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Toxic Polychlorinated Biphenyl Congeners in Sheboygan River (USA) Sediments

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In the U. S. polychlorinated biphenyls (PCBs) were produced in mixtures (Aroclors) of the 209 different PCB congeners. The Aroclors differ not only in the congeners contained in the mixture, but also in the weight percent of the congeners. Until recently almost all environmental and biological samples were analyzed for PCBs by matching the chromatographic pattern to the pattern of pure Aroclors (Webb and McCall 1973; Erickson 1986), and results were reported as an Aroclor or mixture of Aroclors. However, with the refinement of high resolution capillary gas chromatographic techniques, it is now possible to identify and quantify individual PCB congeners in environmental samples (Mullin et al. 1984; Maack and Sonzogni 1988). Note that in this paper congeners will be referred to by their International Union of Pure Applied Chemistry (IUPAC) numbers and by an abbreviation of their structure. For example, 3, 3', 4, 4' tetrachlorinated biphenyl is referred to as congener 77 (34-34).

Interest in individual congener concentrations has also increased because recent toxicological data indicate the potency of congeners varies widely (Safe 1987; Tanabe et al. 1987). Those congeners presently thought to be most toxic are the non-ortho chlorinated PCBs, since these co-planer compounds structurally resemble the highly potent 2,3,7,8-tetrachlorodibenzo-dioxin (TCDD). Congeners 77 (34-34), 126(345-34) and 169 (345-345) are non-ortho chlorinated and most resemble dioxin. They are believed to be the most toxic congeners, at least in terms of dioxin-like properties (Safe et al. 1985; Tanabe et al. 1987). Congener 81 (345-4) also has no ortho chlorines; however, it is structurally different enough from TCDD that it is not considered to be as toxic as the compounds above. The mono-ortho congeners, such as 105

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(234-34), 118 (245-34), 123 (345-24), 114 (2345-4) and 167 (245-345) are also thought to be toxic (have toxic properties related to dioxin), although they are less potent (Safe et al. 1985; Safe 1987).

Unfortunately, most of the congeners mentioned above are difficult to analyze, even by high resolution gas chromatography. These compounds tend to co-elute with other congeners. Special separation techniques are required to identify them. To date, the only separation techniques reported in the literature are (1) carbon column absorption (Stalling et al. 1983) and multidimensional gas chromatography (Duinker et al. 1988). The purpose here is to present results of analyses of river sediments for these toxic PCB congeners using a multidimensional chromatography technique.

MATERIALS AND METHODS

Sediment samples were collected from the Sheboygan River, a Wisconsin tributary to Lake Michigan. The river is polluted with PCBs from the mouth to about 22.6 km (14 miles) upstream. Waste hydraulic fluids containing Aroclor 1248 and Aroclor 1254, were the source of the contamination (David 1990). The polluted section of the river is a U.S. federal "Superfund" site as well as one of the Great Lakes "Areas of Concern" as defined by the U.S./Canadian International Joint Commission.

Sediment cores were collected in December of 1988 and April of 1989 using a metal corer 90 cm (3 ft) long and 7.6 cm (3 in.) in diameter. All samples were collected near the original source of PCBs at Rochester Park (about 22.6 km upstream from the mouth). A hydraulic extruder was used to remove the sediment from the corer. The cores were segmented into 15 cm sections and kept cool (4°C) until analysis.

Sediment was air dried and sieved to form a homogeneous sample. PCBs were extracted from 50 g sediment samples by soxhleting for eight hours with acetone and hexane (1:1). Granular copper was added to the soxhlet flask to insure uniform boiling and to remove sulfur interferences. After concentrating the sample, anhydrous sodium sulfate was added to remove water from the extract. The hexane-acetone solution was then exchanged for 2,2,4-trimethyl pentane (iso-octane). PCBs were separated from other contaminants using Florisil and silica gel. Hexane and 6% ethyl ether were the eluting solvents used for the Florisil fractionation and hexane for the silica gel fractionation. The first silica gel fraction was subsequently used for PCB quantitation. Hexane was exchanged with isooctane prior to gas chromatographic analysis. Samples were concentrated to

10 or 50 mL prior to injection of an aliquot into the gas chromatograph.

