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Concentrations and Profiles of Polychlorinated Naphthalene Congeners in Eighteen Technical Polychlorinated Biphenyl Preparations

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Concentrations and profiles of tri- through octa-chloro-substituted polychlorinated naphthalene (PCN) congeners were determined in eighteen technical polychlorinated biphenyl (PCB) mixtures including Aroclors, Kanechlors, Clophens, Phenoclors, Sovol, and Chlorofen. PCNs were found in all the PCB mixtures at concentrations ranging from 5.2 to 730 $\mu\text{g/g}$. Concentrations of PCNs in Aroclor and Kanechlor mixtures were greater than those of polychlorinated dibenzofurans (PCDFs) present as impurities in these technical PCB preparations. Composition of PCN homologues varied among PCB mixtures. In general, highly chlorinated PCB mixtures contained greater percentages of more-chlorinated naphthalene congeners. Concentrations of PCNs varied by 3-fold among three different lots of Aroclor 1254. On the basis of measured concentrations of PCNs in PCB mixtures and global production estimates of PCBs, PCNs emitted from the use of PCBs was estimated to be 169 tons, which is less than 1% of the production of technical PCN mixtures such as Halowaxes. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) contributed by PCNs in technical PCB mixtures were less than those estimated for coplanar PCB congeners and PCDFs.

Introduction

Polychlorinated naphthalenes (PCNs) were among the first synthetic chemicals; they have been produced since World War I and were used for nearly 70 years in the United States and Europe (1). PCNs were used in capacitor dielectrics, cutting oils, engine oil additives, electroplating stop-off compounds, die casting, ship insulation, wood and paper preservatives, and wire insulation. Production of PCNs in the United States and Europe ceased in the 1980s (2). Unlike polychlorinated biphenyls (PCBs), little information exists on the world production of PCNs. Global production of PCNs has been estimated to be approximately 150 000 metric tons

(3). In addition, other sources such as municipal solid waste incineration (4), metallurgical processes (5), chlor-alkali processes (6), and impurities in technical PCB mixtures (7) contribute to emissions of PCNs into the environment.

PCNs are widespread in the environment. Chlorinated naphthalene (CN) congeners have been found in Arctic and urban air (8,9), drinking water, sediment, and biota (6,10–15), including human tissues (16). Several (approximately 10 of the 25 congeners tested so far) of the PCNs elicit toxic effects similar to those of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) through the Ah-receptor (AhR) mediated mechanism (17,18). The occurrence of PCNs in biota, including humans, and their potential toxic effects are of public health concern. It is therefore important to evaluate potential sources of emission of PCNs into the environment to estimate global inventories and to control emissions.

Occurrence of PCNs as byproducts/impurities in technical PCBs such as Aroclors and Clophens has been reported previously (7,19). However, all of the PCN congeners were not identified in these mixtures because of the lack of analytical standards. PCN content of the PCB mixtures other than Aroclors or Clophens was unknown. In this study, absolute and relative concentrations of individual PCN congeners were measured in eighteen technical PCB preparations including Aroclors (Monsanto, USA), Kanechlors (Kanegafuchi, Japan), Clophens (Bayer, Germany), Phenoclors (Prodelec, France), Chlorofen (Ząbkowice śląskie, Poland), and Sovol (Minchimprom, former USSR). 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. 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) (17).

The determination of PCNs in PCB mixtures requires separation of these compounds to identify and determine individual CN congeners present as byproducts in commercial PCBs. Separation was achieved by the use of silica gel-impregnated active carbon columns and high-pressure liquid chromatography (HPLC). Identification and determination of CN congeners were performed by a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC–HRMS).

Materials and Methods

Technical PCB mixtures investigated included Aroclors 1016 (lot #K02Z), 1232 (#L06B), 1248 (#L03D), 1254 (#6024, 124–191, and L03E), 1260 (L02F), and 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. Composition of chlorobiphenyl congeners in the above PCB mixtures has been examined in detail (20–24). Aroclor standards were obtained from the U. S. Environmental Protection Agency's repository for toxic and hazardous materials (Cincinnati, Ohio). Three different lots of Aroclor 1254 (lots #6024, 124–191, and L03E) were obtained to examine variations in PCN compositions and content with lots. Kanechlor preparations were obtained from deposits at the National Institute for Resources and Environment, Tsukuba, Japan. Original stocks of Aroclor and Kanechlor were available at 1000 mg/mL in hexane. Sovol, Clophens, and Phenoclors were a gift of Dr. N. Kannan, Kiel University, Germany, and were donated as 75 to 450 $\mu\text{g/mL}$ stock solutions in hexane. Lot numbers of Kanechlors, Clophens, Phenoclors, and Sovol were not available. Chlorobiphenyl compositions of these mixtures

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TABLE 1. Concentrations ($\mu\text{g/g}$) of Polychlorinated Naphthalene Homologues in Technical PCB Mixtures

congener	Aroclor						KC-300	KC-400	KC-500	KC-600	Sovol	Chlorofen	Clophen		Phenoclor			
	1016	1232	1248	1254	1260	1262							A40	T64	DP3	DP4	DP5	DP6
tri-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
tetra-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
penta-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
hexa-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
hepta-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
octa-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

are reported elsewhere (21). Chlorofen was obtained as a technical product from the manufacturer in Żabkowice śląskie, Poland (23).

