

Characterization of the Polychlorinated Biphenyls in the Sediments of Woods Pond: Evidence for Microbial Dechlorination of Aroclor 1260 *in Situ*

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PCB-contaminated sediments from the Housatonic River have accumulated in Woods Pond, a shallow impoundment on the river located in Lenox, MA. We used GC/ECD analysis to determine the PCB congener distributions in 181 sediment samples from 94 locations in Woods Pond in order to learn which Aroclors were originally present and whether there was evidence of dechlorination. The congener distributions of all samples showed the hexa-, hepta-, and octachlorobiphenyls (octa-CB) characteristic of Aroclor 1260, but key hexa- and hepta-CBs were decreased by as much as 45% relative to Aroclor 1260, and the tri-, tetra-, and penta-CBs were increased. GC/MS analysis revealed unusual tetra-, penta-, and hexa-CBs, many containing 2,4- and 2,4,6-chlorophenyl rings, which are uncommon in higher Aroclors, and provided strong evidence of dechlorination. A quantitative mother–daughter analysis of key hexa- and hepta-CBs that were decreased relative to Aroclor 1260 and their putative dechlorination products yielded mass balances ranging from 90 to 108%. The data indicate that the PCBs consist of partially dechlorinated Aroclors 1260 and 1254 (~95:5). Relative to Aroclor 1260, the most extensively dechlorinated samples had lost 11–19% of the *meta* chlorines and 2–7% of the *para* chlorines. This modest dechlorination caused a 20–28% decrease in the concentrations of the PCB congeners reported to be most persistent in humans.

Introduction

Polychlorinated biphenyls (PCBs) were widely used as dielectric fluids in capacitors and transformers from 1929 to 1978. Most of the PCBs that were released to the environment adsorbed to organic soils and sediments where they still persist. The environmental fate of PCBs is important because they tend to accumulate in biota and are potentially toxic.

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Commercial PCBs are complex mixtures composed of many congeners, i.e., PCB molecules that differ in the number (from 1 to 10) and position of chlorines (1). In the United States, the most commonly used PCB mixtures were Aroclors 1242, 1254, and 1260, which each contained from 70 to 90 different congeners in various proportions.

PCBs entered the Housatonic River from storm sewer discharges and drainage from transformer manufacturing operations in Pittsfield, MA, and some of the PCB-contaminated sediment accumulated in Woods Pond, a shallow impoundment on the river located 11 mi downstream in Lenox, MA. From 1980 to 1982, Stewart Laboratories conducted a survey of the PCB contamination in the Housatonic River including Woods Pond and reported that the PCBs in the sediments consisted of varying proportions of Aroclors 1254 and 1260 and small amounts (less than 5%) of Aroclor 1242 (2). Aroclor 1260 was used at the transformer manufacturing operations in Pittsfield from 1934 to 1973, and Aroclor 1254 was used from 1973 to 1978, but there is no record that Aroclor 1242 was ever used. The brief usage of Aroclor 1254 was at a time when increased environmental awareness had led to improved procedures for handling PCBs; hence, it is likely that most of the PCB contamination in the Housatonic River originating from Pittsfield was Aroclor 1260.

Reductive dechlorination of PCBs is important because it is expected to reduce the potential toxicity and the persistence of PCBs. *In situ* dechlorination of PCBs attributed to microorganisms in the anaerobic sediments has been documented in the Hudson River (NY), Silver Lake (Pittsfield, MA), the St. Lawrence River (NY), and New Bedford Harbor (MA) (3–8). The 1982 survey of the Housatonic (2) relied on packed column gas chromatography (GC) that did not resolve most individual congeners; hence, tetra- and penta-CB peaks resulting from dechlorination of Aroclor 1260 may have been mistaken for Aroclor 1254. Because of a similar misinterpretation, PCB dechlorination in the Hudson River was not recognized for many years; the elevated levels of mono- and di-CBs observed in the sediments were formed by dechlorination of Aroclor 1242, but they were incorrectly attributed to Aroclor 1221.

We used congener-specific GC with electron capture detection (ECD) and mass spectrometric detection (MSD) to address five questions about the PCBs in the sediments of Woods Pond: (1) Is there evidence of Aroclor 1242? (2) Is there evidence of Aroclor 1254, and if so how much? (3) Is there evidence for *in situ* dechlorination of the PCBs? (4) Can dechlorination of Aroclor 1260 explain the PCB congener distributions in the sediments? (5) What is the impact of any observed dechlorination on PCB bioaccumulation in humans?

Materials and Methods

Sediment Collection and Storage. Between 1989 and 1991, we obtained and analyzed 181 sediment samples from 94 locations in Woods Pond: 42 samples from 24 locations along the southern and eastern shores, 137 samples from 68 locations along the western shore, and one each from a shallow point in the middle and from the oxbow in the north end of the pond. Core samples (30–45 cm) were collected using a Lexan tube (5 cm diameter) and sectioned

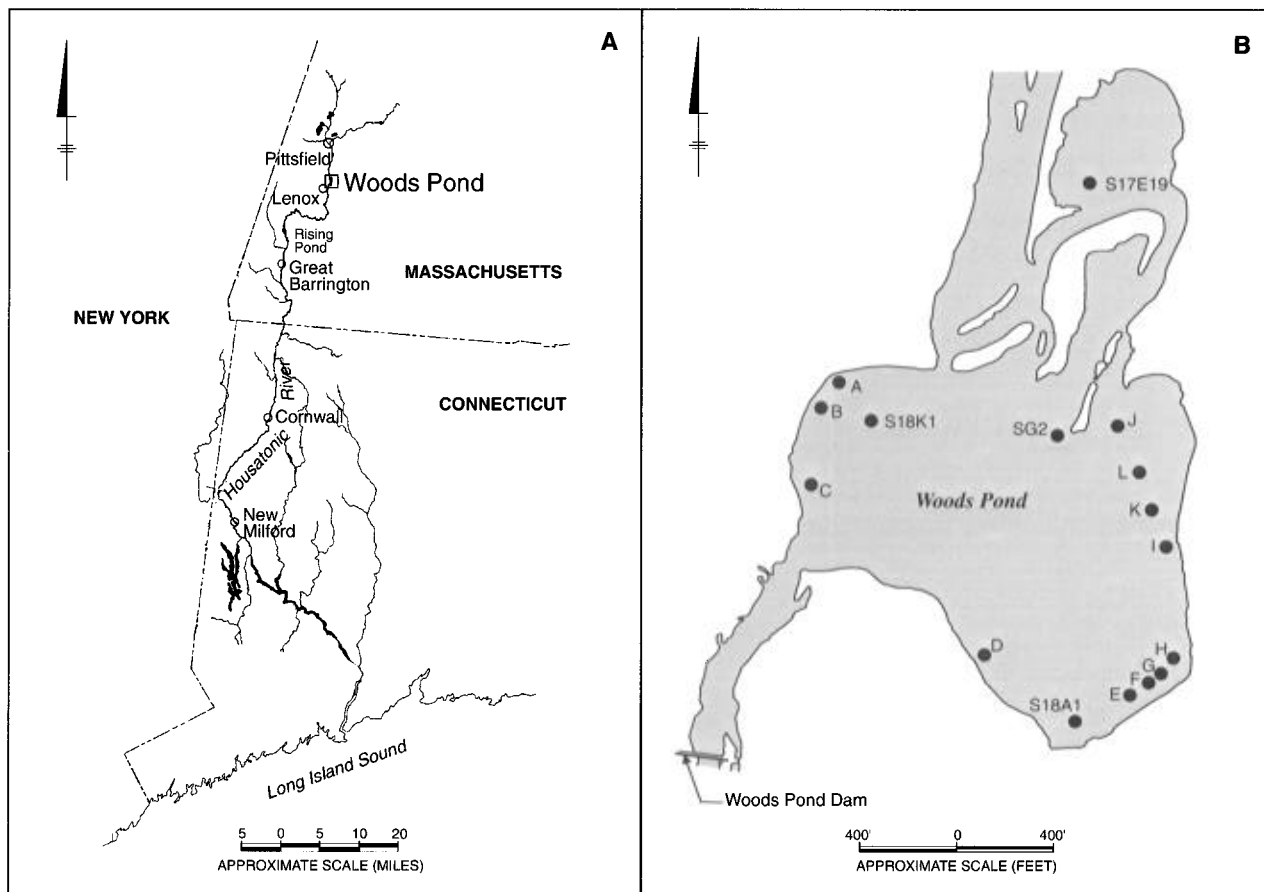


FIGURE 1. Maps showing the location of Woods Pond on the Housatonic River and the areas from which samples were collected. Areas A–D are grids from which samples were collected at multiple locations.

into 15-cm increments, thus generating 2–3 samples each. Bulk samples (1–4 L) that were also intended for biological studies were collected by repeated coring, transferred to glass jars, topped with site water, sealed, and stored at 4 °C. In most cases, only one portion of a bulk sample was analyzed, but five portions were analyzed for sample WP-4, and four portions were analyzed for the samples from sites S18A1 and S18K1. Area A, (Figure 1) is a 14 × 37 m grid from which 21 core samples and 20 bulk samples were analyzed. Areas B–D each represent 9 × 14 m grids from which 12 core samples and three bulk samples were collected at 4.5-m intervals. At locations E–J and sites S17E19, S18A1, S18K1, and SG2, one or two bulk samples were collected.

