700063

December 20, 1998

To: William Ports, NYDDEC

From: Richard Bopp

Re: Report on Task 1

**Overview:**

The Low Resolution Sediment Coring Report (TAMS et al., July, 1988) included a comparison of PCB inventories in cores collected by NYSDEC in 1984 with the low resolution cores collected at the same locations in 1994. The conclusion, that there had been a significant loss of PCBs, elicited a detailed response and numerous objections from General Electric (GE and QEA, August 31, 1998). This task was undertaken to better understand the details of the EPA analysis and to add to the analysis some relevant data from sediment cores that I collected under contract to NYSDEC in 1983.

My analysis, divided into four specific topics is presented below. The new data presented is limited because it is from a single core collected in 1983, however, it does indicate the type of data that could be generated from analysis of eleven other archived cores from that collection. Following the rather technical discussion is a general summary and recommendations.

**Point One; On the Calibration of the 1984 Analyses:**

The sediment samples collected by NYSDEC from the upper Hudson in 1984 were quantified using packed column gas chromatography. The USEPA Low Resolution Sediment Coring Report (July, 1988) concluded that the total PCBs (Aroclor Sum) reported for the 1984 samples represented approximately the tri and higher chlorinated (Tri +) congeners. This was based on application of the 1984 quantification scheme (Brown et al., 1988) to the 1994 congener-specific sample analyses. To do this, it was necessary to specify the congeners associated with several packed column peaks (USEPA, July, 1998, Table 1, page E-4). A best fit indicated that the calculated Aroclor Sum was 1.06 times the concentration of the Tri + congeners.

Since the composition of sediment-associated PCBs had changed via reductive dechlorination between 1984 and 1994, it would have been most useful to have congener-specific analyses of samples collected in or around 1984 for comparing the quantification schemes (Aroclor Sum, Tri +, and Total Congener).

Congener-specific analyses conducted at the NYS Department of Health (DOH) have been reported for samples from a sediment core collected from the Thompson Island Pool

in 1983 (McNulty, 1997). This core, 188.5, was one of twelve collected from the upper Hudson between Fort Edward and Mechanicville as part of a NYSDEC project (Bopp et al., 1985).

Results obtained for the Aroclor Sum quantification of these samples are compared to the Tri + Congeners and Total Congener results in Table 1. They are in general agreement with the EPA analysis. The calculated Aroclor Sum was approximately 1.36 (compared to 1.06) times the concentration of the Tri + congeners (Figure 1). In addition, the Aroclor Sum quantification was always significantly smaller than the Total Congener concentration. As indicated in the EPA analysis, under prediction of Total Congener concentrations would result from reductive dechlorination in the 1983 (1984) samples. The comparison of Aroclor Sum and Total Congener is most significant because the EPA analysis went on to use the Aroclor Sum as a lower limit on the Total Congener concentration in the 1984 samples, an assumption supported by this analysis of the 1983 data.

**Point 2; On Dechlorination in the 1984 Samples:**

The EPA analysis presented no specific information on dechlorination in the 1984 samples. There are, however, data (Brown et al. 1984; Bopp et al. 1985; McNulty, 1997) that show significant dechlorination in upper Hudson sediment samples collected around that time. Samples collected in 1983 have been archived and additional analyses could be performed. Based on the NYSDOH analyses of samples from core 188.5, reductive dechlorination is primarily responsible for the observation that Aroclor Sum values are approximately 0.65 times the Total Congener concentrations (Table 1; Figure 2). Similar levels of dechlorination were observed in several other samples from the 1983 core collection (Bopp et al., 1985). An estimate of Total Congener concentrations in the 1984 samples is required to estimate the re-release of PCBs to the water column between 1984 and 1994.

Based on using the Aroclor Sum as a lower limit of Total Congener concentrations in the 1984 samples, EPA currently estimates a lower bound of 28% re-release of PCBs to the water column from sediments with Aroclor Sum inventories greater than 10.6g/m$^2$ (USEPA, July, 1998, p. 4-45). If it is assumed that the Aroclor Sum values represent 0.65 times the Total Congener concentrations, a re-release of approximately 53% is indicated.

