

ENVIRONMENTAL DECHLORINATION OF PCBs

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Abstract—The polychlorinated biphenyls (PCBs) in sediment and/or fish samples from at least five different locations show changes in gas chromatographic (GC) peak distribution indicative of reductive dechlorination. Several different dechlorination processes, each presumably mediated by a different population of anaerobic bacteria with its own distinctive pattern of PCB congener selectivity, appear to be operating. Six of these processes have been characterized in detail as to the changes occurring in each of the 126 individual PCB congeners or isomer groups detectable by capillary GC or GC-MS on a DB-1 column. The patterns of congener reactivity indicate that the observed transformation processes fall into two broad categories: *o,m,p*-dechlorinations, which remove chlorine atoms from ortho, meta, and para positions, with congener reactivities primarily determined by reduction potential; and *m,p*-dechlorinations, which take chlorines from meta and para positions only, with relative reactivities determined mainly by molecular shape. Both types of dechlorination preferentially remove PCB congeners of toxicological concern, and both produce lower congeners that are biodegradable by environmental aerobes. Thus, dechlorination in anaerobic sediments permits the detoxification and eventual degradation of environmental PCBs.

Keywords—Polychlorinated biphenyl PCB Dechlorination Anaerobic bacteria
Biodegradation

INTRODUCTION

The polychlorinated biphenyls (PCBs) are a family of stable, water-insoluble industrial chemicals that were widely used for nearly 50 years (1929–1978). By 1975, it was estimated that some 57×10^7 kg had been produced in the United States, and about 8×10^7 kg had passed into its soils, sediments, and waters [1]. Until recently, there was widespread opinion that such PCBs, particularly the more highly chlorinated (“higher”) congeners, were resistant to ordinary biodegradative processes, and hence were highly persistent in the environment [1,2].

In 1984, however, it was announced [3], and immediately confirmed [4], that the PCBs in the sediments of the upper Hudson River were undergoing a previously unreported type of compositional alteration [5]. These upper Hudson PCBs all showed depressed proportions of most higher PCB congeners and increased proportions of certain lower congeners, including some that were virtu-

ally absent from the Aroclor composition originally discharged. The gas chromatographic (GC) patterns of individual sediment sections showed that the identities of the specific congeners undergoing significant gain or loss were not quite the same at all locations. Instead, they fell into a small number of repeatedly observed patterns of change, each of which was given a letter designation [3]. The vertical profiles [3] of sediment cores typically showed the extent of such changes in composition to be only minimal near the surface, and maximal within and below the subsurface strata where the total PCB levels were highest. Accordingly, it was concluded that the observed alteration must result from in situ dechlorination rather than differential migration of PCB components.

Since 1984 we have received from investigators of other PCB spill sites gas chromatograms and/or sediment specimens that also showed evidences of dechlorination, but with other selection patterns.

The purpose of this article is to present detailed chemical descriptions of the compositional changes occurring in sediments exhibiting six different dechlorination patterns, namely Patterns B, B', C, and E of the upper Hudson River, and Patterns F and G of Silver Lake (Pittsfield, MA).

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The detailed characterization of chemical change in environmental PCB specimens is made possible by a virtually unique peculiarity of PCB composition. All of the commercial PCB products (e.g., Aroclors) consisted of complex mixtures of chlorinated biphenyl homologs and isomers ("congeners") that were originally produced in fixed relative proportions. The fixed relative proportions occurred because a single manufacturing process, iron-catalyzed chlorination to a fixed weight gain, was used during the entire period of PCB production. However, every chemical, physical, or biological PCB transformation process has its own selectivity pattern (e.g., set of relative transformation rates) for attacking the various individual congeners present in an Aroclor. Thus, an environmentally altered Aroclor will show a new congener distribution (and GC pattern) characteristic of the alteration process; and detailed analysis of that alteration pattern may elucidate the chemical nature of the transformation.

MATERIALS AND METHODS

Description of sites sampled

The flow of the upper Hudson River is controlled by dams that divide the river into a series of stillwaters called reaches. The former Reach 9 received extensive releases of wood wastes from sawmills over the period 1770 to 1950, and of PCBs, mainly Aroclor 1242 released in the period 1952 to 1971, from capacitor manufacturing. Following removal of the old Ft. Edward (New York) Dam in 1973, and heavy flows in 1974 to 1976, there occurred much sediment translocation from the former Reach 9 to Reach 8. The sediments of Reach 8 now consist of sand, silt, and sawdust, with widely varying levels of PCBs. The localization and movement of these sediment-bound PCBs have been extensively studied [6-8].

The sediment samples that were collected for capillary gas chromatographic analysis came almost entirely from the section of Reach 8 between river miles 188.6 and 193.3, that is, above the Thompson Island Dam (RM 188.5) and well below the main point of PCB release (RM 196.1). Fifteen grab samples were collected in October, 1982 and June, 1984, and four 52- to 75-cm cores were taken from "hot spot" [8] areas in June, 1984. In addition, T. J. Tofflemire of the New York State Department of Environmental Conservation gave us one frozen core that had been collected in January, 1977. This core, No. 18-6, was taken within 5 m of core No. 18-8, for which ^{137}Cs levels have

been reported [8]. All cores were cut while frozen into 2.5-cm sections, giving a total of 150 sediment specimens for analysis.

Silver Lake is a 10-ha urban pond in Pittsfield, Massachusetts, which for many years received peripheral municipal solid waste dumpings, sanitary sewage, storm sewage, and industrial discharges. A nearby transformer manufacturing plant used Aroclor 1260 for several decades prior to 1971 and Aroclor 1254 during 1971 to 1977. The Silver Lake bottom sediments consist of a black, oily, methanogenic muck. During 1980 to 1982 about 80 Silver Lake sediment samples were collected by Stewart Laboratories for studies of PCB levels, localization, and movements [9]. We received from Drs. Anna Yoakum and Jack Hall of that organization (now IT Laboratories, Knoxville, TN) copies of many of the original packed-column GC-ECD tracings, along with GC-MS tracings on three samples, and one composite sediment sample for capillary GC analysis.

Through the generosity of other investigators, we also received analytical gas chromatograms of PCBs from upper and lower Hudson River fish, from Dr. Ronald J. Sloan of the New York State Department of Environmental Conservation; from sediments of upper Hudson Reaches 1 to 8 (collected by the N.Y.S. Dept. of Environmental Conservation in 1977) from David R. Hill of OBG Laboratories, Inc., Syracuse, New York; and from Sheboygan Harbor, Wisconsin, sediments, from Victor A. McFarland, U.S. Army Engineers Waterways Experiment Station, Vicksburg, Mississippi.

Analytical procedures

All sediment samples received were air dried, sieved to remove gravel, and extracted in a Soxhlet overnight with 1:1 hexane:acetone. The extracts were evaporated, and the concentrates further extracted with concentrated sulfuric acid, mercury, and florisil. All concentrates were then examined by packed-column GC (Hewlett Packard 5880 gas chromatograph; 6 ft \times 0.25 in. glass column packed with 1.5% SP2250 and 1.9% SP2401 on Supelcoport) to monitor the success of the cleanup and determine the appropriate loading for the capillary column. Capillary gas chromatography was then performed using a fused silica capillary column (J&W Scientific, 30 m \times 0.25 mm i.d.), coated with an 0.25- μm bonded liquid phase of DB-1 (polydimethylsiloxane), and an electron capture detector (ECD) as previously described [3]. In addition, selected samples were run on the same

column with a flame ionization detector (FID) for improved detection and quantitation of the lower congeners, and/or with a ZAB VG analytical organic mass spectrometer to give GC-MS data for the differentiation of nonisomeric congeners. PCB peak quantitation was routinely performed from the DB-1 (ECD) chromatograms employing response factors determined on the corresponding peaks in Aroclor standards by the procedure of Webb and McCall [10], except for the use of a Hall (rather than a Coulson) electrolytic conductivity detector (Tracor Instruments).

