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Congener-Specific Carbon Isotopic Analysis of Technical PCB and PCN Mixtures Using Two-Dimensional Gas Chromatography−Isotope Ratio Mass Spectrometry

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Analysis of stable carbon isotope fractionation is a useful method to study the sources and fate of anthropogenic organic contaminants such as polychlorinated biphenyls (PCBs) in the environment. To evaluate the utility of carbon isotopes, determination of isotopic ratios of $^{13}C/^{12}C$ in source materials, for example, technical PCB preparations, is needed. In this study, we determined $\delta^{13}C$ values of 31 chlorobiphenyl (CB) congeners in 18 technical PCB preparations and 15 chloronaphthalene (CN) congeners in 6 polychlorinated naphthalene preparations using two-dimensional gas chromatography−combustion furnace−isotope ratio mass spectrometry (2DGC−C−IRMS). Development of 2DGC−IRMS enabled improved resolution and sensitivity of compound-specific carbon isotope analysis (CSIA) of CB or CN congeners. $\delta^{13}C$ values of PCB congeners ranged from −34.4 (Delors) to −22.0‰ (Sovol). Analogous PCB preparations with similar chlorine content, but different geographical origin, had different $\delta^{13}C$ values. PCB preparations from Eastern European countries—Delors, Sovol, Trichlorodiphenyl, and Chlorofen—had distinct $\delta^{13}C$ values. PCB mixtures showed increased ^{13}C depletion with increasing chlorine content. $\delta^{13}C$ values for individual CB congeners varied depending on the degree of chlorination in technical mixtures. $\delta^{13}C$ values of CN congeners in Halowaxes ranged from −26.3 to −21.7‰ and these values are within the ranges observed for PCBs. This study establishes the range of $\delta^{13}C$ values in technical PCB and PCN preparations, which may prove to be useful in the determination of sources of these compounds in the environment. This is the first study to employ 2DGC−IRMS analysis of $\delta^{13}C$ values in technical PCB and PCN preparations.

Introduction

Stable isotopic composition of carbon has been used in the study of biogeochemical processes over the last few decades. Variations in the isotopic ratio of $^{13}C/^{12}C$ in environmental matrixes have been used in the understanding of environmental biogeochemistry of natural and synthetic hydrocarbons (*1*−*4*). In recent years, stable carbon isotopic analysis is becoming increasingly popular in understanding sources and fate of anthropogenic organic contaminants in the environment (*5*−*9*). In particular, compound-specific carbon isotope analysis (CSIA) of complex mixtures using gas chromatography−isotope ratio mass spectrometry (GC−IRMS) is emerging as a powerful analytical tool to trace the origin and fate of organic compounds (*10*, *11*).

A few studies have reported on the CSIA of polychlorinated biphenyl (PCB) mixtures such as Aroclors, Kanechlors, and Phenoclors (*5*, *12*, *13*). To our knowledge, no earlier study has reported on CSIA of polychlorinated naphthalenes (PCNs). Similarly, CSIA of PCB mixtures produced in Poland (Chlorofen), former USSR (Sovol and Trichlorodiphenyl), and Czechoslavakia (Delor) has not yet been performed. Although traditional approaches such as fingerprinting, which involves matching of the isomer profiles in samples with that in technical preparations, have been used to determine sources of anthropogenic chemicals, such techniques are more qualitative than quantitative. Therefore, development of alternative approaches is required to complement the existing methods to understand the sources and environmental destiny of man-made chemicals.

Earlier studies of CSIA employed a gas chromatograph (GC) interfaced with an isotope ratio mass spectrometer (IRMS) (*14*, *15*). In this study, we developed two-dimensional gas chromatograph (2DGC)/combustion furnace (C)/IRMS and applied for congener-specific carbon isotopic analysis of PCB and PCN mixtures. The objectives of this study were to develop and validate the 2DGC−C−IRMS technique to determine isotopic analysis of carbon, and to determine congener-specific $\delta^{13}C$ values of CB and CN congeners in several PCB and PCN preparations produced in the United States, Japan, Germany, France, former USSR, Poland, and former Czechoslovakia to establish baseline data for future studies. Two-dimensional gas chromatography enabled increased sensitivity due to the reduction in background, and improved specificity due to the elimination of coeluting compounds.

