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Polychlorinated Naphthalenes in Urban and Arctic Air

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Abstract

Polychlorinated naphthalenes (PCNs) were quantified on a congener-specific basis in air samples collected in Chicago during February-March, 1995 and on a cruise in the eastern Arctic Ocean in the summer of 1996. ΣPCN in the urban/industrialized region of Chicago averaged 68±42 (n=14) pg/m^3 and made a similar contribution to the 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents as some of the coplanar PCBs. The particle-gas partition coeffcient, K_P, was determined for the Chicago samples and was well correlated to the octanol-air partition coefficient. Concentrations over the eastern Arctic Ocean were ΣPCN = 10.0 ± 4.5 pg/m^3 (n=13). The mass distribution profiles of PCNs in air were dominated by the lighter congeners. The 3-Cl and 4-Cl homologs accounted for 94% and 80% of the ΣPCN in Arctic and urban air respectively.

Introduction

Polychlorinated naphthalenes (PCNs) are widespread environmental pollutants which have been quantified in a range of environmental media[1,2] including arctic biota[3,4]. The ubiquitous nature of PCNs is of concern because of their dioxin-like toxicity, which is of similar magnitude to some of the coplanar PCBs[5]. Although the use of PCNs has declined in the past few decades, it is not prohibited in most countries and still occurs in many PCB-like applications such as capacitor fluids, engine oil additives, and electrical insulators[6]. PCNs have also been found in incinerator emissions[7].

This paper summarizes atmospheric levels of PCNs in urban and remote (arctic) regions and describes the particle-gas partitioning of PCN congeners in urban air. The phase distribution of PCNs is a key factor in their transport and deposition away from source regions. The octanol-air partition coefficient, K_{OA}, is a useful descriptor of a chemical's partitioning between the atmosphere and environmental lipids such as vegetation, soil, and the organic portion of atmospheric particulate matter [8-10]. Values of K_{OA} have been recently determined for PCN congeners[12]. Here we investigate the correlation of the particle-gas partition coefficient in urban air with K_{OA}.

Experimental Methods

Air samples were collected using a high volume train consisting of a glass fibre filter (GFF), for the particulate fraction, followed by two polyurethane foam plugs (PUF), for gas-phase compounds. Typical air volumes were as follows: Chicago, 400 m^3; semi-urban Downsview, Ontario, 2500 m^3, eastern arctic, 2500 m^3. Samples were soxhlet extracted in petroleum ether (PUFs) and dichloromethane (GFFs). After volume reduction to 2 mL by rotary evaporation and nitrogen blow-down, the extracts were fractionated on a silicic acid column. Urban and semi-urban samples were further fractionated on a miniature column containing a silicic acid / activated carbon mixture. PCNs and coplanar PCBs were determined by gas chromatography negative ion mass spectrometry (GC-NIMS) on a Hewlett Packard 5890 - MS Engine and quantified against Halowax 1014, a commercial mixture of 2 to 8-Cl PCNs. The details of the sample extraction and clean-up methods, the GC-MS procedure and results for coplanar PCBs are presented elsewhere[11,12]. Recoveries of PCNs ranged from 50% for 3-4 chlorinated congeners to 65-70% for 6-8 chlorinated congeners.

Results and Discussion

Total PCN (ΣPCN) concentrations are summarized in Table 1. ΣPCNs in eastern arctic air (10 pg/m^3 - summer) are lower than values from urban Chicago (68 pg/m^3 - winter) and Augsburg, Germany (150-200 pg/m^3 - summer). Similar reductions in concentration are observed for ΣPCB concentrations from temperate to arctic regions. The ratio ΣPCN/ΣPCB averaged 0.21 in Chicago. This ratio was also calculated for arctic air using the PCN data reported here and ΣPCBs from air monitoring stations in the Canadian (Alert) and Russian (Dunai) arctic[13]. The ΣPCN/ΣPCB in arctic air (0.32) was similar to 0.21 for Chicago.

Table 1. ΣPCN, ΣPCB and TCDD toxicity for PCN-66/67 in urban, semi-urban, and arctic air.

Location	n	ΣPCN (pg/m^3)	ΣPCB (pg/m^3)	PCN 66/67 TEQ(fg/m^3)	reference
Chicago (urban) - winter 1995	14	68	329	0.96	this work and 11, 12
Augsburg(urban) - avg. June 92-Feb.93	- [a]	60	n.d.	n.d.	14
Downsview (semi-urban) - winter 1995	2	17	230	0.45	this work and 11, 12
Eastern Arctic Ocean - summer 1996	13	10	n.d.	0.006	this work
Arctic monitoring stations - summer	9 [b]	n.d.	31	n.d.	13

a) average of nine-month monitoring data from seven stations
b) (Alert - 1993, 1994; Dunai - 1993)
n.d.=not determined

Congener-specific mass percent contributions in Halowax 1014, Chicago air and Arctic air are shown in Figure 1. The numbering system is keyed to the identification of specific PCN congeners in another publication[11]. The 3 and 4-Cl congeners contribute approximately 94% and 80% of the ΣPCN mass in Arctic and urban air respectively. Crookes and Howe (1993) report that Halowax 1001 and 1099, which were used for impregnating capacitors, were the most widely used PCN technical mixtures and accounted for approximately 65% of the market share. These mixtures are dominated by the 3-Cl (40%) and 4-Cl (40%) homologs.