Determination of Total Oil and Grease. Fourteen sediments were freon-extracted and analyzed for total oil and grease (11).

PCB Extraction and Gas Chromatographic Analysis. Quantitative congener-specific analysis of the PCBs in 41 sediment samples was done at Northeast Analytical, Schenectady, NY. The samples were Soxhlet-extracted and analyzed by GC/ECD using a DB-1 poly(dimethylsiloxane) capillary column (J & W Scientific, 30 m × 0.25 mm i.d. × 0.25 μm) as described (6, 10).

For quality assurance (QA), Northeast Analytical performed duplicate sample analysis and matrix spike samples at a frequency of 1 per 20 samples. A surrogate compound, 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl (23456-2346-CB), a congener not found in Aroclors, was added to each sample before extraction. Method extraction blanks, using clean

sand as a matrix, were run with every batch of samples. The results of these and other QA samples were tracked on Shewhart control charts. There was no indication of analytical problems; no samples exceeded chart action limits.

Qualitative congener-specific GC/ECD analysis was done for an additional 140 samples. PCBs were extracted from the samples by shaking wet sediment for 48 h with 5 vol of anhydrous ethyl ether and excess mercury or by shaking air-dried sediment with 5 vol of isooctane and excess mercury. We have compared the PCB congener distributions in samples extracted by both this simpler means and by rigorous Soxhlet extraction and have found no differences. The chromatograms from these samples were visually inspected and compared with the quantitative data.

PCB Peak Assignment and Quantitation. Prior to 1978, when Aroclors were still in production, GE Corporate Research and Development obtained samples of Aroclors 1242, 1254, and 1260 from Monsanto. These provided the basis for our quantitation and were used as calibration standards for all samples. The weight percent contributions of the components of each peak in Aroclors 1242, 1254, and 1260 were determined (10, 11). GC/MS was used to determine which isomer classes were present in each peak and in what proportions. Peaks constituting less than 0.6 wt % of Aroclors 1242, 1254, or 1260 were quantified using published response factors (13) and are identified in Table 1.

Aroclors 1242, 1254, and 1260, each at a concentration of 4 μg/mL (within the linear range of the detector), were

spiked with octachloronaphthalene (OCN) as an internal standard and analyzed separately with each set of samples. The results were used to generate relative response factors for all peaks. PCB extracts were analyzed by packed column GC (12) for an estimate of PCB concentration, then diluted to 2–4 $\mu\text{g}/\text{mL}$, spiked with OCN, and analyzed by capillary GC/ECD.

Our GC analysis resolves the 209 PCB congeners into 118 peaks. The original peak assignments (6, 10) have been updated and verified with authentic standards for all 209 PCB congeners (11). Congener assignments for Aroclor peaks that are composed of coeluting isomers include only those congeners determined to be significant peak components in Aroclors 1260 or 1254 (or, for tri- and tetra-CBs, in Aroclor 1242) as confirmed by quantitative congener-specific analyses of each Aroclor on 12 different GC column phases (G. M. Frame, personal communication).

Congener-Specific GC/MS Analysis of PCBs. Qualitative GC/MS analyses of selected samples and of Aroclors 1242, 1254, and 1260 were performed using a Hewlett-Packard 5890/5971 GC/MSD equipped with an HP G1034C MS Chem Station and a DB-1 capillary column as described above. Chromatographic conditions were similar to those described earlier (10). The two strongest ions of the molecular cluster for each homolog class were measured over elution windows chosen to include all possible PCB congeners in each homolog class, not only those found in Aroclors. The ratios of the two ions for each peak were used to verify that the signal was due to a PCB. Data were collected at 1 cycle/s to provide adequate definition of the capillary GC peaks.

Due to sensitivity limitations of the mass spectrometric detector, PCB extracts from sediment samples had to be concentrated prior to analysis by GC/MS. The high amount of oil in the concentrated sample extracts caused a shift in PCB retention times relative to the Aroclor standards, but because the shift was fairly constant, the PCB peaks could still be identified by using characteristic peak groupings as reference points.

Calculation of PCB Congener Half-Life Values. Half-life values in humans for all resolvable PCB congeners were calculated from the kinetic parameters reported by Brown (14). Brown estimated the relative human accumulations (over 70 years) for 146 PCB congeners by using kinetic and chromatographic data to determine the relative rates of metabolism by P4502B-like cytochromes and the relative rate of nonmetabolic clearance for each congener. The half-life for each individual PCB congener ($t_{1/2}$) was calculated using the equation: $t_{1/2} = 0.6931 / (s_b k_{bi} + k_n)$ where k_{bi} is the relative rate constant for P4502B-type metabolism of PCB_i, k_n is the nonmetabolic PCB clearance rate (yr^{-1}), which has a value of 0.008, and s_b is the relative activity of P4502B as described (14).

Results and Discussion

Characterization of the Site. Figure 1 shows a map of Woods Pond, its location on the Housatonic River, and the areas from which samples were collected. The flow of the Housatonic River is from the north around the oxbow and through a narrow channel in the pond. On either side of this channel, the sediments have accumulated and are relatively undisturbed. The water ranges in depth from about 0.6 to 1.2 m. The sediments are 0.3–1.2 m deep and are composed of a mixture of black humic matter, silt, and sand overlying a clay subsediment.

Results of Congener-Specific PCB Analysis. The sediments contained PCBs in concentrations ranging from 15 to 180 $\mu\text{g}/\text{g}$ (sediment dry weight) and an unidentified hydrocarbon oil in amounts ranging from 5 300 to 32 400 $\mu\text{g}/\text{g}$ (sediment dry weight). The concentration of oil was 100–360-fold higher than that of PCBs in the samples tested. In general, samples with the highest oil concentrations also had the highest PCB concentrations.

The GC profiles and congener distribution profiles of PCBs extracted from sediment samples were compared with those of Aroclors 1254 and 1260. The hexa- through octa-CB peaks of all PCB extracts from Woods Pond were those characteristic of Aroclor 1260, but tri-, tetra-, and penta-CB peaks that were not detected or were barely detected in Aroclor 1260 were present in higher quantities in all samples.

Table 1 compares the quantitative PCB congener distributions of seven sediment samples with those of Aroclors 1254 and 1260 and a 15:85 mixture of these Aroclors. The samples shown were selected because they represent the full spectrum of PCB congener distributions observed in Woods Pond. Duplicate analyses presented for one extract, 8WP, show that the quantitation was very reproducible.

Small amounts of tri- and tetra-CBs were observed in all samples, but roughly 70–90% of the congeners observed were penta-, hexa-, and hepta-CBs corresponding to those in Aroclors 1254 and 1260. The proportions of several major hexa- and hepta-CB peaks in the sediment PCBs were higher than in Aroclor 1254 but were decreased by 11–16% (sample 6WP) or as much as 32–45% (sample A-34-1) relative to Aroclor 1260 (Table 1). Octa-CBs matching those in Aroclor 1260 were present in all samples.