Materials and Methods

Chemicals. Japanese technical PCB preparations (Kanechlors (Kanechlors 300, 400, 500, and 600)), U.S. technical PCB preparations (Aroclors (Lot 505; Aroclors 1221, 1242, and 1254)), and individual CB congeners (2,2′,4-triCB (CB17), 2,3,5,6-tetraCB (CB65), 2,2′,3,5,5′,6-hexaCB (CB151)) were purchased from GL Sciences Inc. (Tokyo, Japan) and Nanogen Analytical Standards (Watsonville, CA). Russian PCB formulations (Sovol and Trichlorodiphenyl (TCP)), and Polish PCB formulation (Chlorofen) were kindly provided by Prof.

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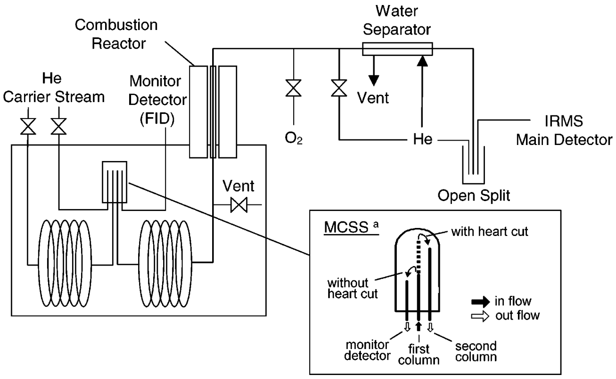

FIGURE 1. Schematic view of the two-dimensional gas chromatography/combustion furnace/isotope ratio mass spectrometer; MCSS: moving capillary stream switching.

Jerzy Falandysz (University of Gdañsk, Poland). German, French, and Czech PCB preparations (Clophens (A30, A40, A50), Phenoclors (DP-3, DP-4, DP-6), and Delors (103, 106)) were also analyzed (*16, 17*). Halowax formulations (Halowax-Kit RC076 (HW 1000, 1001, 1013, 1014, 1051, and 1099)) were obtained from Analab Inc. (Bridgeport, NJ). Technical PCB and PCN preparations were dissolved in *n*-hexane at a concentration of approximately 0.5−3 μg/μL.

2DGC−C−IRMS Analysis. CSIA of PCBs and PCNs was carried out using a 2DGC equipped with Finnigan MAT252 IRMS with a combustion furnace (Figure 1). The 2DGC system was built from a Trace GC 2000 (Thermo Electron, San Jose, CA) equipped with moving capillary stream switching (MCSS) (CE Instruments, Mainz-Kastel, Germany) (*18−21*). The MCSS technique cuts parts of effluents from the first column, and transfers almost all of the target compounds into the second column. The outlet of the first column was diverted to the inlet of the second column, both installed in a dome -shaped glass tip, located inside a GC oven. These cut functions were programmed according to the retention time of target congeners on a monitor detector (flame ionization detector; FID) connected to a dome. The FID was operated at 280 °C, with ultrapure hydrogen and air as makeup gases at a flow of 35 and 350 mL/min, respectively. First and second column flow rates were kept at 1.5−2 mL/min.

Individual PCB and PCN congeners were separated by a less-polar capillary column, DB-5 (30 m × 0.25 mm i.d. × 0.25 μm; J&W Scientific, Foster City, CA), cut by MCSS and separated again on another column (Rtx-200, 15 m × 0.32 mm i.d. × 0.25 μm, Restek Corp., Bellefonte, PA). The column oven temperature for PCBs was programmed from 70 (1 min) to 180 °C at a rate of 15 °C/min, and to 260 °C at 2 °C/min, which was held for 5 min. The column oven temperature for PCNs was programmed from 70 (1 min) to 180 °C at a rate of 15 °C/min, and to 260 °C at 4 °C/min, which was held for 10 min. One μL of PCB and PCN mixtures was injected manually in a splitless mode at 260 °C. PCB and PCN congeners were identified based on the retention times published previously (*16, 17, 22−26*).

Effluents from the second column were combusted to CO_2 in an oxidation reactor through a T-piece connection, at the exit of the chromatographic column. The furnace temperature was held at 940 °C. The combustion reactor consisted of an alumina tube packed with metal oxide (copper, nickel, and platinum wires). Moisture resulting from the combustion was removed from the sample stream via a tubular water separator (Nafion membrane). Reoxidation of the combustion furnace catalysts was performed once a day by oxygen backflow for 20 min.