Of the 75 possible PCN congeners, several show 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) toxicity. The TCDD toxicity of PCN congener(s) 66/67 (peak 6-1 in Fig. 2) in air was compared to the coplanar PCBs using reported TCDD toxic equivalence factors[5]. The results indicate that the TCDD toxic equivalent (TEQ) for PCN-66/67 is significant - approximately 2-5 times greater than for PCB-77 and -169 and approximately 8% of the toxicity attributable to PCB-126[11]. It would be interesting to make the same comparison for the eastern arctic but unfortunately there are no reported values for coplanar PCBs in arctic air.

Particle-gas partitioning is an important factor in the transport of chemicals away from sources and in their deposition from the atmosphere. Figure 2 identifies PCNs in Halowax 1014 on a GC- FID (flame ionization detection) chromatogram and shows GC-NIMS chromatograms of PCNs on the glass fibre filter (particle phase) and the PUF plug (gas phase) in a Chicago air sample. The lighter congeners dominate the gas phase while the heavier congeners are more abundant on particles.

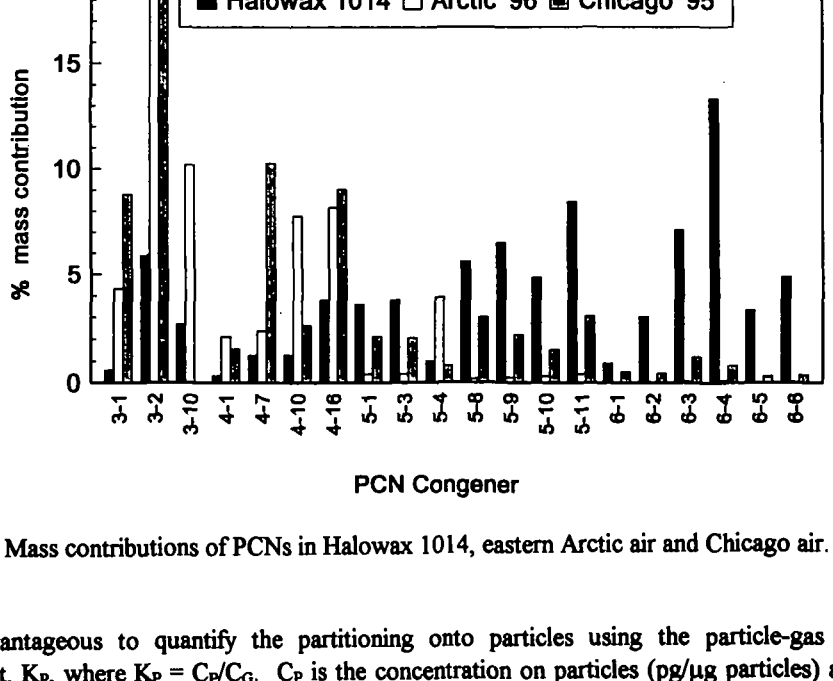

Figure 1. Mass contributions of PCNs in Halowax 1014, eastern Arctic air and Chicago air.

It is advantageous to quantify the partitioning onto particles using the particle-gas partition coefficient, K_P, where $K_P = C_P/C_G$. C_P is the concentration on particles (pg/μg particles) and C_G is the gas-phase concentration in air (pg/m^3). K_P is usually related to the subcooled liquid vapor pressure (p°_L) in plots of log K_P vs log p°_L. However, no vapor pressure data exist for PCNs. Figure 3 is a plot of log K_P versus log K_{OA} in the Chicago air samples where K_{OA} values as a function of temperature were taken from another publication[12]. The excellent correlation demonstrates that partitioning of PCNs onto aerosols is well described by K_{OA}.

