HydroQual, Inc.

MEMORANDUM

| TO: | M. Schweiger-GE |
| :--- | :--- |
| FROM: | J. Haggard - GE |
| CC. Rhea |  |
|  | J. Connolly - HQI |

RE: Hudson River Project: Evaluation of Analytical Bias in the USGS Water Column Database

DATE: January 29, 1998
FILE: GECO 0600

This memorandum documents HydroQual's preliminary analysis of potential analytical biases within the Hudson River water column PCB data set generated by the U.S. Geological Survey (USGS). The principal purpose of this preliminary analysis was to gain insight into the nature of the potential biases and to develop a procedure for a more complete evaluation and possibly a quantification of the bias. This preliminary analysis focused on a subset of the data generated during the late 1980s using capillary column analytical techniques. The remainder of this memorandum presents a brief background on the USGS sampling and analysis program, describes the objectives, methods, and results for this preliminary analysis of the data, and presents recommendations for further consideration.

## I. INTRODUCTION

## Background

The primary objective of the USGS water column PCB monitoring program was to provide baseline PCB transport information prior to the implementation of a New York State sponsored dredging project (Schroeder and Barnes, 1983) ${ }^{1}$. Monitoring began in 1975 at a single station (Waterford, NY) and was expanded to a number of stations (1977-present), including:

[^0]- Glens Falls, NY
- Fort Edward (Rogers Island), NY
- Thompson Island, NY
- Fort Miller, NY
- Schuylerville, NY
- Stillwater, NY
- Waterford, NY
- City of Waterford, NY Water Treatment Plant
- Green Island, NY

The majority of the samples were collected from the Fort Edward, Schuylerville, Stillwater, and Waterford stations. Sampling schedules varied over the years, however, the program focused on elevated flow event sampling.

Samples were collected from bridges using a depth-integrated sampling device equipped with a one-liter sample container. The device was lowered and raised through the water column within the center channel of the river (Schroeder and Barnes, 1983). Whole water samples were shipped to the USGS National Water Quality Laboratories in Doraville, GA (1975-1986) and Denver, CO. (1987-present) for total suspended solids and PCB analysis.

PCB analysis generally followed established protocols and included extraction with a pesticide grade solvent, clean up to remove potential interference agents, PCB separation on either a packed column (1977-1987) or capillary column ${ }^{2}$ (1987present), and PCB detection with an electron capture detector ${ }^{3}$. The procedure used to quantify PCBs in the water samples involved:

- selection of numerous peaks representative of the most closely matched Aroclor(s),
- summing the areas of these peaks, and
- calculation of Aroclor concentrations as the product of the peak areas and a

[^1]composite response factor ${ }^{4}$.
Typically, the Aroclors most often reported by the USGS were Aroclors 1242, 1254, and 1260.

There is potential for a significant analytical bias in the USGS water column data. Due to environmental weathering processes, including partitioning between particulate and dissolved phases, dechlorination, and biodegradation, the congener distribution of PCBs within water column samples collected downstream of sediment PCB deposits deviates from that of the source Aroclors. Therefore, the use of a composite response factor derived from an Aroclor standard may not accurately account for the total PCB concentrations within the sample. Hudson River water column samples collected from stations downstream of Fort Edward, NY contain PCBs which possess a significant proportion of their total mass as mono- and dichlorinated PCBs. The Aroclors used by the USGS to quantify PCBs do not contain these homologs in the same proportions, therefore there is likely a low bias in the USGS data.

Understanding this bias is important for the Hudson River reassessment. The evaluation of remedial alternatives for PCBs within the Hudson River will be conducted using mechanistic mathematical models of PCB fate, transport, and bioaccumulation. These models require calibration to observed temporal and spatial patterns in PCB concentrations within water column, sediments, and fish. Since the USGS data represent the largest historical water column PCB record, it is important to understand, and if possible, quantify the potential biases within the database. Moreover, the USGS data represent a means of understanding: 1) the possible changes in PCB sedimentwater dynamics in response to the large external loadings to the system in the early 1990s, and 2) the magnitude of the sampling bias observed in more recent monitoring data.

## Objectives

The objectives for the analysis of the USGS data described herein were to:

- evaluate the nature and magnitude of potential biases within the USGS Hudson River water column database, and

[^2]- develop protocols for further review of the data.


## Approach

The approach for review of the USGS data involved a number of steps, including:

- obtain copies of chromatograms and supporting documentation on PCB analyses performed by the USGS during the late 1980s,
- review the chromatograms and supporting documentation to develop an understanding of the specific protocols used by USGS personnel in the quantification of PCB concentrations within the samples,
- reevaluate capillary column chromatograms on a limited number of samples to produce a more refined PCB quantification at the chromatographic peak level, and, where possible, calculate PCB homolog and congener distributions,
- compare and contrast results obtained from the different quantification techniques to develop a preliminary understanding of the nature and magnitude of the bias inherent in the USGS analysis scheme, and
- develop specific recommendations for a more complete evaluation of the USGS data.


## III. PRELIMINARY ASSESSMENT OF POTENTIAL ANALYTICAL BIASES

## Methodology

HydroQual obtained copies of gas chromatograms and supporting documentation generated by the USGS for samples analyzed during the late 1980s and early 1990s. The information was organized into gas chromatographic analysis sets that typically included one or more Aroclor standards (typically Aroclor 1242 and 1254), laboratory blanks, matrix spikes, and several water column samples. A listing of the environmental samples received from the USGS is contained in Table 1.

The USGS quantified Aroclor PCB concentrations using a composite response factor derived from a select number of peaks from the capillary column chromatogram.

