

## Characterization of Halogenated Organic Pollutants Using Congener-Specific Carbon Isotopic Analysis

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### 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  $^{13}\text{C}/^{12}\text{C}$  in environmental matrixes have been used in the understanding of environmental biogeochemistry of natural and synthetic hydrocarbons. In recent years, stable carbon isotopic analysis is becoming increasingly popular in understanding sources and fate of anthropogenic organic contaminants in the environment. In particular, compound-specific carbon isotope analysis (CSIA) of complex formulations 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.

A few studies have reported on the CSIA of polychlorinated biphenyl (PCB) formulations such as Aroclors, Kaneclors, and Phenoclor<sup>(1)</sup>. To our knowledge, no earlier study has reported on CSIA of polychlorinated naphthalenes (PCNs). Similarly, CSIA of PCB formulations produced in Poland (Chlorofen), former USSR (Sovol, Trichlorodiphenyl), and Czechoslovakia (Delor) has not yet been performed. Although traditional approaches such as fingerprinting, which involve matching of the isomer profiles in samples with that in technical formulations, 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.

The objectives of this study were to develop and validate two-dimensional gas chromatograph (2DGC)/combustion furnace (C)/ isotope ratio mass spectrometry (IRMS) for isotopic analysis of carbon, and to determine congener-specific  $\delta^{13}\text{C}$  values for CB and CN congeners in several PCB and PCN formulations produced in the US, Japan, Germany, France, former USSR, Poland, and former Czechoslovakia, as well as selected solvents of volatile organic compounds (VOCs) from 4 different manufactures to establish baseline data for future studies.

### Materials and Methods

**Chemicals.** Japanese technical PCB formulations (Kanechlor 300, 400, 500, and 600) were purchased from GL Sciences Inc. (Tokyo, Japan). US technical PCB formulations (Aroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268) were purchased from Nanogen Analytical Standards (Watsonville, CA, USA) and AccuStandard Inc. (New Haven, CT, USA). Russian PCB formulations (Sovol and Trichlorodiphenyl (TCP)), Polish PCB formulation (Chlorofen), German PCB formulations (Clophen A30, A40, A50, T64), French PCB formulations (Phenoclor DP-3, DP-4, DP-6), and Czech PCB formulations (Delor 103, 106) were also analyzed. Halowax formulations, Halowaxes (HW 1000, 1001, 1013, 1014, 1031, 1051, and 1099), were obtained from Analab Inc. (Bridgeport, NJ). Technical PCB and PCN formulations were dissolved in *n*-hexane at concentrations of approximately 0.5-3  $\mu\text{g}/\mu\text{L}$ . Seventeen VOC solvents were purchased from 4 different manufactures (Fig. 1) and were diluted in nonane and methyl-*t*-butyl ether at concentrations of approximately 0.3-3  $\mu\text{g}/\mu\text{L}$ .

**2DGC-C-IRMS analysis.** CSIA of PCBs, PCNs and VOCs was carried out using a 2DGC equipped with Finnigan MAT252 IRMS with a combustion furnace. 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) <sup>(2)</sup>.

Individual PCB and PCN congeners were separated by a less-polar capillary column, DB-5 (30 m x 0.25 mm i.d. x 0.25  $\mu$ m; J&W Scientific, Foster City, CA, USA), cut by MCSS and separated again on another column (Rtx-200, 15 m x 0.32 mm i.d. x 0.25  $\mu$ m, Restek Corp., Bellefonte, PA, USA). The column oven temperature for PCBs was programmed from 70°C (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°C (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 to two  $\mu$ L of PCB and PCN mixtures was injected manually in a splitless mode at 260°C. VOCs were separated by Rtx-VGC (60 m x 0.25 mm i.d. x 1.4  $\mu$ m, Restek Corp., Bellefonte, PA, USA). The column oven temperature for VOCs was programmed from 40°C (4 min) to 80°C at a rate of 5°C/min, and to 220°C at a rate of 20°C/min, which was held for 5 min. One  $\mu$ L of VOC samples was injected manually in a split mode at a split ratio 10 at 230°C. First and second column flow rates were kept at 1.5-2 ml/min.

Effluents from the second column were combusted to CO<sub>2</sub> in an oxidation reactor, at the exit of the chromatographic column. The furnace temperature was held at 940°C. Moisture resulting from the combustion was removed from the sample stream via a tubular water separator (Nafion membrane). CO<sub>2</sub> 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. Isotopic compositions were reported in parts per thousand, per mil (‰), and all values reported are relative to the international standard (Pee Dee Belemnite) by conventional delta ( $\delta$ ) notation. The details of analytical method are discussed elsewhere (3, 4).

