approach similar to the one described for Aroclor 1016, but using a larger number of peaks. Fortunately, Aroclor 1254 and Aroclor 1260 are relatively less important than Aroclor 1242/1016 to the total mass estimate. *We have not yet done an analysis to compare potential implications of the 1977-78 Aroclor 1254 quantitation method.* I suspect, however, that the 1977-78 Aroclor 1254 result should be fairly close to the sum of Aroclor 1254 plus Aroclor 1260 in 1984. *(Need to confirm this?).*

By analogy to the 1984 results, I would suggest that the 1977-78 results should be represented through:

$$3^\circ + \text{sum} = 0.934 \bullet [(1.22 \bullet \text{Aroclor } 1016) + \text{Aroclor } 1254]$$

Further numerical experiments can be pursued here, if warranted.

In using the 1977-78 results, care should be taken on two accounts:

- Note that the 1977 sampling was a broad-scale scan of the upper river, while the 1978 sampling was primarily targeted to hotspots identified in the first round. Spatial analysis of PCB mass (*e.g.*, polygonal declustering) must be applied to account for this targeted sampling, then converted back to concentration.

- The data do not include bulk density, which presents problems for converting concentration to mass. However, constant bulk density **should not** be assumed. This is because there is a strong negative correlation between bulk density and PCB concentration (PCBs are preferentially found in finer-grained, less dense sediments), and assumption of constant density will result in biasing the mass estimate upward. As an alternative, the available information on percent total solids and sample weight should be used to approximate bulk density. Texture class coding may also be useful, although we do not currently have a key to the 1977-78 texture classes in the database. *{May need to follow up with Jim Rhea on this one.}*

1983 NUS Sediment Data: A limited number of samples were collected in 1983 during the NUS feasibility study. Concentrations as Aroclor 1242, 1254, and 1260 were reported, using a method similar to that used by NYSDEC for fish samples: the areas of selected packed-column peaks in the sample are summed and compared to the sum of the areas recorded for the same peaks in a standard Aroclor mixture. We have seen in analysis of the fish data that this type of approach can introduce substantial bias. Because the sample coverage from 1983 is not large, I recommend these data not be used for modeling.

1989 GE Sediment Data: Do not use these data for general modeling. They are focused on special hotspot investigations, and the methodology has not been analyzed.

1990 GE/Harza Sediment Data: The 1990 sediment data give homologue concentrations. The analysis was apparently done on packed column, and we have not received full documentation from GE, despite a pending request. I suspect, however, that the 3° + sum can be used directly from these data.

Other Data Analysis Issues

1984 Sediment Initial Conditions: Sediment concentration data are available for 1984 only in the TIP. Reasonably good coverage below TIP is available only in the 1977-78 NYSDEC surveys and 1990-91 GE surveys. An interpolation to 1984 conditions is required as a starting point for the model. LTI has proposed developing a "projection factor". This involves calculating the average change between 1978 and 1984 in the TIP, then applying a similar reduction from 1978 to estimate 1984 sediment conditions below TIP. I am uncomfortable with this approach because there are several characteristics of the TIP which are systematically different from those downstream:

- In 1978, the TIP still contained large deposits of unstabilized, contaminated sediment left over from the dam removal episode and subject to mass erosion and movement. This is presumably not true below Thompson Island Dam.
- The TIP contained more highly-concentrated PCB deposits than downstream and may show greater impact of biological dechlorination.
- TIP surface sediments may have been recharged by oil-phase PCBs.

Rather than a "projection" method, I would suggest establishing 1984 conditions (for 3°+ sum) by interpolating between 1978 and 1991 conditions, probably using an exponential decline.

Scour Modeling: Based on the STC meeting, it is not clear if the results of the TIP depth-of-scour model are consistent with the long-term HUDTOX model. I am not suggesting a continuous scour model; however, LTI needs to document how the depth-of-scour model informs the HUDTOX model. Presumably, it should constrain the gross resuspension and deposition rates used in HUDTOX?

Partition Coefficients: I do not anticipate any further changes to water column partition coefficient estimates. Hydroqual's estimates will differ from ours because of certain different underlying assumptions, but our numbers are defensible. There may be some changes in sediment partition coefficients following GE's "corrections" to the database. This should primarily affect BZ#4, for which I will need to redo the estimates.

Ed and Al: any more issues you want to raise?

References

Brown, M.P., M.B. Werner, C.R. Carusone, and M. Klein. 1988. Distribution of PCBs in the Thompson Island Pool of the Hudson River. Final Report of the Hudson River PCB Reclamation Demonstration Project Sediment Survey. NYSDEC, Albany, NY

Schroeder, R.A. and C.R. Barnes. 1983. Trends in Polychlorinated Biphenyl Concentration in Hudson River Water Five Years after Elimination of Point Sources. Water-Resources Investigations Report 83-4206. USGS, Albany, NY.

Wershaw, R.L., M.J. Fishman, R.R. Grabbe, and L.E. Lowe, ed.s. 1983. Methods for the Determination of Organic Substances in Water and Fluvial Sediments. USGS Techniques of Water-Resources Investigations, Book 5, Laboratory Analysis, Chapter A3. Open-File Report 82-1004. USGS, Denver, CO.

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MEMORANDUM

To: Vic Bierman (LTI)
Scott Hinz (LTI)
Ed Garvey (TAMS)

Date: Dec. 11, 1996

From: J. B. Butcher

Project. Hudson RRI/FS

Subject: USGS Water Column Data: GE Splits

Pjn: 1182-03

NUMBER OF PAGES: ~~2~~ 3

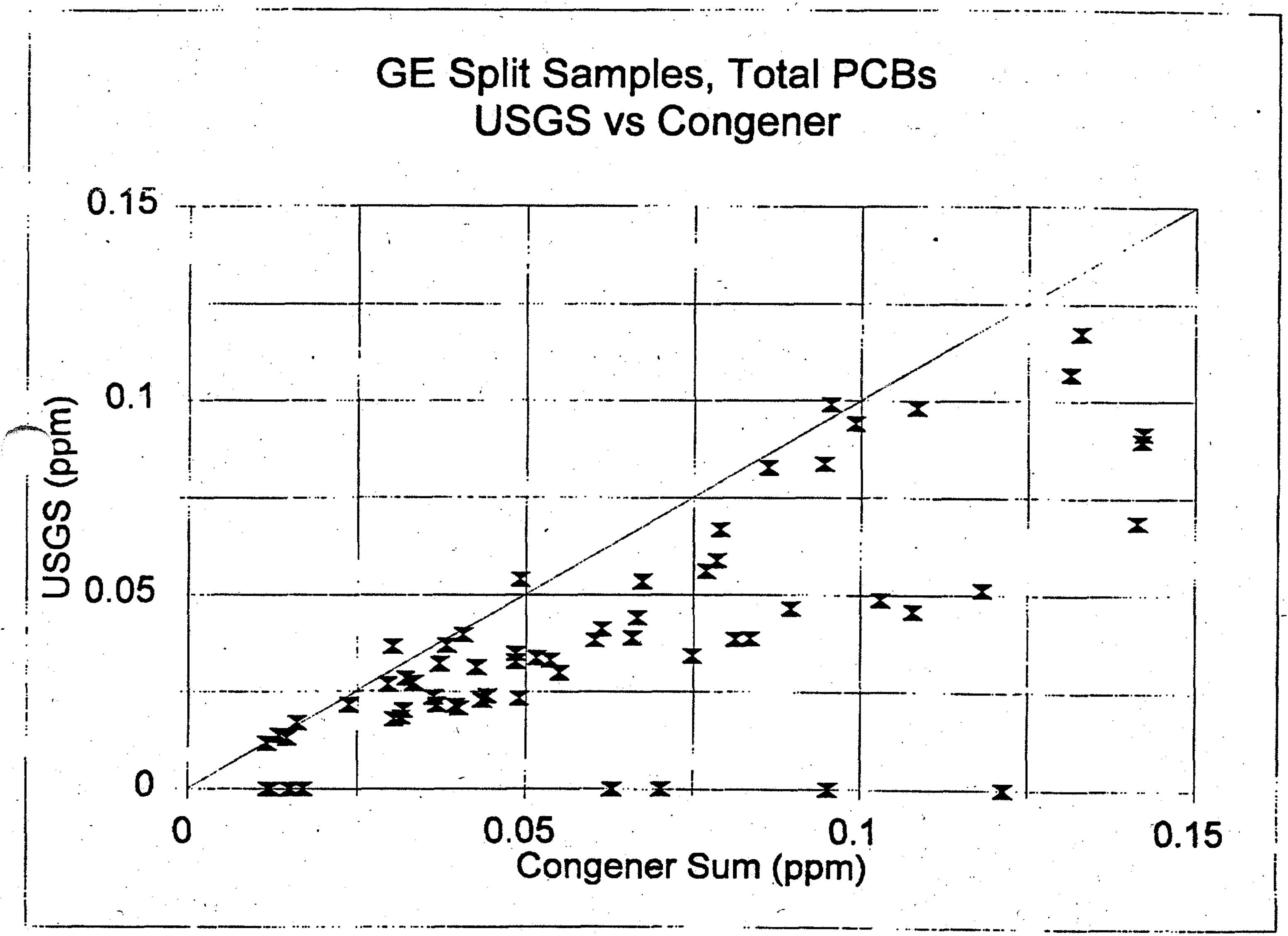
In 1991, GE analyzed split samples by both their capillary column method and the historic USGS method "to provide a baseline reference which could be compared to historical data". NEA conducted PCB quantification "according to USGS protocols", "which is similar to USEPA method 608 (USEPA, 1982) packed column analysis." We are still trying to resolve exact details of the USGS method, but the GE data set yields a direct basis for comparison.

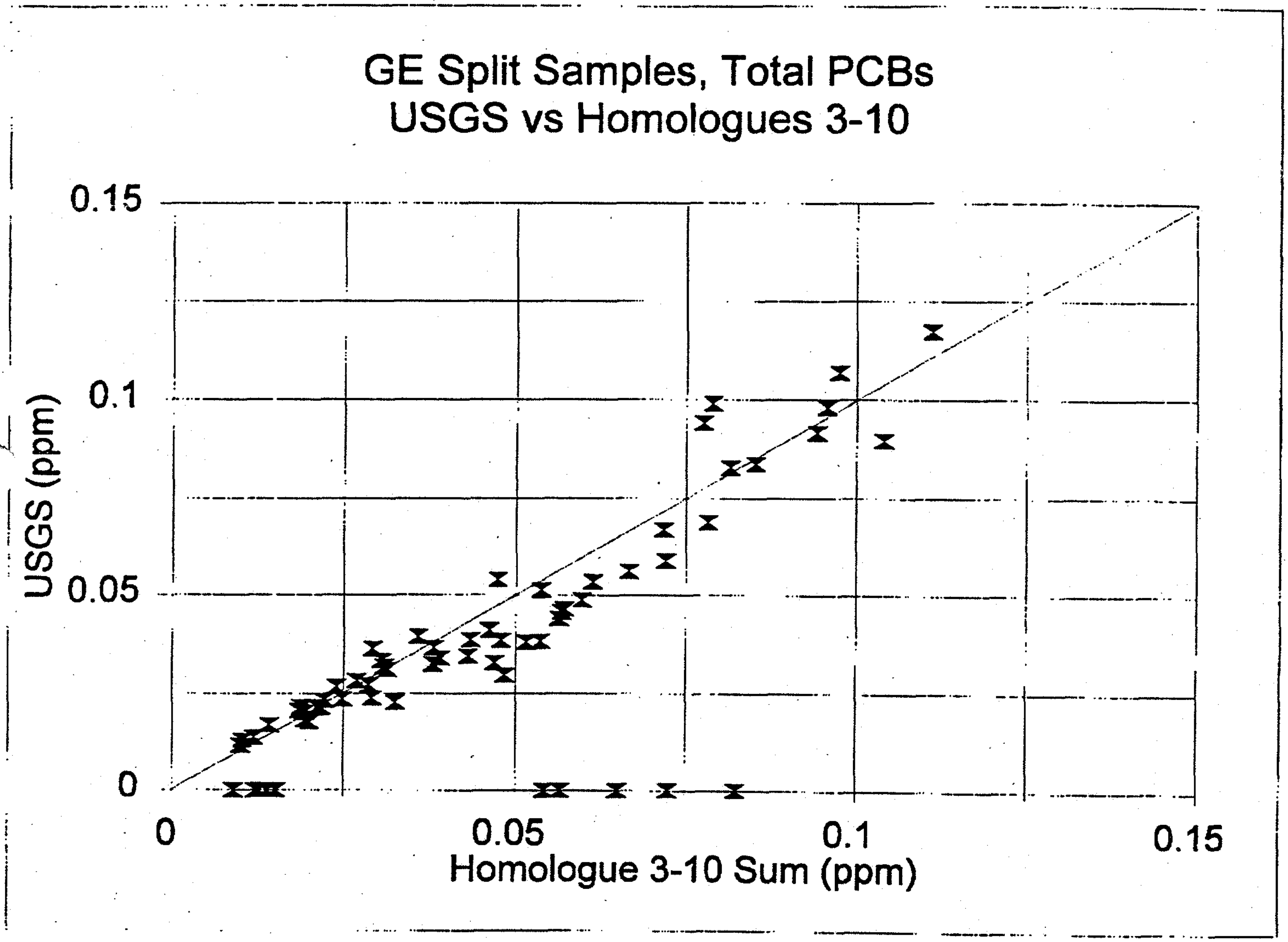
Results of this comparison suggest the USGS packed-column **water column data may be interpreted as a direct estimate of the total (particulate and dissolved) sum of tri- and higher-chlorinated homologues.** We will try to get further confirmation through analysis of the method.