Within each gas chromatographic set, response factors were developed on an Aroclor basis ( $R F_{i}$ ) using select peak areas $\left(A_{i, j}\right)$ and Aroclor standard mass $\left(M_{i}\right)$ as follows:

$$
R F_{i}=\frac{M_{i}}{\sum_{j=1}^{n} A_{i j}}
$$

Aroclor concentrations of water column samples [Aroclors] were determined from the sample chromatogram by summing the areas of the same select peaks ( $\mathrm{A}_{\mathrm{s} . \mathrm{j}}$ ) used to generate Aroclor response factors, multiplying by the Aroclor response factor, and dividing by the volume of sample injected $\left(\mathrm{V}_{s}\right)$ as follows:

$$
\left[\text { Aroclor }_{s}\right]=\frac{R F_{i}\left(\sum_{j=1}^{n} A_{s_{j} j}\right)}{V_{s}}
$$

A listing of the peaks typically used by the USGS to quantify Aroclor 1242 is presented in Table 2.

## Reanalysis of USGS Chromatograms

Reanalysis of the USGS chromatograms involved development of peak specific response factors from twelve Aroclor 1242 standards on a peak height basis, direct measurement of individual peak heights from seven water column sample chromotograms, and recalculation of peak, homolog, and total PCB concentrations in the samples. Peaks were identified based upon elution patterns published for similar columns and chromatographic settings (Frame et al., 1996) ${ }^{5,6}$. The water column samples selected for detailed analysis included three samples each from the Thompson Island and Fort Edward and one from the Schuylerville sampling station.

[^3]
## Calculation of Peak Specific Response Factors

Typically, peak specific response factors used for sample PCB quantification would be calculated from known peak mass and measured peak areas. However, since the USGS did not report peak areas for peaks that may account for a significant portion of the total PCBs of the samples (those eluting prior to peak 8), an alternative response factor was developed based upon peak height. Peak specific response factors for a given Aroclor standard ( $\mathrm{RF}_{\mathrm{i}, \mathrm{j}}$ ) were computed according to the following equation:

$$
R F_{i, j}=\frac{M_{i} \frac{W t \%_{i, j}}{100}}{H_{i, j}}
$$

where $\mathrm{Wt} \%_{\mathrm{i}, \mathrm{j}}$ is the weight percent of peak j within Aroclor I (Frame et al., 1996), and $H_{i, j}$ is the direct measured peak height for peak j within Aroclor I .

The accuracy of using direct measurements of peak heights to estimate Aroclor totals within a sample rather than peak areas was evaluated by direct comparison of the total PCBs in peaks 8 and higher generated by these two methods. The results of these analyses for the seven water column samples are presented in Figure 1. The close agreement between the two methods supports the use of measured peak height for quantification of PCBs within the samples.

## Quantification of PCBs in Peaks 2 and 5

Quantification of PCBs within peaks 2 and 5 required the use of response factors calculated from Aroclor 1232. The more abundant Aroclor 1242 data could not be used since these peaks account for a small percentage of the total PCBs in Aroclor 1242. As an Aroclor 1232 standard was not included in each analytical set, PCB quantification required the use of response factors from one set be applied to other analytical sets. The potential variability this introduces into the analysis was evaluated by examining the variability of response factors for Aroclor 1242 among different analytical sets (Figure 2). Response factors appear to be consistent across the different analytical sets. Therefore, there appears to be little error in using response factor from one set to calculate sample PCB concentrations from another set, as was necessary for peaks 2 and 5. Moreover, the use of average response factors to calculate sample PCB concentrations does not appear to introduce significant errors into the calculation.

## Calculation of Water Column Peak, Homolog, and Total PCB Concentrations

Average peak specific response factors calculated from Aroclor 1232 (peaks 2 and 5 only) and Aroclor 1242 standards were used to compute individual peak concentrations within water column samples. The concentration of each peak in a given sample $\left(\mathrm{C}_{\mathrm{j}, \mathrm{s}}\right)$ was determined using the following formula:

$$
C_{j, s}=\frac{H_{j, s} R F_{i, j}}{V_{s}}
$$

where $V_{s}$ was the reported total olume of the sample extracted and $H_{j, s}$ is the measured height of each peak within the sample. Concentrations for all peaks up to and including peak 50 were computed (Table 3). Based upon an inspection of the gas chromatograms, peaks 2-50 account for the majority of the PCBs within the samples.

The total PCB concentrations and homolog distributions of the samples were computed using the individual peak concentrations. For peaks in which multiple homologs coelute, the homolog distributions were calculated from coelution information published for Aroclors (Frame et al., 1996).

## Approximation of Potential Bias in USGS

A summary of the calculated and USGS-reported total PCB concentrations for the seven samples is presented in Table 4 along with sample locations, date, and average daily flow data for the Fort Edward gauging station the day of sampling. In six out of the seven samples, the peak sum calculations exceeded the reported USGS totals by between 6 and 44 percent. In general, this difference appeared to be associated with lower chlorinated PCBs eluting within peaks 2 , and $5\left(2-C B, 2,2^{\prime}\right.$ and $2,6-C B)$. Adjusting the calculated peak totals by subtracting the contribution of peaks 2 and 5 enhanced the agreement between the USGS reported and peak sum total PCBs (Figure 3).

The calculated homolog distribution from these 1987 samples generally agree with PCB homolog distributions within samples collected and analyzed in 1991 (Figure 4). One notable difference is the elevated weight percent of mono chlorinated biphenyl in samples collected from the Fort Edward station. This will be examined further as additional chromatograms are evaluated. Overall, the similarities between the two homolog calculations support the methodology employed to calculate homolog
distributions from the USGS chromatograms.
This preliminary analysis suggests that the USGS data are biased low, at least at stations downstream of Rogers Island. The analysis performed by the USGS does not account for lower chlorinated PCBs eluting in peaks 2 and 5 of the SPB-5 chromatogram. These peaks account for a significant portion of the total water column PCB loading occurring across the TIP. However, the analysis does account for mono- and dichlorinated PCBs, to the extent that they occur within the Aroclor standards used for calibration of the gas chromatogram. Therefore, it would be inappropriate to simply treat the USGS data as an estimate of tri- and higher chlorinated PCBs, as suggested by the USEPA in recent meetings.