To determine whether the PCBs in the sediments were mixtures of unaltered Aroclors, we compared the average chlorine distributions and PCB homolog distributions of Aroclors 1254 and 1260 and of various mixtures of these Aroclors with those observed in the PCBs extracted from the sediments (Table 2). The average number of chlorines per biphenyl for the sediment PCBs ranged from 5.73 to 6.20 and thus fell between those for Aroclor 1254 (5.10) and Aroclor 1260 (6.38). The average number of chlorines per biphenyl and the chlorine distributions in the sediment PCBs could be approximated by mixtures of the two Aroclors consisting of from 15 to 50% Aroclor 1254, but these are very insensitive measures of PCB composition in environmental samples. The homolog distributions for the sediment samples showed substantial discrepancies from the values calculated for mixtures of Aroclors 1254 and 1260. The tri-, tetra-, and octa-CBs in the sediment PCBs were too high and the penta-CBs too low to be explained by any mixture of the two Aroclors. In addition, for samples A-33-1, WP-4, and A-34-1, the proportions of hexa- and hepta-CBs were too low to be explained by a mixture of Aroclors.

Evaporation and partitioning can also cause changes in PCB congener distribution profiles (3), but these phenomena result in preferential depletion of the most volatile components or water-soluble components, in this case the tri- and tetra-CBs, and are therefore inconsistent with the fact that these homologs are elevated in the sediment PCBs.

Comparison of PCB Homolog Profiles in Aroclors and Sediment PCBs: Evidence for Dechlorination. Because the proportions of tri- and tetra-CBs in the sediment PCBs were higher than could be accounted for by a mixture of Aroclors 1254 and 1260, we used GC/MS to determine

TABLE 1

PCB Congener Distribution^a (mol %)^b in Aroclors 1254 and 1260 and in Sediments from Woods Pond

| sample name | A1254 | A1260 | 15:85 ^c | 6WP | 8WP | 8WPDUP | A-35-2 | 9WP | A-33-1 | WP-4 | A34-1 | | |
|--------------------------|---------------|---------------------------|--------------------|-------|-------|--------|--------|-------|--------|-------|-------|-----|-----|
| location in Woods Pond | | | | S18A1 | S18A1 | S18A1 | A | S18K1 | A | C | A | | |
| PCB concentration (μg/g) | | | | 169.6 | 122.6 | 124.6 | 42.8 | 45.3 | 56.8 | 154.9 | 64.9 | | |
| PCB peak assignment | | | | | | | | | | | | | |
| peak no. ^d | IUPAC No. | congener ID ^e | | | | | | | | | | | |
| 14 | 18; 15 | 25-2; 4-4 | 0.6 | | 0.1 | 0.2 | 0.2 | 0.2 | 0.3 | 0.3 | 0.2 | 0.3 | |
| 15 | 17 | 24-2 | 0.2 | | | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.3 |
| 17 | 16; 32 | 23-2; 26-4 | 0.3 | | | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.4 | 0.3 | 0.6 |
| 21 | 26 | 25-3 | 0.1 | | | 0.1 | 0.2 | 0.2 | 0.1 | 0.4 | 0.2 | 0.3 | 0.5 |
| 22 | 25 | 24-3 | | | | 0.1 | 0.1 | 0.1 | 0.1 | 0.3 | 0.3 | 0.2 | 0.8 |
| 23 | 31 | 25-4 | 0.5 | | 0.1 | 0.2 | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 0.2 | 0.6 |
| 24 | 28 | 24-4 | 0.4 | | 0.1 | 0.3 | 0.3 | 0.4 | 0.4 | 0.7 | 1.0 | 0.3 | 1.5 |
| 25 | 53; 20; 33 | 25-26; 23-3; 34-2 | 0.4 | | 0.1 | 0.1 | 0.2 | 0.2 | 0.3 | 0.5 | 0.9 | 0.9 | 1.0 |
| 26 | 51; 22 | 24-26; 23-4 | 0.1 | | | 0.1 | 0.1 | 0.1 | 0.1 | 0.3 | 0.7 | 0.5 | 0.8 |
| 29 | 46 | 23-26 | 0.1 | | | | | | 0.1 | 0.2 | 0.2 | 0.4 | 0.4 |
| 31 | 52 | 25-25 | 5.6 | 0.4 | 1.2 | 0.7 | 1.1 | 1.1 | 1.4 | 1.8 | 1.4 | 2.7 | 1.8 |
| 32 | 49; 43 | 24-25; 235-2 | 1.4 | | 0.2 | 0.4 | 0.8 | 0.8 | 1.2 | 1.8 | 2.7 | 3.0 | 3.3 |
| 33 | 47 | 24-24 | 0.2 | | 0.1 | 0.2 | 0.4 | 0.4 | 0.9 | 1.7 | 4.4 | 3.4 | 5.2 |
| 37 | 44; [104] | 23-25; [246-26] | 2.5 | 0.1 | 0.4 | 0.3 | 0.5 | 0.5 | 0.4 | 0.6 | 0.4 | 0.8 | 0.5 |
| 38 | 42; 59 | 23-24; 236-3 | 0.4 | | 0.1 | 0.2 | 0.3 | 0.3 | 0.3 | 0.5 | 0.6 | 0.8 | 0.8 |
| 39 | 64; 41; 71 | 236-4; 234-2; 26-34 | 0.9 | | 0.1 | 0.2 | 0.3 | 0.3 | 0.3 | 0.5 | 0.6 | 0.7 | 0.9 |
| 41* | 96 | 236-26 | 0.1 | | | 0.1 | 0.1 | 0.1 | 0.1 | 0.4 | 0.6 | 0.6 | 0.7 |
| 43* | 103 | 246-25 | 0.1 | | | 0.1 | 0.2 | 0.2 | 0.3 | 0.5 | 0.5 | 0.6 | 0.6 |
| 44* | 100 | 246-24 | | | | 0.1 | 0.2 | 0.2 | 0.2 | 0.4 | 0.7 | 0.6 | 0.8 |
| 46 | 74; [94] | 245-4; [235-26] | 0.9 | | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 0.3 | 0.2 | 0.3 |
| 47 | 70 | 25-34 | 3.9 | 0.1 | 0.7 | 0.7 | 0.7 | 0.8 | 0.7 | 0.8 | 0.6 | 0.6 | 0.7 |
| 48 | 95; 102; 66 | 236-25; 245-26; 24-34 | 5.5 | 2.1 | 2.6 | 1.7 | 2.4 | 2.5 | 2.4 | 2.8 | 2.2 | 2.6 | 2.4 |
| 49 | 91 | 236-24 | 1.0 | | 0.2 | 0.2 | 0.3 | 0.3 | 0.4 | 0.7 | 1.5 | 1.2 | 1.6 |
| 50 | 56; 60 | 23-34; 234-4 | 0.9 | | 0.1 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 |
| 51 | 92; 84 | 235-25; 236-23 | 3.4 | 0.5 | 1.0 | 1.1 | 1.3 | 1.4 | 1.4 | 1.4 | 1.1 | 1.5 | 1.2 |
| 52* | 89 | 234-26 | 0.5 | | 0.1 | | | | | | | | |
| 53 | 101; 90 | 245-25; 235-24 | 8.0 | 3.8 | 4.4 | 3.3 | 3.9 | 3.9 | 4.3 | 3.9 | 3.4 | 3.6 | 3.3 |
| 54 | 99 | 245-24 | 2.8 | 0.1 | 0.5 | 1.0 | 1.2 | 1.2 | 1.6 | 1.7 | 1.8 | 1.8 | 1.8 |
| 55* | 119; [150] | 246-34; [236-246] | 0.3 | | | 0.3 | 0.3 | 0.3 | 0.3 | 0.6 | 0.6 | 0.7 | 0.7 |
| 56 | 83; 112 | 235-23; 2356-3 | 0.7 | | 0.1 | 0.2 | 0.2 | 0.2 | 0.2 | 0.3 | 0.2 | 0.3 | 0.2 |
| 57 | 97; [152] | 245-23; [2356-26] | 2.0 | 0.1 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.3 |
| 58 | 87; 117; 115 | 234-25; 2356-4; 2346-4 | 3.8 | 0.5 | 1.0 | 0.6 | 0.6 | 0.6 | 0.4 | 0.5 | 0.4 | 0.4 | 0.5 |
| 59 | 85 | 234-24 | 1.3 | | 0.2 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 |
| 60 | 136 | 236-236 | 0.7 | 1.5 | 1.4 | 0.9 | 1.2 | 1.2 | 1.2 | 1.1 | 0.9 | 1.2 | 0.8 |
| 61 | 110; [148] | 236-34; [235-246] | 8.6 | 1.7 | 2.7 | 2.8 | 2.9 | 2.9 | 2.2 | 2.9 | 1.8 | 2.2 | 1.9 |
| 62* | 154 | 245-246 | 0.1 | | | 0.3 | 0.3 | 0.3 | 0.7 | 0.4 | 0.9 | 0.6 | 0.8 |
| 63 | 82 | 234-23 | 1.0 | | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 64 | 151 | 2356-25 | 0.8 | 3.3 | 3.0 | 2.1 | 2.3 | 2.3 | 2.6 | 2.3 | 2.3 | 2.4 | 2.1 |
| 65 | 135; (124) | 235-236; (345-25) | 1.0 | 1.5 | 1.4 | 1.8 | 2.0 | 2.0 | 1.6 | 1.7 | 1.2 | 1.5 | 1.1 |
| 66 | 144 | 2346-25 | 0.5 | 1.2 | 1.1 | 0.6 | 0.6 | 0.6 | 0.6 | 0.5 | 0.4 | 0.5 | 0.3 |
| 67 | (109); (147) | (235-34); (2356-24) | 0.8 | | 0.1 | 0.6 | 0.6 | 0.6 | 0.5 | 0.7 | 1.1 | 0.8 | 1.2 |
| 69 | 149; 118 | 236-245; 245-34 | 9.7 | 8.1 | 8.3 | 7.6 | 7.9 | 7.9 | 7.4 | 7.1 | 5.7 | 5.6 | 5.4 |
| 70* | 140 | 234-246 | | | | | | | 0.3 | | 0.2 | 0.5 | 0.3 |
| 71 | 134; (114) | 2356-23; (2345-4) | 0.7 | 0.4 | 0.4 | 0.3 | 0.3 | 0.4 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| 72* | 131 | 2346-23 | 0.3 | 0.2 | 0.2 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.3 |
| 73 | 146 | 235-245 | 0.7 | 1.3 | 1.2 | 2.1 | 2.0 | 2.0 | 2.1 | 1.7 | 1.5 | 1.7 | 1.4 |
| 74 | 132; (105) | 234-236; (234-34) | 3.6 | 1.6 | 1.9 | 1.8 | 1.7 | 1.7 | 1.3 | 1.4 | 1.0 | 1.0 | 1.0 |
| 75 | 153 | 245-245 | 4.5 | 12.3 | 11.1 | 11.0 | 10.5 | 10.4 | 10.1 | 9.3 | 7.9 | 8.3 | 7.1 |
| 77 | 141 | 2345-25 | 0.9 | 2.5 | 2.3 | 1.7 | 1.6 | 1.7 | 1.5 | 1.3 | 1.1 | 1.1 | 1.0 |
| 78 | 179 | 2356-236 | 0.1 | 1.9 | 1.6 | 1.6 | 1.5 | 1.5 | 1.8 | 1.6 | 1.5 | 1.6 | 1.3 |
| 79 | 137 | 2345-24 | 0.6 | | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.2 |
| 80 | 130 | 234-235 | 0.6 | 0.3 | 0.3 | 0.9 | 0.7 | 0.8 | 0.6 | 0.5 | 0.4 | 0.5 | 0.4 |
| 81* | 176 | 2346-236 | | 0.5 | 0.4 | 0.3 | 0.3 | 0.3 | 0.4 | 0.3 | 0.3 | 0.3 | 0.3 |
| 82 | 138; 163; 164 | 234-245; 2356-34; 236-345 | 6.9 | 10.8 | 10.2 | 9.2 | 8.8 | 8.7 | 7.4 | 7.5 | 6.4 | 6.6 | 6.0 |
| 83 | 158 | 2346-34 | 0.9 | 1.0 | 1.0 | 0.7 | 0.7 | 0.7 | 0.6 | 0.6 | 0.5 | 0.5 | 0.5 |
| 84 | 129 | 2345-23 | 0.6 | 0.2 | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.1 | 0.2 | 0.2 |
| 85 | 178 | 2356-235 | 0.1 | 0.8 | 0.7 | 0.8 | 0.7 | 0.7 | 0.9 | 0.7 | 0.8 | 0.7 | 0.7 |
| 87* | 175 | 2346-235 | | 0.5 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 |
| 88 | 187 | 2356-245 | 0.3 | 4.8 | 4.1 | 4.5 | 4.1 | 4.1 | 4.5 | 4.0 | 4.1 | 3.9 | 3.7 |
| 89 | 128 | 234-234 | 1.2 | 0.5 | 0.6 | 0.6 | 0.6 | 0.6 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 |
| 90 | 183 | 2346-245 | 0.2 | 2.8 | 2.5 | 2.3 | 2.1 | 2.0 | 2.2 | 1.9 | 2.0 | 1.9 | 1.8 |
| 91 | 167 | 245-345 | 0.6 | 0.4 | 0.5 | 0.9 | 0.8 | 0.8 | 0.6 | 0.5 | 0.5 | 0.5 | 0.5 |
| 92 | 185 | 23456-25 | | 0.7 | 0.6 | 0.5 | 0.4 | 0.4 | 0.5 | 0.4 | 0.5 | 0.4 | 0.4 |
| 93 | 174 | 2345-236 | 0.3 | 4.3 | 3.7 | 3.8 | 3.6 | 3.5 | 3.3 | 3.1 | 3.0 | 3.0 | 2.6 |
| 94 | 177 | 2356-234 | 0.2 | 2.3 | 2.0 | 2.2 | 2.0 | 1.9 | 1.8 | 1.7 | 1.6 | 1.8 | 1.5 |
| 95 | 171; 156 | 2346-234; 2345-34 | 1.0 | 1.6 | 1.5 | 1.5 | 1.3 | 1.3 | 1.2 | 1.1 | 1.1 | 1.0 | 1.0 |
| 98* | 173 | 23456-23 | 0.5 | 0.1 | 0.1 | 0.1 | 0.1 | | | | | | |
| 99* | 201 | 2346-2356 | | 0.3 | 0.2 | 0.3 | 0.3 | 0.7 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 |
| 100 | 172 | 2345-235 | 0.1 | 0.9 | 0.7 | 1.0 | 1.0 | 1.0 | 0.9 | 0.7 | 0.7 | 0.7 | 0.7 |