In the GE database, there are a total of 90 records collected in the Temporal Water Column Monitoring Project between April and August 1991 which were analyzed by both GE's capillary column method and the USGS method. Of these, 25 were below MDL for congener analysis, leaving 65 records.

Figure 1 plots the USGS total versus whole-water sum of congeners. In most instances, the USGS result is less than or equal to the sum of congeners. On the other hand, if the USGS results are plotted against the tri- and higher-chlorinated fraction (Figure 2), most samples lie very close to the line of unity, with the exception of 10 samples which were non-detect by USGS methods and reported as zeros.

If the zeros are omitted, a regression predicting the tri- and higher-chlorinated homologue sum from USGS results has a slope of 0.92 (with intercept) and 1.03 (no-intercept). In both cases, the slope coefficient is not significantly different from 1. It therefore appears that the USGS results can be taken directly as a reasonable approximation of the sum of tri- and higher-chlorinated homologues.


GE Split Samples, Total PCBs
USGS vs Congener
USGS (ppm)
0.15
0.1
0.05
0
0
0.05
0.1
0.15
Congener Sum (ppm)


GE Split Samples, Total PCBs
USGS vs Homologues 3-10

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MEMORANDUM

by Telefax

To: Ed Garvey, Al DiBernardo (TAMS/NJ)
Doug Tomchuk (EPA Region 9)
Vic Bierman, Scott Hinz (LTI)

Date: October 27, 1997

From: J. B. Butcher

Project: Hudson PCBs

Subject: GE Bias Study

Pjn: 1182-09

Number of Pages: 4

Jim Rhea's memo of 10/3/97 presents information which claims to "indicate that PCB concentrations within TID-west samples are unrepresentative of the average concentration passing the TID. PCB concentrations measured in samples collected from this station consistently exceed those in samples collected in the center channel immediately upstream and downstream of the dam. This bias appears to be responsible for the excess loading observed from the TIP since 1991."

While evidence of difference in concentrations between these stations during summer low flow periods does appear clear, the interpretation is not. A more careful examination of the data leads to the following conclusions:

- Even if the estimate of bias is correct, this does not account for all the "excess loading" observed from the TIP; instead, the evidence continues to suggest that there is a summer gain of *at least* 0.5 kg/d total PCBs from the Thompson Island Pool.
- While there is a difference between stations, the conclusion that TID-West observations are biased high, and that this constitutes the entire difference, is only one among a number of possible explanations.
- HydroQual observations on lateral variability of PCB concentrations in the Thompson Island Pool appear to provide evidence that near-shore contaminated sediments ARE a significant source of PCB load to the Pool.

Implications of Alleged Bias

HydroQual's study includes 11 low-flow sample events, collected on 10 different sampling dates. Observations reported at TID-West were in each case higher than those reported for the center channel station above the dam, TIP-18C. On average, the center channel observation was 44% of that at TID-West (note that the "% Difference" reported by HydroQual is calculated in the other direction, being the multiplier applied to center channel observations to obtain the TID-West observation).

Note that these results apply only to summer low flow conditions. Presumably, much greater lateral mixing will occur during more energetic high flow periods, so an estimate of bias from low flow periods only will over-estimate the potential correction in load.

GE's recent corrections to their database resulted in a significant increase in the apparent load gain between the Rogers Island (Rt. 197) and TID-West stations. The older, uncorrected data led to an estimate of approximately 0.5 kg/d load gain across the TIP; using the re-calculated data gives an estimate of about 0.8 kg/d over the 1991-1997 period of record. During summer 1996 and 1997 the re-calculated gain from Rogers Island to TID-West appears to have been about 1.4 kg/d.

If the HydroQual conclusion that the center channel observation is more representative of transport through the Pool is assumed to be correct, and concentrations at this point are assumed to be 44% of TID-West concentrations, this would not eliminate the load gain. Instead, the apparent load gain during summer 1996 and 1997 would be reduced to about 0.5 kg/d total PCBs. In other words, application of the proposed bias correction would almost exactly cancel out the increase in estimated load which resulted from GE's recalculation—and would continue to identify the Thompson Island Pool as a significant source of PCB load.

Interpretation of the Bias

There are a number of alternative explanations, other than simple bias in TID-West observations, which may account for part or all of the difference between TID-West and center channel observations at TIP-18C.

Which observation is biased?

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

From April 1991 through June 1992, GE collected regular monitoring samples at Schuylerville. This period is difficult to interpret, due to large intermittent upstream loads from the Bakers Falls plant.

However, analysis of these data also suggest that TID-West is representative of loads downstream. For the period during which Schuylerville was monitored, the median monthly load gain between Rogers Island and TID-West was 17.8 kg/mo, while the median monthly load gain between Rogers Island and Rt. 29 at Schuylerville was 22 kg/mo.

Diurnal variability

HydroQual does not document time of day of sampling. This may, however, have important consequences if there is a diurnal cycle in concentration patterns. A mechanism for diurnal cycles is provided by hydropeaking power generation at Sacandaga Lake which results in daily variations in flow. During periods of hydropower release, the main channel in TIP might show lower concentrations relative to the near shore areas; when the flow declines, the PCB-enriched nearshore water may then drain back to the main channel.

Horizontal versus vertical variability

An important distinction between sampling locations is that TID-West samples are taken as grabs in shallow water, while TIP-18C samples are vertical composites in approximately 10 feet of water. Part of the difference between stations could represent vertical rather than horizontal variability if composites at TIP-18C have been diluted by low-concentration bottom water. It should be noted that TIP-18C is located in an area with very low sediment PCB concentrations (on the order of 5-10 ppm during 1984), which could lead to reduction in near-sediment water concentrations.

Temperature differences (not documented) may also play a role in concentration differences between stations. During summer daytime sampling, shallow water at TID-West is presumably much warmer than bottom water at TIP-18C. Warmer temperatures will drive more PCBs to the dissolved form; colder temperatures will drive more PCBs to a sorbed form and might reduce the water column concentration during quiescent conditions.

Evidence of Loading from TIP Sediments

The HydroQual results appear to demonstrate that, during summer low flow conditions, PCB concentrations are higher in shallow nearshore areas above Thompson Island Dam than in the main channel. The strong concentration differential suggests that the increased PCBs nearshore must arise from nearby sources (e.g., hotspots 15 through 20), thus allowing limited time for lateral mixing. An unintended consequence of the bias study would thus appear to be a demonstration that these hotspots do indeed constitute a significant source of PCBs to the water column. Even if the nearshore concentrations are biased high relative to total load, it is these shallow nearshore concentrations which are most relevant to biological exposure. Further, highest concentrations in the shallow nearshore areas would appear to be inconsistent with last year's favorite theory of bed transport of NAPL droplets, which should accumulate in the deeper channel areas.

Additional Sampling

In sum, evidence presented to date by GE is inconclusive and subject to several alternative interpretations. Additional sampling and study would be needed to justify an interpretation that TID-West samples are biased for interpreting long-term load leaving the Thompson Island Pool. To attempt to constrain the analysis I would suggest the following items for future monitoring:

1. Resume PCB sampling at Rt. 29, Schuylerville on a regular basis. Also sample at Fort Miller on all occasions when "representativeness" samples are taken in the Thompson Island Pool.
2. Document time of day, stage, and temperature for all samples. Also report continuous logging of stage for 24 hours before and after each representativeness sample.
3. During at least one summer low-flow sampling round, analyze an uncomposited vertical profile at TIP-18C, rather than using a vertical composite.
4. Provide a complete diurnal cycle of measurements at TIP-18C and TID-West. Sampling every four hours over a 24-hour cycle should be adequate.

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MEMORANDUM

To: Ed Garvey (TAMS/NJ)
Al DiBernardo (TAMS/NJ)
Vic Bierman, Scott Hinz (LTI)
Trina v. Stackelberg (MCA)

Date: Oct. 1, 1997

From: J. B. Butcher

Project: Hudson

Subject: Revised GE data and load across TIP

Pjn: 1182-09

On Sept. 15, GE provided a major revision to their database. This included reinterpretation of their standards, plus bias correction factors for four co-eluting peaks. The changes are quite significant, particularly resulting in an increase in reported concentrations of dichloro and trichlor homologues. In addition, the water column monitoring data have been extended through July 1997.

Of particular interest is the effect of the revision on interpretation of load gains across the TI Pool (i.e., between Rogers Island and TI Dam monitoring stations). I have therefore complete redone the earlier analysis of load across the TIP. A revised table and figures are attached. Note that the signature of the TIP load has also changed as a result of the GE corrections: This should be taken into account in the modeling.

A couple of additional points regarding the data are worth noting. First, GE has now deleted the NEA quantitations below the detection limit of 11 ng/l. These data were set to one-half the detection limit, and set to the mean distribution of homologues for a station. Second, GE has also deleted the 1/19/94 observation at Rt. 197 which we had flagged as anomalous. Various other database errors appear to have been fixed, and a few other observations also appear to have been removed. Finally, updated daily flows (used in calculation of load) were obtained from USGS/Troy and have been forwarded to TAMS.

The attached table and figures are largely self-explanatory, and are worth perusing. In general, the revised and extended results further emphasize the importance of the TIP as a source of PCB load, and make theories that this load is somehow derived from NAPL seeps at Hudson Falls appear less likely. Some key points are summarized below:

1. Estimated PCB load gain across the TIP is larger using the revised data. It increases 48% over the DEIR estimate, going from 0.56 to 0.83 kg/d (changing from 203 to 297 kg/yr). Note that GE's claim that TIP gain is equal to the mass loading rate from the Hudson Falls seep is no longer correct.

2. Estimated load gain increases versus earlier estimates for all homologue groups; however, gain

is most dramatic for dichloro homologues. Due primarily to GE corrections to quantitation, estimates of yearly load gain of dichloros originating in the TIP has more than doubled. Dichloro homologues now dominate the TIP signature, while the relative importance of monochloros has decreased.

3. The 1996-1997 data on TIP load gain are consistent with earlier observations, and further support identification of TIP sediment as a significant PCB source.

4. A strong decrease in concentration has been seen at Rogers Island (Rt. 197) since Spring 1995. This decrease is NOT seen at TI Dam. In particular, the summer concentration at TI Dam appears to have been approximately constant since 1993, while the winter concentration has decreased. This fits with interpretation of the TIP source as being mediated by warm-weather biological activity and/or physical processes associated with higher temperatures and receding flows.

5. Load *gain* across the TIP has continued unabated through summer 1997, even though load at Rogers Island has fallen dramatically. This suggests that the theory attributing TIP load to short-term storage of PCB NAPL derived from Hudson Falls is unlikely to be correct.

6. The "signature" of the TIP load during the summer is fairly constant from year to year through 1997, even though the upstream signature has changed over time.