PCB nomenclature

In hopes of improved comprehensibility, individual PCB congeners will be designated by terminology paralleling that commonly used in verbal communication; that is, by numbers indicating the substitution patterns on each ring separately, separated by a dash. Thus, 2,2',3,4',5,5',6-heptachlorobiphenyl (IUPAC [11] No. 187) will be called 2356-245 CB, or simply 2356-245. Groups of PCB congeners having the same total chlorine numbers and numbers of ortho substituents will be described collectively by terms showing each of these numbers separated by a colon; thus, 7:3 will indicate the tri-ortho-substituted heptachlorobiphenyls, including the individual congener 2356-245 CB just cited.

The older packed column gas chromatograms reviewed during the course of the study exhibited up to 33 PCB "peaks" (usually envelopes of unresolved individual congener peaks) at positions that are conventionally denoted by relative retention time (RRT) on an isothermally operated SE-30 packed column (relative to DDE = 100), rather than chemical composition [10]. We noted, however, that within PCB isomer sets the positions of the individual peaks are grouped according to the number of ortho chlorines (see Table 1). Thus, an ortho subset number, like the above 7:3, can be specified for an unidentified single congener capillary peak, or for a multicongener packed-column peak, from its chlorine number and RRT (i.e., GC-MS peak position) alone.

PCB peak identification

The chromatograms of the Aroclor standards and sediment extracts obtained with the DB-1 capillary system exhibited up to 118 peaks resolvable by GC-ECD, which were designated in order as Peaks 1-118. The prior literature does offer PCB congener assignments for most of the GC peaks

given by commercial PCB mixtures on columns coated with pure polydimethylsiloxanes (e.g., OV-1, SE-30, SF-96), but many of the assignments are based upon estimated retention indices [11]. Also available [12] are assignments for most Aroclor 1260 peaks on columns coated with SE-54 (95% dimethylsiloxane-5% diphenylsiloxane copolymer), based on measured relative retention times for all 209 congeners on such columns [13]. Because of disparities and limitations among the earlier assignments, we determined the positions of 70 individual congeners with respect to the Aroclor GC patterns on DB-1 using Aroclor standards spiked with specimens of the commercially available pure congeners. This showed that within isomer sets (distinguishable by GC-MS) the elution sequences on DB-1 very closely paralleled those on SE-54, as might be expected from the chemical similarity of the two coatings. Accordingly, we were able to make assignments for the generally minor DB-1 peaks not adequately identified by our own spiking experiments or the prior literature [11] by use of the observed patterns of relative retention on SE-54 [13]. This indicated that 180 congeners had retention times close enough to one of those of the 118 resolvable GC peaks to require consideration as a possible component thereof. In 22 cases, however, discrimination between nonisomeric coeluting congeners could be made from the mass spectra. In several cases consideration of the relative proportions of the individual chlorophenyl groups in the particular sample being examined indicated that certain of the coeluting isomers would be present at levels too low to merit reporting as significant peak components. Finally, in one case, that of DB-1 Peak 17, the two congeners that coeluted on a DB-1 capillary (23-2 and 26-4 CB), were found to be adequately resolved on the packed column used for the preliminary gas chromatogram. In this case an assessment of isomer distribution could also be made by subjecting the mixture to aerobic microbial biodegradation [14,15], towards which 26-4 is markedly more resistant.

RESULTS

Distribution of PCB alteration patterns in upper Hudson sediments

The 150 DB-1 capillary gas chromatographs of River Reach 8 sediment specimens generally approached the appearance of one of the four major limiting patterns (A, B, B', or C) previously reported [3]. Figure 1 illustrates these patterns as

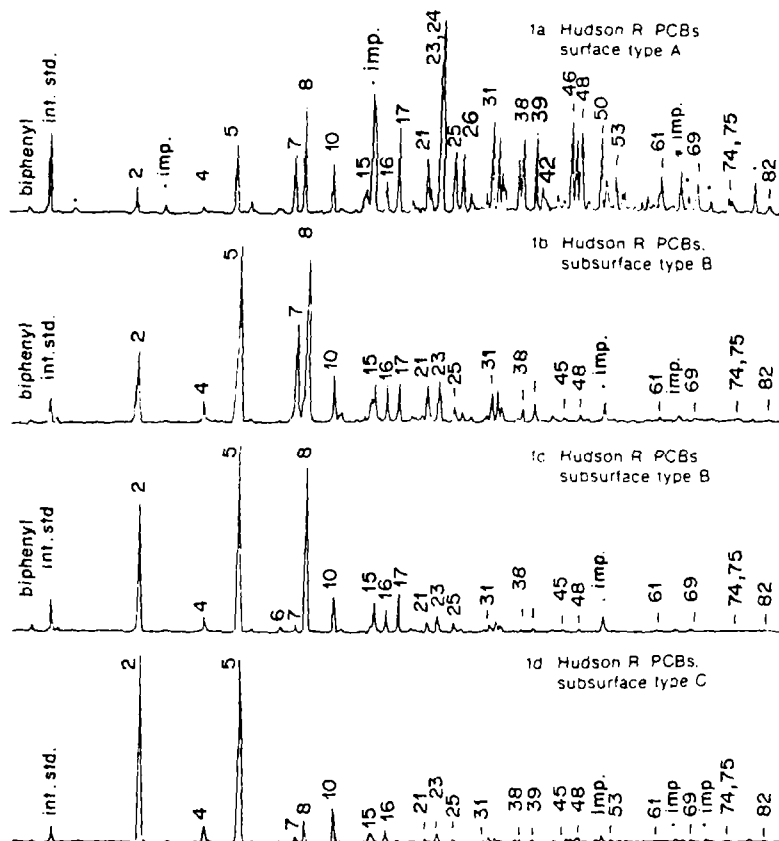


Fig. 1. DB-1 (FID) capillary gas chromatograms of upper Hudson River PCBs showing patterns A, B, B', and C. Peak identifications given in Table 1.

run with a flame ionization detector and low amplification in order to portray the mono- and dichlorobiphenyls in true proportion to the higher congeners. It may be noted that pattern A is qualitatively similar to that of Aroclor 1242 [11], whereas B, B', and C show marked elevation of three, two, or one dichlorobiphenyl peaks, respectively, along with depressions of most of the higher congener peaks. Figure 2 presents the later portions of the same patterns as run with the more usual electron-capture detector and high amplification, so as to better portray the weak peaks produced by the small quantities of higher congeners present. The latter figure also shows a conspicuous variant in the higher congener removal pattern (pattern E) that was seen in about half the specimens showing the lower congeners in patterns B or C.