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 carbon column. Columns (10 cm \times 0.6 cm i.d.) were prepared by packing 0.1 g of silica gel (Kiesel gel, Merck, Darmstadt, Germany; mesh size, 230–400; particle size, 0.04–0.06 mm) followed by 0.5 g of silica gel-impregnated activated carbon and 0.1 of silica gel in glass columns. Silica gel-impregnated activated carbon was prepared by mixing silica gel with activated carbon (Darco G-60, Wako Pure Chemical Industries, Japan) at a ratio of 1:20. Prior to packing, carbon and silica gel were extracted with dichloromethane (DCM) in a Soxhlet apparatus. Glass columns 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 high-pressure liquid chromatography (HPLC model LC-10AD; Shimadzu Corporation, Kyoto, Japan) pump at a flow rate of 3 mL/min. Recoveries and separation of PCNs and PCBs were examined by spiking a mixture of Halowaxes 1014 and 1051 (3:1) and Kanechlors 300, 400, 500, 600 (1:1:1:1) into silica gel-impregnated carbon columns. The 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 non-*ortho* coplanar PCBs. The column was then reversed and eluted with 30 mL of toluene at a rate of 2 mL/min to elute PCN congeners. Recoveries of PCBs and PCNs were between 80% and 100%. Silica gel-impregnated carbon columns were replaced between samples.

Identification and quantification of individual PCN congeners were accomplished with a Hewlett-Packard 6890 series high-resolution gas chromatograph (HRGC) coupled to a JEOL JMS-700 high-resolution mass spectrometer. PCN congeners were separated by a capillary column coated with DB-1701 at 0.25 μm film thickness (30 \times 0.25 mm i.d.; J&W Scientific, Folsom, CA). The column oven temperature was programmed from 80 to 160 $^{\circ}\text{C}$ at a rate of 40 $^{\circ}\text{C}/\text{min}$, and then to 170 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, to 250 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C}/\text{min}$, and to 296 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$, with a final hold time of 10 min. Injector and transfer line temperatures were held at 260 and 250 $^{\circ}\text{C}$, respectively. Helium was used as the carrier gas. The mass spectrometer was operated at an electron impact (EI) energy of 70 eV. CN congeners were determined by selected ion monitoring at the two most intensive ions of the molecular ion cluster. Details of analysis and identification of individual congeners have been described elsewhere (12,25). Detection limit of individual PCN congeners was 1 ng/g.

Results and Discussion

PCN Concentrations and Profiles. Concentrations of total chloronaphthalenes (CN) in 18 technical PCB preparations ranged from 5.2 to 730 $\mu\text{g/g}$ (Table 1). Aroclor preparations

TABLE 2. Concentrations ($\mu\text{g/g}$) and Compositions^a (%) of PCN Congeners in Three Lots of Aroclor 1254

congener	lot #L03E	lot #6024	lot #124–191
tri-CN	0.01 (0.03)	0.02 (0.01)	0.07 (0.04)
tetra-CN	0.25 (0.52)	0.32 (0.19)	0.56 (0.36)
penta-CN	4.26 (9)	23.3 (14)	8.12 (5.2)
hexa-CN	21.8 (46)	95 (56)	65.7 (42)
hepta-CN	17.6 (37)	44.9 (26)	65.8 (42)
octa-CN	3.23 (6.8)	7.80 (4.6)	15 (10)
total	47.2	171.2	155.3

^a Values in parentheses indicate the percentage composition.

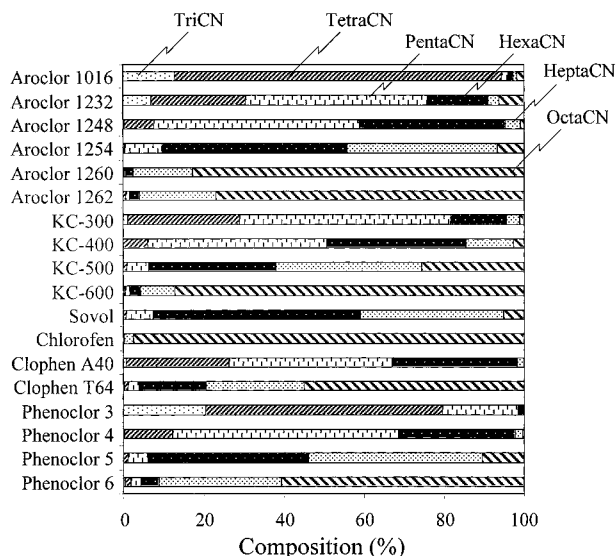


FIGURE 1. Composition (%) of PCN homologues in technical PCB mixtures.