PCB congeners were quantitated using a Siemens Sichromat 2-8 multidimensional gas chromatograph. The instrument was equipped with two 30 m capillary columns (DB-5 and DB-1; J and W Scientific). Each column was connected to an individual ^{63}Ni electron capture detector. The columns were also contained in separate ovens. Eluate from the DB-5 column passed through the column's detector producing a chromatogram similar to that produced in conventional high resolution gas chromatography. However, when a "T-piece" connecting the DB-5 column to the DB-1 column was activated, eluate was diverted to the DB-1 column. Thus, a selected part of the eluate (e.g., the eluate eluting between a specific time interval) was cut to the DB-1 column. The cut is accomplished on a real time basis according to pneumatic (gas flow) differences between the two columns, the timing of which is controlled by the analyst.

The temperature of the oven containing the DB-5 column was ramped from 90°C to 160°C at a rate of 20°C per minute, then from 160°C to 260°C at a rate of 4°C per minute. The final temperature was held for one minute. The temperature of the column containing the DB-1 oven was held at 160°C for 20 minutes and then increased at a rate of 4°C per minute to 240°C. The final temperature was held for eight minutes. The injector temperature was 250°C; the detectors were heated to 300°C. The carrier gas and make-up gas were hydrogen and nitrogen, respectively.

By cutting a portion of the eluate after it passed through the DB-5 column to and through the less polar DB-1 column, increased separation of the compounds in the cut was obtained. The chromatogram produced from the second (DB-1) column and its associated detector represented the response of the cut components, while the chromatogram of the first column (DB-5) represented the rest of the compounds in the injected mixture (the chromatogram for the first column is interrupted by the cut). For a further discussion of the instrument, see Duinker et al. (1988).

For the eight congeners studied, pure standards were used for identification (based on retention times) and quantification. A detector limit of 1 ng/g, based on a signal to noise ratio of approximately 3, was made. Although replicate analyses were made to check results, no alternate method was available to confirm the identification of the congeners in the unknown.

RESULTS AND DISCUSSION

Results of the analyses of Sheboygan River sediment samples for total PCBs and eight "toxic" congeners are summarized in Table 1. Each of these congeners was identified and quantified in at least one of the samples. Note that all sediment core samples analyzed had total PCB concentrations greater than 50 μg/g.

Congeners 118 (245-34), 105 (234-34), and 77 (34-34) were detected in all of the samples reported here. Concentrations ranged from about 5 to 1500 ng/g. The remaining toxic congeners, 81 (245-4), 114 (2345-4), 167 (245-345), 126 (345-34), and 169 (345-345), were detected less frequently in the analyzed samples. Concentrations of these congeners ranged from non-detectable to slightly over 100 ng/g.

Very few measurements of toxic congeners in environmental samples have as yet been reported in the literature. Tanabe et al. (1987) reported various levels of congeners 77 (34-34), 126(345-34), and 169 (345-345) in fish, marine mammals, and terrestrial animals in Japan. Duinker et al. (1988) reported seal blubber from the Dutch Wadden Sea contained 100, 800 and 5200 ng/g of congeners 77 (34-34), 118 (245-34), and 105 (234-34), respectively. Congeners 126 (345-34), 81 (345-4), 167 (245-345), and 114 (23 45-4) were all found in seal blubber at concentrations less than 10 ng/g. Note that for the Sheboygan sediments reported here, congeners 77 (34-34), 118 (245-34), and 105 (234-34) were also found at concentrations higher than the rest of the congeners. To the best of the authors' knowledge, no other data on concentrations of these congeners in aquatic sediment have been published.

Table 2 presents the weight percents of the congeners in the samples. Also included are the weight percents of congeners in several Aroclors as determined by Duinker et al. (1988). The weight percents of the toxic congeners in the sediments were generally lower than those found in Aroclors 1248 and 1254 (the primary PCB mixtures discharged to the river) and in the other Aroclor mixtures listed in Table 2. The weight percents of the most prominent toxic congeners (77, 118, and 105) were about one order of magnitude lower than the weight percents of these congeners in Aroclor 1248. Some weight percents for congener 81 (345-4) were higher than reported for the Aroclors, although the congener was detected only in four of the eight samples reported.