The limited analysis reported herein also suggests that the bias in the USGS data is dependant upon the chlorination level of water column PCBs. Therefore, it is unlikely that a single correction factor (e.g., 20\%) will be able to account for the low bias due to possible seasonal changes in water column PCB chlorination level related to external source loadings and river flow conditions. Nonetheless, since original chromatograms are available for a large number of samples analyzed by the USGS in the late 1980's, it is possible, using the procedures documented herein, to recalculate water column PCB concentrations on a capillary column peak basis. This will enable the development of a more accurate historical water column data set upon which to focus the calibration of fate and transport models currently under development.

## IV. RECOMMENDATIONS

To develop a more thorough understanding of the potential bias in the USGS data, and to develop a more accurate subset of the historical water column PCB record, HydroQual, Inc. recommends the following:

- complete the reanalysis of USGS chromatograms using peak height analysis on remaining capillary column chromatograms,
- quantitatively compare recalculated total PCB concentrations to reported USGS totals, and
- develop specific recommendations for accounting for the bias in model development and calibration.

TABLE 1. List of Hudson River PCB Chromatograms Supplied by the USGS

|  | IDUSGS' | :HudsonRIvert |  | $\begin{aligned} & \text { hatoported } \\ & \text { Arocigor } 1242[\mathrm{dg} \mathrm{~L}] \end{aligned}$ | Rrowroported |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 251.07 | 1724800558 | Waterford | - 4/22/87 | 0.032 |  | 0.020 |
|  | 56 | 1 Waterford | 4/12/87 | 0.020 |  | 0.020 |
|  | 57A | i Waterford | 4/22/87 | 0.020 |  | 0.010 |
|  | 57 B | Waterford | 4/22/87 | 0.020 |  | 0.010 |
|  | 58 | Schuylerville | 4/1/87 | 0.150 |  | 0.060 |
|  | 59A | Schuylerville | 12/30/86 | 0.103 |  | 0.047 |
|  | 598 | Schuylerville | 12/30/86 | 0.009 |  | 0.006 |
|  | 60 | Schuylervilie | 4/15/87 | 0.016 |  | 0.008 |
|  | 72510028A | Fort Edward | 4/1/87 | 0.040 |  | 0.010 |
|  | 28 | Fort Edward | 4/1/87 | 0.040 |  | 0.010 |
|  | 29A | Fort Edward | 4/1/87 | 1.040 |  | 0.480 |
|  | 298 | Fort Edward | 4/1/87 | 0.100 |  | 0.030 |
|  | 30A | Schuylerville | 3/10/87 | 0.010 |  | < 0.01 |
|  | 30 B I | Schuylerville | 3/10/87 | 0.020 |  | 0.010 |
|  | 72520049 | Stillwater | 4/1/87 | 0.099 |  | 0.050 |
| 251.06, 251.05 | 72480047A | Waterford | $4 / 7 / 87$ | 0.038 |  | 0.011 |
|  | 47B | Waterford | 4/7/87 | 0.039 |  | 0.010 |
|  | 48A - | Waterford | 4/9/87 | 0.021 |  | 0.006 |
|  | 48B ! | Waterford | 4/9/87 | 0.039 |  | 0.007 |
|  | 49A | Waterford | 4/9/87 | 0.024 |  | 0.006 |
|  | 49B | Waterford | 4/9/87 | 0.018 |  | 0.008 |
|  | 50A | Waterford | 4/9/87 | 0.014 |  | 0.006 |
|  | 50 B | Waterford | 4/9/87 | 0.010 |  | 0.003 |
| ! | 51A | Waterford | 4/40/87 | 0.019 |  | 0.010 |
|  | 51 B | Waterford | 4/10/87 | 0.015 |  | 0.010 |
| ! | 52A | Waterford | 5/22/87 | 0.033 |  | 0.008 |
|  | 523 | Waterford | 5/22/87 | 0.028 |  | 0.009 |
| ! | 53 | Schuyierville | 4/2/87 | 0.038 |  | 0.012 |
|  | 54A | Waterford | 4/15/87 | 0.012 | 1 | 0.008 |
| ! | 55 | Waterford | 4/22/87 | 0.028 |  | 0.008 |
| ! | 48 | Waterford ! | 4/9/87 |  |  |  |
|  | 72460047 | Waterford | 9/17/87 | 0.148 |  | 0.330 |
| ! | 48 | Waterford | 9/17/87 | 0.980 |  | 1.820 |
|  | 49 | Waterford | 9/17/87 |  |  | 0.040 |
| 268.03, 268.04 | 72670015A1 | Waterford | 9/17/87 | 0.053 |  | 0.013 |
| + | 16A | Rogers Island | 9/17/87 | 0.067 |  | 0.021 |
|  | 16B | Rogers Island | 9/17/87 | 0.031 |  | 0.008 |
| ! | 17A | Waterford | 9/17/87 | 0.041 |  | 0.009 |
|  | 178 | Waterford | 9/17/87 | 0.030 |  | 0.010 |
|  | 18A | Thompson Island | 9/17/87 | 0.090 |  | 0.010 |
|  | 18B | Thompson Island | 9/17/87 | 0.020 |  | 0.006 |
|  | 73370008 | Stillwater | 11/23/87 | 0.009 |  | 0.007 |
| ! | 9 | Fort Miller | 11/24/87 | 0.025 |  | 0.008 |
| I | 10 | Waterford | 11/24/87 | 0.023 |  | 0.009 |
|  | 11 | Fort Edward | 11/24/87 | 0.017 |  | 0.009 |
| 1 | 12 | Schuylerville | 14/24/87 | 0.023 |  | 0.012 |
| 213.01,.02, 03 | 912120168 | Waterford I | 6/25/91 |  | 0.041 |  |
|  | 169 | Waterford | 7/25/91 |  | 0.035 |  |
|  | 170 | Stillwater | 6/28/91 |  | 0.052 |  |
|  | 171 | Stillwater | 7/25/91 |  | 0.048 |  |
| 1 | 172 | Waterford | 4/16/91 |  | 0.014 |  |
| 1 | 173 | Waterford ! | 5/10/91 |  | 0.028 |  |
| ! | 174 | Waterford | 10/24/90 |  | 0.026 |  |
|  | 175 | Waterford | 3/4/91 |  | 0.013 |  |
|  | 176 | Waterford | 1/2/91 |  | 0.007 |  |
|  | 177 | Waterford | 3/5/91 |  | 0.036 | 0.014 |
| ; | 178 | Waterford | 4/9/91 |  | 0.021 |  |
| ' | 179 | Waterford | 4/2/91 |  | 0.013 |  |
|  | 180 | Wateriord | 11/26/90 |  | 0.009 |  |
|  | 181 | Waterford | 10/31/90 |  | 0.032 |  |
|  | 182 | Wateriord | 4/25/91 |  | 0.013 |  |