Attachments: 1 table, 24 figures

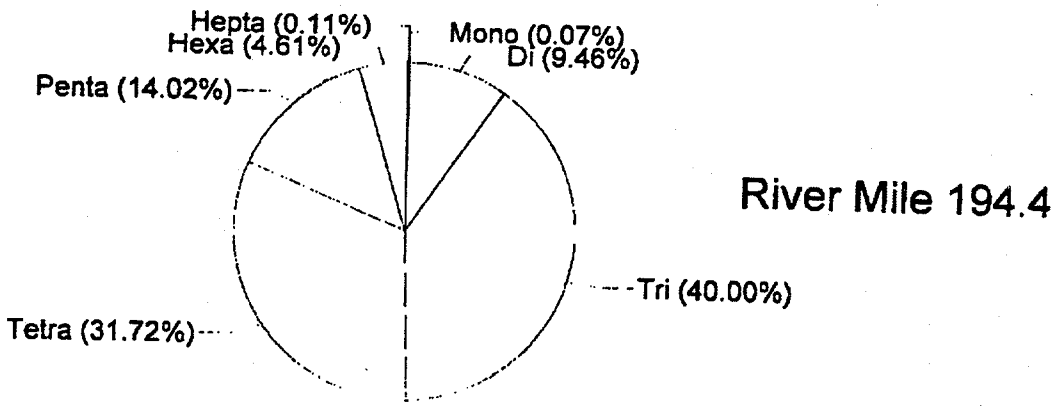
Table 3-21

Cumulative Loading across the Thompson Island Pool by Homologue Group from GE Data April 1991 through July 1997

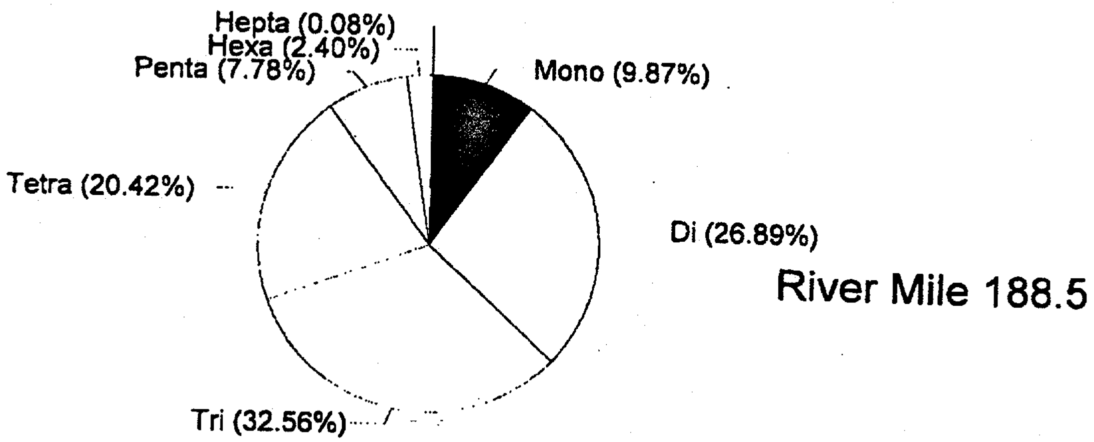
	Total PCBs	Monochloro-Homologues	Dichloro-Homologues	Trichloro-Homologues	Tetrachloro-Homologues	Pentachloro-Homologues	Hexa- and Heptachloro-Homologues
River Mile 194.3 (Rt. 197 Bridge; kg, cumulative)	2298.2	10.2	216.2	973.5	744.0	262.6	90.7
River Mile 188.5 (Thompson Island Dam; kg, cumulative)	4181.1	451.8	1020.2	1432.6	886.6	295.3	93.6
Gain in Load across Thompson Island Pool (kg, cumulative)	1882.9	441.6	804.0	459.1	142.6	32.8	2.9
Gain in Load across Thompson Island Pool (kg/yr)	297.3	69.7	127.0	72.5	22.5	5.2	0.5
Average Loading Rate at River Mile 188.5 (kg/day)	1.83	0.20	0.45	0.63	0.39	0.13	0.04
Average Gain at Thompson Island Dam (kg/d)	0.826	0.194	0.353	0.201	0.0626	0.0144	0.00128

Source: Revised GE data in GE970915.DBF; updated flows from USGS.

JBB, 10/1/97



PCB Homolog Composition Across Thompson Island Pool, GE Monitoring 4/91 - 7/97



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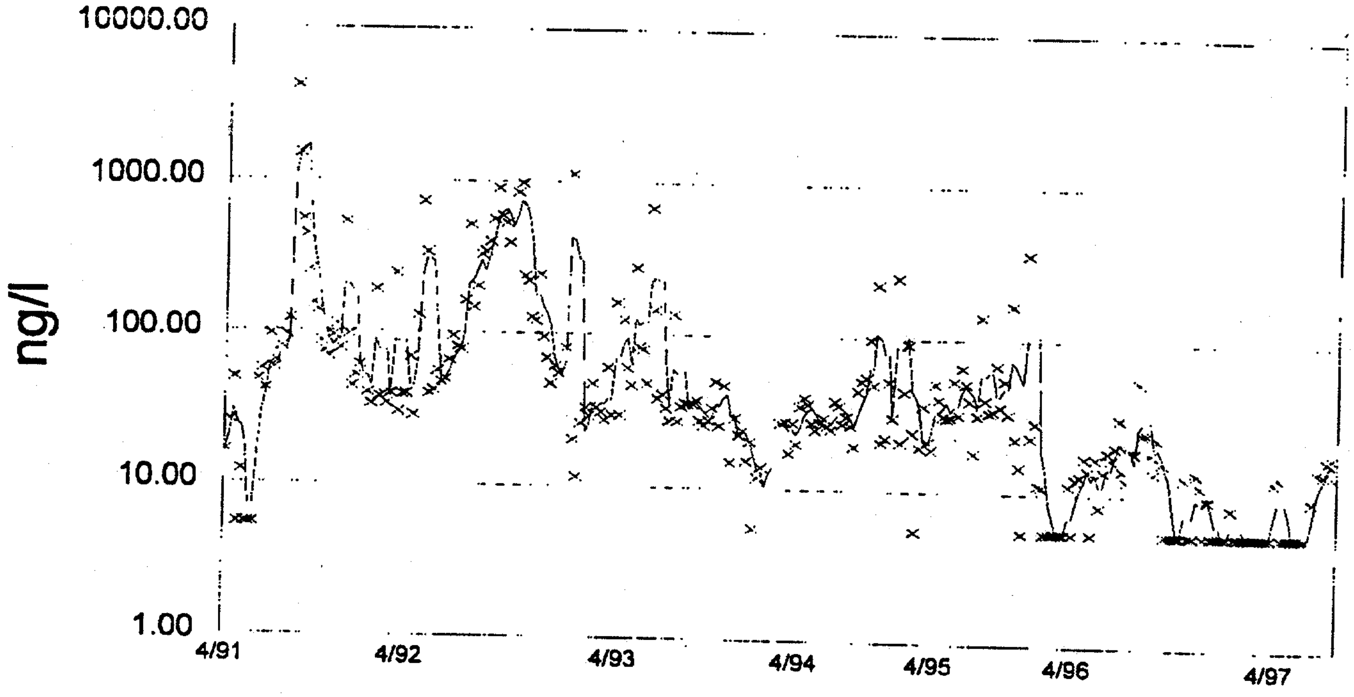
Data Status: GE Revised 970915

Total PCB Concentrations at RM 194.2

GE Data, with Moving Average



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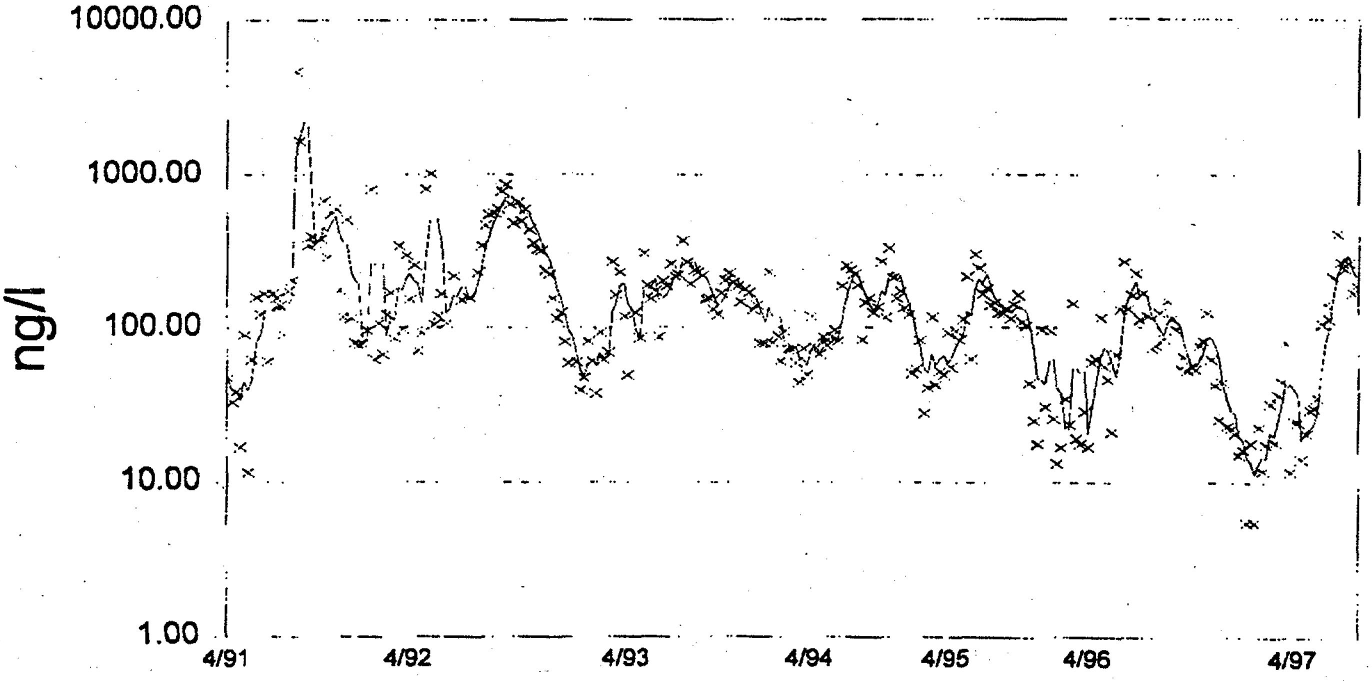
Total PCB Concentrations at TI Dam

GE Data, with Moving Average



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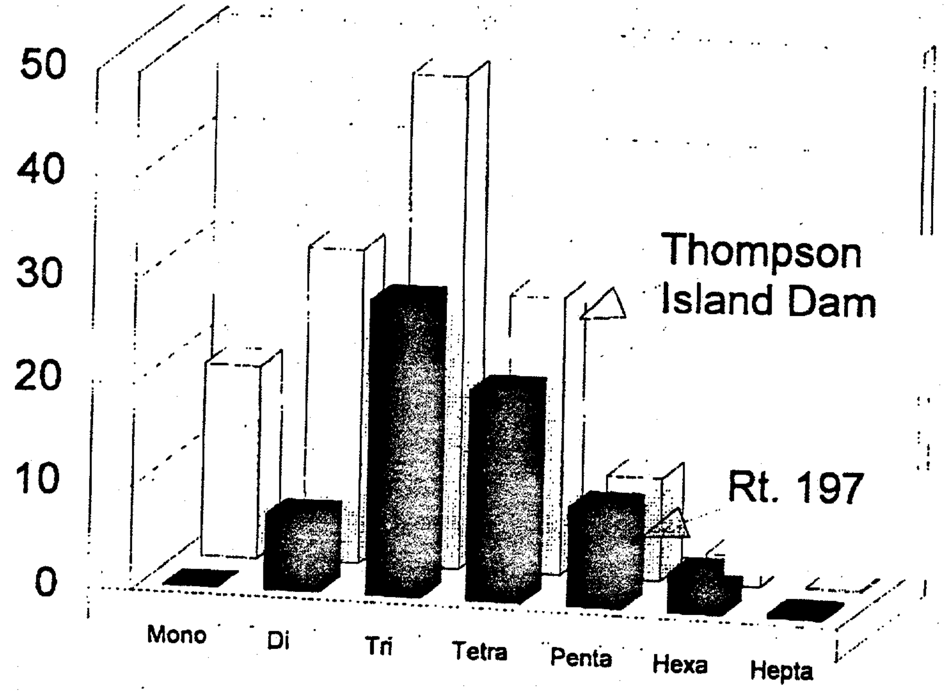
Summer PCB Homolog Concentrations

June-Aug. 1991 GE Data



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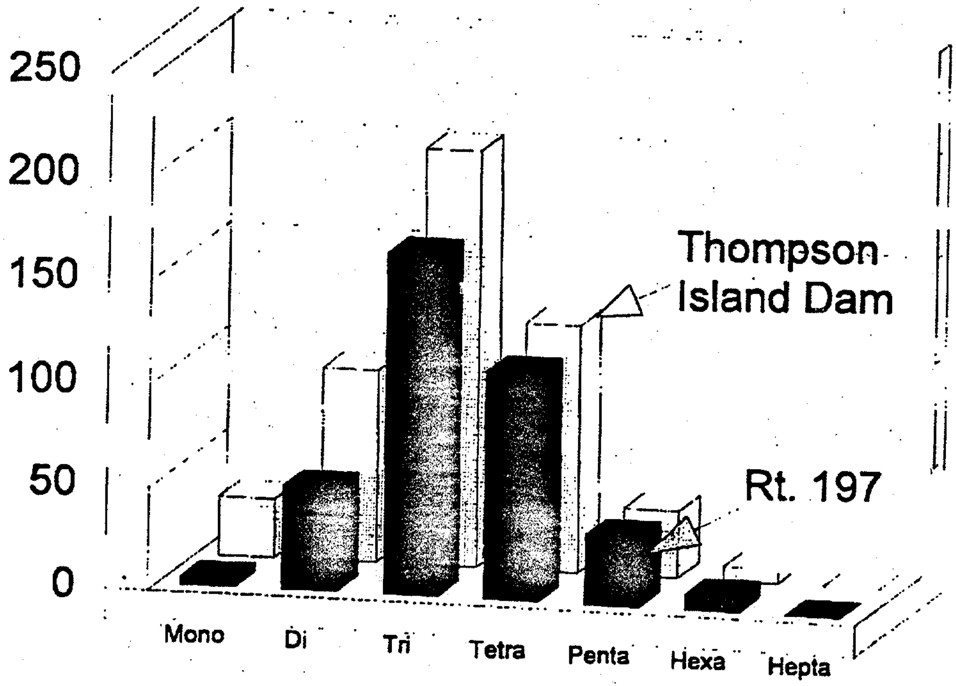
Summer PCB Homolog Concentrations