Table 1 (Continued)

| sample name | | | A1254 | A1260 | 15:85 ^c | 6WP | 8WP | 8WPDUP | A-35-2 | 9WP | A-33-1 | WP-4 | A34-1 |
|-----------------------|-----------|--------------------------|-------|-------|--------------------|-----|-----|--------|--------|-----|--------|------|-------|
| PCB peak assignment | | | | | | | | | | | | | |
| peak no. ^d | IUPAC No. | congener ID ^e | | | | | | | | | | | |
| 101* | 197 | 2346-2346 | | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | | 0.1 |
| 102 | 180 | 2345-245 | 0.7 | 10.2 | 8.8 | 8.6 | 7.9 | 7.8 | 8.3 | 7.1 | 7.8 | 6.9 | 6.9 |
| 103* | 193 | 2356-345 | | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 |
| 106 | 170 | 2345-234 | 0.4 | 3.5 | 3.0 | 2.9 | 2.6 | 2.6 | 2.4 | 2.3 | 2.3 | 2.2 | 2.1 |
| 107 | 190 | 23456-34 | 0.1 | 0.9 | 0.7 | 0.6 | 0.6 | 0.6 | 0.6 | 0.5 | 0.6 | 0.6 | 0.6 |
| 109 | 199 | 2345-2356 | | 1.4 | 1.2 | 1.5 | 1.3 | 1.3 | 1.5 | 1.3 | 1.6 | 1.3 | 1.4 |
| 110 | 196; 203 | 2345-2346; 23456-245 | | 1.8 | 1.5 | 1.6 | 1.4 | 1.4 | 1.7 | 1.4 | 1.9 | 1.5 | 1.7 |
| 112 | 195 | 23456-234 | | 0.7 | 0.6 | 0.7 | 0.6 | 0.6 | 0.6 | 0.6 | 0.7 | 0.6 | 0.6 |
| 115 | 194 | 2345-2345 | | 1.4 | 1.2 | 1.3 | 1.1 | 1.1 | 1.4 | 1.1 | 1.5 | 1.1 | 1.3 |
| 116* | 205 | 23456-345 | | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | | 0.1 |
| 117 | 206 | 23456-2345 | | 0.6 | 0.5 | 0.7 | 0.6 | 0.6 | 0.8 | 0.6 | 1.0 | 0.7 | 0.9 |

^a Where two different homologs coelute, we have used parentheses to indicate homologs that are present in the sediment PCBs and in Aroclor 1254 but not in Aroclor 1260, and brackets to indicate homologs that are present in Woods Pond sediments but not in either Aroclor. This information was derived from GC/MS analyses that will be described later. ^b Quantitation was done by GC/ECD using a DB-1 capillary column as described. Where no value is shown, the value was determined to be 0.0 mol %. ^c Values calculated for a mixture consisting of 15% Aroclor 1254 and 85% Aroclor 1260. ^d For the sake of brevity, we report only peaks that constitute ≥ 0.3 mol % of the total PCBs in at least one sample. Peaks designated by asterisks were quantified with a manual response factor as described. ^e The congener designations denote the positions of the chlorine atoms on each ring of biphenyl, and the hyphen represents separation of the rings.