CO_2 produced by combustion of chromatographic effluents continuously enters the ion source of the MAT 252 IRMS through an open split. Ion currents were monitored at m/z 44, 45, and 46, continuously. Ions were generated by electron impact (70 eV), and accelerating voltage was kept at 10 kV. Isotopic compositions were reported in parts per thousand, per mil (‰), and all values reported are relative to the international standard by conventional delta (δ) notation:

$$\delta^{13}\mathrm{C}\ (‰) = [(R_{\mathrm{sample}}/R_{\mathrm{standard}}) - 1] \times 1000$$

where $R = {}^{13}C/{}^{12}C$. The CO_2 reference gas was calibrated by

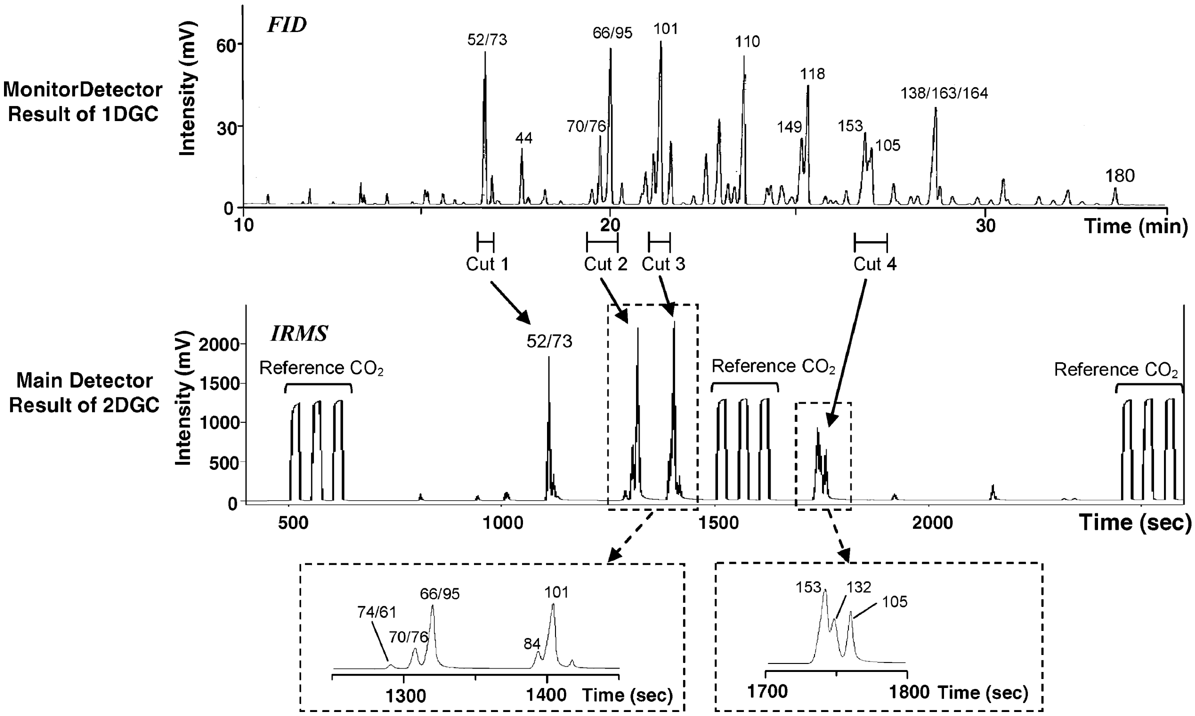

FIGURE 2. Flame ionization detector (FID) chromatogram and isotope ratio mass chromatogram of *m/z* 44 for Kanechlor 500. Peaks are denoted by the IUPAC number of PCB congeners. First and second columns were DB-5 and Rtx-200, respectively.

TABLE 1. Congener-Specific δ^{13}C Values for PCB Congeners in Eighteen Technical PCB Mixtures, by Country and Period of Manufacture