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 Aroclor 1260 (60% chlorine). Among Aroclors, the lowest concentration of PCNs of 5.2 $\mu\text{g/g}$ was present in Aroclor 1016 (42% chlorine), whereas the greatest concentration of 67.2 $\mu\text{g/g}$ 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 Phenoclor were not related to chlorine content. Concentrations of total PCNs in Aroclors 1232 and 1254 were 25 and 13 times less than those reported earlier (7). Lesser concentrations of PCNs in Aroclor 1232 can be explained by the lack of analysis of di-CN in this study, which were reported to be abundant previously (7). Similarly, concentrations of PCNs in Clophen A40 were 8 times less than those reported earlier (7). This difference

TABLE 3. Concentrations of PCN Isomers and Congeners ($\mu\text{g/g}$) in Technical PCB Mixtures

congener	IUPAC No.	Clophen		Phenoclor				Sovol	Chloro fen	KC-300	KC-400	KC-500	KC-600	Aroclor					
		A40	T64	DP3	DP4	DP5	DP6							1016	1232	1248	1254	1260	1262
triCN																			
135	19	0.029	0.032	2.17	0.088	0.035	0.096	0.025	<0.001	0.011	0.001	0.006	0.003	0.031	0.022	0.005	0.001	0.002	0.002
136	20	0.007	<0.001	0.048	<0.001	<0.001	<0.001	0.008	<0.001	0.001	<0.001	0.001	<0.001	0.002	0.001	0.001	<0.001	<0.001	<0.001
146/124	24/14	0.291	0.184	19.9	0.391	0.169	0.629	0.173	0.009	0.13	0.011	0.064	0.033	0.213	0.106	0.042	0.006	0.011	0.013
137	21	0.017	0.009	0.937	<0.001	<0.001	<0.001	0.009	<0.001	0.008	<0.001	0.002	0.001	0.017	0.011	0.003	0.001	0.001	0.001
125	15	0.014	0.007	0.64	<0.001	<0.001	<0.001	0.013	<0.001	0.01	0.003	0.002	0.001	0.033	0.027	0.005	0.001	0.001	0.001
126	16	0.011	0.008	0.49	<0.001	<0.001	<0.001	0.012	<0.001	0.02	0.001	0.003	0.002	0.031	0.02	0.006	0.001	0.001	0.001
167/127	25/17	0.095	0.019	0.983	0.090	<0.001	<0.001	0.017	<0.001	0.062	0.003	0.006	0.002	0.092	0.061	0.014	0.002	0.001	0.003
123	13	0.004	<0.001	0.107	<0.001	<0.001	<0.001	0.014	<0.001	0.004	<0.001	0.001	<0.001	0.004	0.005	0.001	<0.001	<0.001	<0.001
236	26	0.014	<0.001	0.147	<0.001	<0.001	<0.001	0.01	<0.001	0.002	<0.001	0.001	<0.001	0.007	0.005	0.001	<0.001	<0.001	<0.001
145/138	23/22	0.114	0.013	4.9	0.245	0.074	0.206	0.029	0.004	0.063	0.005	0.01	0.004	0.167	0.144	0.029	0.003	0.003	0.007
128	18	0.03	<0.001	0.131	0.088	<0.001	<0.001	<0.001	<0.001	0.027	0.002	0.002	<0.001	0.069	0.074	0.005	0.001	0.001	0.002
tetraCN																			
1357	42	2.39	0.093	7.4	1.01	0.04	0.216	0.077	<0.001	0.11	0.019	0.044	0.029	0.158	0.037	0.044	0.004	0.005	0.016
1246/1247/1257	33/34/37	10.9	0.259	20.7	10.2	0.212	0.584	0.397	0.005	1.06	0.262	0.231	0.088	1.33	0.286	0.596	0.038	0.024	0.082
1467	47	4.5	0.068	9.17	6.34	0.090	0.281	0.173	<0.001	0.42	0.131	0.102	0.036	0.533	0.127	0.318	0.023	0.01	0.034
1367	44	0.113	0.005	0.120	0.052	<0.001	<0.001	0.017	<0.001	0.016	0.002	0.009	0.01	0.027	0.004	0.005	0.001	<0.001	0.001
1235/1256	28/36	0.483	0.025	1.53	0.603	0.12	0.144	0.094	0.003	0.308	0.073	0.029	0.006	0.269	0.067	0.083	0.01	0.002	0.009
1368/1358	45/43	0.664	0.044	11	2.56	0.116	0.252	0.184	<0.001	0.621	0.117	0.108	0.037	0.591	0.133	0.242	0.02	0.011	0.041
1234/1236	27/29	0.046	<0.001	0.322	<0.001	<0.001	<0.001	0.025	<0.001	0.025	0.003	0.005	0.002	0.022	0.006	0.003	0.001	0.001	0.002
1245/1237	32/30	0.155	0.013	1.694	0.163	0.033	0.079	0.056	<0.001	0.24	0.042	0.023	0.007	0.158	0.042	0.052	0.009	0.003	0.011
1267	39	0.549	0.02	1.240	0.54	0.017	0.072	0.029	<0.001	0.311	0.057	0.025	0.007	0.182	0.039	0.077	0.004	0.002	0.01