The 1977 New York State survey of the entire upper Hudson River resulted in about 2,000 packed column gas chromatograms and data printouts. We reviewed these printouts and about 100 of the

original chromatograms. These analytical GC patterns lacked sufficient resolution for discriminating between patterns B and B', or for detecting pattern E. However, all specimens with enough PCB for reliable classification (>1 ppm) did show patterns resembling the Reach 8 patterns A, B/B', or C; and subsurface sections showing patterns B/B' or C were seen in every reach of the river between Ft. Edward and Troy. Thus, the dechlorination processes described here appear to have been well underway over this entire 69-km section of the river by 1977.

Below Troy, in the tidal Hudson, where the PCB levels are considerably lower, the sediment chromatograms are reported to show significant declines in the strong peaks given by mono-ortho-tetrachlorobiphenyls (e.g., 245-4, 25-34, 24-34, and 23-34 CB), which are among those most rapidly attacked by systems B-C (see Table 3), but little gain in the dichlorobiphenyls, thus giving GC patterns superficially resembling mixtures of Aroclors 1016 and 1254 [4]. This would suggest that any

Fig. 2. DB-1 (FID) capillary gas chromatograms of upper Hudson River PCBs showing patterns A, B, B', and C. Peak identifications given in Table 1.

dechlorination had been underway (1977).

As regional distribution of Reach 8 PCBs in the more recent sediments made up of sediments approximately 100 years old, once they had been deposited into the upper Hudson River, the upper

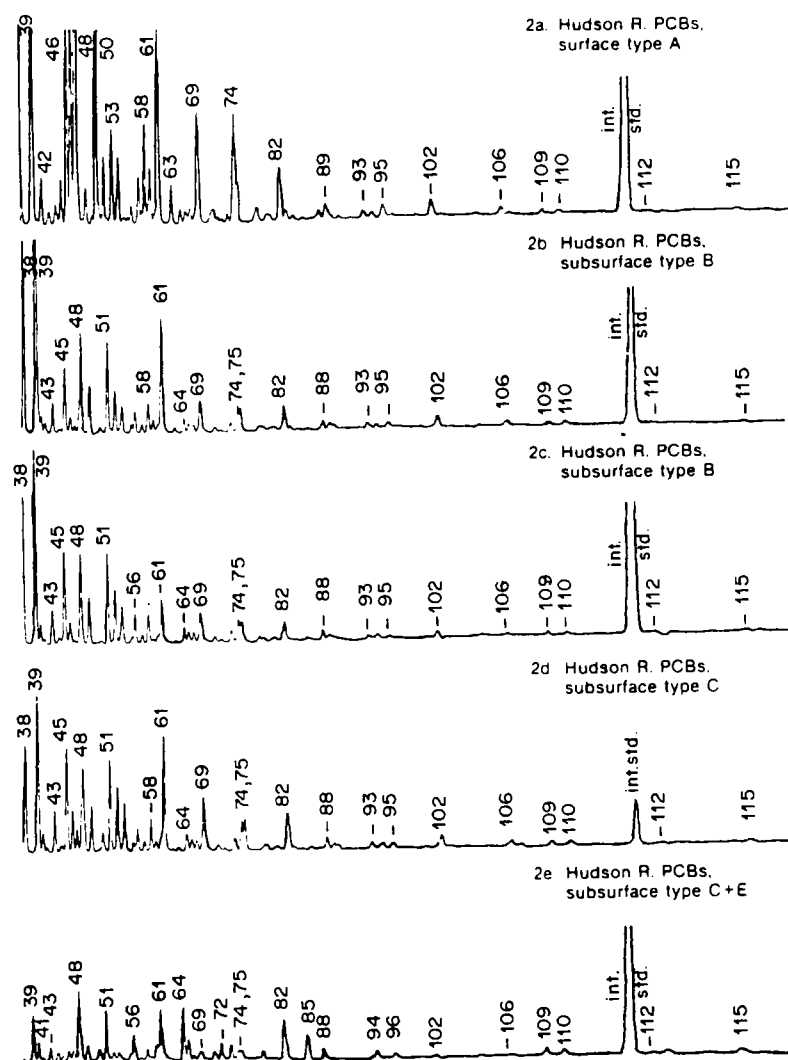


Fig. 2. DB-1 (ECD) capillary gas chromatograms of upper Hudson River PCBs showing patterns A, B, B', and C. Peak identification given in Table 1.

dechlorination process underway in the mid-Hudson had barely started at the time of sampling (1977).

As regards the vertical rather than the horizontal distribution of the alteration patterns, the Reach 8 pattern A characteristically appeared at the more lightly contaminated top ("zone 1") of the sediment column [3], which is known to be made up of a mixture of original and redeposited sediments [6,7], and presumably represents the approximate PCB composition subjected to further dechlorination by systems B, B', C, and E once the sediments became more deeply buried into zone 2. In core sections showing pattern A in the upper 5 to 10 cm, transition to patterns B, B',

or C generally occurred progressively over the next 10 cm.

In quantitative terms, pattern A resembled an approximately 2:1 mixture of Aroclor 1242 and mixed dechlorination products of types B, B', and C, with some (variable) additional loss in mono- and dichlorobiphenyls attributable to elution and/or aerobic biodegradation; some augmentation of hepta- and octa-chlorobiphenyls attributable to the presence of about 1% of Aroclor 1260 and a trace of Aroclor 1268 (which was unambiguously detected in two sediment specimens collected 10-15 km downstream); and possible augmentation with 0 to 5% Aroclor 1254. (Pentachlorobiphenyls, which constitute about 8.5% by weight of Aroclor

1242 and 49% of Aroclor 1254, were found at levels of 9.0–10.5% in pattern A core sections and 10–16% in pattern A surface grab samples. Thus, it was uncertain how much of the relative increase in pentachlorobiphenyls could be attributed to Aroclor 1254 in the initial discharge rather than to simple elutriative or biodegradative loss of lower congeners.)

Although sections exhibiting either patterns B, B', or C appeared in the subsurface portions of every upper Hudson sediment core examined, there was no obvious consistency as to which pattern appeared where. Thus, Core 18-6 showed pattern B over the entire 15 to 55-cm range, accompanied by pattern E in the range 40 to 55 cm, whereas the core TI-2, taken a few meters away, showed B + E near the top of the corresponding subsurface range, B in the middle, and B' near the bottom. The other three Reach 8 cores all showed alterations between 5 to 10-cm sections displaying B, B', or C, with or without E, in different sequences. Presumably, each of the agents effecting PCB dechlorination according to patterns B, B', C, and E has a patchy distribution within the sediments, with minimal overlap between patches occupied by B, B', or C, but full overlap of these with the patches occupied by E.

PCB dechlorination patterns seen in Silver Lake sediments

The Stewart Laboratory survey of the Silver Lake sediments [9] reported "alterations" of the Aroclor in 40 of 72 individual peripheral samples and in all eight of the deepwater samples. The "unaltered" Aroclor in the remaining samples was

reported as a mixture of Aroclor 1260 with Aroclor 1254, which was rarely observed elsewhere in the Pittsfield area. We found, however, that (a) the Aroclor 1260 dechlorination process underway in the Silver Lake sediments is one that would give a congener mixture easily mistaken for Aroclor 1254 in its initial stages, (b) the distribution of residual hexachlorobiphenyl peaks in subsurface samples (by GC-MS) was clearly that of Aroclor 1260 rather than 1254, and (c) the transformer manufacturing plant located next to the lake used Aroclor 1260 exclusively during the period when most of the deposition occurred. Accordingly, it would appear that the PCB subjected to "alteration" by the Silver Lake sediments was initially virtually all Aroclor 1260.

