Organohalogen Compounds, Volume 60, Pages 424-427 (2003)

PRELIMINARY STUDY OF POLYCHLORINATED N-ALKANES IN STANDARD MIXTURES, RIVER WATER SAMPLES FROM JAPAN BY HRGC-HRMS WITH NEGATIVE ION CHEMICAL IONIZATION

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Introduction

Polychlorinated n-alkanes ($C_nH_{2n+2-z}Cl_z$; PCAs) are complex mixtures that have been produced industrially since 1930[1]. They are a group of chemicals manufactured by chlorination of liquid *n*-paraffin or paraffin wax that contain from 30-70% chlorine by weight. They are formed by direct free radical chlorination of *n*-alkane feedstocks with molecular chlorine. Based on the principal *n*-alkane feedstocks, which are derived from petroleum fractions, the commercial PCA mixtures fall into different categories: C_{10}-C_{13} (short), C_{14}-C_{17} (medium), and C_{20}-C_{30} (long). After the ban of polychlorinated biphenyls (PCBs) in the 1980s, PCAs have been used as a temporal substitute of these compounds in some industrial applications[1].

Table 1. The HRGC-HRMS programme adopted in this study.

MS	MAT 95 XL (Thermoquest) Finnigan
Ionization Mode	NCI
Reactor Gas	Isobutane
Trap Current	2.5 x 10-4 mbar
Accel. Volt.	40 V
Emission Current	250μA
Electron Voltage	-5kV
Ion Source Temp.	130°C
Interface Temp.	300°C
Resolution	M/ΔM > 1000 (for LR-scan), 10, 000 (for SIM) with 10% Valley
LR-Scan Range	m/z 30-1000
GC	HP 6890 Series GC System (HEWLETT PACKARD)
Injector	7683 Series Injector (Agilent)
Auto Sampler	7683 Series Auto Sampler (Agilent)
Column	DB-5MS 15m x 0.25mm i.d. (0.1 μ m)
Injection	On-column injection
Injection Volume	2ul (100 ug/mL Toluene)
Injector Temp	100°C (0 min)-100°C/min-300°C (58 min)
Column Temp	100°C (1 min)-10°C/min-300°C (39 min)
He Flow Rate	1 mL/min

A decision to restrict PCAs in metalworking and leather industries in 2004 was informed by EU risk assessment conclusion that suggests a necessity to reduce risks to aquatic organisms arising from these two industrial uses[2]. In the USA, PCAs are listed in the Toxic Release Inventory (TRI) as a result of the USEPA risk assessment[3]. Most available data were collected using thin-layer chromatography and gas chromatography/electron capture detector (GC/ECD). Tomy and his co-workers have established a high-resolution gas chromatography and mass spectroscopy method with negative chemical ionization (HRGC/NCI-HRMS) which enables low-level determination of CPs[4-5]. Tomy and his co-workers have collected environmental data

mainly in Canada and the United Kingdom[6-7]. There are few studies that report about environmental distribution of PCAs in Japan. Reports have documented that average annual production amount of CPs in Japan in the 1990's was estimated to be less than 2.5 10^7 kg. Considering those informations and in order to understand environmental concentrations of PCAs in Japan, in present study we successfully monitored short-chain CPs (SCCPs) by high-resolution GC/NCI-MS in variety of PCA standard mixtures and water samples from Japan for the first time.

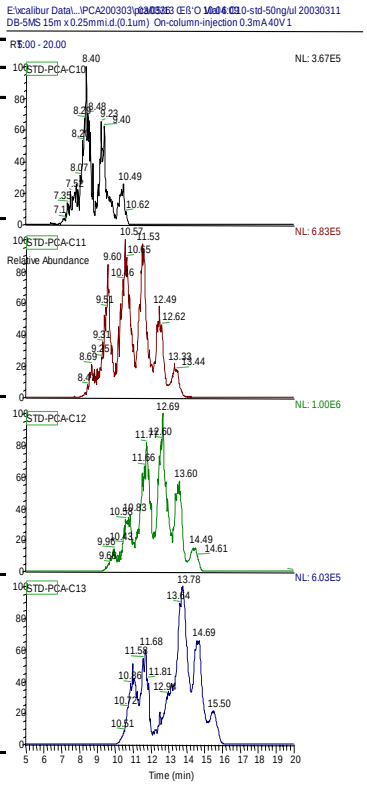
Materials and Methods

The Promochem PCA-technical standard mixtures (PCA-C_{10}, C_{11}, C_{12}, and C_{13}) were analyzed by Thermoelectron Finningan MAT-95XL (HRGC/NCI-HRMS). The HRGC/NCI-HRMS analytical conditions are shown in Table 1. The standard solutions were fractionated with florisil with hexane and dichloromethane as elution solvents with 4 fractions described elsewhere[4-5]. In general,

Table 2. The details of monitoring ion and accurate mass number for Promochem standard.