TABLE 2

Comparison of PCB Homolog Distributions^a (mol %) and Chlorine Distributions in Woods Pond Sediments with Those in Aroclor Mixtures

| sample ID | A1254 | A1260 | 15:85 ^b | 6WP | 8WP | 8WPDUP | 25:75 ^b | A-35-2 | 9WP | A-33-1 | WP-4 | 50:50 ^b | A-34-1 |
|---------------------------------------------|-------|-------|--------------------|------|------|--------|--------------------|--------|------|--------|------|--------------------|--------|
| PCB homolog | | | | | | | | | | | | | |
| dichlorobiphenyls | 0.4 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| trichlorobiphenyls | 2.6 | 0.0 | 0.4 | 0.9 | 1.3 | 1.4 | 0.7 | 1.5 | 2.5 | 2.6 | 2.0 | 1.3 | 4.6 |
| tetrachlorobiphenyls | 19.2 | 0.7 | 3.5 | 4.5 | 6.3 | 6.4 | 5.4 | 7.4 | 11.1 | 14.3 | 15.8 | 10.0 | 17.4 |
| pentachlorobiphenyls | 45.8 | 10.2 | 15.6 | 14.0 | 15.8 | 15.9 | 19.1 | 15.8 | 17.7 | 16.4 | 17.2 | 28.0 | 17.1 |
| hexachlorobiphenyls | 28.6 | 46.4 | 43.7 | 42.1 | 41.3 | 41.4 | 41.9 | 38.8 | 36.4 | 32.0 | 33.2 | 37.5 | 29.6 |
| heptachlorobiphenyls | 3.2 | 35.8 | 30.9 | 31.4 | 29.0 | 28.5 | 27.7 | 29.3 | 26.2 | 27.0 | 25.7 | 19.5 | 24.1 |
| octachlorobiphenyls | 0.1 | 6.2 | 5.3 | 6.3 | 5.5 | 5.7 | 4.7 | 6.2 | 5.3 | 6.6 | 5.3 | 3.2 | 6.0 |
| nonachlorobiphenyls | 0.0 | 0.6 | 0.5 | 0.8 | 0.7 | 0.7 | 0.5 | 0.9 | 0.7 | 1.1 | 0.8 | 0.3 | 1.0 |
| chlorine distribution | | | | | | | | | | | | | |
| <i>ortho</i> Cl per biphenyl | 2.02 | 2.46 | 2.40 | 2.37 | 2.36 | 2.36 | 2.35 | 2.38 | 2.35 | 2.38 | 2.38 | 2.24 | 2.34 |
| <i>meta</i> Cl per biphenyl | 1.95 | 2.57 | 2.47 | 2.48 | 2.42 | 2.42 | 2.41 | 2.40 | 2.27 | 2.19 | 2.20 | 2.26 | 2.08 |
| <i>para</i> Cl per biphenyl | 1.13 | 1.35 | 1.32 | 1.35 | 1.32 | 1.31 | 1.30 | 1.32 | 1.28 | 1.33 | 1.26 | 1.24 | 1.30 |
| total Cl per biphenyl | 5.10 | 6.38 | 6.19 | 6.20 | 6.09 | 6.09 | 6.06 | 6.09 | 5.91 | 5.90 | 5.84 | 5.74 | 5.73 |
| % loss relative to Aroclor 1260 | | | | | | | | | | | | | |
| <i>meta</i> Cl | | | | 3.4 | 5.7 | 5.9 | | 6.7 | 11.4 | 14.5 | 14.4 | | 18.9 |
| <i>para</i> Cl | | | | 0.0 | 2.8 | 3.2 | | 2.8 | 5.2 | 2.0 | 6.9 | | 3.9 |
| <i>meta</i> + <i>para</i> Cl | | | | 2.2 | 4.7 | 4.9 | | 5.3 | 9.2 | 10.2 | 11.8 | | 13.7 |
| ratio: <i>meta/para</i> losses ^c | | | | | 2.1 | 1.9 | | 2.4 | 2.2 | 7.3 | 2.1 | | 4.8 |

^a Quantitation was done by GC/ECD using a DB-1 capillary column as described in the text. The congener distributions are shown in Table 1. No mono- or deca-CBs were detected. ^b Values calculated for mixtures of Aroclors 1254 and 1260 in the proportions shown. ^c Ratio: Percent loss of *meta* chlorines vs percent loss of *para* chlorines.

whether a mixture of Aroclors 1242 and 1254 could account for these homologs. Figure 2 shows that the chromatographic patterns for the tri- and tetra-CBs for sample A-34-1 were distinctly different than those for Aroclors 1242 and 1254. The tri-CBs in A-34-1 included some of those present in the Aroclors, but the relative proportion of peak 22 was much higher in A-34-1 than in the Aroclors, and those of peaks 15, 23, and 24 were much lower than in the Aroclors. Even more striking, the tri-CB components of peaks 25 and 26 were absent in the sediment PCBs although they are major components of Aroclor 1242 (6.0 and 2.8 wt %, respectively) (11). Finally, only one of the components of peak 17 (26-4-CB) was present in the sediment PCBs whereas two are evident in the Aroclors.

The tetra-CB profile for A-34-1 did not resemble that of either Aroclor (Figure 2). The most abundant tetra-CB in A-34-1 was 24-24-CB (peak 33), a congener that is not prominent in Aroclor 1242 and is present in very low

amounts in Aroclor 1254 (Table 1). Conversely, tetra-CB peaks 37, 46, and 50 are all prominent components of Aroclor 1242, and to a lesser extent Aroclor 1254, but were absent or barely detectable in A-34-1. Finally, the tetra-CB components of peaks 25 and 26, respectively, constituted 1.9 mol % in A-34-1, but they constitute only 0.2–0.4 mol % in Aroclors 1242 and 1254 (11).

Since the tri- and tetra-CBs in A-34-1 and several other sediment samples (data not shown) did not correspond to those in Aroclor 1242, we conclude that there is no evidence of Aroclor 1242 in the sediment PCBs.

The selected ion chromatograms for the penta-, hexa-, hepta-, and octa-CBs in Aroclors 1254 and 1260 show that the penta-CB peaks that are most abundant in the Aroclors, i.e., peaks 48, 53, 61, and 69, were also prominent in the sediment PCBs, but a number of striking differences were also apparent. Peaks 49 and 54 were major components of the sediment PCBs but not of either Aroclor; and six