The packed-column GCs of the "altered" sediments showed at least two major patterns of change, designated patterns F and G, and possibly some intermediate ones. The most distinctive feature of pattern F (Fig. 3) was the high level ($\approx 30\%$ of all congeners, vs. 0.0% in Aroclor 1260) of the normally rare 25-3 and 24-3 trichlorobiphenyl congeners (DB-1 peaks 21, 22; RRT 35), along with several diortho-tetrachlorobiphenyls ($\approx 45\%$ of total, vs. 0.3% in Aroclor 1260), but no di- or trichlorobiphenyls having shorter retention times. In pattern G, the RRT 35 peak for the unusual 25-3 and 24-3 trichlorobiphenyls was still fairly prominent, but was accompanied by a group of mono-, di-, and other trichlorobiphenyl peaks (all absent from Aroclor 1260) having shorter retention times. Again, there was no obvious correlation between position in the sediments and selection between dechlorination patterns F and G.

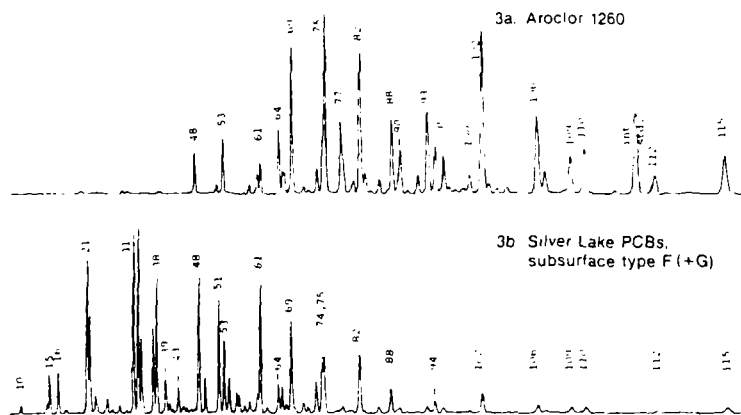


Fig. 3. DB-1 (ECD) capillary gas chromatograms of Silver Lake PCBs showing mainly pattern F, along with Aroclor 1260 reference. Peak identifications given in Table 1.

Dechlorination

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Dechlorinations seen at other sites

Analytical gas chromatograms showing prominent RRT 35 and 47 peaks like those of patterns F and G were also seen in some striped bass from the lower Hudson, and in harbor sediments from Sheboygan, Wisconsin. Conversely, harbor sediments from Waukegan, Illinois showed an Apolane C-87 capillary GC/ECD pattern [16], referred to below as "pattern W," that appeared to be of the same generic family as upper Hudson patterns B, B', C, and E.

Chemical characterization of dechlorination processes

The quantitative analytical data collected during the course of this investigation permitted estimates of the levels of up to 126 individual PCB congeners or isomer groups in the various sediment samples examined. By comparing such levels with those in the Aroclor composition initially discharged we could determine the net total changes effected by the individual transformation systems. In cases where progressive development of a dechlorination pattern appeared in successively deeper sediment sections, it was also possible, for each stage of the conversion, to determine the relative susceptibilities of the individual congeners to undergo change, and to establish that the alterations responsible for patterns B, B', C, and E represented alternative, rather than successive, transformation processes.

Table 1 shows the overall effects of PCB dechlorination systems B, B', C, E, F, and G on the levels of all 126 observable congeners or isomer groups as order-of-magnitude changes. Table 2 gives more precise data on the levels of 9 dechlorination products in representative subsurface sediment specimens showing GC patterns A, B, B', or C, with or without pattern E also present. The relative susceptibilities of about 50 individual congeners to dechlorination by system B are shown in Table 3, while the changes in PCB homolog and ortho-chlorine numbers effected by systems F and G are shown in Table 4.

Simple material balances showed that the environmental dechlorination processes responsible for GC patterns B, B', and C [3], and also pattern W [16], proceeded by loss of only those chlorines located in positions meta or para to the other ring (*m,p*-dechlorination), whereas those responsible for GC patterns F and G involved losses of ortho chlorines as well (Table 4). However, there was no difference between F and G in the extent of ortho

loss, despite a significant difference in total dechlorination. Thus, we cannot exclude the possibility that some part of alteration process G can be attributed to an *m,p*-dechlorination activity, while the remainder of G, along with F, results from an *o,m,p*-dechlorination.

The chemical changes effected by the individual *m,p*- and *o,m,p*-dechlorination systems will be described in turn.

Towards upper Hudson system B, the most reactive of the major congeners present were those of groups 3:1, 4:1, and 5:1 (e.g., the species 34-2, 23-4, 245-4, 25-34, 24-34, 23-34, 234-4, 245-34, and 234-34 CB) (Table 3). Many of the 3:2, 4:2, 5:2, and 6:2 congeners (e.g., 25-2, 23-2, 23-25, 23-24, 234-25, 234-24, 234-23, 245-25, 245-24, 245-23, 245-245, 234-245, and 2345-25 CB) were also fairly reactive. Lower activities were associated with certain 4:2, 4:3, 5:3, and 6:3 group congeners, notably the RRT 47 group (25-25, 24-25, and 24-24 CB) and congeners carrying 2,6-, 2,3,5-, or 2,3,6-substituted rings. The dechlorination apparently converted, presumably stepwise, most of the mono-ortho-substituted congeners (e.g., the 3:1, 4:1, and 5:1 species) to 1:1 and 2:1's (2-, 2-3, and 2-4 chlorobiphenyls); most of the di-ortho congeners to 2:2 and 3:2 species (2-2, 26-, 24-2, 26-3, and 26-4 CB); some of the tri-ortho's to 3:3 and 4:3's (26-2 and 26-25), and some of the tetra-ortho's (present at only trace levels) to a trace of 26-26 CB. (Other unusual congeners formed only at trace levels included the species 35-2, 35-3, and 35-4 CB.) Thus, the net result was the formation of 2-2, 2-3, 2-4, 26-2, 26-3, 26-4, 26-25, and perhaps 2-CB as terminal dechlorination products that appeared in nearly the same relative proportions in all pattern B specimens. As proportions of all PCBs present, the levels of these terminal dechlorination products were all 3 to 8 times higher than in the original 1242 (Table 2). Conversely, those of the isomeric trichlorobiphenyls listed as subject to dechlorination (Tables 1 and 3) were all depressed by factors of 2 to 10.

