

POLYCHLORINATED NAFTALENES AND DLPCBs

INTERCALIBRATION STUDY FOR THE POLYCHLORINATED NAPHTHALENES (PCNS): PHASE 1 RESULTS

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Introduction

Recent investigations have shown that PCNs are ubiquitous in environmental compartments¹ and are capable of long-range transport to arctic environments where they have been detected in air² and biota^{3,4}. The tetrachlorodibenzodioxin (TCDD)-toxic equivalency factors (TEFs) for PCNs have been determined⁵ and results for several congeners are similar in magnitude to the coplanar PCBs. Although overall PCN concentrations in the environment are declining, several congeners associated with combustion processes exhibit increasing contributions⁶. Results from physical chemical property measurements for PCNs^{7,8} demonstrate that PCNs are environmentally mobile and bioaccumulative. This evidence coupled with the occurrence of PCNs in wildlife¹ and in humans⁹, has established the importance of these compounds. The majority of the research on environmental levels of PCNs has been conducted in the past decade by several international research groups using similar methods of gas chromatography with electron capture or mass spectrometry detection (GC-ECD and GC-MS, respectively). However, only in the past few years have individual and isotope-labeled standards for single congeners become available. The bulk of the literature data for PCNs is based on quantification performed using calibrated commercial PCN mixtures as standards (*e.g.*, Harner and Bidleman, 1997 and Helm *et al.*, 1999). Consequently, there is concern regarding the comparability of data acquired using these two methods. This study addresses this issue. Results are presented from the first interlaboratory comparison exercise involving nine international laboratories who are conducting ongoing research on PCNs in the environment.

Materials and Methods

Two unknown test solutions were made from a stock solution of Halowax 1014 (U.S. EPA Repository, Research Triangle Park, NC, USA) prepared to concentrations (Σ PCN) of 1104 $\mu\text{g mL}^{-1}$ and 184 $\mu\text{g mL}^{-1}$, respectively, which were sent to each of the nine participating laboratories. Participants were requested to perform triplicate analyses of each unknown and report numerical data for the Σ 2-Cl, Σ 3-Cl, Σ 4-Cl, Σ 5-Cl, Σ 6-Cl, Σ 7-Cl, 8-Cl, Σ PCN, and for several individual congeners including chloronaphthalene (CN)-19, CN-23, CN-42, CN-47, CN-29, CN-52/60, CN-50, CN-66/67, CN-69, CN-73, and CN-75. Details on the analytical methods used are presented in Table 1. Two laboratories (#3 and #9) reported results by two slightly different methods (Table 1).

Results and Discussion

Reported values for the sums of each of the homolog groups (sum of PCN) and individual PCN congeners for unknowns #1 and #2 are shown in Table 2. The variability between laboratories,

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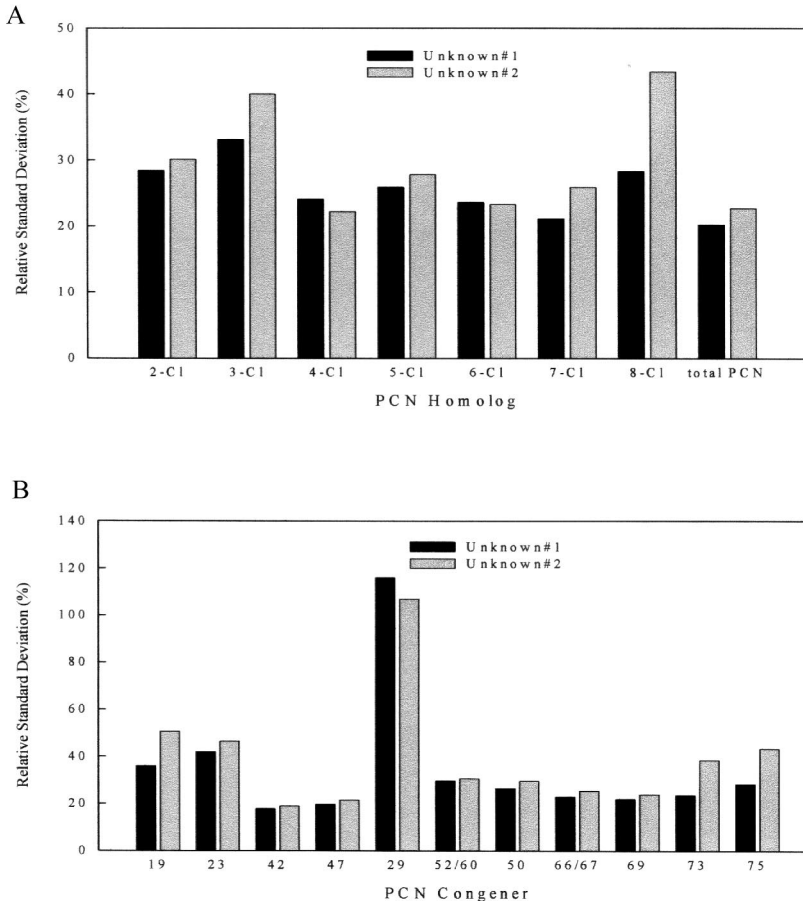


Figure 1. Relative percent standard deviation in reported concentrations for unknowns #1 and #2. Results for sum of homologue groups and total PCN (A) and for selected PCN congeners (B).

expressed as the percent standard deviation relative to the mean (RSD) for Σ PCN, was 20 % for unknown #1 and 23 % for unknown #2 (Fig. 1). The mean (1 Σ D) concentrations reported for unknowns #1 and #2 were 887 (179) ng mL⁻¹ mL⁻¹ and 164 (19) ng mL⁻¹, respectively. These values were 80 % and 83 % of the expected values of 1104 ng mL⁻¹ and 184 ng mL⁻¹ based on the preparation of stock solutions from the solid Halowax 1014 (assuming 100 % purity of the technical crystal).