		Japan (1954−1971)				United States (1930−1975)			Germany (1930−1982)			France (NA)			Czechoslovakia (1959−1984)		Soviet Union (1939−1993)		Poland (1966−1970)
	Cl content (% by weight)	40−42	48	52−54	60	21	40−42	52−54	40−42	48	52−54	40−42	48	60			41	53	70
		KC 300	KC 400	KC 500	KC 600	A 1221[a]	A 1242	A 1254	A30[a]	A40	A50	DP-3[b]	DP-4	DP-6	D 103[b]	D 106	Sovol	TCP	Chlorofen
congener	structure																		
biphenyl						−25.2													
1	2-					−27.2													
3	4-					−24.7													
10/4	2,6-/2,2′-	−23.9					−25.9		−26.5			−27.3			−31.3			−22.7	
8/5	2,4′-/2,3-	−24.0					−26.2		−27.3			−27.7			−31.4			−23.1	
18	2,2′,5-	−25.3	−24.2				−26.9		−28.2	−25.5		−28.9	−25.6		−33.2			−23.9	
16/32	2,2′,3-/2,4′,6-	−25.4	−23.2				−26.7		−28.0	−25.8		−29.2	−24.8		−33.0			−24.7	
31/28	2,4′,5-/2,4,4′-	−25.4	−24.1				−26.7		−27.7	−26.9		−29.0	−25.8		−32.8			−24.8	
33/20/53	2,3′,4′-	−25.6	−24.0				−26.3		−28.1	−26.7		−29.1	−26.6		−33.1			−24.6	
52/73	2,2′,5,5′-/2,3′,5′,6-	−26.4	−25.8	−25.7			−27.7	−26.3	−28.8	−29.2	−27.1	−30.0	−28.0		−34.0		−23.4	−25.1	
43/49	2,2′,3,5-/2,2′,4,5′-	−25.9	−25.5	−24.2			−27.0	−25.0	−28.1	−28.1	−26.0		−27.4		−32.8			−24.6	
47/75/48	2,2′,4,4′-/2,4,4′,6-/2,2′,4,5-		−25.3				−27.2			−26.6			−26.0						
44	2,2′,3,5′-	−26.0	−25.5	−24.9			−27.3	−25.3	−29.0	−28.6	−26.6		−27.3		−33.9			−24.6	
59/42	2,3,3′,6-/2,2′,3,4′-		−25.7				−27.6		−27.2	−28.5		−29.2	−27.3		−31.7			−25.9	
74/61	2,4,4′,5-/2,3,4,5-		−25.1				−26.7			−26.5			−27.9						
70/76	2,3′,4′,5-/2,3′,4′,5′-		−24.8	−22.4			−26.7	−24.0	−28.5	−27.6	−26.1		−27.3		−33.1		−22.0		
66/95	2,3′,4,4′-/2,2′,3,5′,6-		−25.3	−25.8	−25.0		−27.0	−26.5	−28.4	−28.4	−27.2		−27.5	−26.1	−33.1	−31.6	−23.6	−25.2	
89/101/90	2,2′,3,4,6′-/2,2′,4,5,5′-/2,2′,3,4′,5-		−28.5	−27.6	−24.8			−27.4		−31.2	−28.3		−30.7	−26.8		−31.3	−27.1		
110	2,3,3′,4′,6-		−27.5	−26.3				−27.3		−29.9	−28.1		−29.5			−31.2	−25.3		
149/139	2,2′,3,4′,5′,6-/2,2′,3,4,4′,6-			−27.5	−25.9			−27.8			−29.7			−28.6		−32.6			
118/106	2,3′,4,4′,5-/2,3,3′,4,5-		−26.2	−25.9				−26.4		−27.8	−27.4		−29.1			−30.9	−25.1		
153/132/168	2,2′,4,4′,5,5′-/2,2′,3,3′,4,6′-/2,3′,4,4′,5′,6-		−26.4	−27.0	−25.5			−27.2			−28.4			−28.6		−32.0	−25.1		−23.0
105	2,3,3′,4,4′-		−25.8	−26.1				−27.1			−28.2		−29.0				−25.0		
164/163/138	2,3,3′,4′,5′,6-/2,3,3′,4′,5,6-/2,2′,3,4,4′,5′-			−27.1	−25.8			−27.5			−30.5			−28.8		−32.5	−26.4		
182/187	2,2′,3,4,4′,5,6′-/2,2′,3,4′,5,5′,6-				−27.7									−29.8		−34.2			−25.4
174	2,2′,3,3′,4,5,6′-				−27.8									−29.7		−34.2			
180	2,2′,3,4,4′,5,5′-				−27.3									−30.0		−34.4			−24.9
170/190	2,2′,3,3′,4,4′,5-/2,3,3′,4,4′,5,6-				−26.5									−29.4		−33.2			
199	2,2′,3,3′,4,5,5′,6′-				−28.9														−26.6
203/196	2,2′,3,4,4′,5,5′,6-/2,2′,3,3′,4,4′,5,6′-				−28.2														−25.8
194	2,2′,3,3′,4,4′,5,5′-				−28.5														−25.8
206	2,2′,3,3′,4,4′,5,5′,6-																		−27.8
	mean	−25.3	−25.5	−25.9	−26.8	−25.7	−26.9	−26.5	−28.0	−27.8	−27.8	−28.8	−27.5	−28.6	−32.8	−32.5	−24.8	−24.5	−25.6
	maximum	−23.9	−23.2	−22.4	−24.8	−24.7	−25.9	−24.0	−26.5	−25.5	−26.0	−27.3	−24.8	−26.1	−31.3	−30.9	−22.0	−22.7	−23.0
	minimum	−26.4	−28.5	−27.6	−28.9	−27.2	−27.7	−27.8	−29.0	−31.2	−30.5	−30.0	−30.7	−30.0	−34.0	−34.4	−27.1	−25.9	−27.8

[a] A1221, A1242, and A1254 are Aroclors; A30, A40, and A50 are Clophens. [b] DP-3, DP-4, and DP-6 are Phenoclors; D103 and D106 are Delors.