For systems B' and C, the differences were quantitative rather than qualitative, except for the unambiguous formation of 2-chlorobiphenyl as a major product. Above DB-1 peak 39, the chromatograms were quite similar to that of pattern B, although system B' may have shown a little more activity than B or C towards congeners 236-34 and 2356-34 CB. Below this range, both B' and C showed significantly more reduction of the 25-25, 25-24, 24-2, and 2-3 CBs than did B. In addition, system C was sufficiently active towards 26-4 and

Table 1. Changes in PCB congener distributions effected by upper Hudson River and Silver Lake dechlorination systems

Packed column (RRT) ^a	DB-1 peak No. ^b	Total:ortho Cl No.	Congeners in peak ^c	Change in congener level ^d					
				Hudson River				Silver Lake	
				B	B'	C	E	F	G
	1	0:0	biphenyl	±±	++	++			
11	2	1:1	2-	±±±±	++++	++++			e
14	3	1:0	3-	+	+	±			e
14	4	1:0	4-	++	++	++			e
16	5	2:2	2-2, 26-	++++	++++	++++			++++
	6	2:1	25-, 24-	--	±±	±±			+++
	7	2:1	2-3	+++	--	±± ^c			+++
21	8	2:1	2-4, 23-	++++	++++	±±±			++
24	10	3:3	26-2	+++	+++	+++			+++
	12	2:0	3-3	±	-	±			
	13	2:0	3-4, 34-	±±	--	±±			
28	14	3:2	25-2	---	---	---			++
28	14	2:0	4-4	±±±	---	±±± ⁱ			
28	15	3:2	24-2	±±± ^e	---	---			+++
30	16	3:2	26-3, 236-	+++	+++	+++			+++
32	17	3:2	23-2, 26-4	±±± ^h	±±±	--- ^h			++
	19	3:1	35-2	++	++	++			++
	19	4:4	26-26	+	+	+			+
	20	3:1	245-	-	-	-			
35	21	3:1	25-3	+++ ^e	±±±	±±		++++	++-
35	22	3:1	24-3	+++ ^e	±±±	±±		+++	++-
37	23	3:1	25-4	---	---	---		++	+-
37	24	3:1	24-4	---	---	---			
	24	4:3	246-2	-	-	-		++	++
40	25	3:1	34-2, 23-3, 234-	---	---	---			
40	25	4:3	25-26	++	±±	+++		++	i
40	26	3:1	23-4	---	---	---		++	
40	26	4:3	24-26	---	---	---		++	i
	27	4:3	236-2	---	---	---	--	++	i
	28	3:0	35-3	±	±	±		+	
	29	4:3	23-26	---	---	---		++	i
	30	3:0	35-4	±	±	±			
47	31	4:2	25-25, 35-26	+++ ^e	---	---		++++	+++
47	32	4:2	24-25	±±± ^e	---	---		++++	+++
47	33	4:2	24-24	+++ ^e	±±±	---		+++	---
	34	4:2	245-2, 246-4	---	---	---		++	
54	37	4:2	23-25	---	---	---		+++	j
54	38	3:0	34-4	---	---	---	--		
54	38	4:2	23-24, 236-3 ^k	±±±	±±±	±±±		+++	j
58	39	4:2	26-34, 236-4, 234-2, 25-35	---	---	---	--	++	++
	40	4:1	24-35					++	
	41	5:4	236-26	+	+	+		+	+
	42	4:2	23-23	---	---	---		+	
	43	5:3	246-25	±	±	±		+	
	43	4:1	235-3	±	+	+	-	++	
	44	5:3	246-24	±	±	±		+	
	44	4:1	245-3	±	-	-		+	
	45	4:1	235-4, 23-35	±±	++	++	--	+	
70	46	4:1	245-4	---	---	---	--	+	
	46	5:3	235-26	±	±	±		+	
70	47	4:1	25-34, 345-2	---	---	---	--	+	
70	48	4:1	24-34	---	---	---	--	+	
70	48	5:3	236-25, 245-26	±±	±±	±±	±±	±±±	---

continued

Table 1. continued

Packed column (RRT) ^a	DB-1 peak No. ^b	Total:ortho CI No.	Congeners in peak ^c	Change in congener level ^d					
				Hudson River				Silver Lake	
				B	B'	C	E	F	G
	49	5:3	236-24	±±	±±	±±	--	++	--
78	50	4:1	23-34, 234-4	---	---	---	---		
84	51	5:3	236-23, 235-25	±±	±±	±±	--	++	--
	52	5:3	234-26	-	-	-	-		
84	53	5:2	245-25, 235-24	--	±±	±±	--	---	---
	54 ¹	5:2	236-35				+		
84	54	5:2	245-24	--	--	±±	--	++	
	55	5:2	2356-3, 246-34	±	±	±	-	++	
	55	6:4	236-246				+		
	56	5:2	235-23, 2346-3	±	+	±	±	++	
98	57	5:2	245-23, 2345-2	---	---	---	---	±	
	57	6:4	2356-26		+	+		+	
98	58	5:2	234-25, 2346-4	--	--	--	--	--	--
98	59	5:2	234-24	--	--	--	--	±	
	60	6:4	236-236	±±	±	±	+	---	
	61	4:0	34-34	---	---	---	---		
104	61	5:2	236-34	--	--	±±	--	±±±	---
	62	6:3	245-246	±			±	+	
112	63	5:2	234-23	---	---	---	---	±	
117	64	6:3	2356-25	±	±	±	++	---	---
	65	6:3	235-236	±	±	±	+	--	--
	65	5:1	345-25	-	±	-	-	±	
	66	6:3	2346-25	-	±	-	-	---	---
	67	5:1	235-34, 234-35	-	-	-	-	-	
	67	6:3	2356-24				±		
125	69	5:1	245-34, 2345-3	--	--	--	--	±±±	
125	69	6:3	236-245	---	---	---	---	---	---
	70	6:3	2346-24, 234-246				±	+	
	71	5:1	2345-4	-	-	-	-	+	
	71	6:3	2356-23, 2345-26	±	±	±	±	--	--
	72	5:1	345-23	-			-	+	
	72	6:3	235-235, 2346-23	±	±	±	+	-	
	73	6:3	235-245	±	±	±	±	--	--
	73	7:4	2356-246					±	
146	74	5:1	234-34	---	---	---	---	---	---
146	74	6:3	234-236	---	---	---	---	---	---
146	75	6:2	245-245	---	---	±±	--	---	---
	76	6:2	246-345				±	±	
160	77	6:2	2345-25	-	-	-	-	---	---
160	78	7:4	2356-236	±	±	±	±	---	---
	79	6:2	234-235	-	±	±	-	--	
	80	6:2	2345-24	-	±	±	-	--	
	81	7:4	2346-236	-	±	±	-	--	
174	82	6:2	234-245, 2356-34	---	---	---	---	---	---
	83	6:2	2346-34	-	-	-	-	--	
	84	6:2	2345-23	-	-	-	-	-	
	85	7:3	2356-235	±	±	±	+	--	--
	87	7:3	2346-235				-	-	
203	88	7:3	2356-245, 2345-246	- ^m	±	±	- ^m	---	---
203	89	6:2	234-234	-	-	-	-	---	---
203	90	7:3	2346-245	-	±	±	-	---	---
	91	6:1	245-345	-			-	---	
232	92	7:3	23456-25	- ^m	-	±	-	---	---
232	93	7:3	2345-236, 23456-24	±	±	±	-	---	---
232	94	7:3	2356-234	±	±	±	±	---	---

continued

Table 1. continued

Packed column (RRT) ^a	DB-1 peak No. ^b	Total:ortho Cl No.	Congeners in peak ^c	Change in congener level ^d					
				Hudson River				Silver Lake	
				B	B'	C	E	F	G
244	95	6:1	2345-34	—	—	—	—	—	—
	95	7:3	2346-234					—	—
	96	8:4	2356-2356		±	±	± ⁿ	—	—
	99	8:4	2346-2356, 23456-246	±	±	±	±	—	—
	100	7:2	2345-235, 23456-35	±	±	±	—	—	—
280	102	7:2	2345-245	— ^m	— ^m	— ^m	—	—	—
	103	7:2	2356-345				—	—	—
	104	7:2	2346-345				—	—	—
	105	8:4	23456-236				—	—	—
332	106	7:2	2345-234	— ^m	— ^m	— ^m	—	—	—
332	107	7:2	23456-34		±	±	—	—	—
372	109	8:3	2345-2356	±	±	±	±	—	—
372	110	8:3	2345-2346, 23456-245	±	±	±	— ^m	—	—
	111	7:1	2345-345				—	—	—
448	112	8:3	23456-234	±	±	±		—	—
	113	9:4	23456-2356	±	±	±		—	—
528	115	8:2	2345-2345	±	±	±		—	—
	117	9:3	23456-2345		±			—	—

^aRetention time (relative DDE = 100) of corresponding low-resolution PCB peak envelope seen on isothermal SE-30 packed columns [11].