TABLE 1 cont'd
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|  | $\begin{aligned} & \text { USGSS } \\ & \text { NOMber } \end{aligned}$ | Hudson River Samplling Station | Date: 7 | Prerreportod |  Aroclor 1248 If́g Ll] | Fhanireportodetel Aroclor 1254 Tug L |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 183 | Waterford | 3/21/91 |  | 0.012 |  |
|  | 184 | Stillwater | 1/2/91 |  | 0.008 |  |
|  | 185 | Stillwater | 4/25/91 |  | 0.023 | 0.049 |
|  | 186 | Stillwater | 3/4/91 |  | 0.017 |  |
|  | 187 | Stillwater | 10/24/90 |  | 0.039 | 0.014 |
|  | 188 | Stillwater | 4/9/91 |  | 0.042 |  |
|  | 189 | Stillwater | 4/2/91 |  | 0.004 |  |
|  | 190 | Stillwater | 5/10/91 |  | 0.018 |  |
|  | 191 | Stillwater | 11/26/90 |  | 0.012 |  |
|  | 192 | Stillwater | 4/16/91 |  | 0.037 | 0.015 |
|  | 193 | Stillwater | 10/31/90 |  | 0.024 |  |
| 254.01, .02, .03, . 04 | 912530581 | Fort Edward | 5/22/90 |  | 0.024 |  |
|  | 582 | Fort Edward | 10/24/90 |  | 0.499 | 0.053 |
|  | \| 583 | Waterford | 5/30/90 |  | 0.029 |  |
|  | 584 | Waterford | 7/17/90 |  | 0.03 |  |
|  | 585 | Stillwater | 7/17/90 |  | 0.218 | 0.169 |
|  | 586 | Fort Edward | 10/31/90 |  | 0.022 |  |
|  | 587 | Waterford | 6/13/90 |  | 0.031 |  |
|  | ) 588 | Fort Edward | 5/22/90 |  | 0.023 |  |
|  | 589 | Stillwater | 5/30/90 |  | 0.045 |  |
|  | 590 | Stillwater | 6/13/90 |  | 0.035 |  |
|  | + 591 | Fort Edward | 4/25/91 |  | trace |  |
|  | 592 | Fort Edward | 3/5/91 |  | 0.019 |  |
|  | ! 593 | Fort Edward | 1/2/91 |  | trace |  |
|  | - 594 | Fort Edward | 3/4/91 |  | trace |  |
|  | - 595 | Fort Edward | 3/21/91 |  | trace |  |
|  | 596 | Fort Edward | 4/2/91 |  | 0.003 |  |
|  | 597 | Fort Edward | 4/9/91 |  | 0.014 |  |
|  | 598 | Fort Edward | 5/10/91 |  | 0.007 | - |
|  | 600 | Fort Edward | 4/16/91 |  | 0.006 |  |
| $!$ | 601 | Fort Edward | 6/28/91 |  | 0.033 |  |
|  | 602 | Fort Edward | 8/30/91 | 0.040 | 0.042 | 0.005 |
|  | 603 | Stillwater | 8/30/91 |  | 0.048 | 0.005 |
| ! | - 604 | Fort Edward | 8/20/91 | 0.047 | 0.051 | 0.005 |
| ! | - 605 | Fort Edward | 7/25/91 |  | 0.018 |  |
|  | 606 | Fort Edward | 8/30/91 | 0.031 | 0.036 | 0.005 |
| I | 607 | Fort Edward | 8/30/91 | 0.032 | 0.032 | 0.005 |
| ! | 608 | Waterford | 8/20/91 |  | 0.027 | 0.005 |
|  | 609 | Stillwater | 8/20/91 | ; | 0.037 | 0.005 |
|  | 610 | Waterford | 8/30/91 |  | 0.017 | trace |
| 4.02 | 73570018 | Schuylerville | 12/18/87 | 0.019 |  | 0.0052 |
|  | 19 i | Fort Miller | 12/18/87 | 0.016 |  | 0.0051 |
|  | 20 | Waterford | 1218/87 | 0.019 | . | 0.006 |
|  | 21 | Stillwater | 1218/87 | 0.018 |  | 0.003 |
|  | 22 | Fort Edward | 12/17/87 | 0.013 |  | 0.009 |
| 42.01, 82.01 | 80400029A | Fort Edward | 2/2/88 | 0.010 |  | $<.01$ |
|  | 30 | Waterford | 2/2/88 | 0.020 |  | $<.01$ |
|  | 31 | Stillwater i | 2/2/88 | 0.010 |  |  |
|  | 32 | Fort Miller | 2/3/88 | 0.010 |  |  |
|  | 80750066 | Fort Miller | 2/24/88 | 0.040 |  |  |
|  | 68 | Waterford | 2126/88 | 0.010 |  |  |
|  | 69 | Fort Edward | 4/1/87 | 0.080 |  | 0.01 |
|  | 70 | Stillwater | 2/26/88 | 0.010 |  |  |
|  | 71 i | Fort Edward | 2/26/88 | 0.005 |  |  |
| 233.02, 236.01 | 912350297 | Fort Edward | 9/14/90 |  | 0.015 |  |
| $\square 1$ | 98 | Fort Edward | 9/14/90 |  | 0.015 |  |
|  | 99 | Waterford | 8/17/90 | \| | 0.023 |  |
|  | 300 | Fort Edward | 3/20/90 |  | 0.003 |  |
|  | 1 | Stillwater | 5/22/90 | I | 0.058 | 0.023 |
|  | 2 | Stillwater | 9/14/90 |  | 0.018 |  |
|  | 3 | Stillwater | 8/17/90 |  | 0.014 |  |
|  | 4 | Fort Edward | 3/20/90 |  | trace |  |
|  | 5 | Waterford I | 5/22/90 |  | 0.039 | trace |