**Point 3; On Quantifying Congener-Specific Analyses as if they were Packed Column Analyses:**

As mentioned above, this procedure, which essentially calibrates the Aroclor Sum quantification of the 1984 samples, depends on the specification of congeners associated with several packed column peaks. For calculating Aroclor 1242 concentrations, it also

depends on the weight percent associated with the packed column peaks at RRT .28, .47, and .58.

For weight percents, the EPA relied on Aquatec analyses of standards. There were some significant discrepancies between these values and the other two common sources of compositional information, Schulz et al. (1989) and Webb and McCall (1973) (Table 3), however, they did not make a major difference in A 1242 quantification.

More significant was the choice of which congeners to include in the packed column peaks. This is particularly important for the packed column peak at RRT .28. The EPA analysis considered only BZ 15, 17 and 18.

It is important to note that the packed column chromatograms of significantly dechlorinated samples do not resemble chromatograms of A 1242 standards. Inspection of packed column chromatograms from our 1983 samples reveals that the peak at RRT .28 can be identified, but that it is poorly separated from a major peak at about RRT .30 (containing dechlorination products BZ 24 and 27). If the A 1242 quantification of the 1984 sediment samples assigned a significant portion of the RRT .30 peak to RRT .28, the values of Aroclor Sum reported would have been higher than predicted from the EPA analysis. Thus, the reported Aroclor Sum values could be much closer to the Total Congener concentrations and significantly greater than 1.06 times (or 1.36 times) the Tri + concentrations. This would imply that the 28% re-release of PCBs to the water column from sediments with Aroclor Sum inventories greater than 10.6g/m$^2$ would be closer to a best estimate than a lower bound.

To address this question in detail, it would be most helpful to examine any additional data that are available from the 1984 sediment sample analyses, including individual packed column peak quantifications, estimates of homolog distributions and, ideally, chromatograms.

**Point 4; Packed Column and Congener Analyses of the Same Samples:**

The 1983 samples from core 188.5 that were analyzed by the congener-specific method at the NYSDOH had previously been analyzed by packed column chromatography in my laboratory. The packed column chromatograms were recently quantified for A 1242 using the peaks at RRT .28, .47, and .58. The procedure was similar to the A 1242 quantification scheme used for the 1984 samples except that in this case peak heights rather than peak areas were used. Since A 1242 comprises about 90% of the Aroclor Sum values in this core (Table 1), this quantification yields an estimate of Aroclor Sum concentrations.

A 1242 concentrations are compared to Total Congener concentrations and Tri + concentrations in Table 2. The results show that Aroclor Sum concentrations are significantly greater than Tri + congener concentrations and average about 0.85 times the

Total Congener concentrations.

Between 1984 and 1994, EPA currently estimates a lower bound of 28% re-release of PCBs to the water column from sediments with Aroclor Sum inventories greater than 10.6g/m$^2$ (USEPA, July, 1998, p. 4-45). If it is assumed that the Aroclor Sum values represent 0.85 times the Total Congener concentrations, a re-release of approximately 39% is indicated.

**Summary and Recommendations**

My analyses of congener-specific data and packed column chromatograms from some upper Hudson sediment samples collected in 1983 indicate that Aroclor Sum concentrations fall between Tri + and Total Congener concentrations. This is in general agreement with the EPA's use of Aroclor Sum concentrations as a lower limit on Total Congener concentrations.

Interpretation of the 1984 sediment data is critically limited by the fact that chromatograms were not available for inspection and analysis. It should be determined whether chromatograms or individual packed-column peak data on these samples exists.

Observations in this report should be shared and discussed with EPA for the purpose of preparing a response to General Electric's comments.

The 1984 to 1994 sediment PCB inventory comparison is only one facet of the upper Hudson PCB mass balance. Additional important constraints will be provided by detailed analysis of the water column data, the focus of Task 3.