		Monitoring Ion m/z		
SCCPs	***Components***	(M-Cl)-	(M+2-Cl)-	(M+4-Cl)-
PCA-C10	$C_{10}H_{18}Cl_4$	243.0474	245.0445	
	$C_{10}H_{17}Cl_5$	277.0084	279.0055	
	$C_{10}H_{16}Cl_6$	310.9695	312.9665	
	$^{13}C_{12}$-PeCB	337.9201[a]	337.9201[b]	
PCA-C11	$C_{11}H_{20}Cl_4$	257.0631	259.0602	
	$C_{11}H_{19}Cl_5$	291.0241	293.0212	
	$C_{11}H_{18}Cl_6$	324.9851	326.9822	
	$C_{11}H_{17}Cl_7$		360.9432	362.9403
	$C_{11}H_{16}Cl_8$		394.9042	396.9013
	$^{13}C_{12}$-PeCB	337.9201[a]	337.9201[b]	
PCA-C12	$C_{12}H_{22}Cl_4$	271.0787	273.7585	
	$C_{12}H_{21}Cl_5$	305.0397	307.0368	
	$C_{12}H_{20}Cl_6$	339.0008	340.9979	
	$C_{12}H_{19}Cl_7$		374.9589	376.956
	$C_{12}H_{18}Cl_8$		408.9199	410.917
	$^{13}C_{12}$-HpCB	405.8422[a]	407.8393[b]	
PCA-C13	$C_{13}H_{24}Cl_4$	285.0944	287.0915	
	$C_{13}H_{23}Cl_5$	319.0554	321.0525	
	$C_{13}H_{22}Cl_6$		355.0135	357.0107
	$C_{13}H_{21}Cl_7$		388.9745	390.9716
	$C_{13}H_{20}Cl_8$		422.9356	424.9326
	$^{13}C_{12}$-HpCB	405.8422[a]	407.8393[b]	

[a]monitor ion $[M+2]^-$, [b]monitor ion $[M+4]^-$



for standardizing the analysis, we conducted the analysis using a DB-5 MS column with 200 ng of technical CP standards (Promochem, Unichlor 70A, 40-90, 502-50, Chlorafin 40, Diablo 700X and Chlorawax 500C). Total ion concentrations in low-resolution conditions were measured in all standard solutions, and the mass range and its area were proposed (monitored m/z for Promochem standards and chromatograms are shown in Table 2). The total ion concentration chromatograms showed typical broad peaks and the calibration curves of standard materials were made at 0.5, 1, 5, 20, 50 ng/μL standard solutions.

Table 3. EI-NCI ratio of chlorine (%) components.

Promochem Standard	
PCA-C10	Cl_4:32%, Cl_5:47%, Cl_6:21%
PCA-C11	Cl_4:3%, Cl_5:31%, Cl_6:49%, Cl_7:15%, Cl_8:1%
PCA-C12	Cl_4:1%, Cl_5:20%, Cl_6:54%, Cl_7:23%, Cl_8:2%
PCA-C13	Cl_4:2%, Cl_5:20%, Cl_6:54%, Cl_7:21%, Cl_8:3%
Internal Standard	
$^{13}C_{12}$-PeCB	$^{13}C_{12}$-2,3,3',5,5'-PeCB
$^{13}C_{12}$-HpCB	$^{13}C_{12}$-2,2',3,3',4,4',5HpCB

The recovery standards were total $^{13}C_{12}$-total PCBs (25 ng/μL of 20 μL each) that were syringe spiked in each standard vials. The electron ionization (EI) and NCI chlorine components are shown in Table 3. As you can see the chlorine % varied with carbon chain length with 4-6 Cl in PCA-C10 and 4-8 Cl in PCA-C11 to PCA-C13.

Results and Discussion

The total scan mass spectra revealed the presence of $[M-Cl]^-$, $[M-HCl]^-$, and $[H+Cl]^-$. $[M-Cl]^-$, $[M+2-Cl]^-$, and $[M+4-Cl]^-$, were monitored for quantitation. Only C_{10} (Cl_{4-6}), C_{11} (Cl_{4-8}), C_{12} (Cl_{4-8}), and C_{13} (Cl_{4-8}) present in the Promochem Standard were quantified. The cleanup procedure is appropriate with florisil and hexane and dichloromethane as elution solvents. The usage of internal standard of total PCBs was acceptable due to good recovery percentage. The HRGC-HRMS conditions were found to be ideal.