June-Aug. 1992 GE Data



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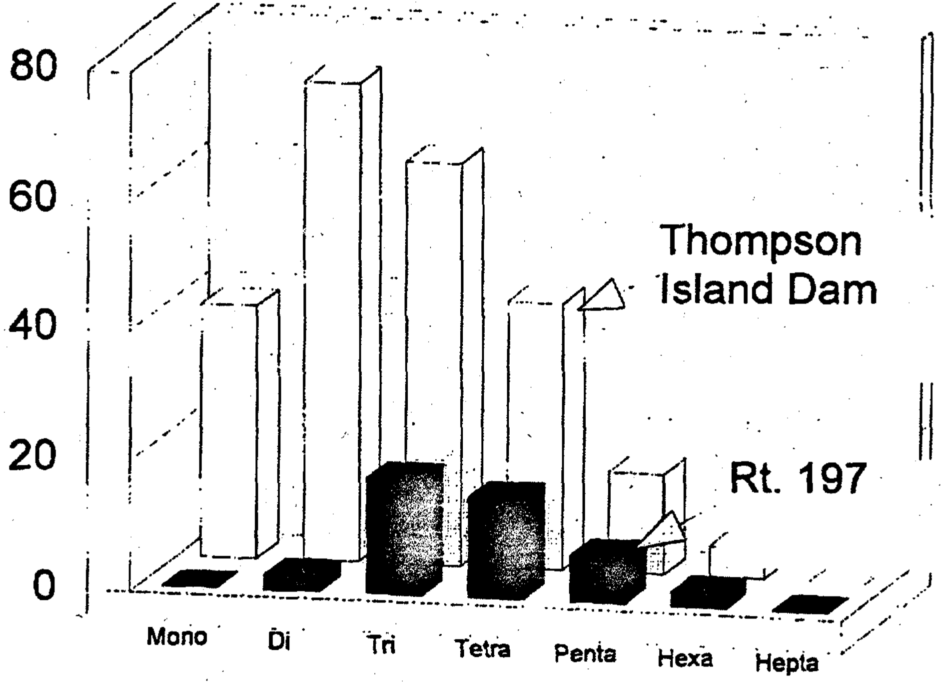
Summer PCB Homolog Concentrations

June-Aug. 1993 GE Data



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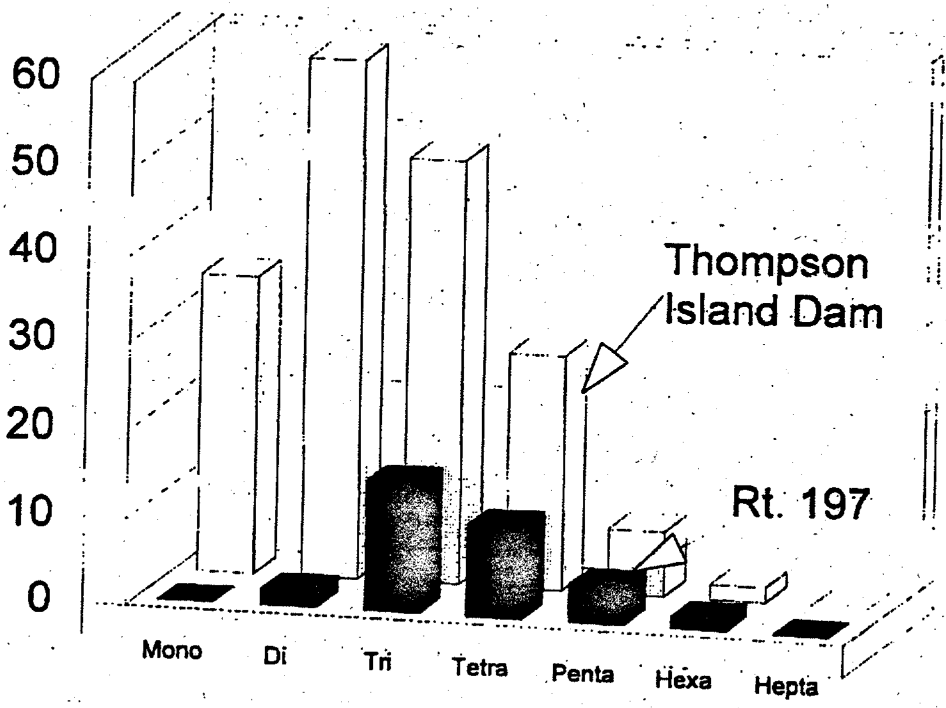
Summer PCB Homolog Concentrations

June-August 1994 GE Data



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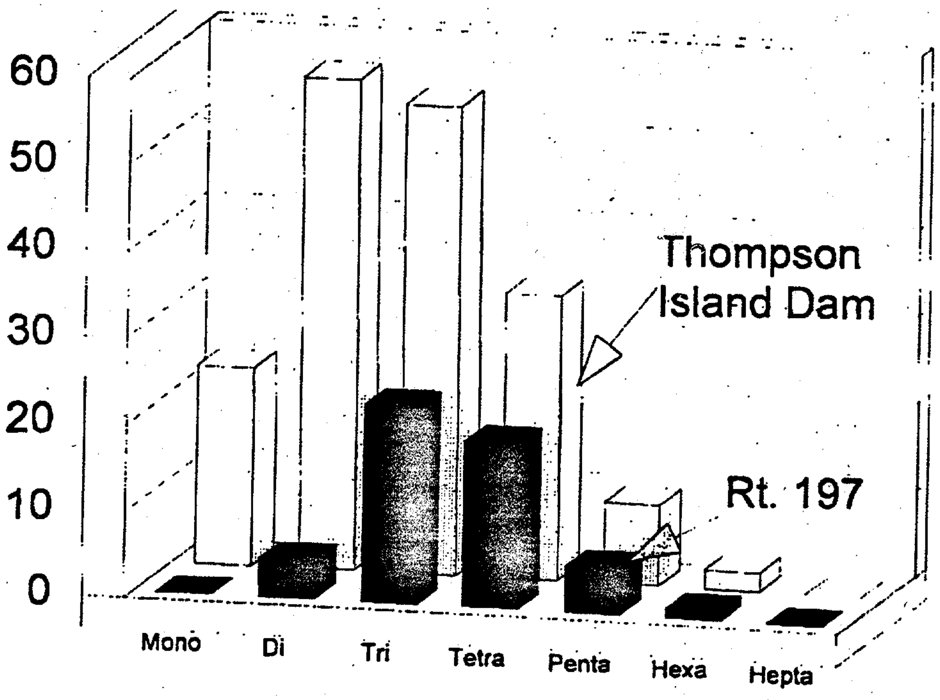
Summer PCB Homolog Concentrations

June-August 1995 GE Data



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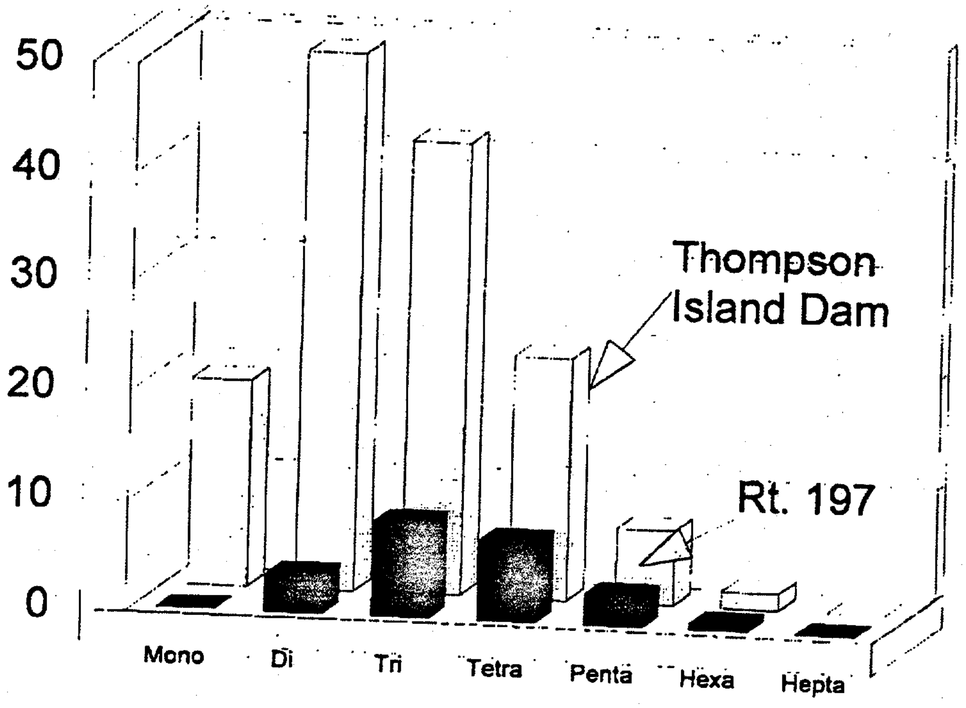
Summer PCB Homolog Concentrations
June-August 1996 GE Data



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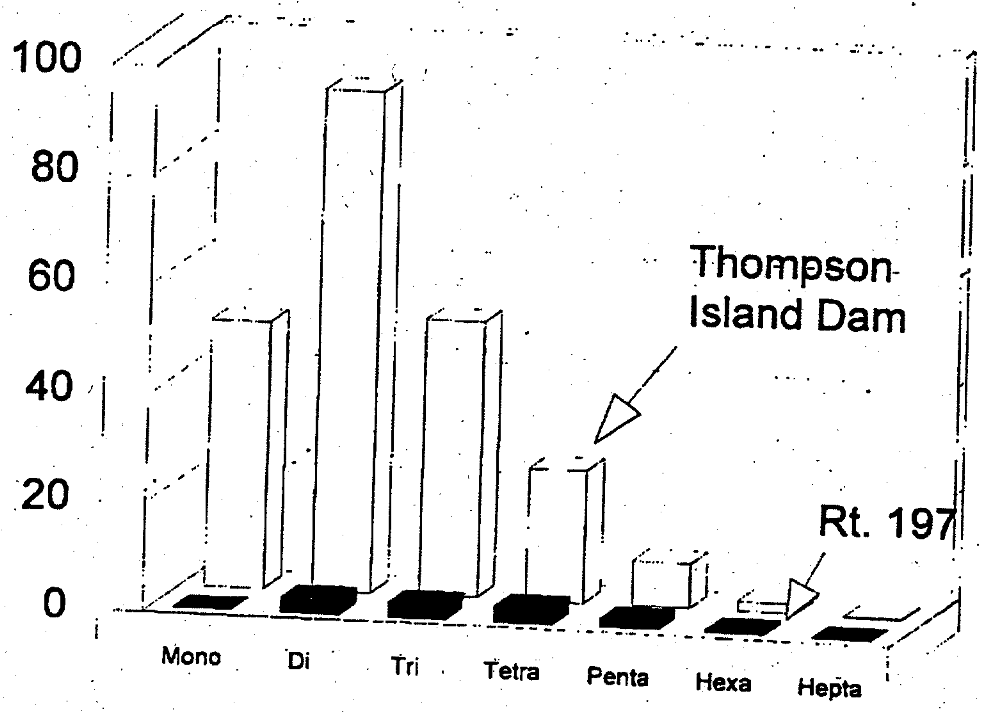
Summer PCB Homolog Concentrations