1248	35	0.474	0.032	7.25	1.09	0.169	0.317	0.134	<0.001	0.802	0.115	0.081	0.02	0.307	0.135	0.163	0.014	0.008	0.028
1258	38	2.53	0.074	22	12.3	0.422	0.764	0.45	0.003	3.4	0.797	0.343	0.076	0.634	0.46	1.13	0.081	0.025	0.09
2367	48	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1268	40	0.028	0.004	0.489	0.168	<0.001	<0.001	0.017	<0.001	0.134	0.023	0.011	0.003	0.024	0.016	0.025	0.002	0.001	0.004
1458	46	3.34	0.113	3.13	19.8	1.99	0.209	3.197	0.005	0.728	0.168	0.124	0.007	0.023	0.197	0.289	0.033	0.009	0.031
1238	31	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.039	0.021	0.036	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
1278	41	0.195	0.018	1.27	0.666	0.133	0.058	0.069	<0.001	0.816	0.198	0.072	0.011	0.004	0.065	0.14	0.007	0.004	0.01
pentaCN																			
12357/12467	52/60	4.83	1.48	5.34	36.9	5.72	0.468	10.9	0.014	1.33	1.39	1.53	0.309	0.027	0.403	2.98	0.773	0.048	0.105
12457	58	<0.001	0.023	0.377	3.06	0.159	0.079	1.11	<0.001	0.133	0.104	0.068	0.021	0.001	0.036	0.223	0.045	0.004	0.009
12468	61	3.55	0.171	6.97	40.2	0.948	0.534	4.84	<0.001	2.27	1.59	0.882	0.146	0.011	0.484	3.02	0.442	0.042	0.098
12346	50	<0.001	0.044	1.17	5.96	0.159	0.189	0.84	<0.001	0.621	0.528	0.181	0.033	0.003	0.111	0.67	0.091	0.012	0.025
12356	51	<0.001	0.092	1.1	7.56	0.282	0.157	1.365	<0.001	0.791	0.766	0.236	0.049	0.004	0.162	1.198	0.144	0.017	0.044
12456	57	9.65	0.117	2.74	34.7	1.31	0.283	6.987	0.009	2.15	2.31	1.08	0.113	0.008	0.333	2.83	0.639	0.033	0.059
12367	54	0.799	0.015	0.147	0.628	<0.001	0.11	<0.001	0.006	0.067	0.055	0.054	0.03	0.001	0.01	0.077	0.01	0.002	0.007
12478	62	16.8	0.256	3.48	47.7	1.92	0.393	6.539	0.013	3.34	3.22	1.53	0.155	0.011	0.456	3.875	0.608	0.041	0.085
12358	53	4.42	0.048	2.67	38	0.608	0.393	6.023	0.009	2.8	2.56	1.11	0.129	0.008	0.419	3.252	0.591	0.035	0.08
12368	55	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
12458	59	0.894	0.078	3.43	40.8	5.4	0.88	8.82	0.021	2.31	1.88	1.64	0.188	0.01	0.568	3.58	0.753	0.051	0.1
12345	49	<0.001	<0.001	0.391	0.742	<0.001	<0.001	0.951	<0.001	0.409	0.188	0.086	0.011	0.001	0.039	0.123	0.079	0.005	0.01
12378	56	0.567	<0.001	0.216	2.12	1.05	2.48	0.491	<0.001	0.633	0.52	0.23	0.022	0.002	0.051	0.296	0.089	0.024	0.023
hexaCN																			
123467/123567	66/67	10.4	4.01	0.49	8.63	16.2	2.58	25.5	0.099	0.471	1.43	3.69	0.496	0.006	0.11	1.72	2.21	0.249	0.6
123457/123568	64/68	9.35	2.75	0.367	19.5	19.6	2.04	83.9	0.164	0.841	1.98	5	0.456	0.01	0.165	2.51	3.68	0.228	0.26
123578	69	7.12	4.81	0.429	37.6	45.7	1.48	92.7	0.196	1.37	3.59	13.4	0.627	0.017	0.263	4.16	5.63	0.234	0.275
124568/124578	71/72	3.13	1.5	0.367	42.4	45.5	1.13	109	0.245	0.721	1.84	20.1	0.838	0.018	0.277	4.21	6.56	0.271	0.238
123456	63	2.11	1.17	0.332	13.1	11.1	0.76	32.8	0.097	0.801	2.16	4.79	0.277	0.009	0.116	1.849	2.131	0.132	0.15
123458	65	0.13	<0.001	<0.001	13.4	2.55	0.408	30.2	0.081	0.32	0.733	3.69	0.205	0.005	0.099	1.37	1.62	0.077	0.052
123678	70	<0.001	0.212	<0.001	0.243	1.95	1.97	2.52	<0.001	0.014	0.049	0.138	0.036	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
heptaCN																			
1234567	73	1.61	15.3	0.199	3.24	53.7	46.7	105	5.19	0.734	2.97	16.9	3.82	0.026	0.109	0.838	8.29	7.19	11.4
1234568	74	0.153	5.85	0.012	5.2	99.5	23	157	3.57	0.294	1.1	41.2	5.41	0.021	0.069	0.837	9.3	2.86	13.3
octaCN																			
12345678	75	0.079	47.4	<0.001	2.34	37.8	138	38.6	398	0.398	0.879	41.3	94.4	0.098	0.433	0.378	3.23	55.5	50.5
total		102.5	86.4	147.9	460.3	354.6	227.5	730.8	408	32.2	33.9	160.3	108.1	5.23	6.8	43.3	47.2	67.2	65.8