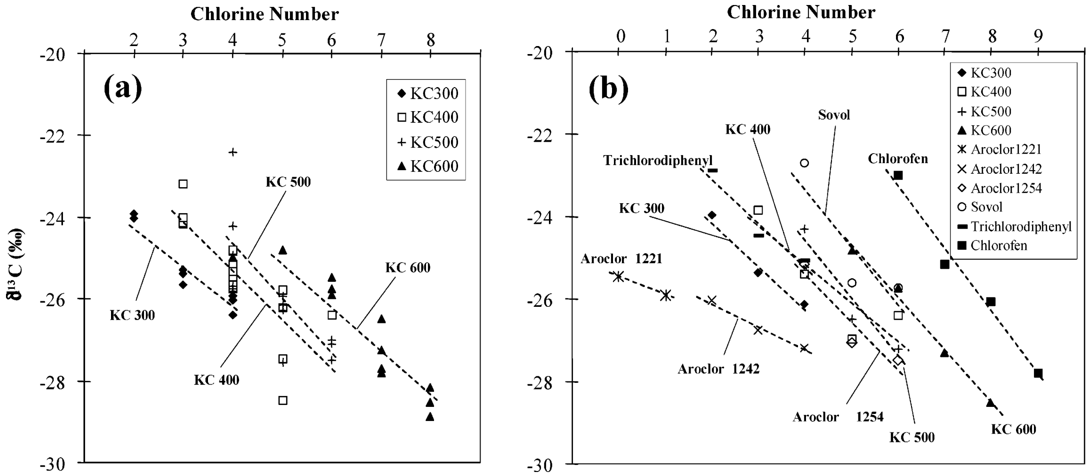

FIGURE 3. **$\delta^{13}C$ values for selected PCB congeners and homologues in several PCB preperations: (a) profile of PCB congeners in Kanechlors, and (b) profile of PCB homologues in several technical PCB mixtures. $\delta^{13}C$ values for each homologue are represented by average of congener values.**

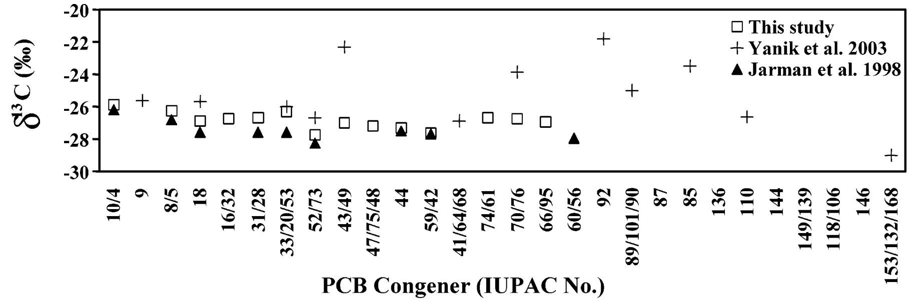

FIGURE 4. **$\delta^{13}C$ values for Aroclor 1254 determined in this study compared with those reported earlier by Jarman et al. (*12*) and Yanik et al. (*13*).**

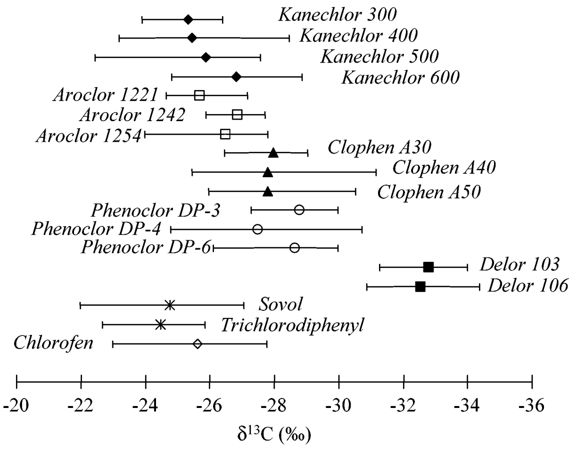

FIGURE 5. **Plot of mean and range of $\delta^{13}C$ values in commercial PCB mixtures.**

isotopic ratio reference gas from Oztech Co. (Dallas, TX) (SHOKO-944C), $\delta^{13}C = -40.84$ versus the Pee Dee Belemnite.

