IDENTIFICATION OF ENVIRONMENTAL PCB TRANSFORMATION PROCESSES

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ABSTRACT

PCBs in the environment may undergo various niche-specific transformations, including evaporative loss, biological oxidation, and reductive dechlorination. Each of these processes may be identified by characteristic changes in the congeneric composition of the residual PCBs. A compositional δ value, defined by the relationship of the total non-*ortho* to *ortho* chlorines in the PCB mixture, can provide a summary index of environmental alteration.

KEYWORDS

Polychlorinated biphenyls; PCBs; biodegradation; dechlorination

INTRODUCTION AND RESULTS

Complex and highly characteristic changes in congener distribution are exhibited by PCB specimens that have been altered (or "weathered") by known environmental transformations such as evaporative or elutriative loss [1], microsomal metabolism [2,3], aerobic microbial cometabolism [4,5], or anaerobic microbial dechlorination [1,5-8]; or to postulated environmental alterations such as photochemical dechlorination [9] or anaerobic metabolism [10]. We have found the precise patterns of compositional change effected by each of these process categories to vary somewhat with the specific organism or enzyme involved, but still to show many common generic features (Table 1).

We have also found a useful pair of summary indices of PCB composition to be the ratios of *ortho* chlorine atoms to biphenyl residues and of total non-*ortho* (i.e., *meta* plus *para*) chlorine atoms to biphenyls, which ratios can be calculated from the chlorine positions and mole fractions of all the PCB congeners present. The relationship between these parameters for the formerly commonly used 1200 series Aroclors is linear (Figure 1) indicating that the original composition of the Aroclor mixture responsible for an environmental accumulation would have yielded a point falling on that trend line. Thus, any vertical departure from the trend line, defined as the m,p-chlorination δ value, can serve as an overall index of environmental alteration. General trends in such δ values are indicated in Table 1. We have observed δ's ranging from +1.47 for metabolized Aroclor 1242 in capacitor workers to -2.15 for microbially oxidized Pattern B* dechlorinated Aroclor 1248 ("Pattern X*") in Sheboygan riverside sediments.

Anaerobic microbial dechlorination is the most important process for PCB transformation and detoxication in aquatic sediments [1,5-8]. The congener selectivity patterns displayed vary considerably from site to site, and even from stratum to stratum, indicating mediation by a variety of microbial activities, whose distinguishing features are summarized in Table 2. Many of these activities have now been reproduced in laboratory culture [5,8]. Inter-pattern comparisons indicate that the Type C environmental dechlorination [6,7] arises from the

Table 1. Recognition Features for Environmental PCB Alteration Processes

Alteration Process (and environmental niche)	Effect on Residual PCB[a]				
	lower cong'rs	higher cong'rs	o-Cl per BP	m,p-Cl per BP	δ value
Physical Alternation					
1. Evap'n, elut'n (from soil, sediment surface)	--	(-)	0	+	+
2. Photolysis (in large lakes, seas)	+ +	--	--	-	+ +
Eucaryotic Oxidative Metabolism					
3. Via cyt. P-450-IA1 (chloracne pts; some animals)	--	(-)	+	+	±
4. Via cyt. P-450-IIB2 (normal man; most animals)	--	-	±	+	+ +
Prokaryotic Oxidative Cometabolism					
5. Via 2,3-dioxygenase (aerobic soils, sediments)	-	0	+	+	±
6. Via 3,4-(+ 2,3-)" " (aerobic soils, groundwater)	--	(-)	+	+	±
Anaerobic Dechlorination and Metabolism					
7. m,p-dechlorination (aquatic sediments)	+ +	--	0	--	--
8. o,m,p-dechlorination (aquatic sediments[b])	+ +	--	-	--	-
9. anaerobic metabolism (aquatic sediments[c])	-	0	±	+	+

a. Key: --, -, (-), ±: large, small, marginal, or variable decrease in indicated component; + +, +, ±: large, small, or variable increase in indicated component; 0: no change. b. Thus far, seen only in sediments of Silver Lake, Pittsfield, MA, USA (Processes F, G). c. Thus far, seen only in cultures of sediments from upper Hudson River (Ft. Miller, NY, USA [10]).
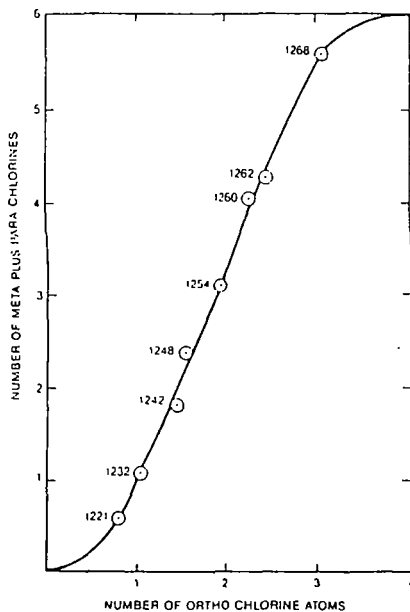