## References

Bopp, R.F., H.J. Simpson, and B.L. Deck, 1985. Release of Polychlorinated Biphenyls from Contaminated Hudson River Sediments. Report to NYSDEC, June 30, 1985.

Brown Jr., J.F., R.E. Wagner, and D.L. Bedard, 1984, PCB Transformations in Upper Hudson Sediments. *Northeast. Environ. Sci., 3*, pp 167-179.

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.

General Electric and Quantitative Environmental Analysis, August 31, 1998, Comments of the General Electric Company on Low Resolution Sediment Coring Report, July 1998.

McNulty, A., 1997, *In-Situ* Anaerobic Dechlorination of Polychlorinated Biphenyls in Hudson River Sediments, Master's Thesis, Rensselaer Polytechnic Institute.

Schulz, D.E., G. Petrick, and J.C. Duinker, 1989, Complete Characterization of Polychlorinated Biphenyl Congeners in Commercial Aroclor and Clophen Mixtures by Multidimensional Gas Chromatography-Electron Capture Detection. *Environ. Sci. Technol. 23*, pp. 852-859.

Webb, R.G., and A.C. McCall, 1973, Quantitative PCB Standards for Electron Capture Gas Chromatography. *J. Chromatogr. Sci. 11*, pp. 366-373.

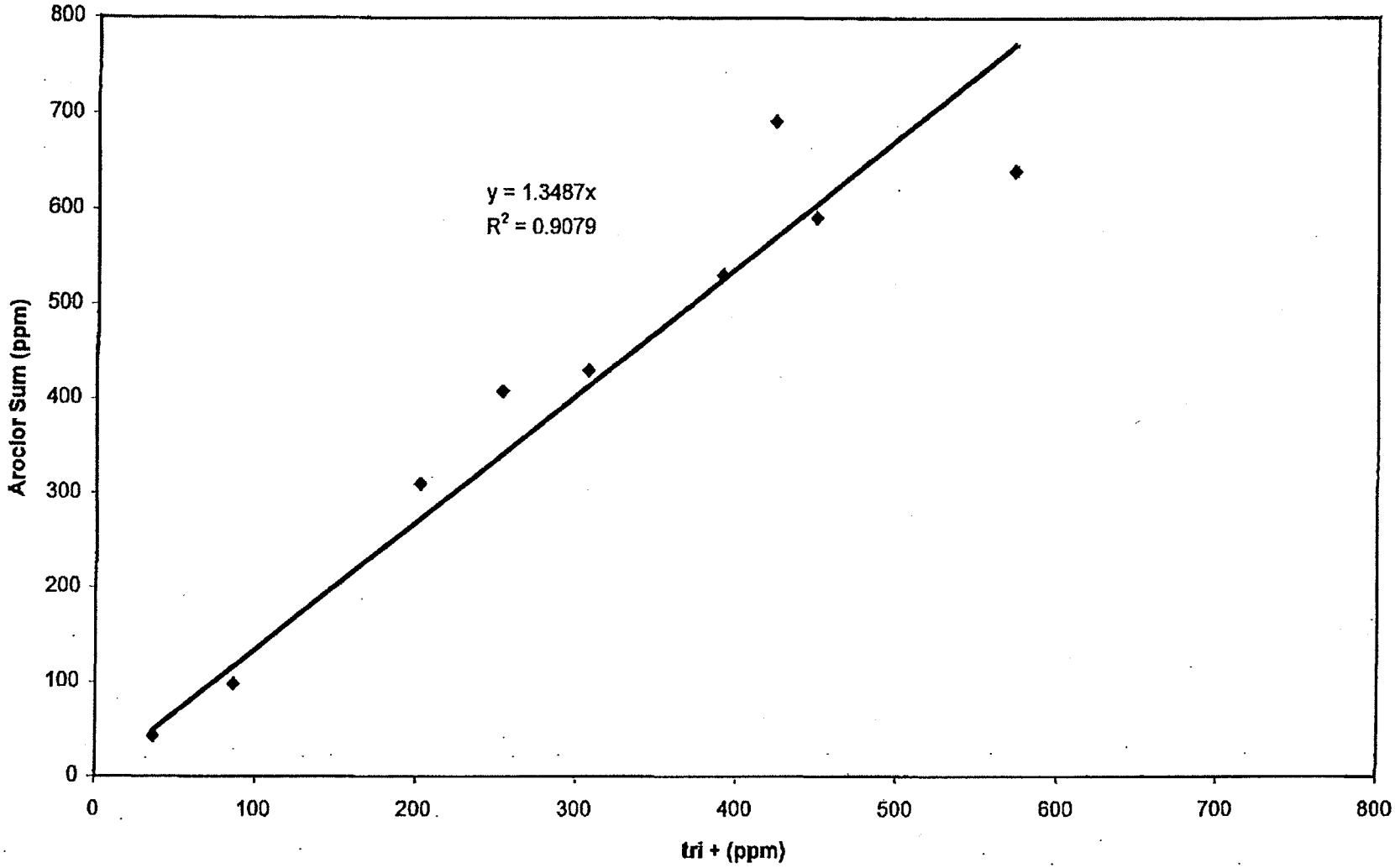
**Core 188.5 ollected 19 July 1983**

| | NYSDOH Congener Analysis | | | Calculated as if packed | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| depth (cm) | total PCBs ppm | tri + % | tri+ ppm | A 1242 (ppm) | A 1254 (ppm) | A 1260 (ppm) | Aroclor Sum | A Sum/tri + | Calc.Tot./Cong.Tot. |