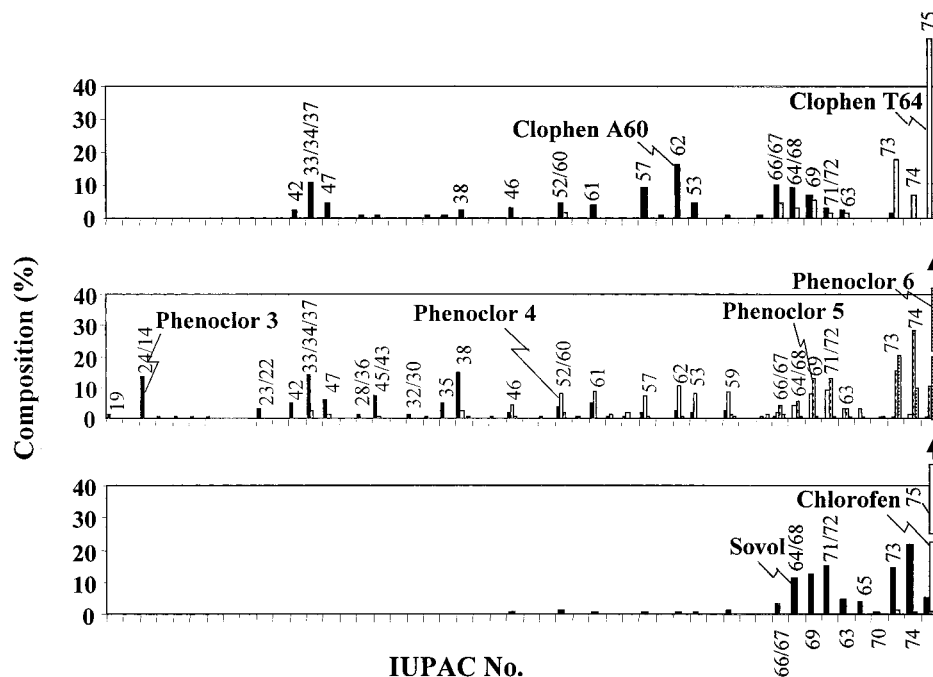


FIGURE 2. Relative composition (%) of individual PCN isomers and congeners in Phenoclor, Sovol, and Chlorofen.

primarily appears to be due to variations in tri-CN concentrations. Although the earlier study had reported the occurrence of 440 $\mu\text{g/g}$ tri-CN in Clophen A40 (7), in this study the concentration of this homologue was 0.63 $\mu\text{g/g}$. Mono-, di- and tri-CN are relatively more volatile congeners than the higher chlorinated congeners. Loss of these congeners during storage of PCB mixtures in the laboratory (though all the mixtures were stored at 4 °C) could be a possibility for the lesser concentrations of tri-CN. Furthermore, variations in analytical conditions for the synthesis of PCBs can alter the composition and concentrations of PCNs. Differences in the composition of PCB mixtures originating from different lots have been reported (26,27).

Absolute and relative concentrations of PCN congeners were determined in three different lots of Aroclor 1254 (Table 2). PCN concentrations varied 3-fold among the three lots. The composition of PCN homologues varied slightly among the three lots. Hexa-CN was the predominant homologue in lots L03E and 6024, whereas both hexa- and hepta-CNs accounted for equal proportions in lot 124–191. These results provide evidence for the variations in PCN content in technical PCB mixtures among lots.

The presence of PCNs in PCB mixtures can be explained by the chlorination of naphthalene, which would occur simultaneously with the chlorination of biphenyl during the production of PCBs, because technical biphenyl contains naphthalene (28). Thus, the chlorination profiles of PCNs formed as byproducts in the technical synthesis of PCBs are expected to follow the chlorination profile of the parent chlorobiphenyl mixture. The average degree of chlorination of the CNs was greater than the corresponding degree of the chlorobiphenyls. For example, hexachlorobiphenyls were the predominant chlorobiphenyl homologues in Aroclor 1260, whereas octa-CN accounted for 83% of the total PCNs in this PCB mixture. This may be due to the greater reactivity of naphthalene than that of biphenyl (29). Concentrations of PCN homologues followed a general trend in most of the PCB mixtures. In general, percentage of individual CN homologues was related to the degree of chlorination of the PCB mixture. Lower-chlorinated PCB mixtures contained relatively greater percentages of less-chlorinated naphthalene congeners, whereas the higher-chlorinated PCBs contained

TABLE 4. 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	435 100 000	39	16 969
UK	Aroclors	66 748 000	39	2 603
Japan	Kanechlors	59 119 000	84	4 966
Germany	Clophens	123 552 000	95	11 737
France	Phenoclor	201 679 000	298	60 100
former USSR	Sovol	100 000 000	730	73 000
total				169 375

greater proportions of more-chlorinated naphthalenes (Figure 1).