Figure 1. Relationship between numbers of *ortho* and non-*ortho* chlorine atoms per biphenyl residue in commercial Aroclors.

Table 2. Congener Selectivity Patterns Shown by Environmental PCB Dechlorination Systems[†]

System	Source	Position and Range of Attack	Higher PCB Removal Pattern	Range of Reactivities for PCBs with Indicated Mono- or Dichlorophenyl Group					
				3,4-	2,3-	2,5-	2,4-	4-	3-
B	Upper + mid-Hudson R (NY) + cultures	m,p-L	III-4	4	4	2b	1	0?	1?
B'	Upper Hudson R (NY)	m,p-L	III-4	4	4	2-3b	2	0?	2
B*	Sheboygan R (WI)	m,p-L	III-4	4	4	3b	1	0?	2
C	Upper Hudson R (NY) + cultures	m,p-L	III-4	4	4	4	3-4	4	2
E	Upper Hudson R (NY) + cultures	m,p-H	II-4	?	?	?	?	?	?
F	Silver Lake (Pittsfield, MA)	o,m,p-H	III-4	4	<3	0	0	0	0
G	Silver Lake (Pittsfield, MA)	o,m,p-M	III-4	4	4	2-3b	0?	?	2
H	(Several sites [1] + cultures)	m,p-L	II-3	3	2	0	0	0	0
H'	(Several sites [1] + cultures)	m,p-L	II-3	3	3	0	0	0	0
H*	Sheboygan R + Harbor (WI)	m,p-L	II$^+$-3	3	2	0	0	0	0
J	New Bedford (MA) cultures	m,p-L?	III-4	4a	3	0	0	0	0
M	Upper Hudson R (NY) cultures	m,p-LL	I-4	4a	4	4	0	0	2
N	Woods Pond (MA) + cultures (on 1260)	m,p-M	III-4	?	?	?	0	?	?
Q	Upper Hudson R (NY) cultures	m,p-L	III-4	4	4	0?	3-4	4	0?
W	Waukegan Harbor (IL)	m,p-L?	II$^+$-3	3-4	3-4	2b	0	0?	2

[†]KEY. Chlorine positions attacked: m,p = meta, para; o,m,p = ortho, meta, para; underline indicates preference. Chlorination range attacked: L, M, H = mild preference for lower, medium, or higher congeners, respectively; LL = strong preference for lower congeners. Pattern of attack on higher congeners: I = 236-XY > 234-XY >> 245-XY, etc. II = 234-XY > 245-XY > 235-XY >> 236-XY; 2345-XY, 2346-XY >> 2356-XY. II$^+$ = ditto except 234-XY ≃ 245-XY. III = 234-XY ≥ 245-XY > 236-XY > 235-XY but range of relative reactivities small; 2345-XY, 2346-XY, 2356-XY all reactive. Effect of opposite ring substitution pattern on reactivity of indicated chlorophenyl group (or 245-chlorophenyl group in a higher congener): 0 = indicated group never dechlorinated; 1 = only congeners lacking 2'-substitition attacked; 2 = congeners substituted 2' but not 2'X' attacked; 3 = congeners substituted 2'X' but not 2'6' attacked; 4 = all congeners carrying indicated group attacked. Modification of usual 2'6'-substitution effects on reactivity: a = 2'6'-substituted congeners attacked at least as easily as less ortho-substituted types. b = indicated ortho-substituted type may be more reactive than non-ortho-substituted species (e.g., 25-3, 25-4 CB).

combined activities of systems M and Q; Type H´ [1] probably from activity H with small contributions from either B, M, or J, depending on the site; and Type G [7] possibly from the unusual *o,m,p*-dechlorinating activity F followed by a more normal *m,p*-dechlorination, such as the readily cultured activity N.

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