| 0-2 | 75 | 48.8 | 37 | 41 | 2 | 0.3 | 43 | 1.18 | 0.57 |
| 2-4 | 187 | 46.1 | 86 | 91 | 6 | 1.1 | 98 | 1.14 | 0.52 |
| 4-8 | 615 | 49.9 | 307 | 403 | 23 | 4.1 | 431 | 1.40 | 0.70 |
| 8-12 | 827 | 47.2 | 390 | 500 | 25 | 6.1 | 531 | 1.36 | 0.64 |
| 12-16 | 974 | 46.1 | 449 | 557 | 28 | 7.0 | 592 | 1.32 | 0.61 |
| 16-20 | 1212 | 47.2 | 572 | 592 | 38 | 10.1 | 640 | 1.12 | 0.53 |
| 20-24 | 855 | 49.5 | 423 | 651 | 34 | 7.9 | 692 | 1.64 | 0.81 |
| 24-28 | 442 | 57.2 | 253 | 381 | 22 | 5.6 | 409 | 1.62 | 0.92 |
| 28-32 | 397 | 50.9 | 202 | 293 | 13 | 4.5 | 310 | 1.54 | 0.78 |

**Core 188.5** ***Collected 19 July 1983***

| depth (cm) | NYSDOH Analysis total PCBs ppm | NYSDOH Analysis tri+ ppm | Packed Chromatogram Quantification A 1242 (ppm) | A 1242/tri + | A 1242/Tot.Cong. |
|---|---|---|---|---|---|
| 0-2 | 75 | 37 | 58 | 1.58 | 0.77 |
| 2-4 | 187 | 86 | 103 | 1.19 | 0.55 |
| 4-8 | 615 | 307 | 310 | 1.01 | 0.50 |
| 8-12 | 827 | 390 | 428 | 1.10 | 0.52 |
| 12-16 | 974 | 449 | 727 | 1.62 | 0.75 |
| 16-20 | 1212 | 572 | 1250 | 2.19 | 1.03 |
| 20-24 | 855 | 423 | 888 | 2.10 | 1.04 |
| 24-28 | 442 | 253 | 461 | 1.82 | 1.04 |
| 28-32 | 397 | 202 | 529 | 2.62 | 1.33 |

## Samples from Core 188.5



## Samples from Core 188.5