ISOMER-SPECIFIC ANALYSIS OF POLYCHLORINATED NAPHTHALENES IN SEVERAL POLYCHLORINATED BIPHENYL PREPARATIONS

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Introduction

Polychlorinated naphthalenes (PCNs) were used for wide variety of purposes; capacitor dielectrics, cutting oils, engine oil additives, etc. This has resulted in significant environmental contamination, even though the production of PCNs in the United States and Europe was ceased in the 1980s. Although global production of technical PCNs such as Halowaxes has been estimated to be approximately 150,000 metric tons (1), very little was known about other sources that contribute to emissions of PCNs into the environment. A few studies have indicated the occurrence of PCNs in a few PCB mixtures. In this paper, concentrations and profiles of polychlorinated naphthalene (PCN) congeners were determined in eighteen technical polychlorinated biphenyl (PCB) mixtures including Aroclors, Kanechlors, Clophens, Phenoclors, Sovol and Chlorofen. Total amount of PCNs emitted from the use of PCBs was estimated based on the concentrations of PCNs in PCB mixtures and the reported global production of PCBs. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) equivalents (TEQs) contributed by PCNs in technical PCB formulations were estimated based on the concentrations of AhR active PCN congeners and toxic equivalency factors (TEF). Amount of coplanar PCBs and PCDFs present in these mixtures were also measured and discussed.

Materials and Methods

Technical PCB mixtures investigated include, Aroclors 1016 (lot #K02Z), 1232 (#L06B), 1248 (#L03D), 1254 (#6024, 124-191 and LO3E), 1260 (L02F), 1262 (#L02G), Kanechlors 300, 400, 500, and 600 (KC-300, KC-400, KC-500 and KC-600), Clophens A40 and T64, Phenoclors 3,4,5, and 6 (DP3, DP4, DP5 and DP6), Sovol, and Chlorofen.

Stock solutions of PCB mixtures were prepared in hexane and the highest available concentrations were used for the separation of PCNs from PCBs using silica gel-impregnated activated carbon mini-column (ACMC). ACMC (100 mm X 6 mm i.d.) were prepared by packing 0.1 g of silica gel (Kiesel gel 60, Merck, mesh size, 230-400) followed by 0.5 g of silica gel-dispersed activated carbon and 0.1 of silica gel in glass columns of 6 mm i.d.. Silica gel-impregnated activated carbon was prepared by mixing silica gel with activated carbon (Darco G-

60, Wako Pure Chemical Industries) at a ratio of 1: 20. Prior to packing, carbon and silica gel were extracted with dichloromethane (DCM) and toluene in a Soxhlet apparatus. ACMC were pre-cleaned by eluting with 30 mL of toluene followed by reverse elution with 1% DCM in hexane (25 mL) and hexane (20 mL) using a HPLC (LC-10AD; Shimadzu Corporation) pump at a flow rate of 3 mL/min. Recoveries and separation of PCNs and PCBs were examined by spiking a mixture Halowaxes 1014 and 1051 (3:1) and Kanechlors 300, 400, 500, 600 (1:1:1:1) into ACMC. First fraction eluted with hexane (6 mL) using the HPLC pump at a flow rate of 1 mL/min contained most of the *ortho*-substituted PCB congeners whereas the second fraction eluted with 25 mL of 1% DCM in hexane at a rate of 2 mL/min contained mono-ortho and part of non-*ortho* coplanar PCBs. The column was then reversed and eluted with 30mL of toluene at a rate of 2 mL/min to elute PCN, part of non-*ortho* coplanar PCBs and PCDF congeners. Recoveries of PCBs, PCNs and PCDFs were between 78% and 104%.

Identification and quantification of individual PCN congeners were accomplished with a Hewlett-Packard 6890 series II high-resolution gas chromatograph (HRGC) coupled to a JEOL JMS-700 high resolution mass spectrometer. Details of analysis and identification of individual congeners of PCNs, PCDF and coplanar PCBs have been described elsewhere (2, 3).

Results and Discussion

Concentrations of total chloronaphthalenes (CN) in 18 technical PCB preparations ranged from 5.2 to 730 μg/g (Table 1). Aroclor preparations contained relatively lesser concentrations of PCNs than the other PCB mixtures. Concentrations of total PCNs in Aroclors tend to increase with increase in chlorine content except in Aroclor 1262 (62% chlorine by weight), which contained slightly lesser concentrations of PCNs than in Aroclor 1260 (60% chlorine). Among Aroclors, the lowest concentration of PCNs of 5.2 μg/g was present in Aroclor 1016 (42% chlorine) while the greatest concentration of 67.2 μg/g was found in Aroclor 1260 (60% chlorine). The pattern of increase in PCN concentrations with the increase in chlorine content in PCB mixtures was also evident for Kanechlors. However, concentrations of PCNs in Phenoclors were not related to chlorine content.