Anaerobic reductive dechlorination of PCBs, similar to that reported by Brown et al. (1987), Quensen et al. (1988), and Rhee et al. (1989), has been reported to

Table 1. Concentration of various toxic PCB congeners in Sheboygan River sediment samples of different total PCB concentrations.

Total PCB in Sample (μg/g)	Congener (IUPAC Number) 77	118	105	167	114	126	169	81
				(ng/g)				
50.3	31	140	80	44	ND[a]	ND	ND	ND
1050	360	1480	490	80	110	10	19	90
76.9	24	129	27	ND	ND	9	9	ND
97.8	21	318	41	ND	ND	ND	ND	ND
256	46	395	15	ND	ND	ND	ND	75
73.4	5	103	11	ND	ND	ND	ND	ND
97.5	11	162	6	ND	ND	ND	11	ND
124	16	86	11	ND	ND	ND	ND	50

[a]ND = not detected (concentration less than 1 ng/g)

Table 2. Weight percent of various toxic PCB congeners in Sheboygan River sediment samples and weight percent of congeners in several aroclors[a].

Total PCB in Sample (μg/g)	Congener (IUPAC Number) 77	118	105	167	114	126	169	81
				(weight %)				
50.3	0.06	0.27	0.15	0.09	- -[b]	- -	- -	- -
1050	0.03	0.14	0.05	0.01	0.01	<0.01	<0.01	0.01
76.9	0.03	0.16	0.04	- -	- -	0.01	0.01	- -
97.8	0.02	0.33	0.04	- -	- -	- -	- -	- -
256	0.02	0.15	0.01	- -	- -	- -	- -	0.03
73.4	0.01	0.14	0.01	- -	- -	- -	- -	- -
97.5	0.01	0.17	0.01	- -	- -	- -	0.01	- -
124	0.01	0.07	0.01	- -	- -	- -	- -	0.04
Aroclor 1242	0.50	1.80	0.33	<0.01	<0.01	<0.01	<0.01	<0.01
Aroclor 1248	0.30	3.35	0.55	<0.01	<0.01	<0.01	<0.01	<0.01
Aroclor 1254	<0.01	8.45	2.03	0.05	<0.01	0.08	0.08	<0.01
Aroclor 1260	<0.01	1.15	0.08	0.15	<0.01	0.05	0.05	<0.01

[a]Aroclor weight percents from Duinker et al. 1988
[b]Congeners not detected in samples (weight percents less than 0.002%).

occur in Sheboygan River sediments (David 1990). Dechlorination of non-ortho chlorinated congeners has been found to occur more readily than dechlorination of ortho chlorinated PCBS (Brown and Wagner 1990). Congeners 77 (34-34), 118 (245-34), and 105 (234-23) are all non-ortho chlorinated PCBs, suggesting that dechlorination might play a role in the depletion.

Of the toxic congeners, congener 118 (245-34) was found in Sheboygan River sediments in the highest weight percent. Congener 118 is also found in all the Aroclors in Table 2 in the highest weight percent of the toxic congeners. It also appears to be the most common toxic congener in environmental samples. It was found in highest concentrations (relative to other toxic congeners) in seal blubber (Duinker et al. 1988), as well as in the sediments collected for this study. Congener 118, unlike the other toxic congeners, can often be resolved and quantified without multidimensional gas chromatography or other special techniques. It has thus been reported in a variety of matrices, such as fish and the blood of sport fish eaters (Maack and Sonzogni 1988; Fiore et al. 1989 and Sonzogni et al. 1991).

The eight toxic PCBs studied here appear to be present in the sediment, but in relatively low concentrations compared to total PCBs or other more abundant congeners. The concentrations of the eight congeners are low relative to the congeners with which they co-elute as well. For example, toxic congener 77 (34-34) co-elutes with congener 110 (236-34), but 77, in the sediments studied here, made up less than 4 percent of the total of the co-eluting pair. It should again be emphasized that the toxic congeners have been so labeled because of their dioxin-like structure and the potential health effects of dioxin. More research needs to be conducted on the toxicological effects of the PCB congeners. The effects of exposure to environmental levels needs to be considered as well as toxicological endpoints other than that for dioxin. For example, the neurotoxicological impacts of specific congeners or combinations of congeners needs to be studied. Perhaps new analytical tools, such as multidimensional gas chromatography, will help make such research more feasible.

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