TABLE 1 cont'd
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Table 2. Peaks Most Commonly Used by USGS to Quantify Aroclor 1242

| DB-5 Peak | *IUPAC | ${ }^{*}$ PCB |
| :---: | :---: | :---: |
| Number | Number | Congeners |
| 14 | 15,18 | $44^{\prime}, 252^{\prime}$ |
| 15 | 17 | $242^{\prime}$ |
| 17 | 16,32 | $232^{\prime}, 264^{\prime}$ |
| 23,24 | 31,28 | $254^{\prime}, 244^{\prime}, 2462^{\prime}$ |
| 25 | $20,33,53$ | $233 \prime^{\prime}, 234,342^{\prime}, 252^{\prime} 6$ |
| 32 | 43,49 | $2352^{\prime}, 242^{\prime} 5$ |
| 34 | 48 | $2452^{\prime}, 2464^{\prime}$ |
| 38 | $37,42,59$ | $344^{\prime}, 232^{\prime} 4,2363^{\prime}$ |
| 39 | $41,64,71$ | $2342^{\prime}, 2364^{\prime}, 263^{\prime} 4,253^{\prime} 5$ |

*IUPAC Numbers and Congener I.D.'s from Frame et al., 1996

## Schuylerville (4/3/87)

1232 Standard Concentration $=12 \mathrm{ng}$
1242 Standard Concentration $=68.4 \mathrm{ng}$
Sample Volume $=955.7 \mathrm{~mL}$


## Thompson Island (4/4/87)

1232 Standard Concentration $=12 \mathrm{ng}$
1242 Standard Concentration $=68.4 \mathrm{ng}$
Sample Volume $=958.8 \mathrm{~mL}$

| Peak \# | Aroclor Standard Used ${ }^{1}$ | Average Response Factor ${ }^{2}$ | Sample Measured Peak Height ${ }^{3}$ | Concentration [ug/L] |
| :---: | :---: | :---: | :---: | :---: |
| 2 | Aroclor 1232 | 0.246 | 48 | 0.0123 |
| 5 | Aroclor 1232 | 0.209 | 44 | 0.0096 |
| 8 | Aroclor 1242 | 0.031 | 20 | 0.0006 |
| 10 | Aroclor 1242 | 0.030 | 65 | 0.0020 |
| 14 | Aroclor 1242 | 0.050 | 127 | 0.0066 |
| 15 | Araclor 1242 | 0.037 | 70 | 0.0027 |
| 16 | Araclor 1242 | 0.026 | 57 | 0.0016 |
| 17 | Aroclor 1242 | 0.029 | 146 | 0.0045 |
| 21 | Aroclor 1242 | 0.024 | 35 | 0.0009 |
| 22 | Aroclor 1242 | 0.033 | 16 | 0.0005 |
| 23\& 24 | Aroclor 1242 | 0.041 | 144 | 0.0062 |
| 25 | Aroclor 1242 | 0.029 | 62 | 0.0019 |
| 26 | Aroclor 1242 | 0.022 | 84 | 0.0019 |
| 27 | Aroclor 1242 | 0.023 | 58 | 0.0014 |
| 29 | Aroclor 1242 | 0.043 | 20 | 0.0009 |
| 31 | Aroclor 1242 | 0.021 | 143 | 0.0032 |
| 32 | Aroclor 1242 | 0.019 | 143 | 0.0029 |
| 34 | Aroclor 1242 | 0.017 | 103 | 0.0018 |
| 37 | Aroctor 1242 | 0.018 | 143 | 0.0026 |
| 38 | Aroclor 1242 | 0.032 | 112 | 0.0037 |
| 39 | Aroclor 1242 | 0.019 | 143 | 0.0029 |
| 46 | Aroclor 1242 | 0.015 | 89 | 0.0014 |
| 47 | Aroclor 1242 | 0.018 |  | 0.0000 |
| 48 | Aroctor 1242 | 0.017 |  | 0.0000 |
| 49 | Aroclor 1242 | 0.047 | 19 | 0.0009 |
| 50 | Aroctor 1242 | 0.015 | 110 | 0.0018 |
|  |  |  |  |  |

Peak Weight Percents from Frame et al., 1996 Used in Computation of Peak Specific Response Factors
${ }^{1}$ Aroclor Standard Used in Computation of Peak Specific Response Factor
${ }^{2}$ Aroclor 1242 Response Factors are the Average of 12 Selected Aroclor Standards; Aroclor 1232 Response Factors Computed from 1 Standard
${ }^{3}$ Peak Height Measured Using 1:100 Engineers Scale from Actual Chromatograph

- USGS Reported Aroclor 1242 Concentration

Fort Edward（4／6／87）
1232 Standard Concentration $=12 \mathrm{ng}$
1242 Standard Concentration $=68.4 \mathrm{ng}$
Sample Volume $=955.2 \mathrm{~mL}$

