Interlaboratory Study for the Polychlorinated Naphthalenes (PCNs): Phase II Results

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Introduction

Polychlorinated naphthalenes (PCNs) are a class of halogenated compounds that are similar to the polychlorinated biphenyls (PCBs) as they were at one time widely used in applications ranging from dielectics to fabric water repellents[1]. PCN use was generally abandoned in North America in the early 1970s; however, the persistence of these compounds has led to continued detection of PCNs in environmental samples [2]. The high dioxin-like toxicity of certain PCNs has led to the continued analysis of these compounds by several groups around the world[3].

To help establish the comparability of PCN data, an interlaboratory comparison exercise was conducted in 2001 with the results published previously[4]. The exercise coordinators distributed two Halowax 1014 solutions with different concentrations and requested that the participants report the concentrations of selected PCN congeners, PCN homologs, and total PCNs in these two solutions. On average, the laboratories were within 14% of the target value for SPCNs. Individual congener and homolog results varied among the participants more than SPCN results.

The next logical step in the interalabortory comparison process was to distribute natural matrix reference materials with measurable PCNs. These materials would better assess the ability of laboratories to measure PCNs in environmental matrix samples. An air particulate and a sediment Standard Reference Material (SRM), SRM 1649a Urban dust and SRM 1944 New York/New Jersey Waterway Sediment, respectively, were chosen for Phase II of the exercise. This paper presents the results from that exercise with recommendations on usage of SRMs as control materials for PCN analysis.

Materials and Methods

For Phase II, three test materials were distributed to seven laboratories. Two of the materials were SRM 1649a Urban Dust and SRM 1944 New York/New Jersey Waterway Sediment. SRM 1649a was collected from the Washington DC area in 1976 and 1977 using a baghouse specially designed for this purpose[5]. SRM 1944 was collected from New York Bay and Newark Bay in October 1994 and freeze-dried prior to sieving and bottling[6]. Both materials have certified values for a number of PCB congeners, polycylic aromatic hyrdrocarbons, and chlorinated pesticides. Prior to use in the exercise, the materials were screened for the presence of measurable PCN congeners. An additional Halowax 1014 solution was also distributed to the participants. This stock solution was prepared by weighing neat Halowax 1014 and dissolving in a known volume of isooctane. Based on mass and the dilution factors used to prepare the test solution sample, the concentration (SPCN) of the unknown solution sample was 1104 ng mL^{-1}. The solution was used as a control material since the PCN congener concentrations are known and these concentrations were validated from the analytical results of the 2001 exercise in which this material was used [4].

Participating laboratories were requested to perform three measurements on the materials and provide values for PCNs in the 2-8 chlorinated homolog groups, SPCN, and congeners 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. The methods for analysis were not prescribed; rather laboratories were free to use the method of their choice.

Results and Discussion

Five laboratories submitted results from this exercise. All laboratories used gas chromatography mass spectrometry (GC/MS) for analysis. Three laboratories operated their mass spectrometers in the electron impact mode (one low resolution and two high resolution), and the other two laboratories used low resolution MS with negative chemical ionization. Four laboratories separated the PCNs using a 5% methyl substituted polysiloxane GC column, while one

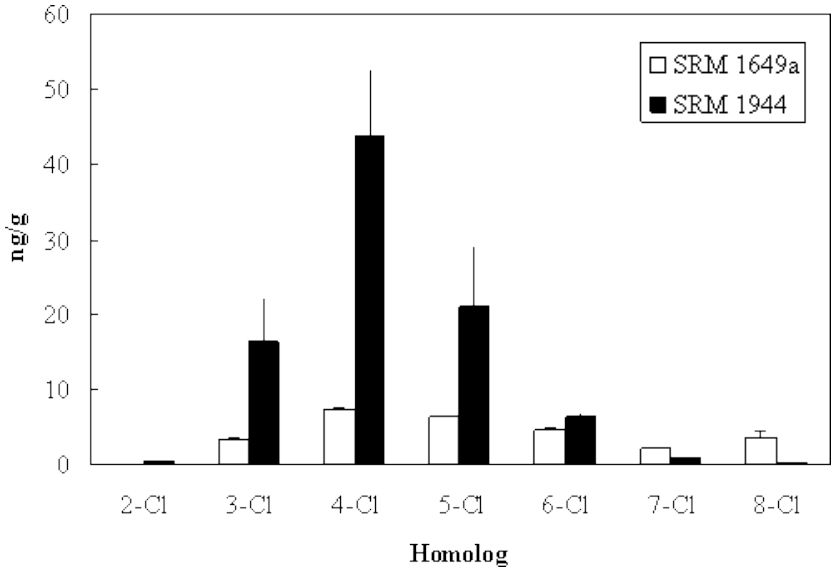
laboratory used a 50% methyl substituted polysiloxane column. Extraction and cleanup steps were only indicated by two laboratories.

Results from the exercise are shown in Table 1. The agreement of the participants on the control material was quite good with a pooled value of 1066 ng/mL (73 ng/mL) (mean (1 SD)) versus a target value of 1104 ng/mL. PCNs were approximately three times higher in SRM 1944 than in SRM 1649a. In general, the relative standard deviation among laboratories for all homologs or individual congeners was 10% or less suggesting reasonably good agreement among laboratories. The profiles of PCN homolog groups in the two SRMs is shown in Figure 1. The distribution of homologs is more even in SRM 1649a while SRM 1944 is dominated by the contribution of the 3-5 chlorinated homologs. Based on the results of this study, either SRM should be a reasonable control material for PCN analysis

Table 1: Summary of results from Phase II of the PCN interlaboratory study.

Compound(s)	1649a			SRM 1944			Control Material (Halowax 1014)		
	mean	1SD	n	mean	1 SD	n	mean	1 SD	n
Homologs									
S2-Cl	0.107	--	1	0.461	--	1	10.7	0.07	2
S3-Cl	3.41	0.087	4	16.4	5.7	3	110	15	4
S4-Cl	7.31	0.33	4	43.9	8.6	3	166	22	4
S5-Cl	6.36	0.068	4	21.1	7.8	3	388	24	4
S6-Cl	4.68	0.21	4	6.50	0.43	3	348	55	4
S7-Cl	2.11	0.16	4	0.800	0.04	3	52.6	5.4	4
8-Cl	3.48	0.92	5	0.148	0.11	4	1.53	0.22	4
SPCN	27.4	1.14	4	89.0	22	3	1066	73	4
Congeners									
CN-19	0.177	0.005	4	1.26	0.36	3	6.24	0.98	4
CN-23	0.864	--	4	3.47	1.8	3	27.6	4.2	4
CN-42	0.152	0.019	5	2.55	0.64	4	4.03	0.78	4
CN-47	0.408	0.056	5	5.16	2.8	4	14.8	2.0	4
CN-29	NA	NA		NA	NA		NA	NA	
CN-52/60	0.491	0.035	5	2.66	0.36	4	41.1	5.2	4
CN-50	0.207	0.019	5	0.929	0.38	4	11.1	1.7	4
CN-66/67	0.282	0.026	5	0.687	0.23	4	9.68	0.90	4
CN-69	1.06	0.061	5	1.60	0.20	4	76.7	8.4	4
CN-73	0.976	0.122	5	0.482	0.074	4	10.5	0.71	4
CN-75	3.48	0.92	5	0.148	0.11	4	1.53	0.22	4

Figure 1: PCN homologs in SRMs 1649a and 1944.



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