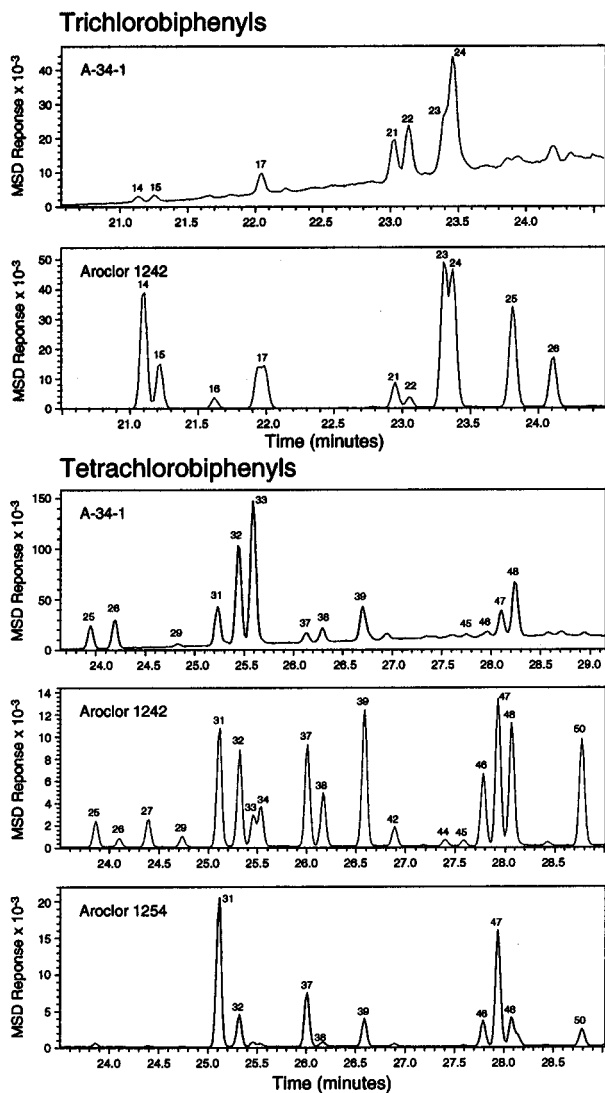


FIGURE 2. Selected ion chromatograms for trichlorobiphenyls ($m/z = 256$) and tetrachlorobiphenyls ($m/z = 290$) in sediment sample A-34-1 and in Aroclors 1242 and 1254. No data are presented for Aroclor 1260 because the tri- and tetra-CBs are very minor components of that Aroclor. Samples shown in Figures 2 and 3 were analyzed by GC/MS as described, and the components in each peak are identified in Table 1. The trichlorobiphenyls for Aroclor 1254 (not shown) occur in the same relative proportions as those of Aroclor 1242, but constitute only 2.8 mol % of the PCBs.

additional penta-CB peaks (37, 41, 43, 44, 46, and 55) were present in the sediment PCBs but not in either Aroclor.

The chromatograms of the hexa-CBs (Figure 3) are very similar for both Aroclors and match those of the sediment PCBs fairly closely. However, in sample A-34-1 we also detected five additional hexa-CB peaks that were not detected in either Aroclor (peaks 55, 57, 61, 62, and 70) and one (peak 67) that was significantly elevated. The hepta- and octa-CBs from sediment samples matched those for Aroclor 1260 (data not shown) and thus support the interpretation that the original contaminant was primarily Aroclor 1260.

We conclude that the congener distribution of the sediment PCBs cannot be explained by any combination of unaltered Aroclors 1242, 1254, and 1260.

The tri- through hexa-CBs that were significantly elevated in A-34-1 relative to Aroclors 1254 and 1260 are listed in Table 3. Most of these contain 2,4- (24-) or 2,4,6-chloro-

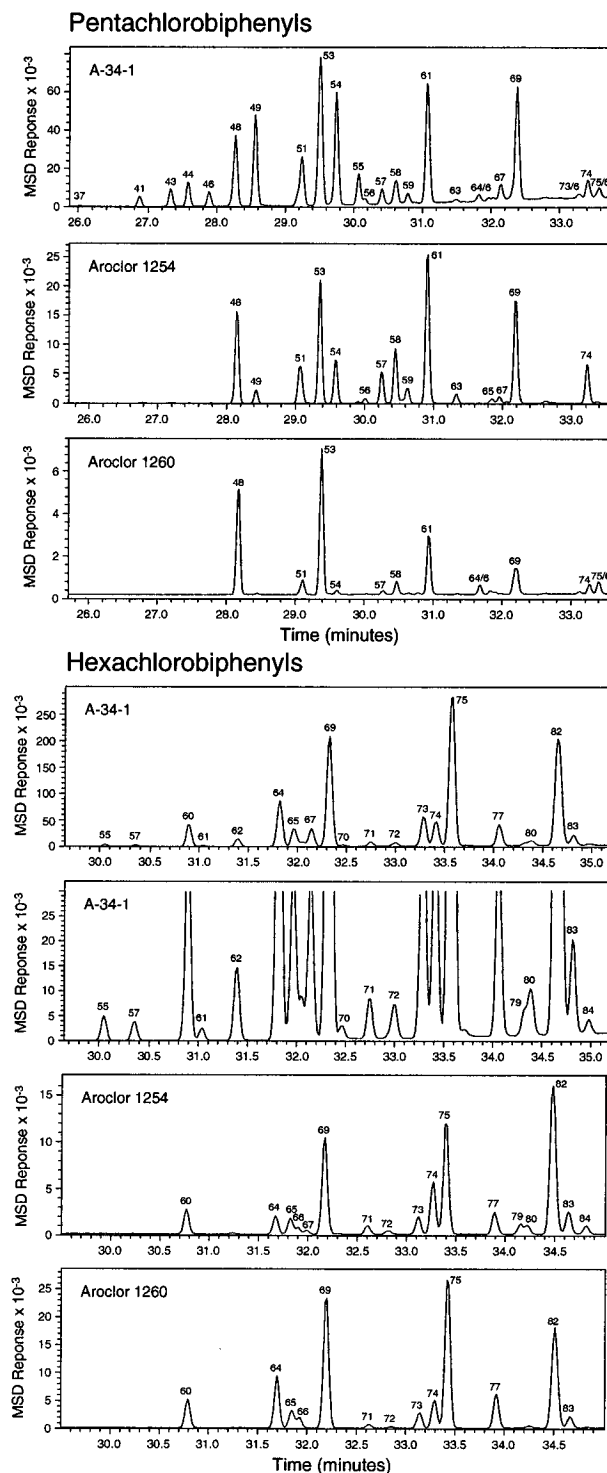


FIGURE 3. Selected ion chromatograms for pentachlorobiphenyls ($m/z = 324$) and hexachlorobiphenyls ($m/z = 360$) in sediment sample A-34-1 and in Aroclors. A-34-1 included six unique penta-CB and five hexa-CB peaks that were not present in the Aroclors. An expanded plot is included for sample A-34-1 to show that the small peaks are well defined. Fragments of hexa-CBs are evident for peaks 64, 73, and 75 in the pentachlorobiphenyl profiles and are noted.

phenyl groups, which are fairly uncommon substitution patterns in higher Aroclors. Many of these congeners coelute with homologs that are present in higher amounts and therefore could not be quantified by GC/ECD, but where such coelutions do not occur, congener-specific GC/ECD analysis confirmed the elevation of these congeners in many other sediment samples (Table 1). These

TABLE 3

Congeners That Are Unique or Elevated Relative to Aroclors 1254 and 1260

| tri-CB | | tetra-CB | | penta-CB | | hexa-CB | |
|--------|----------|----------|--------------|----------|----------|---------|----------|
| peak | congener | peak | congener | peak | congener | peak | congener |
| 17 | 26-4 | 25 | 25-26 | 37 | 246-26 | 55 | 236-246 |
| 21 | 25-3 | 26 | 24-26 | 41 | 236-26 | 57 | 2356-26 |
| 22 | 24-3 | 29 | 23-26 | 43 | 246-25 | 61 | 235-246 |
| 24 | 24-4 | 32 | 24-25; 235-2 | 44 | 246-24 | 62 | 245-246 |
| | | 33 | 24-24 | 46 | 235-26 | 67 | 2356-24 |
| | | 38 | 23-24; 236-3 | 49 | 236-24 | 70 | 234-246 |
| | | 45 | 235-4 | 54 | 245-24 | | |
| | | | | 55 | 246-34 | | |
| | | | | 67 | 235-34 | | |

data provide strong evidence for PCB dechlorination because it is difficult to explain elevated levels of so many uncommon congeners in any other way. PCBs with 24- and 246-chlorophenyl rings could result from *meta* dechlorination of PCBs containing 234-, 245-, 2345-, and 2346-chlorophenyl groups; such PCBs are fairly common in Aroclor 1260.

Characterization of *in Situ* PCB Dechlorination. Relative to Aroclor 1260, the major hexa- and hepta-CBs in all 181 sediment samples from Woods Pond were significantly decreased, and specific tri-, tetra-, and penta-CBs were increased. On a mole percent basis, the largest losses were those of 236-245-CB, 245-245-CB, 234-245-CB, 2345-245-CB, and 2345-234-CB. Smaller losses of 2345-25-CB, 2345-236-CB, 2356-25-CB, 235-245-CB, and 2345-246-CB/2356-245-CB were also evident. These losses were balanced by elevated amounts of congeners that are virtually absent in Aroclor 1260, i.e., 25-25-CB, 24-25-CB, and 24-24-CB and many other congeners with 24- and 246-chlorophenyl groups that are not found in Aroclor 1260 (Table 3).