June-August 1997 GE Data



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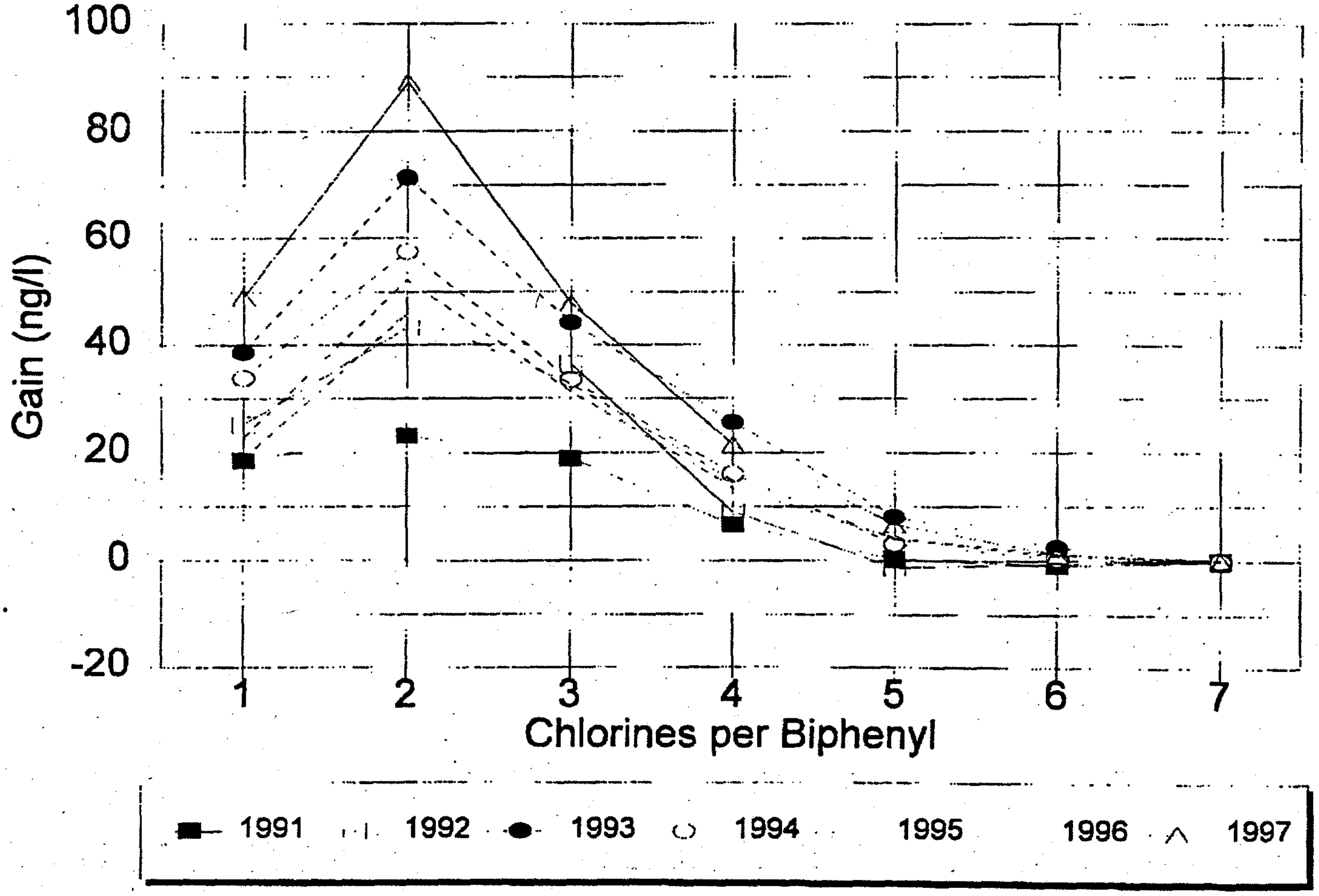
Summer Change in Conc. across TIP



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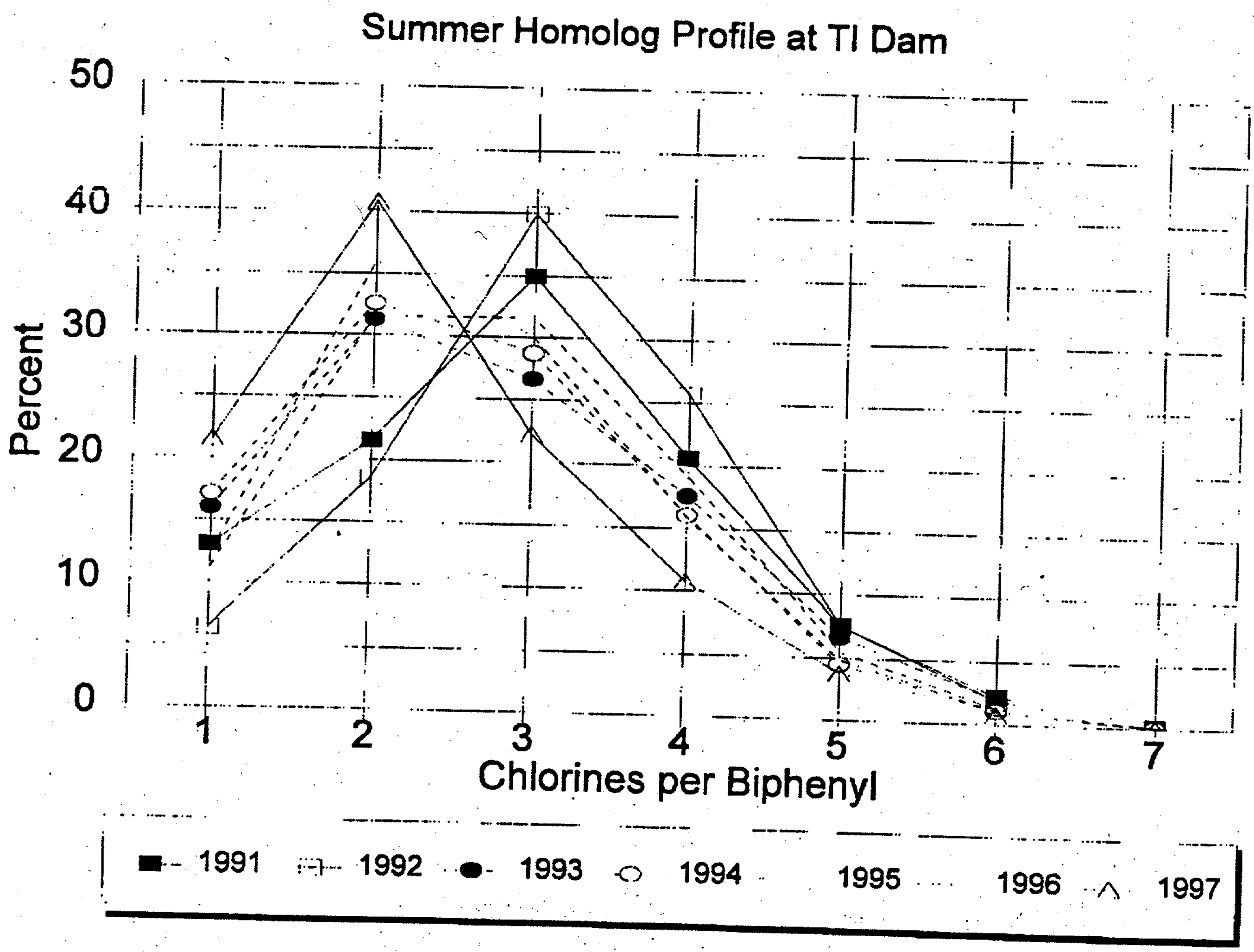

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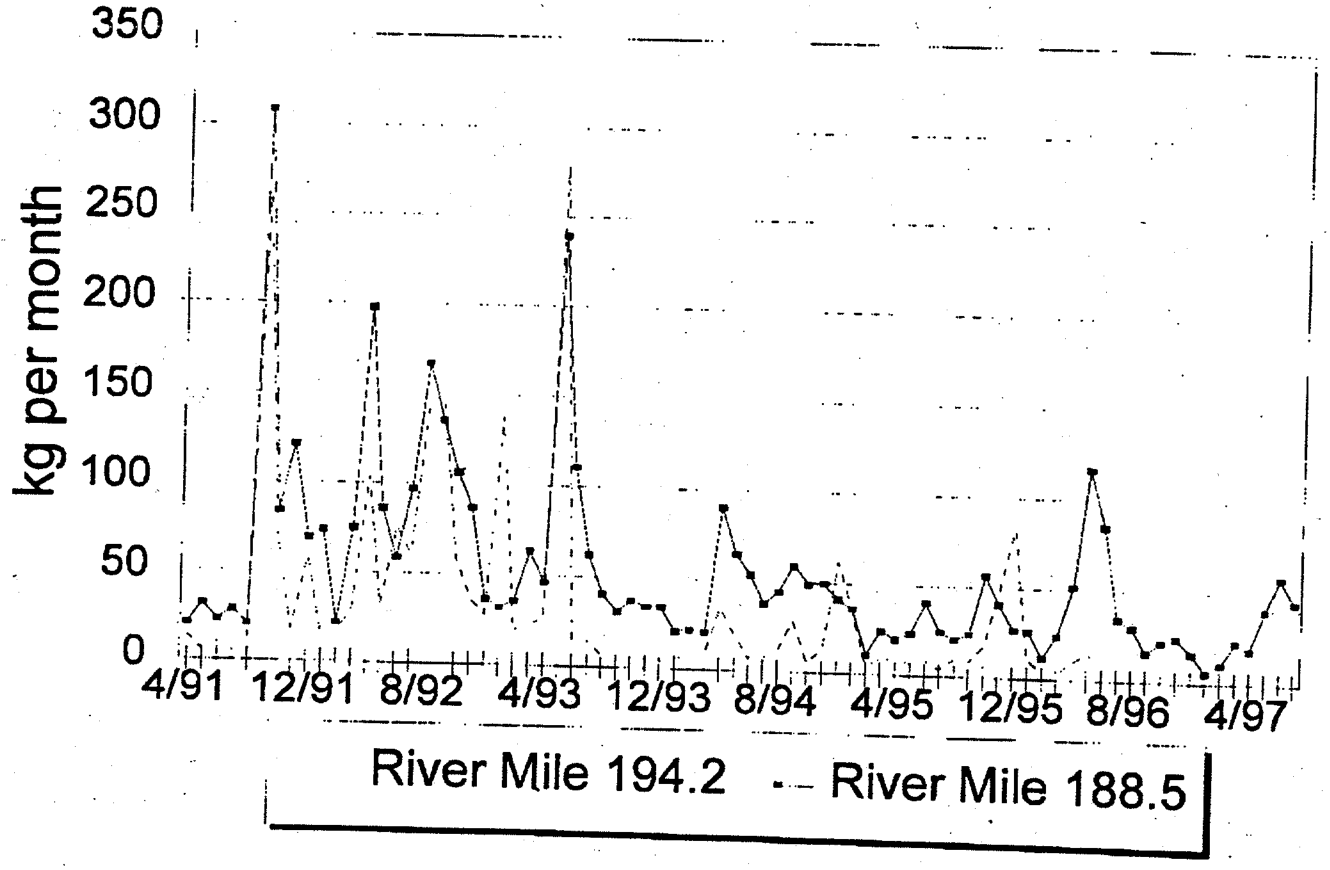
Monthly PCB Load, Thompson Is. Pool