Several studies have reported the occurrence of polychlorinated dibenzofurans (PCDFs) as impurities in technical PCB preparations (30–32). Concentrations of total PCDFs in Kanechlors 300, 400, 500, and 600 were 7.5, 26, 7.2, and 5.4 $\mu\text{g/g}$, respectively (31), which were approximately 4, 1.3, 22, and 20-fold less than those of the sum of tri- through octa-CN concentrations in the corresponding mixture. Similarly, concentrations of PCNs (tri- through octa-CN) in Aroclors were 9–12 times greater than those of total PCDFs (31).

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 (Table 3). 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, Phenoclor 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

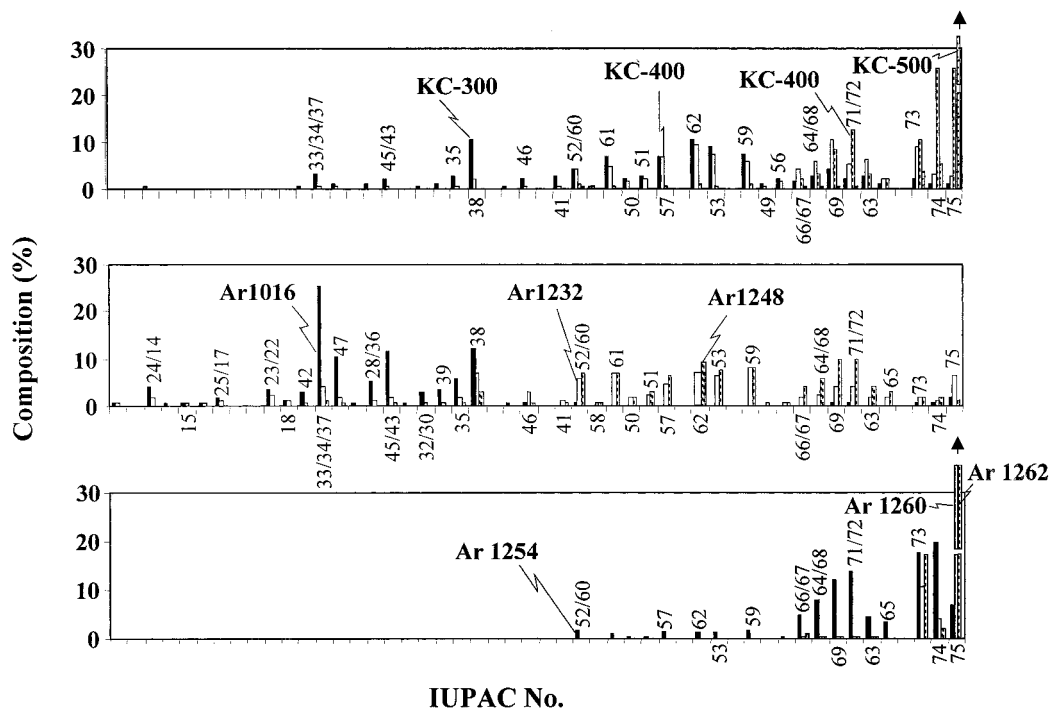


FIGURE 3. Relative composition (%) of individual PCN isomers and congeners in Aroclors and Kanechors.

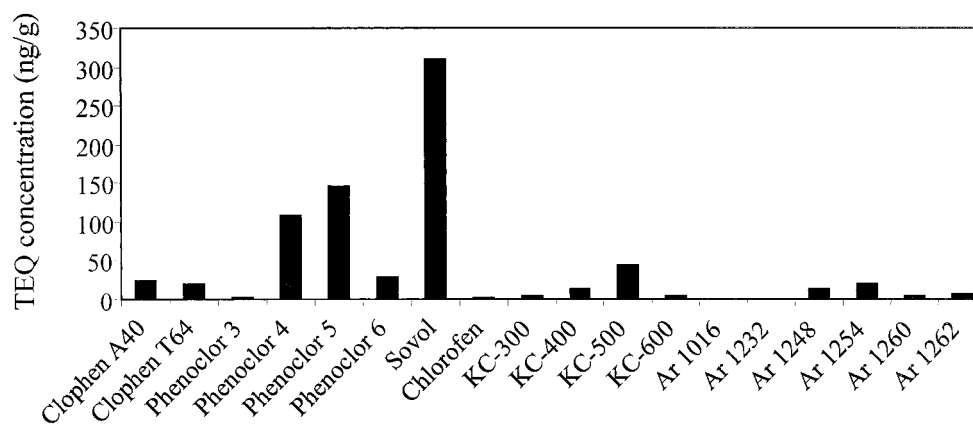


FIGURE 4. Concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) contributed by PCNs in various technical PCB mixtures.