Table 4. Concentrations (ng/L) of SCCPs in river water and sewage treatment plant (STP) influent/effluent samples.

Samples	STP A influent	STP A effluent	STP B influent	STP B effluent	STP C influent	STP C effluent
Total C10	30	11	41	21	40	9.9
Total C11	73	15(21)	77	14(22)	149	5.9(18)
Total C12	50 (53)	<5.0	77	<5.0 (4.2)	83	<5.0 (0.96)
Total C13	67 (72)	<5.0 (3.1)	68	<5.0 (0.98)	83	<5.0 (2.3)
Total SCCPs	220 (230)	26 (35)	260	35 (48)	360	16 (31)

Samples	Iwabuchi Suimon	Kasaibashi	Hirakata Ohashi	Yodogawa Ozeki
Total C10	7.7	8.1	9.5	7.6
Total C11	12(16)	23(27)	<5.0(11)	<5.0(11)
Total C12	<5.0 (3.2)	<5.0 (3.0)	<5.0 (2.7)	<5.0 (2.7)
Total C13	<5.0 (1.9)	<5.0 (39)	<5.0 (0.48)	<5.0 (0.44)
Total SCCPs	20 (29)	31 (39)	9.5 (24)	7.6 (22)

Detection limit is 5 ng/L

Results in parentheses are data when distinguishable peaks lower than the detection limit are counted.

Our analytical results showed that Promochem standard solutions are suitable to use as reference standard materials for environmental water samples analyzed in this study, because chromatograms of the standards and the environmental water samples were similar to each other. We analyzed influent/effluent samples at three sewage treatment plants and four river water samples from two rivers in Japan. The three sewage treatment plants (A-C) release their effluent to a river in Tokyo Prefecture. Iwabuchi Suimon and Kasaibashi are located along Arakawa River in

Tokyo, and Hirakata Ohashi and Yodogawa Ozeki are located along Yodogawa River in Osaka Prefecture. Sampling from a river was done on the same day in June 2002. Each sample (six litter/sample) was taken once. The PeCB and HpCB act as internal standard for PCA-C10/C11 and PCA-C12/C13, respectively (Table 3) with their m/z ion.

The concentrations of SCCPs in the water samples are presented in Table 4. The total SCCPs ranged from 7.6-220 ng/L. The STP influent samples had maximum concentrations, while the effluent and river water samples had about one order of magnitude lower concentrations than the STP influent. It is apparent that sewage treatment plant efficiently reduced SCCPs to considerably low levels. The removal efficiencies of PCA in the sewage treatment plants decrease as carbon numbers increased. The lowest removal efficiency is 47% of $C_{10}H_{16}Cl_6$.

The PCA-C11 was predominant in water with the following order of contamination; $C_{11}H_{17}Cl_7$> $C_{11}H_{16}Cl_8$> $C_{12}H_{19}Cl_7$>$C_{13}H_{22}Cl_6$> $C_{13}H_{21}Cl_7$> $C_{12}H_{20}Cl_6$> $C_{11}H_{18}Cl_6$ > $C_{11}H_{19}Cl_5$> $C_{13}H_{20}Cl_8$> $C_{12}H_{18}Cl_8$> $C_{12}H_{21}Cl_5$> $C_{13}H_{23}Cl_5$. The highest $C_{11}H_{17}Cl_7$ were scanned in Chlorowax 500C and Unichlor standard with mass area % of 16 and 17, respectively. The final results were based on 3 injection data for quality assurance.

Literature Cited

1. Tomy, G.T., Fisk, A.T., Westmore, J.B., Muir, D.C.G. (1998). Reviews of Environmental Contamination and Toxicology, 158, 53-128.
2. European Union, PE-CONS 3617/02
3. European Union Risk Assessment Report (Alkanes, C10-13, Chloro-), 1999.
4. Tomy, G.T., Stern, G.A., Muir, D.C.G., Fisk, A.T., Cymbalisty, C.D., Westmore, J.B. (1997). Analytical Chemistry, 69, 2762-2771.
5. Tomy, G.T., Muir, D.C.G., Stern, G.A., Westmore, J.B. (2000). Environmental Science and Technology, 34, 1615-1619.
6. Tomy, G.T., Stern, G.A. (1999). Analytical Chemistry, 21, 4860-4865.
7. Tomy, G.T., Stern, G.A., Lockhart, W.L., Muir, D.C.G. (1999). Environmental Science and Technology, 33, 2858-2863.