Quality Assurance/Quality Control. The stability of the 2DGC−C−IRMS system and background were checked daily. CBs17, 65, and 151 were analyzed at the beginning and at the end of sample measurements for quality control. The standard deviation of repeated measurements of these three standards was <0.4‰ throughout the analysis ($n = 60$). Samples containing different concentrations, ranging from 7 to 62 ng carbon, were analyzed in triplicate to test the combustion of carbon to CO_2 under the system conditions specified above. Peak areas were linear ($R^2 > 0.99$) and $\delta^{13}C$ values were stable with a corresponding standard deviation that ranged from 0.06 to 0.26 for the three PCB congeners.

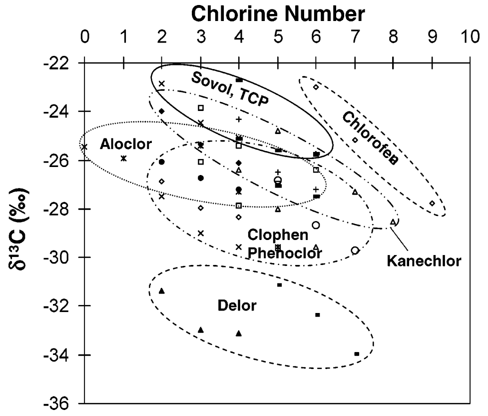

FIGURE 6. **Plot of ranges of $\delta^{13}C$ values for various PCB preparations.**

Each sample was analyzed several times. Calculated isotope ratios were reported as below the limit of obtaining stable data if peak area was not above the threshold amount (300 mV).

Results and Discussion

Technical PCBs. Two-dimensional gas chromatographic separation enabled significant improvement in the resolution and sensitivity of individual CB isomers by at least an order of magnitude better than the traditional one-dimensional GC−IRMS method. FID and 2DGC−IRMS chromatograms of Kanechlor 500 are shown in Figure 2. The FID chromatogram shows separation of PCB congeners in Kanechlor 500 on the first column. Only selected congeners were transferred into the second column by MCSS for the determination of $\delta^{13}C$ (Figure 2). For example, CB 105 was separated on the

TABLE 2. Congener-Specific $\delta^{13}C$ Values for PCN Congeners in Halowax Mixtures

	Cl weight (%)	23	27	49	55	60	49
PCN congener	structure	HW 1000	HW 1001	HW 1013	HW 1014	HW 1051	HW 1099
2/1	2-/1-	−23.6					
5/6/7/12	1,4-/1,5-/1,6-/2,7-	−26.3	−22.4				
9	1,8-	−25.5					
21/24/14	1,3,7-/1,4,6-/1,2,4-		−24.7	−23.0			−24.1
23	1,4,5-		−23.5				−22.2
33/34/37	1,2,4,6-/1,2,4,7-/1,2,5,7-		−25.3	−24.3	−24.0		−24.4
38/40	1,2,5,8-/1,2,6,8-		−25.6	−24.4	−22.9		−24.6
46	1,4,5,8-		−25.1	−23.9	−23.0		−24.0
52/60	1,2,3,5,7-/1,2,4,6,7-				−23.0		
61	1,2,4,6,8-			−24.4	−22.9		
59	1,2,4,5,8-			−25.2	−23.5		
71/72	1,2,4,5,6,8-/1,2,4,5,7,8-				−25.6		
65	1,2,3,4,5,8-				−26.0		
73/74	1,2,3,4,5,6,7-/1,2,3,4,5,6,8-					−21.7	
75	1,2,3,4,5,6,7,8-					−24.9	
	average	−25.1	−24.4	−24.2	−23.9	−23.3	−23.8
	maximum	−23.6	−22.4	−23.0	−22.9	−21.7	−22.2
	minimum	−26.3	−25.6	−25.2	−26.0	−24.9	−24.6