^bNumbered according to sequence of 118 Aroclor PCB peaks seen by DB-1 GC-ECD; where further resolution of same peak was made by GC-MS, two sets of total:ortho chlorine numbers are given.

^cFor abbreviations used, see text. Where isomers are believed present in quite different proportions, the major isomer is underlined.

^dAbsolute change in congener level, as weight % of all PCBs present, indicated by number of + 's or - 's; thus, + + + +, 10-100%; + + +, 1-10%; + +, 0.1-1%; +, <0.1% for increases; — — — —, — — —, etc. for decreases. Where observed level within factor of 1.5 of original, absolute level present similarly indicated by number of = 's. For Hudson River systems, changes are indicated relative to pattern A (slightly modified Aroclor 1242); for Silver Lake systems, relative to Aroclor 1260.

^eSizeable increase in monochlorobiphenyl(s) seen, but packed column GCs did not permit reliable differentiation.

^fSharper decreases observed in some pattern C sediments; may indicate need to subdivide group into C and C'.

^gIn successively deeper core sections, peak appeared to first increase, then decrease.

^hAerobic biodegradation indicated this peak to be nearly half 23-2 in Aroclor 1242 but largely 26-4 in Hudson River subsurface sediments. Change for 26-4 alone, + + + in B and presumably B', — — — in C.

ⁱGroup 4:3 considerably larger than in pattern F, but packed-column GCs did not permit resolution of individual congener peaks.

^jThis 4:2 pair weaker than in pattern F, but not resolved by packed-column GC.

^kThis congener believed to be minor component of peak 38 in Aroclor 1242, but more prominent in dechlorinated specimens.

^lWeak peak seen on leading edge of peak 54.

^mAmount of decrease marginal by criterion used.

ⁿAbsolute increase marginal by criterion used, but increase relative to neighboring 8:3's appeared unequivocal.

2-4 to prevent the accumulations of these congeners that were seen in B and B'. As a result, higher proportions of the PCBs were dechlorinated all the way down to the 1:1, 2:2, 3:3, or 4:4 stages (Table 2). In the 27 subsurface samples showing high total PCB levels and transformation patterns B' or C, the levels of 2-chlorobiphenyl (which constituted 0.72% of the original Aroclor 1242) ranged between 28 and 52%, indicating a 39- to 72-fold increase.

The presence of system E along with B or C made little difference to the levels of the mono-, di-, and trichlorobiphenyls (Tables 1,2). The effects on the tetrachlorobiphenyls were modest: enhanced clearance of 236-2, 236-3, 235-3, and 235-4 CB, all of which may be formed in small amounts during the operation of B, B', or C, and of any residual 4:1 species. Instead, system E was distinguished by markedly increased clearance of most higher congeners. In the example shown in

Peak No.

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Table 2. Content of major dechlorination products (as weight percent of total PCB) in Hudson River sediment sections showing patterns A, B, B', C, and E

Peak No.	Congeners in peak	Peak distribution pattern ^a						
		1242	A	B	B + E	B'	C	C + E
2	2-	0.7	5.1 ^b	13.6	15.6	39.3	32.6	33.8
5	2-2, 26-	2.6	8.1	18.7	19.0	22.4	36.0	39.0
7	2-3	1.3	2.8	8.9	5.7	0.3	0.6 ^c	1.8
8	2-4, 23-	6.2	9.2	15.8	17.7	12.5	3.4	4.1
10	26-2	0.9	2.3	2.9	4.1	3.1	4.9	5.2
15	24-2	4.4	6.2	4.0	6.1	1.9	1.0	2.1
16	26-3	0.8	2.2	3.8	4.3	3.5	3.4	3.8
17	26-4, 23-2	5.0	4.5	4.1	5.7	2.8	1.4	1.1
21	25-3	1.2	2.4	3.0	2.0	1.0	0.9	0.7

^aThe specific specimens showing the indicated distributions were for "1242," Aroclor 1242 standard; A, 1977 core 18-6 (river mile 188.6, E side), 2.5-5-cm section; B, core 18-6, 32.5-35-cm section; B + E, core 18-6, 40-42.5-cm section; B', 1984 core T1-2 (near 18-6 site), 57.5-60-cm section; C, 1984 core R2 (river mile 190.0, W side), 25-27.5-cm section; C + E, 1984 core 13.2 (river mile 193.3, W side), 7.5-10-cm section.

^bObserved levels of this congener in upper Hudson surface grab samples exhibiting pattern A were usually 5-12% but occasionally extended over the range 1-25%; its measurement was also more sensitive to analytical error than those of other congeners.

^cMost sediment sections showing pattern C contained 2-3 times as much of this congener.

Table 3. Numbers of half-losses shown by various PCB congeners in an upper Hudson deposit showing a well-developed pattern B^a

Subst. on presumably less reactive ring	Substitution pattern on presumably more reactive ring									
	34	23	234	245	2345	23456	236	25, 24	4	3
4	5	~2 ^{b,c}	5	5	>1 ^c		~1 ^c	1.5	>1 ^c	1 ^{b,d}
2	5	~2 ^c		>1 ^c			0.7	>1 ^b	0 ^b	0 ^b
24, 25	5	3.5	2	1.5	2	1	0.5 ^d	0.1 ^b		
234	4	2.5	1.5	1.5 ^d	0.7		<0.5 ^d			
245	3.5	2	1.5 ^d	1.5	0.7		<0.5 ^d			
2345	>1 ^c	>1 ^c	0.7	0.7						
26	1	1								
236	1	0.3 ^d	<0.5 ^c	<0.5 ^d	~0.5 ^c					

^aNumber of half-losses equal to $-\log_2$ (fraction of original congener level still remaining). Sediment specimen from river mile 188.6 E side, 1977 Core 18-6, 32.5-35-cm section; same as shown in Figures 1 and 2. Local stratigraphy characterized by ¹³⁷Cs [8]; estimated age 15 ± 5 yr.

^bNet clearance may be reduced by simultaneous regeneration via dechlorination of higher congeners.

^cEstimate of clearance complicated by interfering peaks.

^dBoth rings may be comparably reactive; part of indicated clearance may be attributable to other ring.

Figure 2e and Table 1, there was $\approx 90\%$ removal of 245-245, 2345-245, and 2345-234 CB, and substantial attack on all other congeners carrying a chlorine in the 4-position of either ring. Concomitantly, several new and characteristic dechlorination products appeared: 2356-25 and 2356-235 CB most prominently, along with lesser amounts of 236-35, 236-236, 236-235, 235-235, 2356-24, and possibly 2356-2356.