Isomer-specific analysis of PCN congeners revealed the presence of almost all the PCN congeners, except congeners 48 (2,3,6,7-TeCN) and 55 (1,2,3,6,8-PeCN), in at least one of the PCB mixtures analyzed. 1,2,3,8-Tetra-CN congener (31) was detected only in Kanechlor preparations. Chlorofen, a Polish PCB preparation with 64% chlorine by weight, contained octa-CN accounting for 98% of the total PCNs (Figure 2). Chloronaphthalene congeners 64/68 (1,2,3,4,5,7-/1,2,3,5,6,8-HxCNs), 69 (1,2,3,5,7,8-HxCN), 71/72 (1,2,4,5,6,8-/1,2,4,5,7,8-HxCNs), 73 (1,2,3,4,5,6,7-HpCN) and 74 (1,2,3,4,5,7,8-HpCN) accounted for 75% of the total PCNs in Sovol. Some of the most abundant CN congeners in less chlorinated PCB mixtures such as Kanechlors 300 and 400, Phenoclors 3 and 4, Aroclors 1016 and 1232 include tetra-CN congeners 33/34/37 and 38 and penta-CNs 52/60 and 62 (Figure 3). The highly chlorinated PCB mixtures contained predominant amounts of octa-CN (75), which accounted for greater than 80% of the total PCN concentrations in Kanechlor 600 or Aroclor 1260.

Although the concentrations of PCNs in technical PCB mixtures vary depending on the production

conditions, PCNs formed as a byproduct in PCB mixtures can be estimated approximately. Total quantities of PCBs produced in the USA, UK (Aroclors), Japan (Kanechlors), Germany (Clophen), France (Phenoclors) and the former USSR (Sovol) and mean concentrations of PCNs present in these mixtures were used to estimate PCNs formed as a by-product (Table 2). This was estimated to be approximately 169 tons, which is 0.1% of the total world production of technical PCN mixtures of 150,000 tons (1). This estimate did not include the content of mono- and di-CNs, which were not measured in PCB mixtures. Similarly, PCB mixtures produced in Italy, Spain, Poland and the former Czechoslovakia were not examined. Although this is an approximate estimate, it can be safely mentioned that PCNs emitted from the use of PCB mixtures would be less than 1% of the PCNs produced as technical preparations such as Halowaxes.

Several of the PCN congeners elicit toxic effects similar to those of TCDD through the AhR mediated mechanism. TEFs (relative potency of congener to that of 2,3,7,8-TCDD) derived from H4IIE rat hepatoma cells have been reported for several chlorinated naphthalene congeners. TEQs contributed by PCNs in PCB mixtures varied from 0.07 to 310 ng/g. PCN-TEQs were less than 20 ng/g in all Aroclors analyzed. The greatest PCN-TEQs were observed in Sovol and highly chlorinated Phenoclor mixtures. The major PCN congeners that contributed to TEQs include hexa-CNs 63, 69, and hepta-CN congener 73. In highly chlorinated PCB mixtures such as Chlorofen, Phenoclor 6, Kanechlor 600, and Aroclors 1260 and 1262, congener 73 accounted for greater than 50% of the total PCN-TEQs. In other PCB mixtures, congener 69 accounted for approximately 50% of the total TEQs.

In summary, the results of this study suggest that PCNs are commonly found in PCB mixtures at concentrations of up to several hundred micrograms per gram. The concentrations of PCNs present as impurities in technical PCB mixtures were greater than those of PCDFs, although PCNs contributed relatively less to AhR-mediated toxic potentials than those of PCDFs. Understanding the composition of PCNs in technical PCB mixtures has additional benefits. The CN composition in PCB mixtures varied considerably among different commercial preparations. Therefore, the profile of selected PCN congeners can be used to identify the type of PCB mixtures released into the environment.

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TABLE 1. Concentrations (μg/g) of Polychlorinated Naphthalene Homologs in Technical PCB Mixtures

	AR 1016	AR 1232	AR 1248	AR 1254	AR 1260	AR 1262	KC 300	KC 400	KC 500	KC 600	Sovol	Chlorofen	CL A40	CL T64	PC DP3	PC DP4	PC DP5	PC DP6
T3-CN	0.67	0.48	0.11	0.01	0.02	0.03	0.34	0.03	0.10	0.05	0.31	0.01	0.63	0.27	30.4	0.90	0.28	0.93
T4-CN	4.26	1.61	3.17	0.25	0.10	0.37	9.03	2.03	1.24	0.34	4.92	0.02	26.4	0.77	87.3	55.4	3.34	2.98
P5-CN	0.09	3.07	22.1	4.26	0.31	0.64	16.9	15.1	8.62	1.21	48.9	0.07	41.5	2.32	28.0	258.4	17.6	5.97
H6-CN	0.07	1.03	15.8	21.8	1.19	1.57	4.54	11.8	50.9	2.93	376.6	0.88	32.2	14.4	1.99	134.8	142.5	10.4
H7-CN	0.05	0.18	1.67	17.6	10.0	12.7	1.03	4.08	58.2	9.23	261.5	8.76	1.76	21.2	0.21	8.43	153.2	69.7
O8-CN	0.10	0.43	0.38	3.23	55.5	50.5	0.40	0.88	41.3	94.4	38.6	398.3	0.08	47.4	ND	2.34	37.8	137.6
Total	5.2	6.8	43.3	47.2	67.2	65.8	32.2	33.9	160.3	108.1	730.8	408.0	102.6	86.4	147.9	460.3	354.6	227.5

AR : Aroclor, KC : Kanechlor, CL : Clophen, PC : Phenoclor

TABLE 2. Estimated Production of PCNs from Technical PCB Mixtures

Country	PCB mixture	PCB production (kg)	Mean PCN conc (mg/kg)	Amount of PCNs in PCBs (kg)
US	Aroclors	435100000	39	16969
UK	Aroclors	66748000	39	2603
Japan	Kanechlors	59119000	84	4966
Germany	Clophens	123552000	95	11737
France	Phenoclors	201679000	298	60100
former USSR	Sovol	100000000	730	73000
Total				169375