| Peak ${ }^{\text {\％}}$ | Aroclor Standard Used ${ }^{1}$ | Average Response Factor ${ }^{2}$ | Sample Measured Peak Height ${ }^{3}$ | Concentration［ug／L） |
| :---: | :---: | :---: | :---: | :---: |
| 2 | Aractor 1232 | 0.246 | 49 | 0.0126 |
| 5 | Aroclor 1232 | 0.209 | 12 | 0.0026 |
| 8 | Arocior 1242 | 0.031 | 20 | 0.0006 |
| 10 | Aroctor 1242 | 0.030 | 32 | 0.0010 |
| 14 | Aroctor 1242 | 0.050 | 88 | 0.0046 |
| 15 | Aroctor 1242 | 0.037 | 33 | 0.0013 |
| 16 | Arocior 1242 | 0.026 | 29 | 0.0008 |
| 17 | Aroclor 1242 | 0.029 | 101 | 0.0031 |
| 21 | Aroclor 1242 | 0.024 |  | 0.0000 |
| 22 | Aroclor 1242 | 0.033 |  | 0.0000 |
| 23824 | Arocior 1242 | 0.041 | 82 | 0.0035 |
| 25 | Aroclor 1242 | 0.029 | 39 | 0.0012 |
| 26 | Arocior 1242 | 0.022 | 14 | 0.0003 |
| 27 | Arocior 1242 | 0.023 | 46 | 0.0011 |
| 29 | Arocior 1242 | 0.043 | 18 | 0.0008 |
| 31 | Aroclor 1242 | 0.021 | 142 | 0.0032 |
| 32 | Aroclor 1242 | 0.019 | 92 | 0.0019 |
| 34 | Aroclor 1242 | 0.017 | 52 | 0.0009 |
| 37 | Aroclor 1242 | 0.018 | 142 | 0.0026 |
| 38 | Arocior 1242 | 0.032 | 56 | 0.0019 |
| 39 | Aroclor 1242 | 0.019 | 112 | 0.0023 |
| 46 | Aroclor 1242 | 0.015 | 41 | 0.0006 |
| 47 | Aroclor 1242 | 0.018 | 95 | 0.0017 |
| 48 | Aroclor 1242 | 0.017 | 141 | 0.0026 |
| 49 | Aroclor 1242 | 0.047 | 23 | 0.0011 |
| 50 | Aroclor 1242 | 0.015 | 56 | 0.0009 |
| Y Reported valuePercent Low Blas,$~$ |  |  |  |  |

Thompson Island 1 （9／17／87）
1232 Standard Concentration $=12 \mathrm{ng}$
1242 Standard Concentration $=12 \mathrm{ng}$
Sample Volume $=\mathbf{9 5 8 . 8} \mathrm{mL}$

| Peak \＃ | Aroclor Standard Used＇ | Average Response Factor ${ }^{2}$ | Sample Measured Peak Height ${ }^{3}$ | Concentration［ug ${ }^{\text {L }}$ ］ |
| :---: | :---: | :---: | :---: | :---: |
| 2 | Aroclor 1232 | 0.246 | 25 | 0.0064 |
| 5 | Aroclor 1232 | 0.209 | 107 | 0.0233 |
| 8 | Aroclor 1242 | 0.051 | 46 | 0.0025 |
| 10 | Arocior 1242 | 0.058 | 75 | 0.0045 |
| 14 | Aroclor 1242 | 0.050 | 83 | 0.0043 |
| 15 | Aroctor 1242 | 0.037 | 65 | 0.0025 |
| 16 | Aroctor 1242 | 0.026 | 59 | 0.0016 |
| 17 | Aroctor 1242 | 0.029 | 98 | 0.0030 |
| 21 | Aroclor 1242 | 0.024 | 29 | 0.0007 |
| 22 | Aroctor 1242 | 0.033 | 12 | 0.0004 |
| 23\＆ 24 | Aroclor 1242 | 0.041 | 129 | 0.0055 |
| 25 | Aroclor 1242 | 0.029 | 42 | 0.0013 |
| 26 | Aroclor 1242 | 0.022 | 37 | 0.0009 |
| 27 | Aroclor 1242 | 0.023 | 9 | 0.0002 |
| 29 | Aroclor 1242 | 0.043 |  | 0.0000 |
| 31 | Aroctor 1242 | 0.021 | 87 | 0.0019 |
| 32 | Aroclor 1242 | 0.019 | 76 | 0.0015 |
| 34 | Aroclor 1242 | 0.017 | 56 | 0.0010 |
| 37 | Aroclor 1242 | 0.018 | 79 | 0.0014 |
| 38 | Aroclor 1242 | 0.032 | 42 | 0.0014 |
| 39 | Aroclor 1242 | 0.019 | 72 | 0.0015 |
| 46 | Arocior 1242 | 0.015 | 35 | 0.0005 |
| 47 | Aroclor 1242 | 0.018 | 55 | 0.0010 |
| 48 | Aroclor 1242 | 0.017 | 72 | 0.0013 |
| 49 | Aroclor 1242 | 0.047 | 9 | 0.0004 |
| 50 | Aroclor 1242 | 0.015 | 45 | 0.0007 |

[^4]Thompson Island 2 (9/17/87)
1232 Standard Concentration $=12 \mathrm{ng}$
1242 Standard Concentration $=12 \mathrm{ng}$
Sample Volume $=959.7 \mathrm{~mL}$

| Peak \# | Aroclor <br> Standard Used ${ }^{\dagger}$ | Average Response Factor ${ }^{2}$ | Sample Measured Peak Height ${ }^{3}$ | Concentration [ug/L] |
| :---: | :---: | :---: | :---: | :---: |
| 2 | Aroctor 1232 | 0.246 | 25 | 0.0064 |
| 5 | Arocior 1232 | 0.209 | 53 | 0.0116 |
| 8 | Aroclor 1242 | 0.051 | 25 | 0.0013 |
| 10 | Arocior 1242 | 0.058 | 35 | 0.0021 |
| 14 | Aroclor 1242 | 0.050 | 40 | 0.0021 |
| 15 | Aroclor 1242 | 0.037 | 30 | 0.0012 |
| 16 | Aroclor 1242 | 0.026 | 26 | 0.0007 |
| 17 | Arocior 1242 | 0.029 | 46 | 0.0014 |
| 21 | Aroclor 1242 | 0.024 | 13 | 0.0003 |
| 22 | Aroclor 1242 | 0.033 | 5 | 0.0002 |
| 23\&24 | Arocior 1242 | 0.041 | 60 | 0.0026 |
| 25 | Aroctor 1242 | 0.029 | 20 | 0.0006 |
| 26 | Aroctor 1242 | 0.022 | 17 | 0.0004 |
| 27 | Arocior 1242 | 0.023 | 10 | 0.0002 |
| 29 | Aroctor 1242 | 0.043 |  | 0.0000 |
| 31 | Aroctor 1242 | 0.021 |  | 0.0000 |
| 32 | Arocior 1242 | 0.019 | 31 | 0.0006 |
| 34 | Aroclor 1242 | 0.017 | 22 | 0.0004 |
| 37 | Aroclor 1242 | 0.018 | 35 | 0.0006 |
| 38 | Aroctor 1242 | 0.032 | 17 | 0.0006 |
| 39 | Aroctor 1242 | 0.019 | 30 | 0.0006 |
| 46 | Arocior 1242 | 0.015 | 13 | 0.0002 |
| 47 | Aroclor 1242 | 0.018 | 20 | 0.0004 |
| 48 | Aroctor 1242 | 0.017 | 29 | 0.0005 |
| 49 | Aroclor 1242 | 0.047 | 3 | 0.0001 |
| 50 | Aroclor 1242 | 0.015 | 18 | 0.0003 |