Averaging Estimate on GE Data



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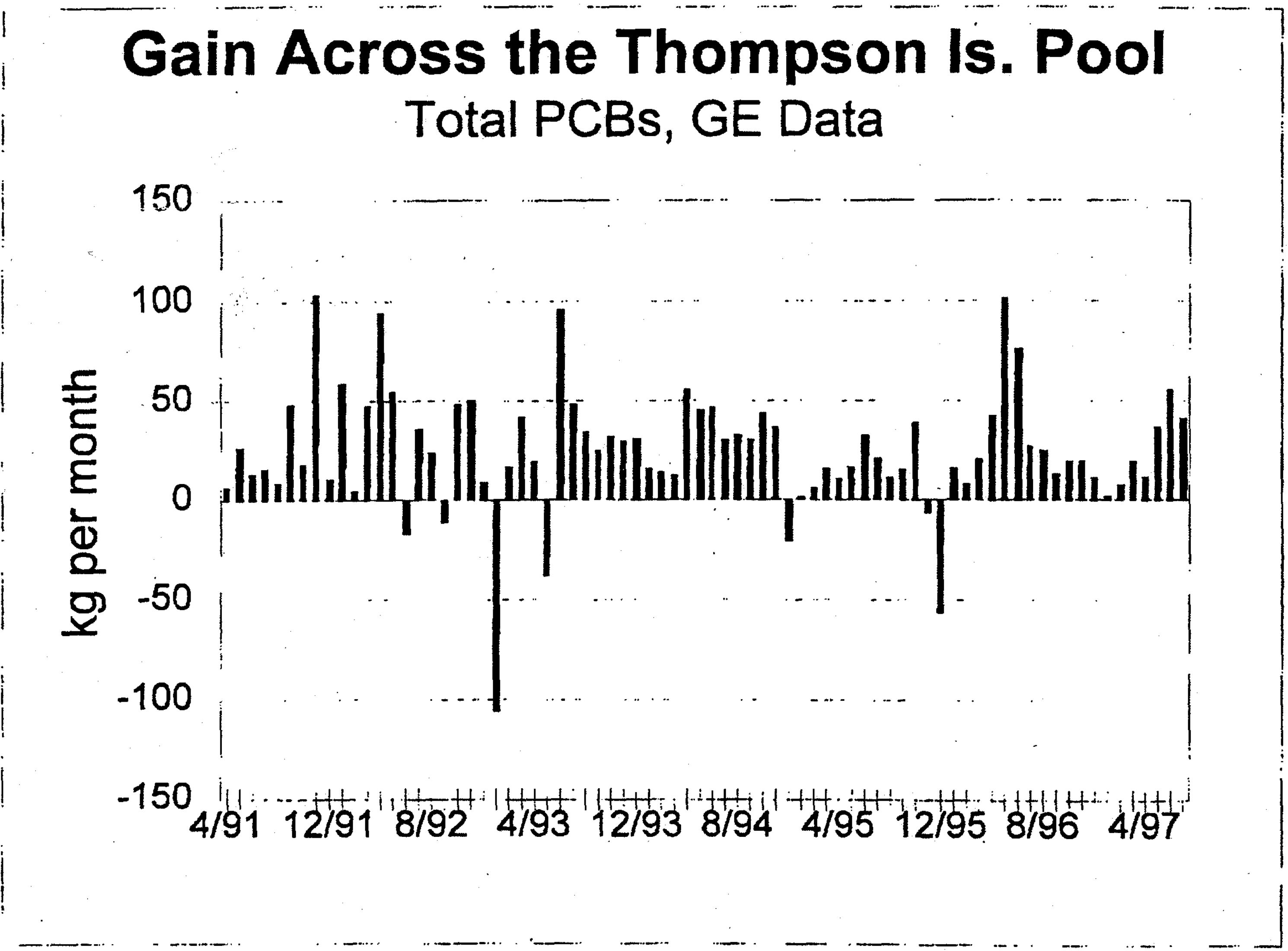

Gain Across the Thompson Is. Pool

Total PCBs, GE Data

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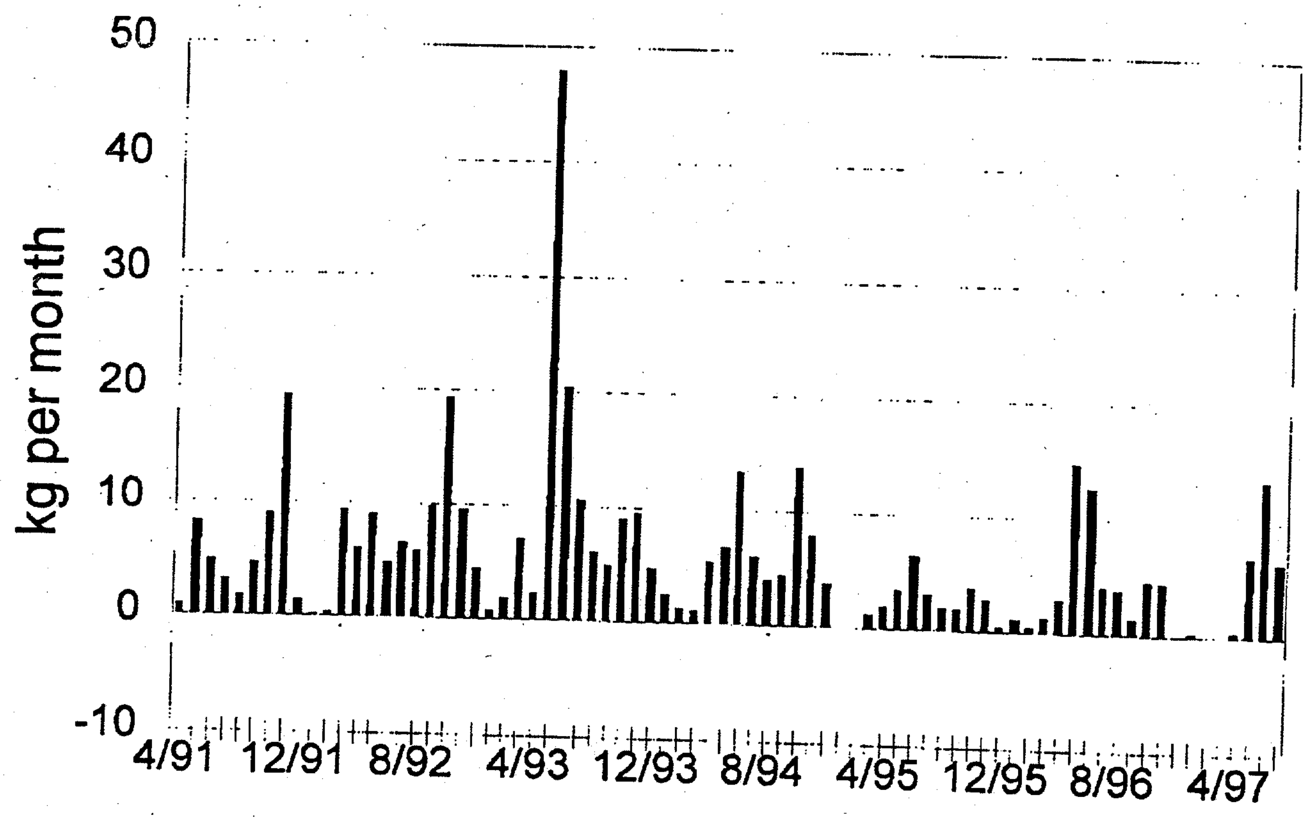
Gain Across the Thompson Is. Pool

Mono-Chloro Homologs, GE Data



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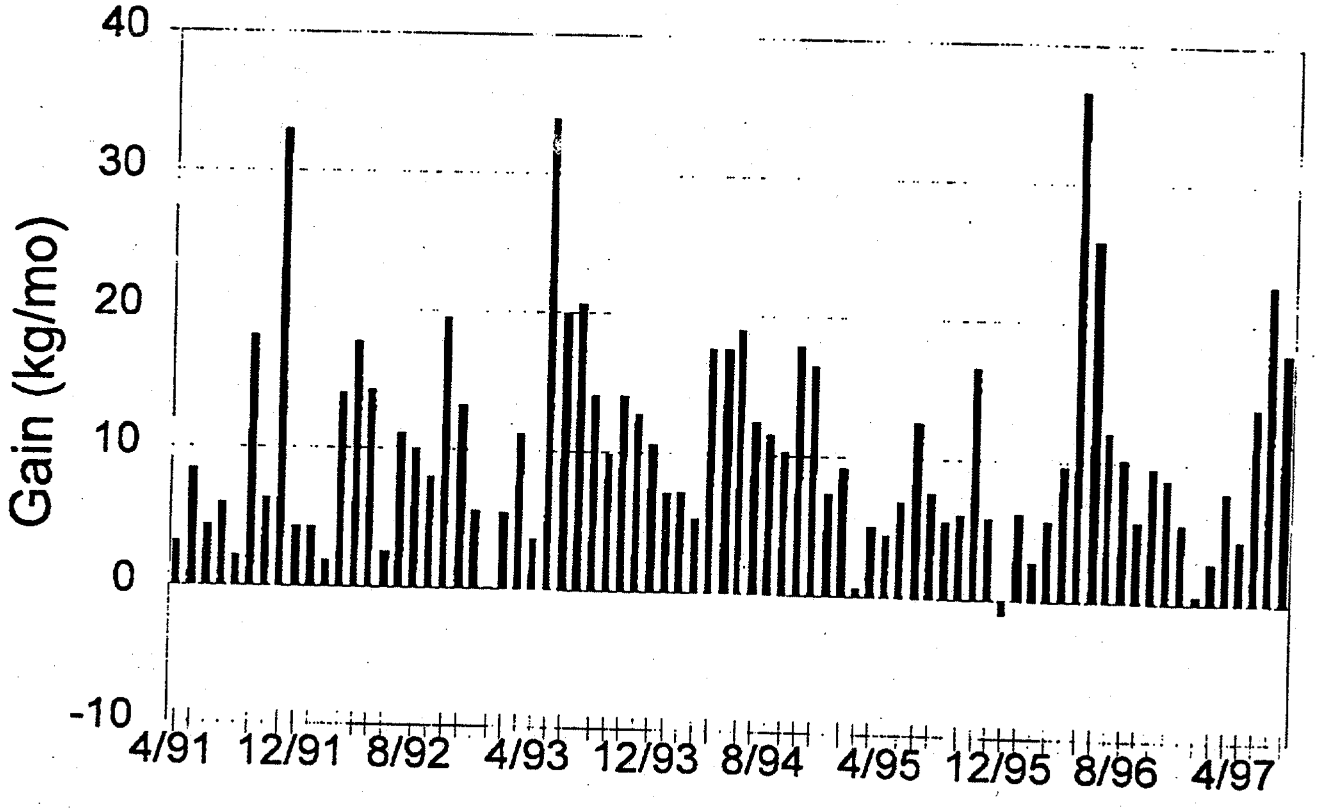
Gain Across the Thompson Is. Pool

Di-Chloro Homologs, GE Data



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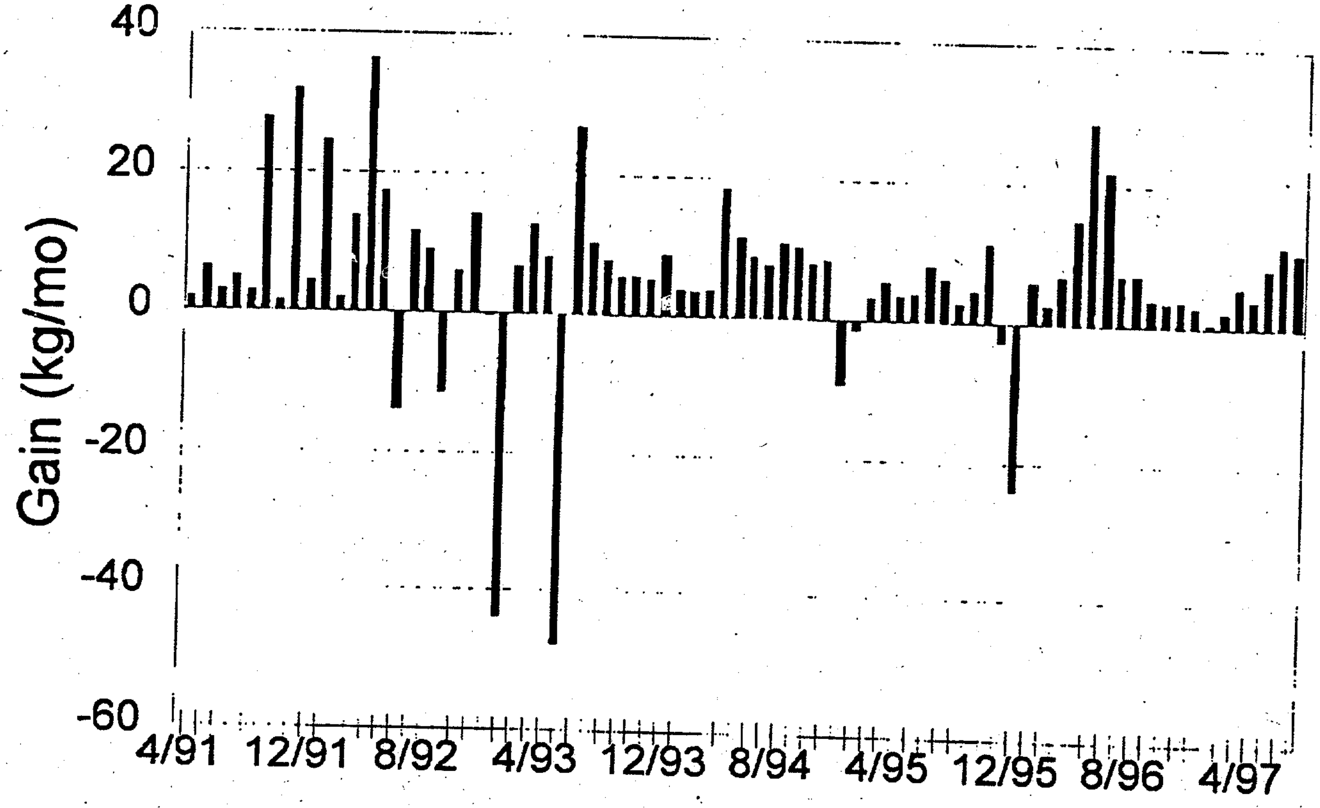
Gain Across the Thompson Is. Pool