## Results and discussion

**Technical PCB formulations.**  $\delta^{13}\text{C}$  values for 31 CB congeners in 25 kinds of technical PCB formulations from different suppliers were measured.  $\delta^{13}\text{C}$  values of individual CB congeners ranged from -34.4 (CB180, Delor 106) to -22.0‰ (CB70/76, Sovol), and varied from 2 to 6‰ within PCB series (Fig. 1).  $\delta^{13}\text{C}$  values decreased with an increase in chlorination of technical PCB formulations (Fig. 2). It was worthy to mention that lower chlorinated CB congeners had higher  $\delta^{13}\text{C}$  values in each technical PCB formulation and it might be influenced by isomer specific isotopic partitioning. Interestingly,  $\delta^{13}\text{C}$  values for Delors, Chlorofen, Sovol, and TCP had distinct  $\delta^{13}\text{C}$  values compared to other technical PCB formulations (Fig. 3). In general, Delors had more depleted  $\delta^{13}\text{C}$  than other technical PCB formulations. On the other hand, Sovol, Chlorofen, and Trichlorodiphenyl had higher  $\delta^{13}\text{C}$  values compared to other technical PCB formulations analyzed in this study. A striking feature was that the products of different manufactures defined different trends, in  $\delta^{13}\text{C}$  versus chlorine number diagram (Fig. 3).

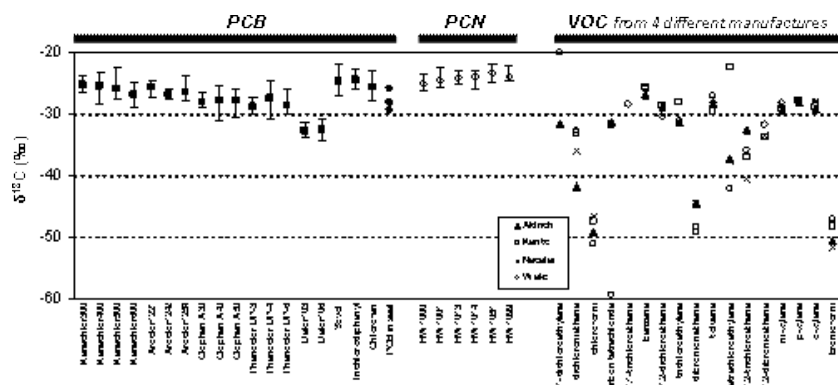


Fig.1 The range of  $\delta^{13}\text{C}$  values for PCB and PCN mixtures, and VOC solvents from different manufactures.

**Technical PCN formulations.**  $\delta^{13}\text{C}$  values of 15 individual congeners in Halowaxes ranged from -26.3 (CN5/6/7/12, HW 1000) to -21.7‰ (CN73/74, HW 1051) (Fig. 1). This range was comparable to that found for technical PCB formulations. Similar to that found for PCBs,  $\delta^{13}\text{C}$  values decreased with increasing chlorination in Halowax series (Fig. 2). Furthermore,  $\delta^{13}\text{C}$  values for individual CN congeners increased with increasing chlorination of technical formulations. For instance,  $\delta^{13}\text{C}$  values of 1,4,5,8-tetraCN (CN46) in Halowaxes 1001, 1013, and 1014 were -25.1, -23.9, and -23.0‰, respectively, suggesting a  $^{13}\text{C}$  depletion with decreasing chlorination in the same