## Rogers Island 1 ( $9 / 17 / 87$ )

1232 Standard Concentration $=12 \mathrm{ng}$
1242 Standard Concentration $=12 \mathrm{ng}$
Sample Volume $=959.5 \mathrm{~mL}$

| Peak \# | Aroclor Standard Used ${ }^{\prime}$ | Average Response Factor ${ }^{2}$ | Sample Measured Peak Height ${ }^{3}$ | Concentration [ught] |
| :---: | :---: | :---: | :---: | :---: |
| 2 | Aroclor 1232 | 0.246 | 33 | 0.0085 |
| 5 | Aroclor 1232 | 0.209 | 25 | 0.0055 |
| 8 | Aroclor 1242 | 0.051 | 42 | 0.0022 |
| 10 | Aroclor 1242 | 0.058 | 32.5 | 0.0020 |
| 14 | Aroclor 1242 | 0.050 | 116 | 0.0060 |
| 15 | Aroclor 1242 | 0.037 | 92 | 0.0036 |
| 16 | Aroclor 1242 | 0.026 | 30 | 0.0008 |
| 17 | Arocior 1242 | 0.029 | 115 | 0.0035 |
| 21 | Aroclor 1242 | 0.024 |  | 0.0000 |
| 22 | Arocior 1242 | 0.033 |  | 0.0000 |
| 23824 | Aroctor 1242 | 0.041 | 143 | 0.0061 |
| 25 | Aroctor 1242 | 0.029 | 60 | 0.0018 |
| 26 | Arocior 1242 | 0.022 | 75 | 0.0017 |
| 27 | Aroclor 1242 | 0.023 | 28 | 0.0007 |
| 29 | Arocior 1242 | 0.043 | 12 | 0.0005 |
| 31 | Aroclor 1242 | 0.021 | 103 | 0.0023 |
| 32 | Araclor 1242 | 0.019 | 91 | 0.0018 |
| 34 | Aroclor 1242 | 0.017 | 61 | 0.0011 |
| 37 | Aroclor 1242 | 0.018 | 107 | 0.0020 |
| 38 | Aroctor 1242 | 0.032 | 66 | 0.0022 |
| 39 | Aroclor 1242 | 0.019 | 95 | 0.0019 |
| 46 | Aroclor 1242 | 0.015 | 59 | 0.0009 |
| 47 | Aroclor 1242 | 0.018 | 95 | 0.0017 |
| 48 | Aroclor 1242 | 0.017 | 113 | 0.0021 |
| 49 | Aroclor 1242 | 0.047 | 11 | 0.0005 |
| 50 | Aroclor 1242 | 0.015 | 70 | 0.0011 |
|  |  |  |  | $4+\square$ $\square$$\quad 0.0606$ |

- Peak Weight Percents from Frame et al., 1996 Used in Computation of Peak Specific Response Factors

Aroclor Standard Used in Compulation of Peak Specific Response,Factor
${ }^{2}$ Aroclor 1242 Response Factors are the Average of 12 Selected Arocior Standards; Aroclor 1232 Response Factors Computed from 1 Standard
${ }^{3}$ Peak Height Measured Using 1:100 Engineers Scale trom Actual Chromalograph
4 USGS Reported Aroclor 1242 Concentration

## Rogers Island 2 (9/17/87)

1232 Standard Concentration $=12 \mathrm{ng}$
1242 Standard Concentration $=12 \mathrm{ng}$
Sample Volume $=960.8 \mathrm{~mL}$.

| Peak \# | Aroclor Standard Used ' | Average Response Factor ${ }^{2}$ | Sample Measured Peak Height ${ }^{3}$ | Concentration [ug/L] |
| :---: | :---: | :---: | :---: | :---: |
| 2 | Aroclor 1232 | 0.246 | 32 | 0.0082 |
| 5 | Aroclor 1232 | 0.209 | 19 | 0.0041 |
| 8 | Aroclor 1242 | 0.051 | 38 | 0.0020 |
| 10 | Aroclor 1242 | 0.058 | 19 | 0.0011 |
| 14 | Aroclor 1242 | 0.050 | 54 | 0.0028 |
| 15 | Aroclor 1242 | 0.037 | 36 | 0.0014 |
| 16 | Aroclor 1242 | 0.026 | 16 | 0.0004 |
| 17 | Aroclor 1242 | 0.029 | 59 | 0.0018 |
| 21 | Aroclor 1242 | 0.024 | 12 | 0.0003 |
| 22 | Aroclor 1242 | 0.033 | 7 | 0.0002 |
| 23\& 24 | Aroclor 1242 | 0.041 | 70 | 0.0030 |
| 25 | Aroclor 1242 | 0.029 | 29 | 0.0009 |
| 26 | Aroctor 1242 | 0.022 | 32 | 0.0007 |
| 27 | Aroclor 1242 | 0.023 | 16 | 0.0004 |
| 29 | Aroclor 1242 | 0.043 | 6 | 0.0003 |
| 31 | Aroclor 1242 | 0.021 | 48 | 0.0011 |
| 32 | Aroctor 1242 | 0.019 | 42 | 0.0008 |
| 34 | Araclor 1242 | 0.017 | 27 | 0.0005 |
| 37 | Aroclor 1242 | 0.018 | 57 | 0.0010 |
| 38 | Araclor 1242 | 0.032 | 29 | 0.0010 |
| 39 | Aroclor 1242 | 0.019 | 47 | 0.0009 |
| 46 | Aroclor 1242 | 0.015 | 22 | 0.0003 |
| 47 | Aroclor 1242 | 0.018 | 34 | 0.0006 |
| 48 | Aroctor 1242 | 0.017 | 45 | 0.0008 |
| 49 | Araclor 1242 | 0.047 | 3 | 0.0001 |
| 50 | Arocior 1242 | 0.015 | 31 | 0.0005 |