The compositional change presented by pattern F was sharply different from any of the above. A typical sediment section (Table 3, Fig. 3) showed 90 to 98% removal of all hexa-, hepta-, and octachlorobiphenyls originally present with almost no discrimination between isomers, and slower removal of the pentachlorobiphenyls, particularly those of type 236-XY. There were also 80% and 90% net removals of tri-ortho and tetra-ortho-

Table 4. Distributions^a of PCB isomer groups in Silver Lake sediment specimens exhibiting peak distribution patterns predominantly F or G

Isomer group	Mole percent ^a in specimen ^b of type:		
	1260	F(+G)	G(+F)
Monochlorobiphenyl	0	0.1	17 ^c
Dichlorobiphenyl	0	0.1	17
Trichlorobiphenyl	0	32 ^d	26 ^e
Tetrachlorobiphenyl	0.6	50	31
Pentachlorobiphenyl	16	12	6
Hexachlorobiphenyl	53	5	3.4
Heptachlorobiphenyl	25	0.5	0.6
Octachlorobiphenyl	5	0.1	0.1
ortho-Cl per biphenyl	2.5	1.8 ^f	1.8 ^f
<i>m,p</i> -Cl per biphenyl	3.6	2.1	1.2
Total Cl per biphenyl	6.1	3.9	3.0

^aApproximate distribution in each case estimated from relative sizes of parent ion peaks in packed column GC/MS.

^bSpecimen F(+G), Silver Lake 1982 core C1, 48-64-cm section; specimen G(+F) 1982 core C2, 80-96-cm section; for location map, see Ref. 9.

^cEstimated from a single GC-MS of another specimen showing mono- and dichlorobiphenyls at equal levels.

^dMade up of 4% congeners of type 3:2, from admixed pattern G; 28% of type 3:1, mainly 25-3 and 24-3.

^eMade up of 9% type 3:1, still mainly 25-3 and 24-3; 13% type 3:2; 3% type 3:3.

^fAbout two-thirds of ortho chlorine loss from tri- and tetra-ortho congeners: these types depleted 90% and 80% respectively; remaining third from di-ortho congeners, mainly responsible for 3:1, 2:1, and 1:1 formation.

substituted congeners, respectively. The products were mainly of types 3:1 and 4:2, made up predominantly of PCB congeners containing all the possible combinations among 3-, 2,3-, 2,4- and 2,5-chlorophenyl groups. The product mixture also contained two unusual series of congeners: first, the 3-chlorophenyl derivatives, such as the major products 25-3 and 24-3 CB already noted and the minor products 35-3, 235-3, 245-3, and probably also 23-3, 236-3, and 2356-3; and second, the 2,4,6-chlorophenyls: PCB congeners 246-2, 246-25, 246-24, 236-246, 245-246, 246-345, 2356-246, and possibly 234-246, most of which are barely detectable in the commercial Aroclors; all gave small but distinct peaks. Conversely, there were only minor amounts of the 26-X and 26-XY CB species that are prominent among the B, B', or C dechlorination products of Aroclor 1242. Evidently, system F has the ability to attack all penta-, tetra-, and trichlorinated rings except for those substituted

2,4,6 or possibly 2,3,6; but no mono- or dichlorinated rings except those substituted 3,4. Thus, the terminal dechlorination products contained rings substituted 3, 2,3, 2,4, 2,5, 3,5, 2,4,6, and 2,3,6, but with few substituted 2,6 or 4, and none substituted 2.

The system G specimen for which packed-column GC-ECD and GC-MS data was available (Table 3) showed the same extensive, indiscriminant removal of hexa-, hepta-, and octachlorobiphenyls as system F; considerably more removal of pentachlorobiphenyls, notably the 236-25 and other 236-XY congeners that were somewhat persistent in F; less accumulation of 4:2 congeners, particularly those of the 23-2X type; and less accumulation of the 3:1 group. Instead, there was greater formation of 4:3 species (not resolved in the packed column GCs, but presumably 25-26, 24-26, and 236-2, as in the F(+G) composite shown as Fig. 3), along with those of types 3:2, 3:3, 2:1, 2:2, and 1:1. Still prominent were 3-chlorophenyl derivatives: 2-3, 26-3, and possibly 23-3 CB (in addition to the remaining 25-3 and 24-3); however, 2-chlorophenyls (as in 2-2, 2-3, 24-2, and probably 2-CB) were equally apparent. Thus, "system G" may represent a combination of an *o,m,p*-dechlorinating system like F with some kind of an *m,p*-dechlorination system; however, the latter differs somewhat from those of the upper Hudson in its congener selectivity pattern.

DISCUSSION

Structure-reactivity relationships for PCB dechlorination

Table 5 summarizes the foregoing observations as to the relative reactivities of the various PCB-forming chlorophenyl groups toward dechlorination systems B, B', C, E, and F. These chlorophenyl groups are listed in order of decreasing electron affinity, as indicated by a reduction interrupt potential (E_2d) measured at an amalgamated platinum electrode [17,18].

Table 5 shows that for system F there is a simple correlation between reduction potential and reactivity: where the E_2d is less negative than about -1.94 V dechlorination occurs; otherwise it does not. Conversely, for system B, B', and C there is no such simple relationship: even the group with the most negative potential (3-chlorophenyl; $E_2d + -2.108$) is dechlorinated by two of these three systems (B' and C), but several chlorophenyl groups with considerably greater electron affinities are not attacked by any of them. It would appear that the chlorine atoms that are inaccessible to sys-

Table 5. Comparison between reduction potentials reported [22] for single-ring chlorinated biphenyls and estimated relative reactivities of PCB rings towards dechlorination

Chlorination pattern	E _{2d} (V) ^a	Est. rel. reactivity ^b to system:		
		F	E	B, B', C
23456	-1.566	+++	++	+
2345	-1.679	+++	+++	++
345	-1.696	+++	+++	++
235	-1.783	++	±	-
2346	-1.784	+++	++	++
2356	-1.787	+++	-	-
245	-1.837	++	+++	++
234	-1.852	++	+++	++
34	-1.871	++	++	+++
35	-1.897	±	±	-
236	-1.937	±	±	±
25	-1.942	-	-	±±
23	-1.956	-	++	+++
246	-1.966	-	c	c
24	-1.982	-	-	±±
4	-2.056	-	-	±±
2	-2.097	-	-	-
26	-2.107	-	-	-
3	-2.108	-	-	±±

^aReduction interrupt potentials, as measured in dimethylsulfoxide solution at an Hg-Pt electrode, versus a saturated calomel electrode [17].

^bKey, +, ++, +++, increasing reactivity; -, no observed reactivity; ±, reactivity uncertain or observed only in species favorably substituted on opposite ring.