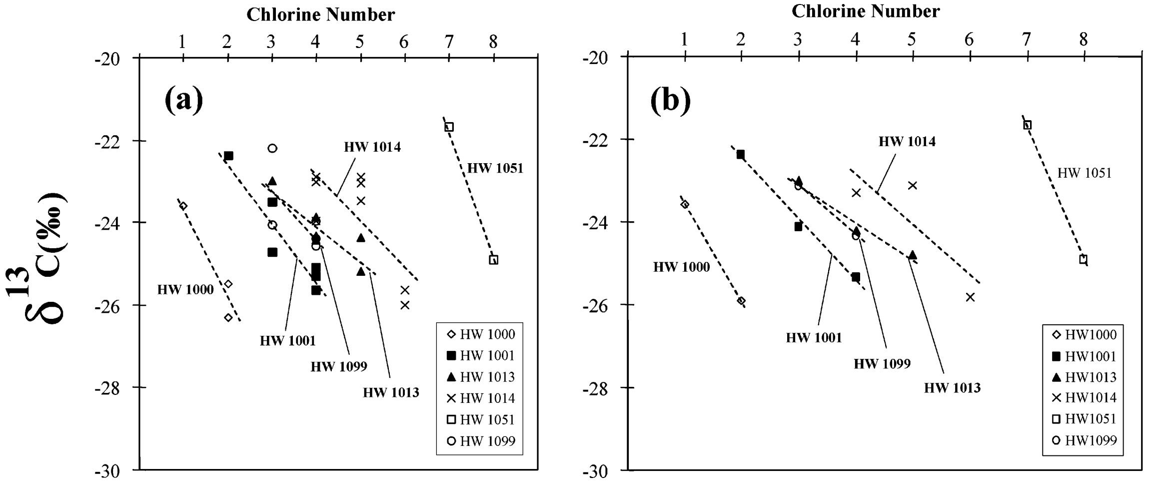

FIGURE 7. $\delta^{13}C$ values for selected PCN (a) congeners and (b) homologues. $\delta^{13}C$ values for each homologue are represented by average of congener values.

second column from other coeluting peaks. The isotopic composition of the reference gas, CO_2, was measured at multiple time points within a single chromatographic analysis (Figure 2). In CSIA, using single GC−C−IRMS, all organic compounds in samples are transferred to the oxidation furnace and combusted to CO_2. This results in high background and low sensitivity since the combustion furnace has to handle a large amount of carbon for oxidation. In a 2DGC−C−IRMS by MCSS, only target compounds, which are selected based on retention times identified using the monitor detector (FID, in this case), are transferred to the oxidation furnace via a second column. The background signal of m/z 44 is significantly reduced to 10 mV even at high temperature (260 °C) due to the avoidance of column bleed or solvent peaks. The $\delta^{13}C$ value for the test sample is calculated by comparison between reference isotope ratios and that of the sample. Estimated sensitivity of carbon using 2DGC−C−IRMS is less than 7 ng, which corresponds to 10−20 ng of individual PCB congeners. Such an improvement in resolution and sensitivity would also benefit CSIA analysis of environmental matrixes.

Thirty-one PCB congeners were selected in 18 technical PCB preparations for the determination of $\delta^{13}C$. $\delta^{13}C$ values of individual PCB congeners ranged from −34.4 (CB180, Delor 106) to −22.0‰ (CB70/76, Sovol) (Table 1). $\delta^{13}C$ values decreased with an increase in chlorination of technical PCB mixtures (Figure 3). It is worthy of mention that lower chlorinated CB congeners had higher $\delta^{13}C$ values in each technical PCB mixture, which might be influenced by isomer specific isotopic partitioning. However, the adverse phenomenon was found in $\delta^{13}C$ values of individual CB congeners between the same series of technical PCB mixtures. For example, $\delta^{13}C$ value for tetra CB−CB44 in Kanechlor 300 was lower than $\delta^{13}C$ values for the same congeners in Kanechlor 500. Jarman et al. (*12*) reported that CB70 (2,3′,4′,5-) was isotopically heavier than CB52 (2,2′,5,5′-) in technical PCBs. Mean $\delta^{13}C$ values for various CB homologues in several technical PCB preparations are shown in Figure 3. Similar to the studies by Jarman et al. (*12*) and Drenzek et al. (*5*), in general, increase in chlorination of a technical mixture resulted in increased depletion of ^{13}C.

$\delta^{13}C$ values of CB congeners determined in this study were compared with those reported earlier (Figure 4) (*12*, *13*). Whereas $\delta^{13}C$ values for several CB congeners were comparable among the three investigations, variations did exist for a few congeners. Particularly, $\delta^{13}C$ values of certain coeluting CB congeners 43/49 and 70/76 varied highly, by approximately 4‰ between this study and that by Yanik et al. (*13*). On the other hand, $\delta^{13}C$ values for CB153 and CB138 were within ±0.5‰ among the three investigations. Drenzek et al. (*5*) reported $\delta^{13}C$ values for bulk Aroclors from three different suppliers and found a narrow range, with a mean value of -26.17 ± 0.37‰ ($n = 10$). There was no apparent bias in $\delta^{13}C$ values between suppliers. The accuracy of GC−C−IRMS analysis is generally greater than 0.5‰ (*27*). Therefore, the observed discrepancy in $\delta^{13}C$ values for individual CB congeners between studies is less likely due to analytical variation. The variations in $\delta^{13}C$ values for CB congeners between this study and those of others may be due to the source of the material (suppliers) and the analytical conditions. As mentioned earlier, 2DGC technique allowed high resolution of individual congeners and significantly reduced noise (background) due to low column bleed and avoidance of solvent peaks.