Tri-Chloro Homologs, GE Data



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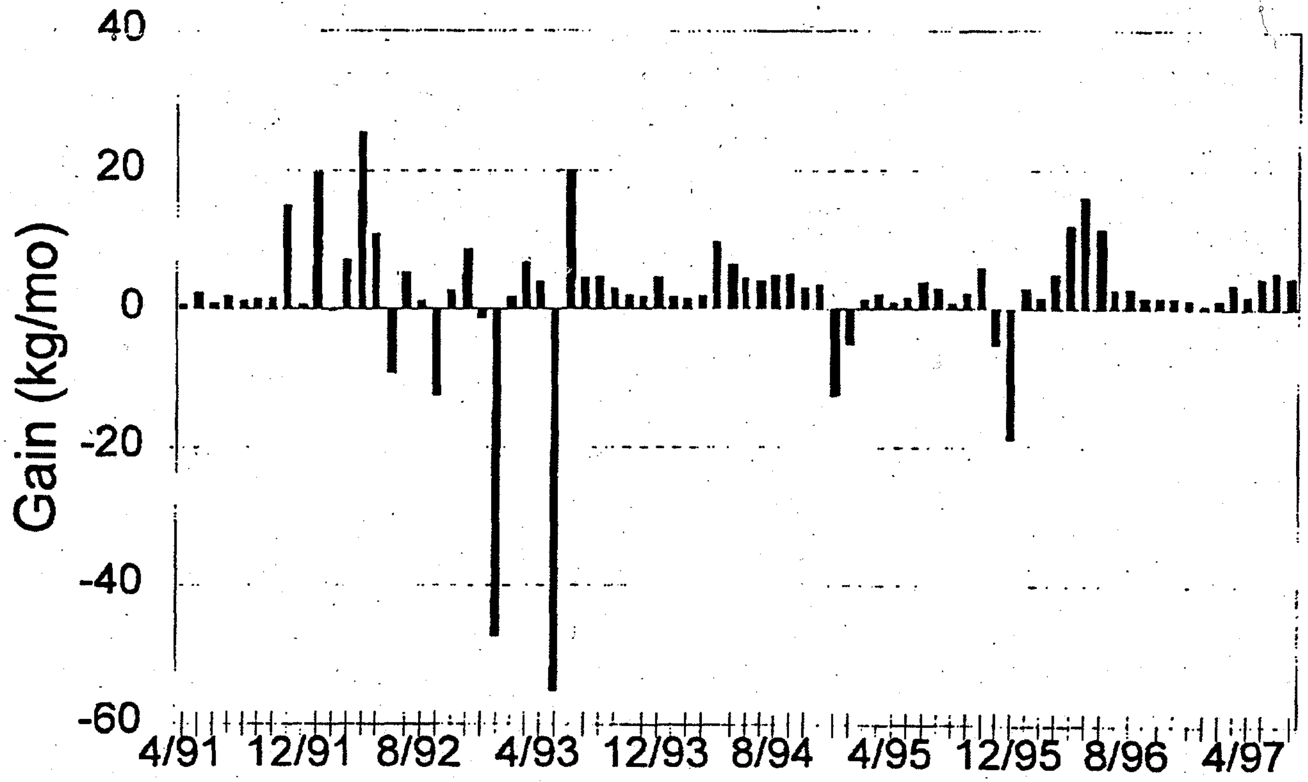
Gain Across the Thompson Is. Pool

Tetra-Chloro Homologs, GE Data



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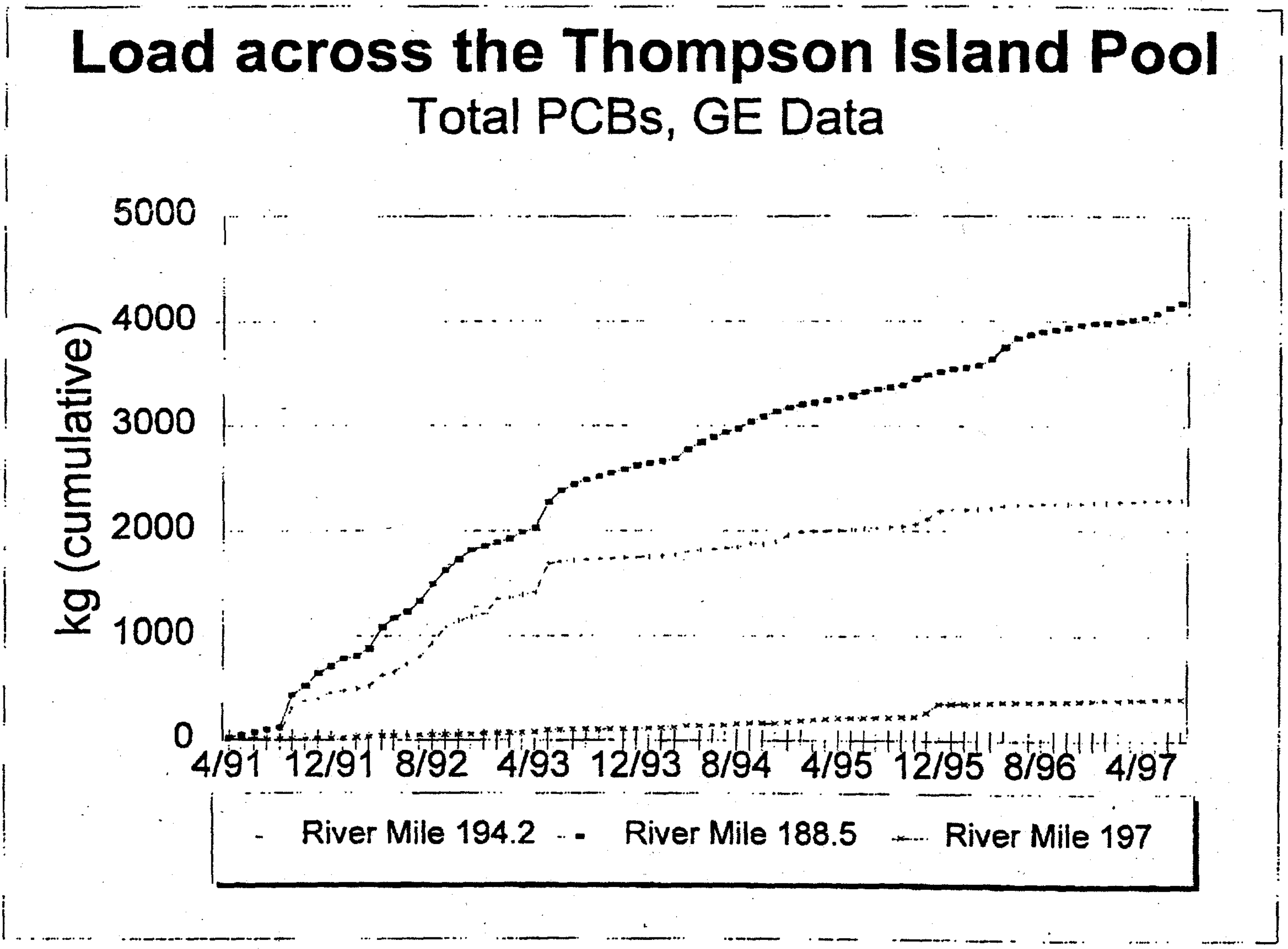

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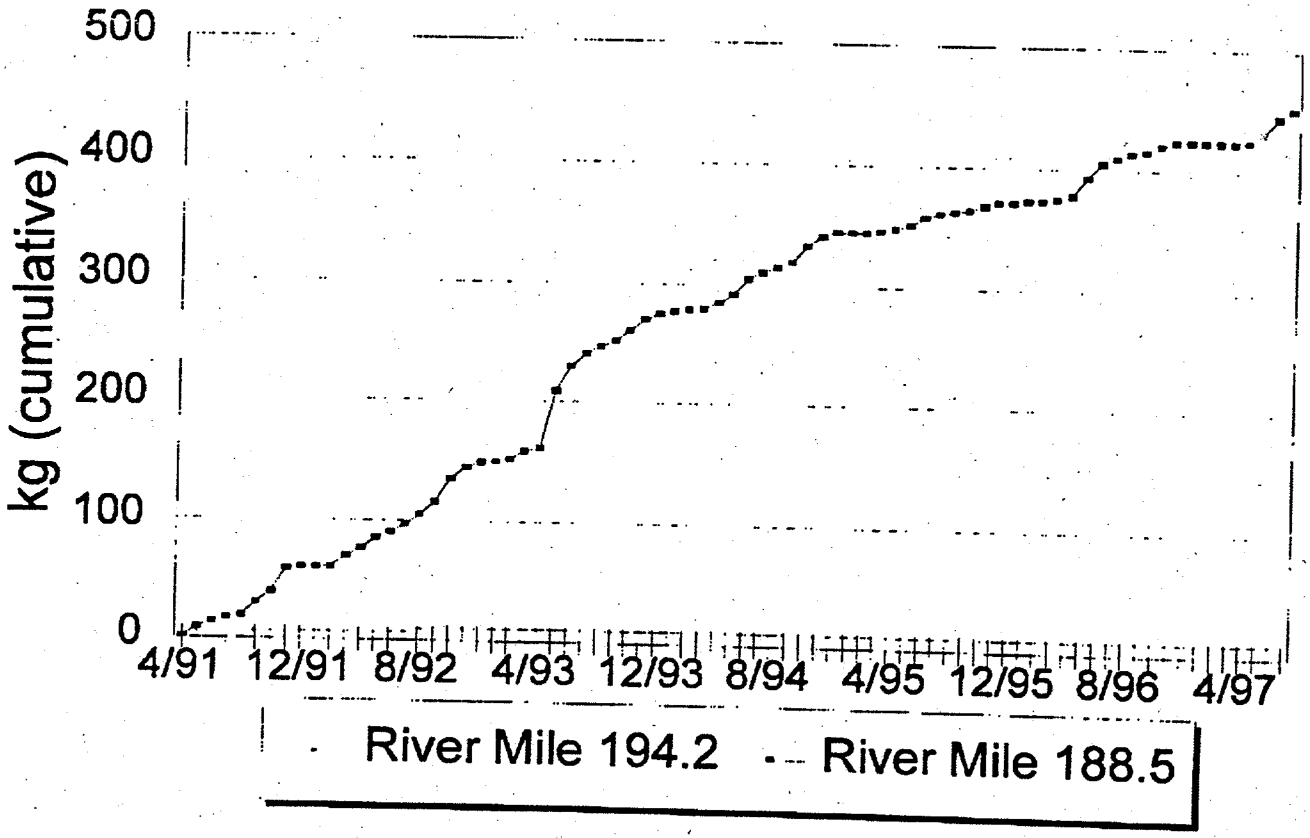
Load across the Thompson Island Pool

Mono-chloro Homologs, GE Data



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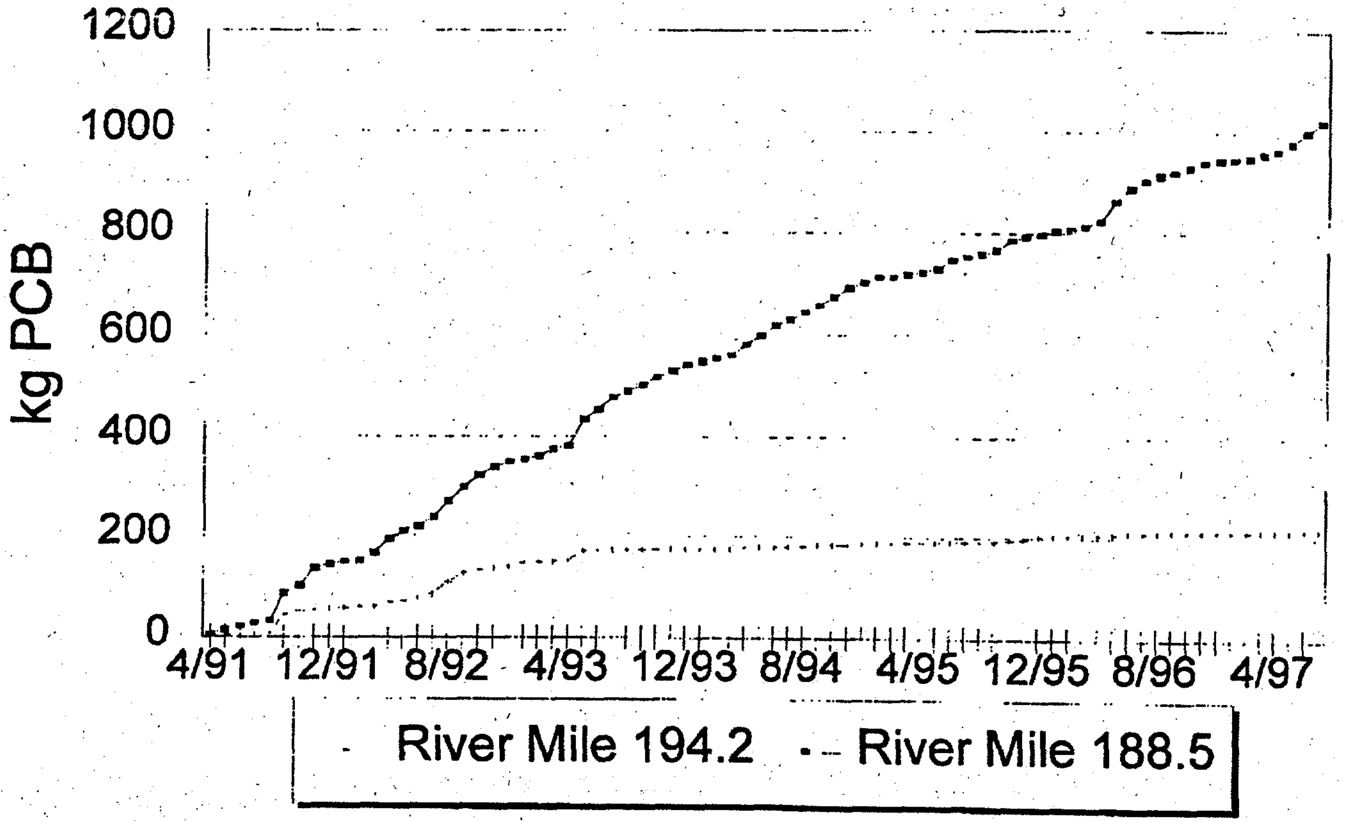
Load Across the Thompson Island Pool