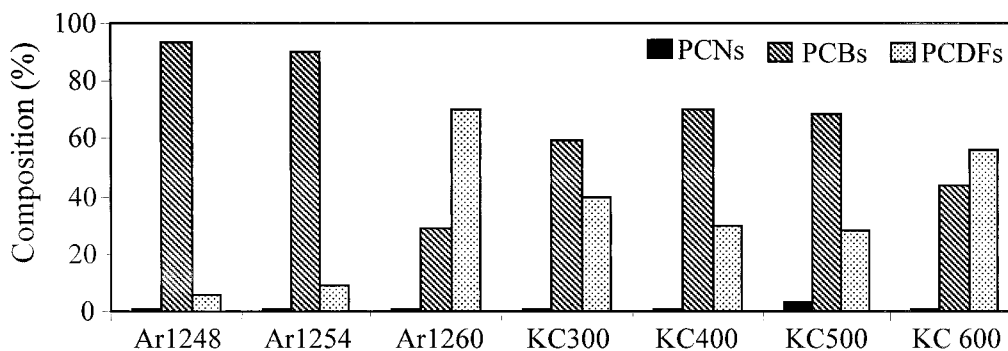


FIGURE 5. Relative contribution of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) of PCBs, PCDFs, and PCNs in technical PCB mixtures.

contained predominant amounts of octa-CN (75), which accounted for greater than 80% of the total PCN concentrations in Kanechlor 600 and Aroclor 1260.

Emission Estimates of PCNs from PCBs. 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 (Kanechors), Germany (Clophen), France (Phenoclor), and the former USSR (Sovol) and mean concentrations of PCNs present in these mixtures were used to estimate PCNs formed as a byproduct (Table 4) (32). 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 (3). This estimate did not include the content of mono- and di-CN, which were not measured in PCB mixtures. Similarly,

PCB mixtures produced in Italy, Spain, Poland, and the former Czechoslovakia were not examined. Further, this estimate is based on the assumption that PCN concentrations measured in these mixtures are representative for all the PCB mixtures produced. 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.

Total national or global production estimates for PCNs are difficult to obtain, but it is known that the annual production from the largest PCN manufacturer, Koppers Company, Pittsburgh, USA, in 1956 was 3200 metric tons, which declined to 2300 metric tons in 1972. The production of technical PCNs by Koppers Company was ceased in 1977 (2).

Toxic Equivalents. Some PCN congeners elicit toxic effects similar to those of TCDD through the AhR-mediated mechanism (18). TEFs (relative potency of congener to that of TCDD) derived from H4IIE rat hepatoma cells have been reported for several chlorinated naphthalene congeners (17). TEQs contributed by PCNs (sum of TEQs of PCN congeners 54, 56, 57, 63, 64/68, 66/67, 69, 70, and 73) were estimated by an additive model by multiplying concentrations of AhR-active PCN congeners by their corresponding TEFs and summing the products. However, all the PCN congeners have not been tested for their dioxin-like potency. 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 (Figure 4).

The greatest PCN-TEQs were observed in Sovol and highly chlorinated Phenoclor mixtures. The major PCN congeners that contributed to TEQs include hexa-CN 63 and 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.

Concentrations of TEQs contributed by non- and mono-ortho coplanar PCBs in various Aroclors have been reported earlier (33,34). TEQs contributed by non- and mono-ortho coplanar PCBs (sum TEQs of chlorobiphenyls 77, 126, 169, 105, 114, 118, 123, 156, 157, and 189) and PCDFs (sum TEQs of ten 2,3,7,8-substituted congeners) were estimated in Aroclors and Kanechlors (24,31,34) to compare with those contributed by PCNs (Figure 5). TEFs for coplanar PCBs, PCDFs, and PCNs derived using H4IIE rat hepatoma cells were used in the calculation (17,35). When H4IIE bioassay-derived TEFs were used to estimate coplanar PCB-TEQs, PCDF-TEQs, and PCN-TEQs in Aroclors and Kanechlors, coplanar PCBs accounted for 50–150 times greater TEQs than those of PCNs. TEQs contributed by PCDFs were greater than those of coplanar PCBs in Aroclor 1260 and Kanechlor 600. Overall, contribution of PCNs to TEQs in Aroclors and Kanechlors was less than 1% 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.

Literature Cited

- (1) Hayward, D. *Environ. Res.* **1998**, *76*, 1–18.