Means and ranges of $\delta^{13}C$ values in 18 technical PCB mixtures are shown in Figure 5. $\delta^{13}C$ values of technical PCB preparations ranged from −34.4‰ (Delors) to −22.0‰ (Sovol). However, within a PCB series, $\delta^{13}C$ value varied from 2 to 6‰. Interestingly, $\delta^{13}C$ values for Delors, Chlorofen, Sovol, and Trichlorodiphenyl had distinct $\delta^{13}C$ values compared to other technical PCB preparations (Figure 6). In general, Delors had more depleted ^{13}C than other technical PCB preparations. On the other hand, Sovol, Chlorofen, and Trichlorodiphenyl had higher $\delta^{13}C$ values compared to other technical PCB mixtures analyzed in this study.

Technical PCNs. $\delta^{13}C$ values of fifteen individual congeners in Halowaxes ranged from −26.3 (CN5/6/7/12, HW 1000) to −21.7‰ (CN73/74, HW 1051) (Table 2). This range is comparable to that found for technical PCB preparations. Similar to that found for PCBs, $\delta^{13}C$ values decreased with increasing chlorination in Halowax series (Figure 7). Furthermore, $\delta^{13}C$ values for individual CN congeners increased with increasing chlorination of technical mixtures. For instance, $\delta^{13}C$ values of 1,4,5,8-tetraCN (CN46) in Halowaxes 1001, 1013, and 1014 were −25.1, −23.9, and −23.0‰, respectively, suggesting an ^{13}C depletion with decreasing chlorination in the same congeners in each Halowax. This is the first report of $\delta^{13}C$ values of individual congeners of PCNs. These values provide baseline data for future studies to understand biogeochemical processes of these complex mixtures.

These results indicate that the number and substitution pattern of chlorine atoms effect the ^{13}C fractionation of the individual congeners in a systematic fashion. Variations in isotopic ratios among technical preparations from different countries may be related to the manufacturing process and is probably related to a kinetic isotope effect at the positions of chlorination. During production, biphenyl or naphthalene is reacted with chlorine and iron chloride (*28*−*30*). In this process, hydrogen bonded to ^{12}C may be replaced by chlorine relatively easily to hydrogen bonded to ^{13}C. Geographical differences in the $\delta^{13}C$ values among PCB preparations, particularly those of Delors, Sovol, Trichlorodiphenyl, and Chlorofen, suggest possible differences in the raw materials used in production and production processes.

$\delta^{13}C$ values determined for PCB and PCN congeners were similar to those from petroleum and terrestrial plants (Figure 8). However, these values are apparently different from those of carbonates and marine plants (*31*, *32*). This suggests that carbon for the production of industrial chemicals comes primarily from fossil petroleum. Individual congeners of PCBs and PCNs, however, exhibit a wide range of $\delta^{13}C$ values, some of which are lower than those associated with terrestrial petroleum. Although it is necessary to obtain more information regarding $\delta^{13}C$ values of manmade chemicals, CSIA by accurate instrumental methods such as 2DGC seems to be a promising tool to reveal isotopic partitioning by unknown environmental and geochemical processes. Production processes in industries and human activities such as waste incineration may be the reasons for the observed variations in $\delta^{13}C$ values. Further studies will focus on measuring $\delta^{13}C$ values for PCBs and PCNs in environmental matrixes.

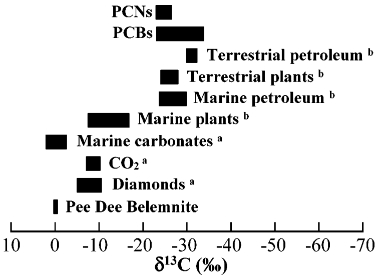

FIGURE 8. $\delta^{13}C$ values of some important carbon reservoirs and chlorinated hydrocarbons. Values for petroleum, plants, CO_2, diamond, and Pee Dee Belemnite are from refs *31* (a) and *32* (b).

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