Di-chloro Homologs, GE Data



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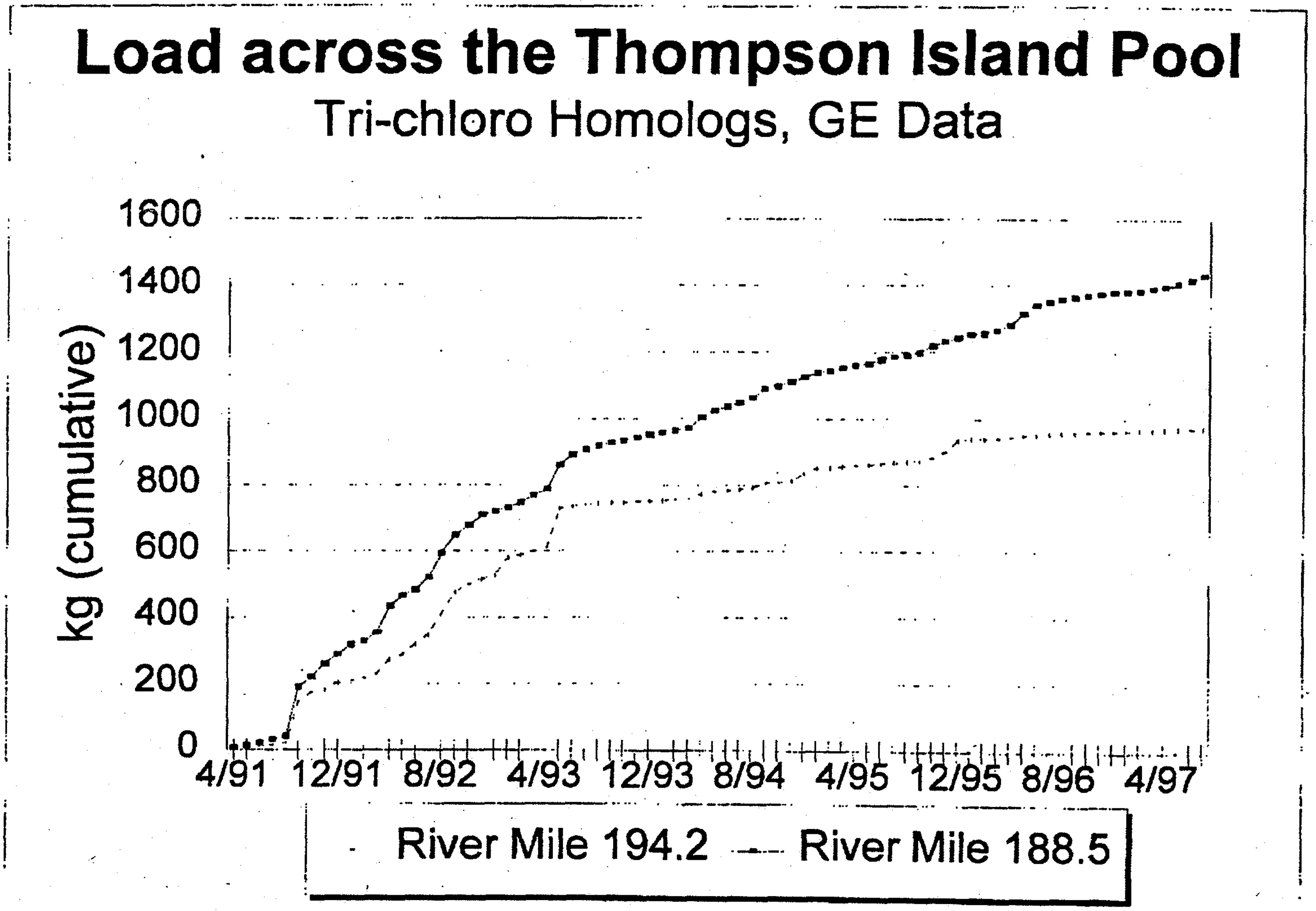

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Load Across the Thompson Island Pool

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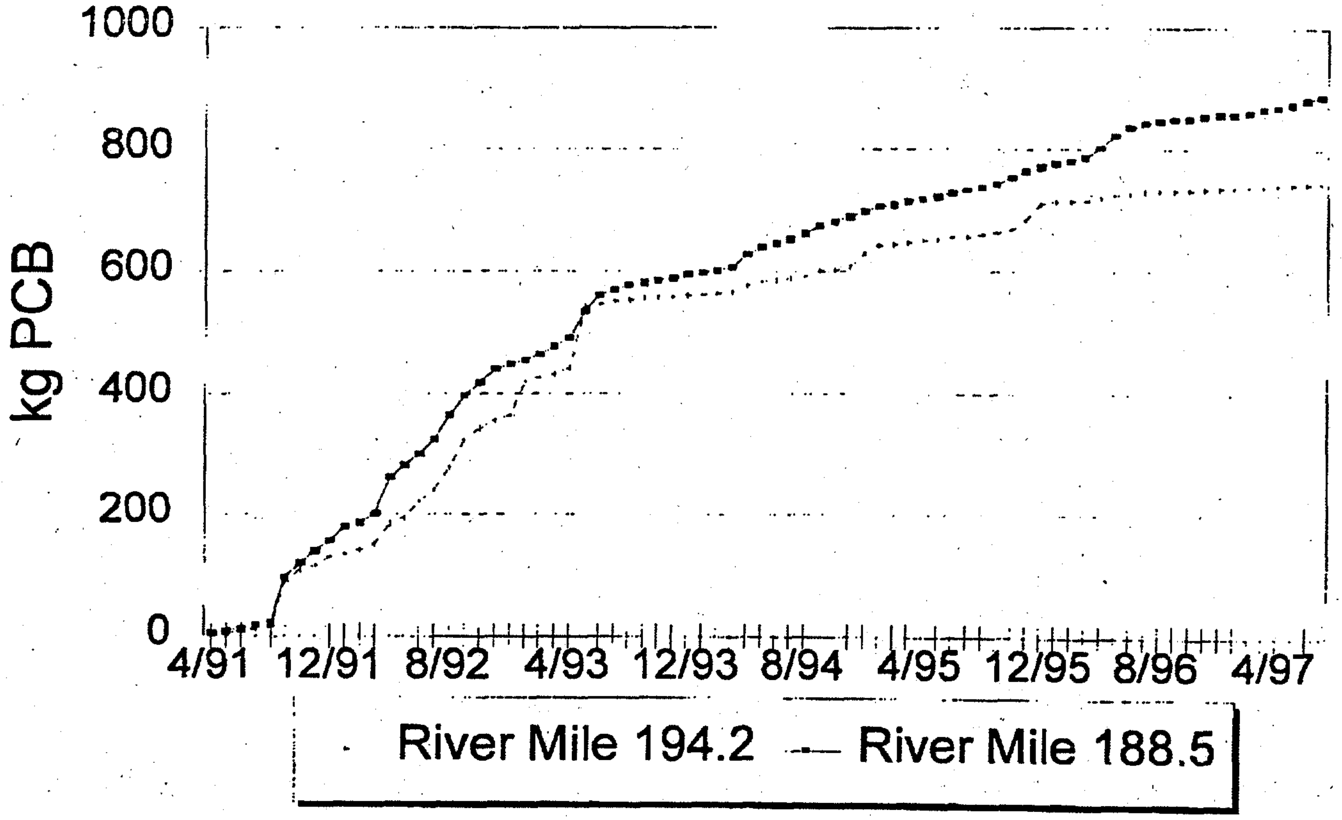

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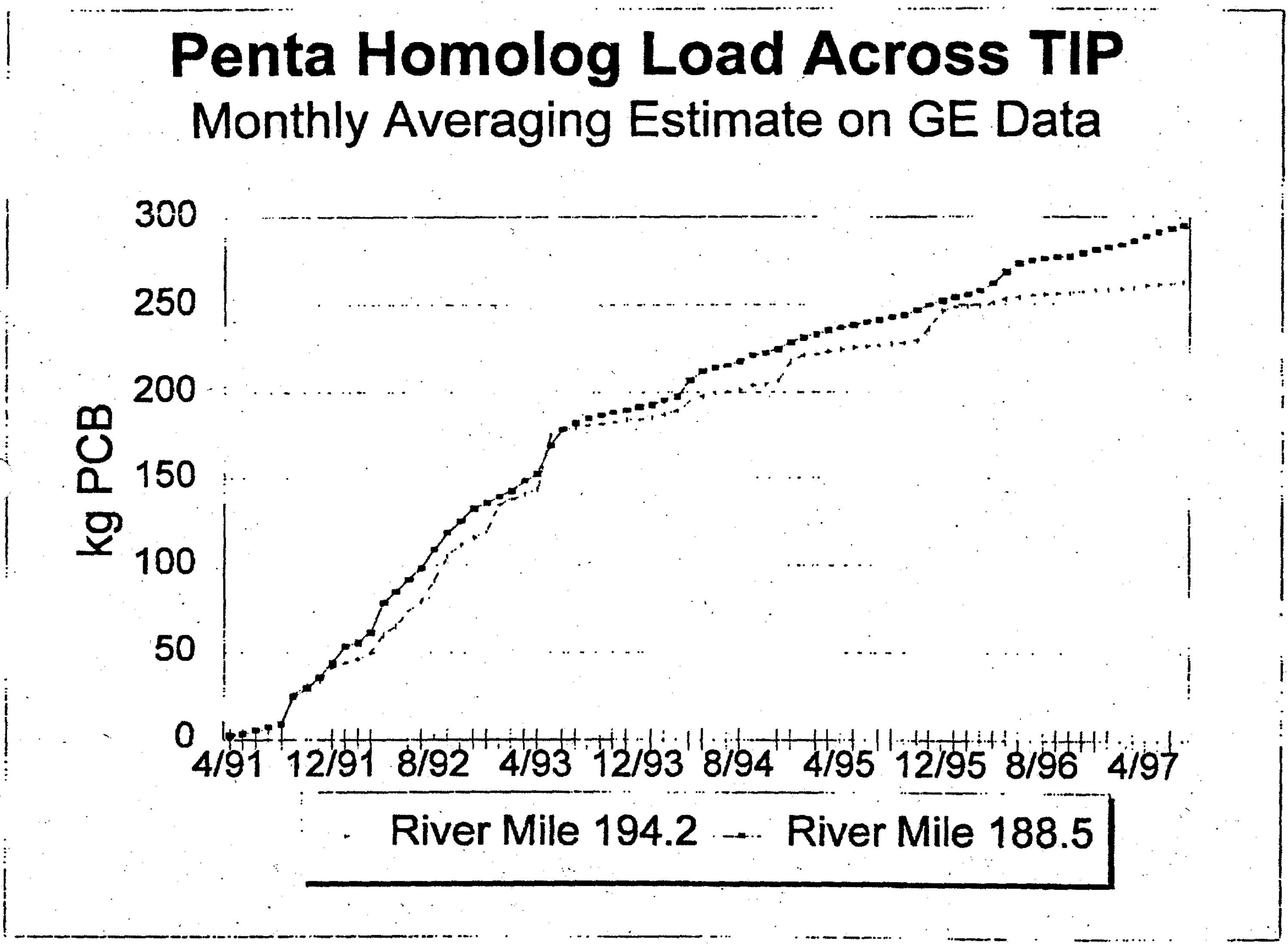

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