* Peak Weight Percents from Frame et al., 1996 Used in Computation of Peak Specific Response Factors
- Aroclor Slandard Used in Computation of Peak Specific Response Factor
${ }^{2}$ Aroclor Standard Used in Computation of Peak Specific Response Factor 1242 Response Factors are the Average of 12 Selected Aroclor Standards; Aroclor 1232 Response Factors Computed from 1 Standard
${ }^{3}$ Peak Height Measured Using 1:100 Engineers Scale from Actual Chromatograph
- USGS Reported Aroclor 1242 Concentration

TABLE 4. Summary of Recolculated USGS Water Column PCBs

| Location | Date | Approx. Fow | $\begin{gathered} \text { Calculated } \\ \text { Peak } 2 \text { (ug } /)^{\prime \prime} \end{gathered}$ | $\begin{gathered} \text { Calculated } \\ \text { Peak } 5[\text { ugh }]^{2} \end{gathered}$ | Sum Peaks $2 \& 5$ [ughl | Calculated Peak Sum $[u g /]^{3}$ | USGS Reported 1242 Total fughl | Percent <br> Low Blas | Percent <br> Peaks 2 \& 5 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Thompson Isiand 1 | 9/17/87 | 7500 cts | 0.0064 | 0.0233 | 0.0298 | 0.0700 | 0.05 | 29 | 43 |
| Thompson isiand 2 | 9/17/87 | 7500 cts | 0.0064 | 0.0116 | 0.0180 | 0.0354 | 0.02 | 44 | 51 |
| oogers Island 1 | 9/17/87 | 7500 cts | 0.0085 | 0.0055 | 0.0139 | 0.0606 | 0.07 | -11 | 23 |
| Rogers Istand 2 | 9/17/87 | 7500 cfs | 0.0082 | 0.0041 | 0.0923 | 0.0355 | 0.03 | 13 | 35 |
| Schuyderville | 4/3/87 | 20000 cfs | 0.0113 | 0.0151 | 0.0264 | 0.0715 | 0.04 | 44 | 37 |
| Thomoson Istand | 4/4/87 | 20000 cts | 0.0123 | 0.0096 | 0.0219 | 0.0748 | 0.07 | 6 | 29 |
| Fort Edward | 4/6/97 | 20000 cts | 0.0126 | 0.0026 | 0.0152 | 0.0533 | 0.04 | 25 | 29 |

' SPB-5 Peak 2 Contains Congener 2 Mono Chborinated Bhphenyls
${ }^{2}$ SPB-5 Peak 5 Contains Congeners 2, 2" and 2, 6 DC Chominated Biphenyls
${ }^{3}$ Total From Table 3

FIGURE 1. Comparison of Reported and Calculated Aroclor 1242 Totals Using Peak Area and Peak Height Methods


## FIGURE 2

Mean Response Factors for Twelve Aroclor 1242 Standards


[^5]Figure 3.
Comparison of USGS Reported and Calculated Peak Totla PCB Concentration
(A) with and (B) without DB-5 Peaks 2 and 5.



Figure 4.
Comparison of Water Column PCB Homolog Distributions Calculated from 1987 USGS Chromatograms and Reported for 1991 GE Data





[^0]:    ${ }^{1}$ Schroeder, R.A. and C.R. Barnes. 1983. Polychlorinated Biphenyl Concentrations in Hudson River Water and Treated Drinking Water at Waterford, New York. U.S. Geological Survey. Water Resources Investigation Report 83-4188. Albany, New York.

[^1]:    ${ }^{2}$ The USGS used either a 30 meter Supelco, Inc. SPB-5 or J\&W, Inc. DB-5 capillary column from 1987-1991.
    ${ }^{3}$ Personal communication between Robert Wagner of Northeast Analytical, Inc. and Ralph White and Duane Wydoski of the USGS in Denver, CO.

[^2]:    ${ }^{4}$ A composite response factor is defined as the Aroclor standard mass divided by the total area of the select chromatographic peaks used for Aroclor quantification.

[^3]:    ${ }^{5}$ Frame, G.M. et al., 1996. Comprehensive, Quantitative, Congener-specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns. Chemosphere 33:603-623.
    ${ }^{6}$ Pattern matching referenced DB-1 column elution patterns. The SPB-5 column produces a PCB elution pattern similar to that of the DB-1 column.

[^4]:    ＊Peak Weight Percents from Frame et al．， 1996 Used in Computation of Peak Specific Response Factors
    －Aroclor Standard Used in Computation of Peak Specific Response Factor
    ${ }^{2}$ Aroclor 1242 Response Factors are the Average of 12 Selected Aroclor Standards；Aroclor 1232 Response Factors Computed from 1 Standaro
    ${ }^{3}$ Aroclor 1242 Response Factors are the Average of 12 Selected Aroclor Standards；
    －Peak Height Measured Using 1：100 Engineer

[^5]:    ${ }^{1}$ Response Factors Calculated as Concentration of PCB Injected Divided by Peak Height Measured Using 1:100 Scale