The results of CSIA of PCB and PCN indicate that the number and

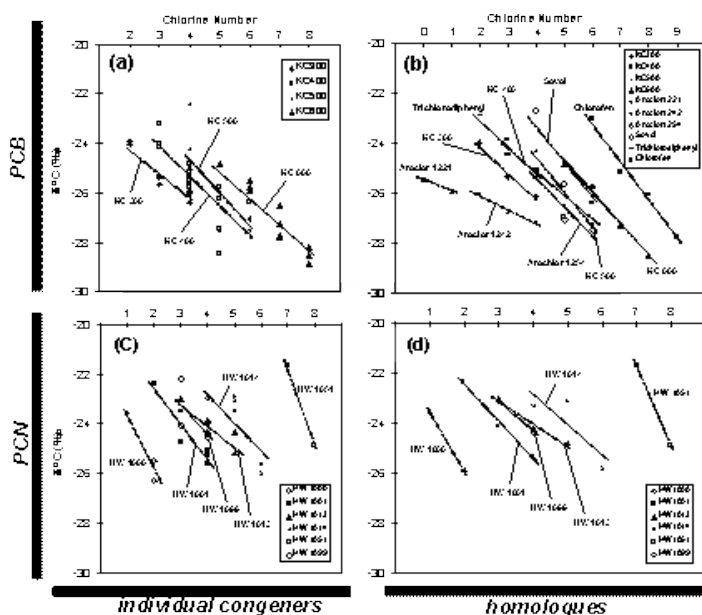


Fig.2 The isotopic compositions of PCBs and PCNs. (a) Profile of PCB congeners in Kanechlor, (b) profile of PCB homologues in several technical PCB formulations, (c) profile of PCN congeners in Halowaxes, and (d) profile of PCN homologues in Halowaxes.  $\delta^{13}\text{C}$  values for each homologue are represented by average of congener values.

substitution pattern of chlorine atoms affect the  $^{13}\text{C}$  fractionation of individual congeners in a systematic fashion. Variations in isotopic ratios among technical formulations from different countries may be related to the manufacturing process and is probably related to kinetic isotope effects at the positions of chlorination. During production, biphenyl or naphthalene is reacted with chlorine and iron chloride. In this process, hydrogen bonded to  $^{12}\text{C}$  may be replaced by chlorine relatively easily to hydrogen bonded to  $^{13}\text{C}$ . Geographical differences in the  $\delta^{13}\text{C}$  values among PCB formulations, particularly those of Delors, Sovol, TCP, and Chlorofen, suggested possible differences in the raw materials used in production. In the case of VOCs, there are also different sources of carbon. The main ones are ethylene, methanol and methane, existing as or produced from natural hydrocarbons, petroleum.

$\delta^{13}\text{C}$  values determined for CB and CN congeners were similar to those from petroleum and terrestrial plants (Fig. 4), as well as  $\delta^{13}\text{C}$  values for VOC having benzene nucleus such as toluene and xylene had similar to petroleum (Fig. 1, 4). However, these values were apparently different from those of carbonates and marine plants<sup>(6, 7)</sup>. This suggests that carbon for the production of industrial chemicals comes primarily from fossil fuel, petroleum. Individual congeners of CB and CN, however, exhibited a wide range of  $\delta^{13}\text{C}$  values, some of which were lower than those associated with terrestrial petroleum. Although it is necessary to obtain more information regarding  $\delta^{13}\text{C}$  values of man-made 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  $\delta^{13}\text{C}$  values. We have started measuring CSIA of PCBs in biota samples (Fig. 1), sediments and other sources of PCBs and PCNs in the environment such as fly ash. These results would provide baseline data to understand biogeochemical processes and the fate of man-made chemicals in the environment.

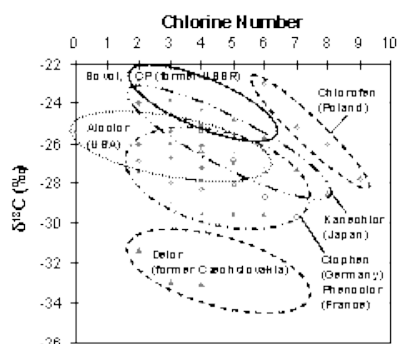


Fig.3 Plot of ranges of  $\delta^{13}\text{C}$  values for various PCB mixtures.

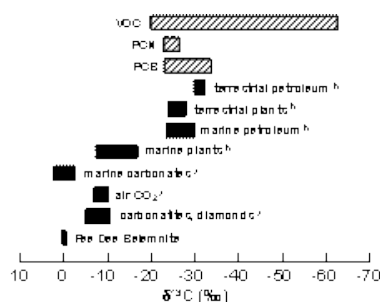


Fig.4 The  $\delta^{13}\text{C}$  values of some important carbon reservoirs and halogenated organic pollutants. Values for petroleum, plant,  $\text{CO}_2$ , diamond, and Pee Dee Belemnite by ref. 6 (a), 7 (b).

### Acknowledgments

We thank critical comments provided by Dr. N.Hanari, Miss. S.Taniyasu and the staff of AIST. We thank Dr. Noma for giving us PCN samples, and Dr. M. Okada, Prof. K. Amano (Ibaraki University, Japan), Prof. T. Yoshinari (Wadsworth Center, USA) and Prof. T. Katase (Nihon University, Japan) for helpful discussions.

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