PCBs in the sediment samples were dechlorinated from both *meta* and *para* positions (Table 2). The slight decrease in *ortho* chlorines is most likely an artifact because we did not observe any products of *ortho*-dechlorination. Based on the chlorine substitution pattern of those congeners that were decreased or increased relative to Aroclor 1260, we propose in Figure 4 a scheme of *meta*- and *para*-dechlorination that demonstrates how many of the elevated tetra- and penta-CBs observed in Woods Pond sediments could have been formed by dechlorination of the four major hexa- and hepta-CB components of Aroclor 1260 that showed large decreases. The congeners that were elevated relative to Aroclor 1260 are underlined in Figure 4. We propose that there are various routes of dechlorination for each of the major hepta- and hexa-CBs and several routes of formation for most of the tetra- and penta-CBs. For example, 24-25-CB, 24-24-CB, and 245-24-CB can each be formed from all four of the major Aroclor components that decreased: 234-245-CB, 245-245-CB, 2345-234-CB, and 2345-245-CB. Therefore, the large increases of these three congeners relative to Aroclor 1260 are consistent with the proposed dechlorination.

Many of the penta-CBs that would be produced by dechlorination (Figure 4) match those that are found in Aroclor 1254. Thus, dechlorination of Aroclor 1260 would generate a population of penta-CBs containing those found in Aroclor 1254, but in different relative proportions. Hence the penta-CB distribution for A-34-1 (Figure 3) supports the interpretation that many of these penta-CBs were

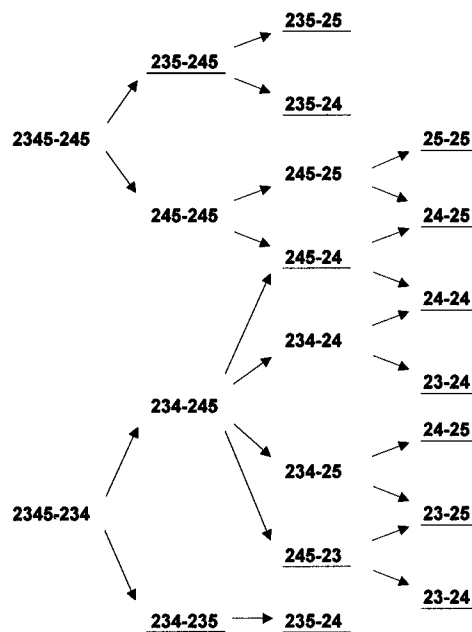


FIGURE 4. Proposed routes of dechlorination for major hexa- and heptachlorobiphenyl components of Aroclor 1260. Congeners that were elevated in the sediment samples relative to Aroclor 1260 are underlined. One putative dechlorination product, 235-24-CB, comigrates with an isomer, 245-25-CB, that we propose is further dechlorinated. The total PCBs in that peak (peak 53) showed little change relative to Aroclor 1260, but we propose that the composition of the peak changed from mainly 245-25-CB to mainly 235-24-CB.

formed by dechlorination of Aroclor 1260. Furthermore, unusual penta-CBs such as 246-25-CB and 246-24-CB that were observed in the sediment PCBs could be generated by *meta*-dechlorination of the 2346-chlorophenyl ring of 2346-25-CB and 2346-245-CB. The latter congeners were both decreased in the sediment PCBs relative to Aroclor 1260 (Table 1).

Mass Balance for *in Situ* Dechlorination. The mass balances for the congeners included in the dechlorination scheme proposed are shown for all seven sediment samples in Table 4. Relative to Aroclor 1260, the parent congeners in the sediment samples decreased by 5.0 to 14.6 mol % and the presumptive dechlorination products increased by 4.5 to 13.9 mol %. The calculated mass balances are excellent, ranging from 90 to 108%, thus the increases in tetra- and penta-CBs completely account for the observed decreases in the major hexa- and hepta-CBs. Hence, we conclude that the PCB congener distributions in Woods Pond sediments result from dechlorination of Aroclor 1260.

Contribution of Aroclor 1254 in the Sediment PCBs. Two observations suggest that there was a small amount Aroclor 1254 in the PCBs that contaminated Woods Pond. First, the proportion of 236-34-CB (peak 61), which constitutes 8.6 mol % of Aroclor 1254, was substantially elevated relative to Aroclor 1260 in several of the sediment samples (Table 1). This congener could be formed by dechlorination of two congeners in Aroclor 1260, i.e., 236-345-CB (a component of peak 82) and 2346-34-CB (peak 83), but the losses observed in those congeners relative to Aroclor 1260 were not great enough to account for the elevated levels of 236-34-CB in samples 6WP, 8WP, and 9WP. Hence, it is more likely that part of the observed increase in this congener relative to Aroclor 1260 was due to a small contribution from Aroclor 1254.

TABLE 4

Quantitative Mother–Daughter Analysis of Key Hexa- and Heptachlorobiphenyls and Their Putative Dechlorination Products

| peak no. | congener ID | mol % in sample ^a | | | | | | | | |
|----------|--------------------------------|------------------------------|-----------------------------------------------|------|--------|--------|-------|--------|-------|--------|
| | | Aroclor 1260 | increase or decrease relative to Aroclor 1260 | | | | | | | |
| | | | 6WP | 8WP | 8WPDUP | A-35-2 | 9WP | A-33-1 | WP-4 | A-34-1 |
| 31 | 25-25 | 0.4 | 0.3 | 0.7 | 0.7 | 1.0 | 1.4 | 1.0 | 2.3 | 1.4 |
| 32 | 24-25; 235-2 | 0.0 | 0.4 | 0.7 | 0.7 | 1.2 | 1.8 | 2.7 | 3.0 | 3.3 |
| 33 | 24-24 | 0.0 | 0.2 | 0.3 | 0.3 | 0.8 | 1.6 | 4.4 | 3.4 | 5.2 |
| 37 | 23-25; [246-26] ^b | 0.1 | 0.3 | 0.4 | 0.4 | 0.3 | 0.6 | 0.3 | 0.7 | 0.4 |
| 38 | 23-24; 236-3 | 0.0 | 0.2 | 0.3 | 0.3 | 0.3 | 0.5 | 0.6 | 0.8 | 0.8 |
| 51 | 235-25; 236-23 | 0.5 | 0.6 | 0.8 | 0.8 | 0.8 | 0.9 | 0.6 | 1.0 | 0.7 |
| 53 | 245-25; 235-24 | 3.8 | -0.5 | 0.2 | 0.2 | 0.5 | 0.1 | -0.3 | -0.1 | -0.4 |
| 54 | 245-24 | 0.1 | 1.0 | 1.1 | 1.1 | 1.6 | 1.6 | 1.7 | 1.7 | 1.7 |
| 57 | 245-23; [2356-26] ^b | 0.1 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.2 |
| 58 | 234-25; 2356-4; 2346-4 | 0.5 | 0.1 | 0.1 | 0.1 | -0.1 | 0.0 | -0.1 | -0.1 | 0.0 |
| 59 | 234-24 | 0.0 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 |
| 73 | 234-245 | 1.3 | 0.8 | 0.7 | 0.7 | 0.8 | 0.4 | 0.2 | 0.4 | 0.1 |
| 80 | 234-235 | 0.3 | 0.6 | 0.5 | 0.5 | 0.4 | 0.3 | 0.1 | 0.2 | 0.1 |
| | sum | 7.1 | 4.5 | 6.5 | 6.6 | 8.4 | 9.9 | 11.7 | 13.7 | 13.9 |
| 75 | 245-245 | 12.3 | -1.3 | -1.8 | -1.8 | -2.2 | -3.0 | -4.4 | -3.9 | -5.2 |
| 82 | 234-245; 2356-34; 236-345 | 10.8 | -1.5 | -2.0 | -2.0 | -3.3 | -3.2 | -4.3 | -4.2 | -4.8 |
| 102 | 2345-245 | 10.2 | -1.6 | -2.3 | -2.4 | -1.9 | -3.1 | -2.4 | -3.3 | -3.3 |
| 106 | 2345-234 | 3.5 | -0.6 | -0.8 | -0.8 | -1.0 | -1.2 | -1.1 | -1.2 | -1.3 |
| | sum | 36.7 | -5.0 | -6.9 | -7.1 | -8.4 | -10.5 | -12.3 | -12.7 | -14.6 |
| | mass balance (%) | | 90 | 94 | 93 | 100 | 95 | 95 | 108 | 95 |

^a Data are taken from Table 1. ^b Brackets denote a homolog that is present in the sediment samples but not in Aroclor 1260.