Standard deviations were similar for each homologue group and Σ PCN, ranging from ~20-40 %. A marked increase occurred for the 8-Cl PCN (CN-75) in the more dilute unknown #2 where the RSD was 43 %, which likely represents an increase in uncertainty with the approach to the analytical detection limit of PCN congeners for some laboratories for the 8-Cl PCN. Of the approximately 160 data values included in Figure 1, only three values were identified as outliers via a Grubb's Single Iteration Outlier Test. These came from laboratory #8 for unknown #2 (values for Σ 2-Cl, Σ 6-Cl and Σ PCN).

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Table 1. Summary of instrument and quantification details for participating laboratories.

Lab I.D. #	Analytical Instrument	GC Column (length)	Quantification external or internal standard	Quantification response factor (RF) or calibration curve (CC)	Type of standard 1 = tech. mixture 2 = individual congeners 3 = 1 and 2
2	<i>GCMS-EI</i>	CP-SIL8CB, 50 m	internal	CC	1
3A	<i>GCMS-NICI</i>	DB5-MS, 60 m	internal	CC	1
3B	<i>GCMS-NICI</i>	DB5-MS, 60 m	internal	CC	2
4	<i>GCMS</i>	DB5-MS, 30 m	internal	CC	2
5	<i>GCECD</i>	DB5, 60 m	external	RF	2
6	<i>GCMS</i>	DB5, 30 m	internal	RF	2
7	<i>HRGC-HRMS</i>	Ultra2, 25 m	external	RF	2
8	<i>HRGC-HRMS</i>	DB5-MS, 60 m	internal	RF	3
9A	<i>GCMS-NICI</i>	DB5, 60m	internal	RF	1
9B	<i>GCMS-NICI</i>	Rt-bDEXcst, 30 m	internal	RF	1
10	<i>HRGC-HRMS</i>	DB17, 30m	external	RF	2

^aGC–gas chromatography; MS–mass spectrometry; ECD–electron capture detection
HR–high resolution; EI–electron impact; NICI–negative ion chemical ionisation.

Table 2. Consensus values for reported concentrations in unknowns #1 and #2.

	Unknown#1				Unknown#2			
	Consensus (ng/mL)	1 SD (ng/mL)	RSD (%)	<i>n</i>	Consensus (ng/mL)	1 SD (ng/mL)	RSD (%)	<i>n</i>
Homolog								
S2-Cl	8.66	1.3	15	3	1.45	0.22	15	3
S3-Cl	78.6	26	33	7	13.9	5.6	40	8
S4-Cl	122	29	24	9	22.4	5.0	22	9
S5-Cl	318	82	26	9	54.9	15.3	28	9
S6-Cl	312	73	24	9	56.4	8.0	14	8
S7-Cl	48.2	10	21	8	8.52	2.2	26	8
S8-Cl	1.64	0.46	28	7	0.307	0.13	43	6
SPCN	887	179	20	8	164	19	11	7
Congener								
19	4.57	1.6	36	8	0.911	0.46	51	8
23	22.1	9.2	42	7	3.77	1.8	47	7
42	3.07	0.54	18	9	0.531	0.10	19	9
47	10.8	2.1	20	8	1.93	0.41	22	8
29*	5.62	6.51	116	3	0.922	0.98	107	3
52/60	34.6	10	30	9	5.94	1.8	31	9
50	9.77	2.6	27	8	1.76	0.52	30	8
66/67	8.57	2.0	23	9	1.46	0.37	25	9

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69	65.9	14	22	8	11.38	2.7	24	8
73	9.78	2.3	24	8	1.80	0.69	39	8
75	1.64	0.46	28	7	0.307	0.13	43	6

*Outliers not removed - see text for explanation

For the analysis of individual congeners, some cases laboratories reported co-elution problems for selected congeners and in these instances the data were excluded from the analysis. For instance laboratory #6 reported coelution of congeners 73 and 74; laboratory #10 reported coelution of congeners 29/27 and 23/22. The variability between labs for the two unknowns is shown in Figure 1B. As was observed for the homologue and total PCN results there is little difference between the RSD for the two unknowns despite the fact that unknown #2 is six times more dilute than unknown #1. For all of the selected congeners except one (CN-29), the RSDs are similar to those in in Figure 1A and are in the range of 20-50 % (Table 2). The very high RSD for CN-29 relative to other PCN congeners (~100 % with no outliers removed) can be attributed to a number of factors. First, this congener does not occur in commercial Halowax 1014 (from which the unknown solutions were derived). Therefore, any reported values for CN-29 must be due to an assignment error. Only three of the nine laboratories reported a value for CN-29. One additional laboratory (#10) indicated that CN-29 co-eluted with CN-27 (analysis performed on a DB-17 column), which does occur in technical Halowax 1014. This result was excluded. Of the remaining approximately 225 data values in Figure 1, none were identified as outliers.

In summary, the laboratories that took part in this study quantified PCNs in a consistent manner despite variations in their methodologies, instrumentation, and types of standards that were employed. These results provide credence for the reported PCN concentrations in the literature and indicates that currently used methodologies are satisfactory and that a standardized method is not necessary. In Phase 2 of the intercalibration exercise, Standard Reference Materials (SRMs) of atmospheric particulate matter and marine sediment will be distributed. This aspect of the study will challenge the entire methodology (sample extraction, clean-up and quantification) providing a more comprehensive basis for comparing interlaboratory performance.

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