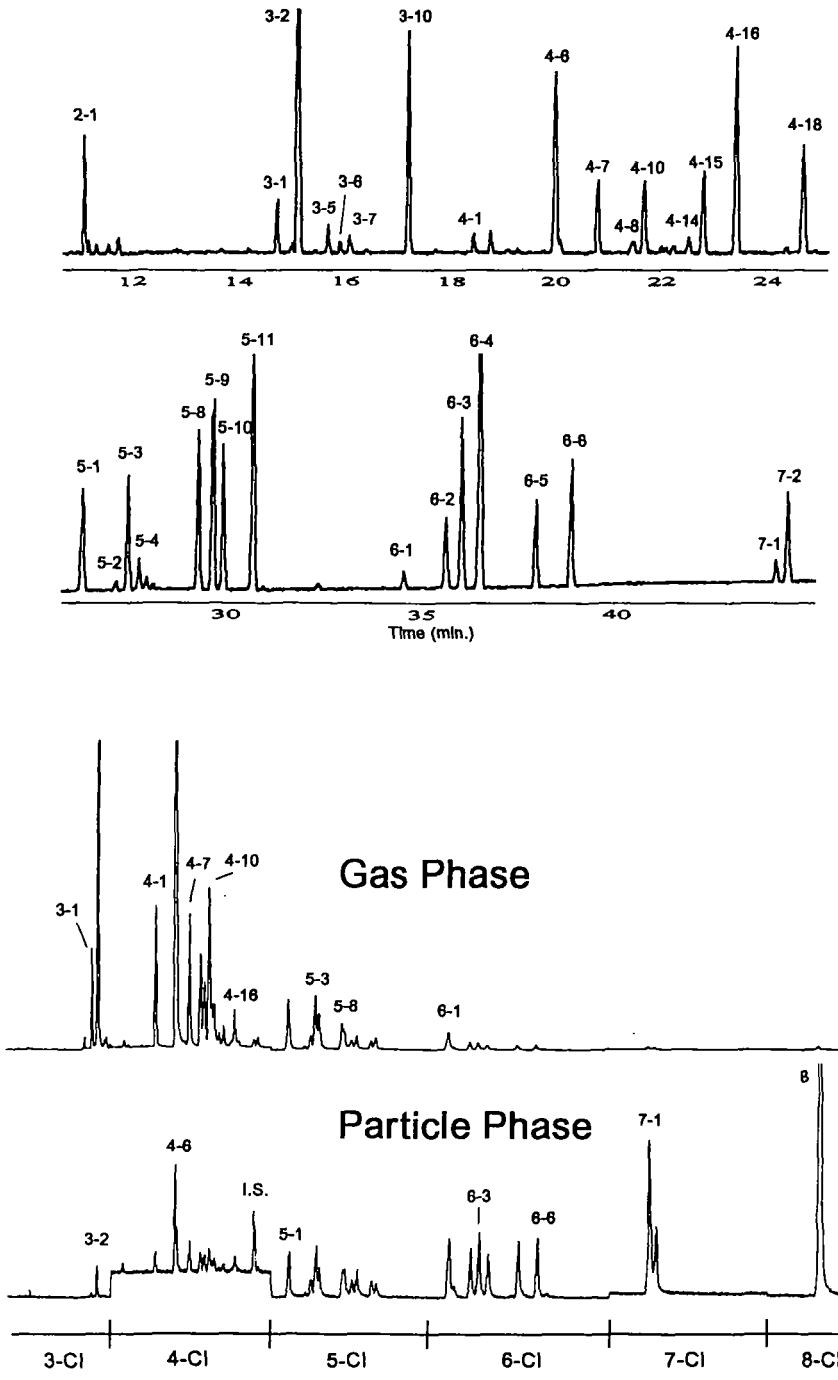

Figure 2. Chromatograms of Halowax 1014 (GC-FID), particle phase PCNs and gas phase PCNs (GC-NIMS, DB-5). Scale for particle phase is expanded by 20 times compared to gas phase.

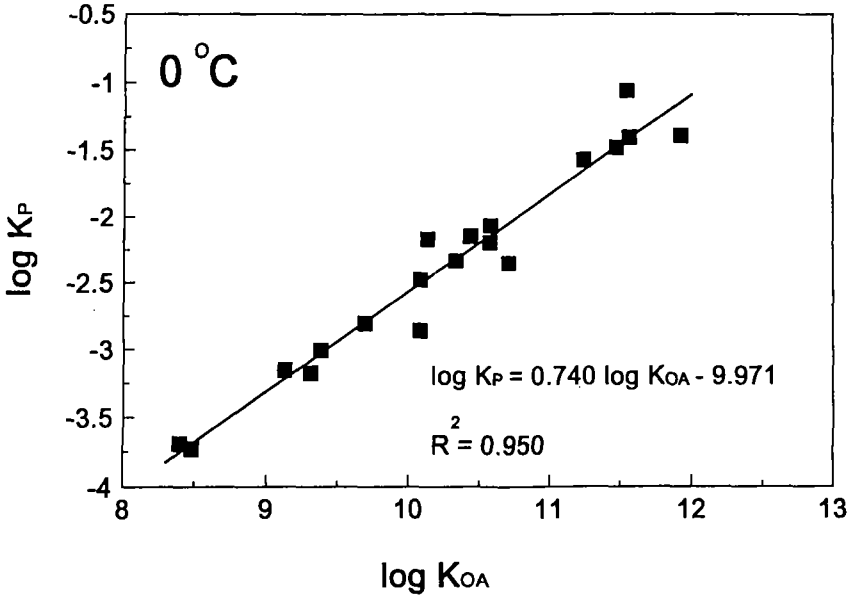

Figure 3. Log-log plot of K_P versus K_{OA} for PCNs in Chicago air

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