Second, the amounts of 25-3-CB, 24-3-CB, 25-4-CB, and 24-4-CB cannot be fully explained by the dechlorination of Aroclor 1260. These tri-CBs are most likely produced from dechlorination of 24-34-CB (a component of peak 48), 25-34-CB (peak 47), and 245-34-CB (a component of peak 69). Figure 2 shows that 24-34-CB and 25-34-CB were significant components of the sediment PCBs, but they are very minor components of Aroclor 1260 (11) and cannot account for the amounts of the daughter products seen in some of the samples. The proportions of these parent congeners are 7–20-fold higher in Aroclor 1254 than in 1260 (11), hence a 5–15% contribution from Aroclor 1254 would provide sufficient parent congeners to explain the observed proportions of these tri-CBs in the sediment.

A comparison of the octa-CBs in 6WP, the sediment that shows the least transformation, with those in Aroclor 1260 provides a good means of assessing the relative contribution of Aroclor 1254. The proportions of three key octa-CBs (peaks 109, 110, and 115) deviate only 4–7% from those in Aroclor 1260 (Table 1). Since there are virtually no octa-CBs in Aroclor 1254, any dilution with Aroclor 1254 would result in a proportional decrease in these homologs. Thus, we conclude that the PCBs that contaminated Woods Pond contained no more than 5% Aroclor 1254.

Identification of Microbial PCB Dechlorination Processes in Woods Pond. Brown and Wagner reported that the PCB congener distribution in Woods Pond sediment resembles the pattern that would result from microbial dechlorination processes H and H', which are active in New Bedford Harbor (3). But although dechlorination of Aroclor 1260 by Processes H and H' would generate a congener distribution profile similar to that observed in Woods Pond, these dechlorination processes remove primarily *para* chlorines (3, 16) whereas the dechlorination in Woods Pond removed primarily *meta* chlorines (Table 2). Furthermore, the variability in the ratio of *meta* to *para* dechlorination in Woods Pond (Table 2) indicates that two distinct

microbial dechlorination processes were active. Our laboratory experiments with microcosms of Woods Pond sediments confirm this. Dechlorination Processes P and N can be selectively stimulated in Woods Pond sediment by the addition of a PCB congener that acts as a preferred substrate for one of the processes (15, 16).

Process P is highly selective and removes only *para* chlorines flanked by at least one *meta* chlorine. In Aroclor 1260, the target substrates for Process P are penta- and hexa-CBs containing 234-, 245-, or 2345-chlorophenyl groups, and the key products are tetra- and penta-CBs containing 25-, 235-, and to a lesser extent 23-chlorophenyl groups, especially 25-25-CB, 24-25-CB, 23-25-CB, and 235-25-CB (15, 17).

Process N selectively removes *meta* chlorines, but only those that are flanked by at least one chlorine in either the *para* or the *ortho* position (15, 18, 19). In Aroclor 1260 the primary targets are penta- through octa-CBs. Congeners containing 234-, 245-, or 2345-chlorophenyl groups are dechlorinated to tri-, tetra-, and penta-CBs containing 24-chlorophenyl groups, and congeners containing 2346-, 236-, and 34-chlorophenyl rings are dechlorinated to tri-, tetra-, and penta-CBs containing, respectively, 246-, 26-, and 4-chlorophenyl groups (15, 16, 18, 19). The primary products are 24-24-CB, 24-25-CB, 24-26-CB, 25-26-CB, and 246-24-CB (15, 16, 19).

All of the changes observed in the sediment PCBs relative to Aroclor 1260 are consistent with what would be expected from various combinations of Processes N and P. A decrease in the number of *para* chlorines per biphenyl and elevated levels of 23-25-CB, 25-25-CB, 235-25-CB, and in more dechlorinated samples, 25-3-CB and 24-3-CB, provide evidence of Process P dechlorination. A decrease in the number of *meta* chlorines per biphenyl and elevated amounts of 24-4-CB, 26-4-CB, 25-26-CB, 24-26-CB, 24-24-CB, 236-24-CB, 245-24-CB, and 2356-24-CB provide evidence of Process N dechlorination. The increases in 24-25-CB are consistent with both dechlorination processes.

TABLE 5

Effect of Dechlorination on Relative Persistence of PCBs in Humans^a

| metabolic susceptibility ^b | half-life in human (yr) | mol % in sample | | | | | | | |
|-----------------------------------------------------|-------------------------|-----------------|------|------|--------|------|--------|------|--------|
| | | A1260 | 6WP | 8WP | A-35-2 | 9WP | A-33-1 | WP-4 | A-34-1 |
| very rapidly cleared; not seen in tissues | <0.01 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| soon cleared; rarely seen in tissues | 0.01–0.10 | 1.6 | 1.8 | 2.4 | 2.8 | 3.9 | 4.9 | 5.4 | 6.1 |
| slightly persistent; barely detectable in tissues | 0.1–1.0 | 34.4 | 35.5 | 39.0 | 39.0 | 42.7 | 41.9 | 44.4 | 47.5 |
| moderately persistent; usually detected in tissues | 1.0–10.0 | 17.8 | 19.2 | 18.3 | 17.3 | 17.2 | 16.4 | 15.5 | 16.0 |
| highly persistent; always detectable after exposure | 10–100 | 46.2 | 43.5 | 40.2 | 40.8 | 36.1 | 36.8 | 34.7 | 33.3 |
| % decrease of highly persistent congeners | | | 5.8 | 13.0 | 11.7 | 21.2 | 20.3 | 24.9 | 27.9 |

^a These data are based on relative metabolic rates and relative human accumulations for all resolvable PCB components reported by Brown (14).

^b The half-life categories and descriptions for metabolic susceptibility are from John F. Brown, Jr. (personal communication).

Most sediment samples showed evidence of both Processes P and N, but the extent of dechlorination and the relative contributions of the two dechlorination processes, as indicated by the losses of *para* vs *meta* chlorines, varied considerably among samples (Table 2). The highest dechlorination was seen in sediments from the western shore, but the extent of dechlorination was quite variable even for samples collected close to each other. There was no correlation between the concentrations of oil or PCBs and the extent or pattern of dechlorination. For example, the concentration of oil in sample WP-4 was 23 800 µg/g, yet the PCBs in this sample were more extensively dechlorinated than in sediment samples that had only 6600–8900 µg/g of oil.

Impact of PCB Dechlorination in Woods Pond. The extent of dechlorination in Woods Pond is modest compared with the dechlorination of Aroclor 1254 observed in nearby Silver Lake (refs 5 and 6 as reinterpreted in ref 16) or the dechlorination of Aroclor 1242 in the upper Hudson River (5, 6, 20). All 181 samples collected from Woods Pond showed evidence of dechlorination, but even those showing the most extensive dechlorination had lost only 13.7% of the *meta* and *para* chlorines. In the upper Hudson, and to a lesser extent in Silver Lake, nearly all *meta* and *para* chlorines were dechlorination targets. In Woods Pond *meta*-dechlorination was favored over *para*-dechlorination, and only *meta* and *para* chlorines located adjacent to other chlorines were removed by dechlorination.

Even though the PCB dechlorination in Woods Pond was modest, it substantially reduced the concentrations of the congeners that are reported to be most persistent in humans (14). Relative to Aroclor 1260, the most extensively dechlorinated sediment PCBs showed decreases of 20–28% in the congeners with half-lives in humans of 10–100 yr and corresponding increases in congeners with half-lives of 0.01–1.0 yr (Table 5). Hence *in situ* dechlorination in Woods Pond has significantly reduced the human bioaccumulation potential of the PCBs and, consequently, potential health risks associated with PCB bioaccumulation. As dechlorination proceeds, an even greater impact can be anticipated. Additional experiments will be required to determine the rate at which *in situ* PCB dechlorination is proceeding in Woods Pond.

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