^cLevels of appropriate congeners too low to permit reactivity estimate.

tems B, B', and C are those in positions ortho to the other ring (e.g., 2 or 6), or meta to a chlorine that is itself meta to the other ring (as in the 3,5-, 2,3,5-, or 2,3,5,6-CPs). The latter restriction may be relaxed slightly in system E, where at least the 235-3 and 235-4 CBs are attacked. The most reactive chlorophenyls towards systems B, B', and C would appear to be 2,3- and 3,4-CP (Table 3). Their reactivities are moderately reduced by further chlorination on either the reacting ring (shown by the horizontal progressions on Table 3) or on the opposite ring (shown by the corresponding vertical progressions). These inhibitions are also less marked in system E, resulting in enhanced removal of penta-, hexa-, and heptachlorobiphenyls containing 2,3,4-, 2,3,6-, 2,4,5-, 2,3,4,5-, 2,3,4,6-, and 2,3,4,5,6-substituted rings. Nevertheless, the persistence of tri- and tetra-ortho-chlorinated congeners (containing mainly 2,3,5-, 2,3,6-, and 2,3,5,6-substituted rings) in the pattern E product

mixtures shows that E is still an *m,p*- rather than an *o,m,p*-dechlorinating system.

The patterns of steric effects exhibited by the *m,p*-dechlorinating systems B, B', C, and E would appear to define the spatial configuration of the dechlorinating agents involved as presenting a roughly conical cavity with a reducing (or hydrogenating) site located near the apex (Fig. 4). For para (4-) chlorine removal, a PCB molecule would be able to fit into such a cavity lengthwise, with only minimal steric hindrance by other pendant chlorine atoms, mainly those in ortho positions. For meta (3-) chlorine removal, however, the PCB molecule would have to come into the cavity at an angle, which would result in severe steric hindrance if there were other chlorines present at positions 5 or 6 (i.e., on the opposite side of the reacting ring), and particularly if there were also more than one chlorine on the opposite ring. For ortho (2-) chlorine removal, the PCB molecule would have to be rotated through a larger angle than permitted by the cavity structure; hence, no *o*-dechlorination occurs.

Microbiological implications

As pointed out earlier [3], there are no known environmental chemical agents having the negative reduction potentials or other chemical activities needed to reductively dechlorinate simple aromatic chlorine compounds, such as the PCBs, and no simple chemical agents of any type that show the steric selectivities just described for the environmental *m,p*-dechlorination agents. Accordingly, these agents—and possibly the *o,m,p*-dechlorinating ones as well—must be enzymes, presumably associated with anaerobic environmental bacteria analogous to those known to effect position-sensitive dechlorinations of chlorobenzoates [19] and chlorophenols [20]. It has recently been observed that several synthetic PCB congeners not present in Aroclor 1242 (e.g., 2,3,4,5,6-pentachlorobiphenyl) can be partially dechlorinated by a 32-week anaerobic incubation with unsterilized, but not with sterilized, upper Hudson sediments, indicating microbial mediation (J.F. Quensen III, S.A. Boyd, and J.M. Tiedje, private communication, 1986).

Since the PCB nucleus is not destroyed by the dechlorination process, it would appear that these anaerobes are using the PCB molecules simply as electron acceptors rather than as carbon sources. In order to assess the thermodynamic feasibility of such a process, we performed standard thermochemical calculations of the free-energy change

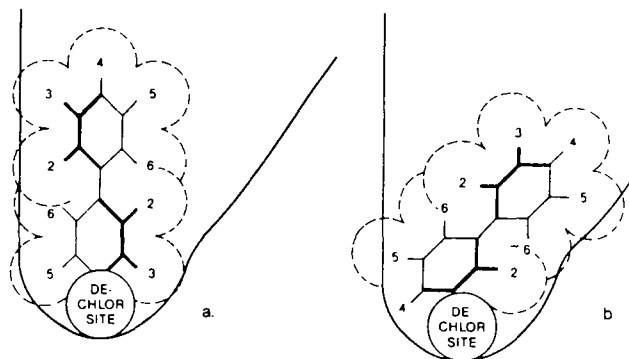


Fig. 4. Schematic of *m,p*-dechlorinating agent active site, showing position taken by PCB molecule during (a) *p*-chlorine or (b) *m*-chlorine removal. Dotted arcs show interference radii of other chlorine substituents, if present at indicated positions.

associated with the oxidation of glucose by various oxidants, taking monochlorobenzene and hexachlorobenzene (for which handbook data were available) as models that should span the range occupied by the PCBs. The results (Table 6) showed that oxidation by chlorinated aromatics would indeed offer a greater free-energy gradient than that provided by the other environmental oxidants commonly available to anaerobes, namely CO_2 and sulfate. Thus, any anaerobe having enzyme systems with the PCB-dechlorinase activity needed to capture this potential energy should be at a competitive advantage. Presumably, the appearance of characteristic sets of PCB dechlorination products in localized patterns in the sediments of the upper Hudson River, Silver Lake, Waukegan Harbor, and Sheboygan Harbor results from the local expansion of anaerobic bacterial populations having such dechlorinase activities.

Environmental implications

Previously, the only known route for the environmental destruction of the more heavily chlorinated PCBs had been photolysis by solar near-ultraviolet light [21]. This process effects the dechlorination of higher to lower PCB congeners, which are more slowly photolyzed. Modeling studies have shown that solar photolysis may reduce the levels of the higher PCBs in large lakes or the oceans with half-times of a year or two [21]. However, the major accumulations of PCBs that lie buried in aquatic sediments are obviously inaccessible to sunlight. Thus, their dechlorination by other agents present in these environmental reservoirs removes what would otherwise be a major blockage to PCB degradation in nature.

Table 6. Standard free-energy change for the oxidation of glucose to CO_2 and H_2O using various oxidants

Oxidant	Reduced product	ΔG (kcal/mol)
O_2	H_2O	-676.10
C_6Cl_6	C_6H_6	-410.16
$\text{C}_6\text{H}_5\text{Cl}$	C_6H_6	-369.50
SO_4^{2-}	S_8	-131.78
CO_2	CH_4	-95.63

Dechlorination, whether by sunlight or bacteria, does not usually accomplish the complete destruction of a PCB molecule. Instead, it converts the more heavily chlorinated PCB species to lower congeners that are readily biodegradable by aerobic bacteria [2,14,15]. Thus, a two-step process, consisting of dechlorination followed by oxidative biodegradation, may be required for complete PCB destruction.

The partially dechlorinated PCB mixtures remaining after dechlorination by aquatic sediments are already sharply depleted in those congeners that are of concern as regards to either persistence, P448 cytochrome induction, or toxicity in higher animals. Available information indicates that the more persistent congeners in man are those having 4,4'-substitution along with additional 2,5-substitution on at least one ring, as in chlorobiphenyls 245-4, 245-24, 245-34, 245-245, 245-234, 2345-34, 2345-245, 2345-234, etc. [12]. Thymotoxicity in rats, along with P448 cytochrome induction, is shown by PCB congeners having 4,4'-substitution accompanied by at least two chlorines in meta

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positions and no more than one ortho chlorine, which should be adjacent to a meta chlorine [22]. The PCB congeners that are actually detectable in the commercial Aroclors and also meet this criterion include 34-34, 2345-4, 234-34, and 2345-34 CB. From Tables 1 and 4 it is apparent that both the persistent and the potentially toxic congener groups are among those most readily removed by dechlorination systems B, B', C, E, F, and G. Extensive removal of congeners 34-34, 245-34, and 234-34 from Aroclor 1248 by the sediments of Waukegan Harbor ("system W") is also indicated by the available data [16]. Thus, anaerobic dechlorination, while not immediately reducing the total mass of chlorinated biphenyl in an environmental deposit, can effect its detoxification.

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