- (2) Crookes, M. J.; Howe, P. D. *Environmental Hazard Assessment: Halogenated Naphthalenes*. Department of the Environment: London, UK, 1993.
- (3) Falandysz, J. *Environ. Pollut.* **1998**, *101*, 77–90.
- (4) Imagawa, T.; Yamashita, N. *J. Environ. Chem.* **1996**, *6*, 495–501.
- (5) Benfenati, E.; Mariani, G.; Faneli, R.; Zuccotti, S. *Chemosphere* **1991**, *22*, 1045–1052.
- (6) Kannan, K.; Imagawa, T.; Blankenship, A. L.; Giesy, J. P. *Environ. Sci. Technol.* **1998**, *32*, 2507–2514.
- (7) Haglund, P.; Jakobsson, E.; Asplund, L.; Athanasiadou, M.; Bergman, Å. *J. Chromatogr.* **1993**, *634*, 79–86.
- (8) Harner, T.; Bidleman, T. F. *Atmos. Environ.* **1997**, *31*, 4009–4016.
- (9) Harner, T.; Kylin, H.; Bidleman, T. F.; Halsall, C.; Strachan, W. M. J.; Barrie, L. A.; Fellin, P. *Environ. Sci. Technol.* **1998**, *32*, 3257–3265.
- (10) Espadaler, I.; Eljarrat, E.; Caixach, J.; Rivera, J.; Martí, I.; Ventura, F. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 410–414.
- (11) Furlong, E. T.; Carter, D. S.; Hites, R. A. *J. Great Lakes Res.* **1988**, *14*, 489–501.
- (12) Kannan, K.; Yamashita, N.; Imagawa, T.; Decoen, W.; Khim, J. S.; Day, R. M.; Summer, C. L.; Giesy, J. P. *Environ. Sci. Technol.* **2000**, *34*, 566–572.
- (13) Falandysz, J.; Strandberg, L.; Bergqvist, P.-A.; Kulp, S. E.; Strandberg, B.; Rappe, C. *Environ. Sci. Technol.* **1996**, *30*, 3266–3274.
- (14) Falandysz, J.; Rappe, C. *Environ. Sci. Technol.* **1996**, *30*, 3362–3370.
- (15) Järnberg, U.; Asplund, L.; de Wit, C.; Egeback, A.-L.; Wideqvist, U.; Jakobsson, E. *Arch. Environ. Contam. Toxicol.* **1997**, *32*, 232–245.
- (16) Lundén, C.; Norén, K. *Arch. Environ. Contam. Toxicol.* **1998**, *34*, 414–423.
- (17) Villeneuve, D. L.; Kannan, K.; Khim, J. S.; Falandysz, J.; Blankenship, A. L.; Giesy, J. P. *Arch. Environ. Contam. Toxicol.* **2000**, (in press).
- (18) Blankenship, A.; Kannan, K.; Villalobos, S.; Villeneuve, D. L.; Falandysz, J.; Imagawa, T.; Jakobsson, E.; Giesy, J. P. *Environ. Sci. Technol.* **2000**, *34*, 3153–3158.
- (19) Vos, J. G.; Koeman, J. H.; Van der Mass, H. L.; ten Noever de Brauw, M. C.; de Vos, R. H. *Food Cosmet. Toxicol.* **1970**, *8*, 625–633.
- (20) Ivanov, V.; Sandell, E. *Environ. Sci. Technol.* **1992**, *26*, 2012–2017.
- (21) Kannan, N.; Schulz-Bull, D. E.; Petrick, G.; Duinker, J. C. *Int. J. Environ. Anal. Chem.* **1992**, *47*, 201–215.
- (22) Schulz, D. E.; Petrick, G.; Duinker, J. C. *Environ. Sci. Technol.* **1989**, *23*, 852–859.
- (23) Falandysz, J.; Yamashita, N.; Tanabe, S.; Tatsukawa, R. *Int. J. Environ. Anal. Chem.* **1992**, *47*, 129–136.
- (24) Boonyathumanondh, R.; Watanabe, S.; Laovakul, W.; Tabucanon, M. *Fresenius' J. Anal. Chem.* **1995**, *352*, 261–267.
- (25) Olivero, J.; Kannan, K. *J. Chromatogr.* **1999**, *849*, 621–627.
- (26) Kodavanti, P. R. S.; Kannan, N.; Yamashita, N.; Derr-Yellin, E. C.; Ward, T. R.; Burgin, D. E.; Birnbaum, L.; Tilson, H. A. *Environ. Health Perspect.* **2000**, (in press).
- (27) Frame, G. M. *J. High Resolut. Chromatogr.* **1999**, *22*, 533–540.
- (28) Albro, P. W.; Parker, C. E. *J. Chromatogr.* **1979**, *169*, 161–168.
- (29) Clar, E.; Zander, M. *J. Chem. Soc.* **1958**, 1861–1865.
- (30) Buser, H.-R. *Environ. Health Perspect.* **1985**, *60*, 259–267.
- (31) Wakimoto, T.; Kannan, N.; Tatsukawa, R.; Masuda, Y. *Chemosphere* **1988**, *17*, 743–750.
- (32) Giesy, J. P.; Kannan, K. *Crit. Rev. Toxicol.* **1998**, *28*, 511–569.
- (33) Hong, C.-S.; Bush, B.; Xiao, J.; Qiao, H. *Arch. Environ. Contam. Toxicol.* **1993**, *25*, 118–123.
- (34) Schwartz, T. R.; Tillitt, D. E.; Feltz, K. P.; Peterman, P. H. *Chemosphere* **1993**, *26*, 1443–1460.
- (35) Giesy, J. P.; Jude, D. J.; Tillitt, D. E.; Gale, R. W.; Meadows, J. C.; Zajack, J. L.; Peterman, P. H.; Verbrugge, D. A.; Sanderson, J. T.; Schwartz, T. R.; Tuchman, M. L. *Environ. Toxicol. Chem.* **1997**, *16*, 713–724.

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