Polychlorinated Naphthalenes and Coplanar Polychlorinated Biphenyls in Arctic Air

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Introduction

Polychlorinated naphthalenes (PCNs) are widespread environmental pollutants which have been reported in a range of environmental media *(1,2)* including arctic biota *(3)*. The ubiquitous nature of PCNs is of concern because of their dioxin-like toxicity *(4)*, which is of similar magnitude to some of the coplanar PCBs. Although the use of PCNs has declined in the past few decades, they are not prohibited in most countries and still occur in many PCB-like applications. They are found in incinerator emissions *(6)* and have recently been reported in urban air *(7,8)*. Polychlorinated biphenyls (PCBs) are also a concern in the Arctic environment. Unlike the PCNs, levels of PCBs in arctic air *(9)* and biota have been fairly well monitored, especially in the past decade. However, levels of coplanar PCBs, the most toxic congeners, have not been reported in air. Coplanar PCBs have no ortho-substituted chlorines and are structurally similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin.

This paper summarizes atmospheric levels and relative dioxin type toxicities of PCNs and coplanar PCBs over the Eastern Arctic Ocean and two land-based arctic monitoring stations (Alert, NWT-Canada and Dunai Island, Russia).

Experimental Methods

Eastern Arctic Ocean

A total of 34 air samples was collected on a cruise of the eastern Arctic Ocean (Fig. 1) using a high volume train consisting of a glass fiber filter (GFF) followed by two polyurethane foam plugs (PUF). Flow rates were approximately 0.4 m^3 min^{-1}. PUF plugs were soxhlet extracted using petroleum ether and volume was reduced to 2 mL by rotary evaporation and nitrogen blow-down. Extracts were fractionated on a column of silicic acid overlaid with neutral alumina. PCNs and PCBs were eluted in fraction F1 with 30 mL petroleum ether. The F1

portions were further fractionated on a mini carbon column to separate the mono- and non-ortho PCBs from the multi-ortho congeners. The first fraction (F1-1) was eluted with 5 mL 30% dichloromethane in cyclohexane and contained the multi-ortho and a portion of the mono-ortho PCBs. The second fraction (F1-2) was eluted 5 mL toluene and contained the PCNs, non-ortho PCBs and the remainder of the mono-ortho congeners. PCB-103 was added as an internal standard to all samples. Non-ortho PCBs (congeners 77, 81, 126, 169) and PCNs in fraction F1-2 and mono-ortho PCBs (congeners 105, 114, 118, 156) in fraction F1 were determined by gas chromatography negative ion mass spectrometry (GC-NIMS) on a Hewlett Packard 5890GC-5989B MS Engine using a 30 m DB-5MS column (0.25 mm i.d., 0.25 μm film). PCNs were quantified against Halowax 1014, a commercial mixture of 2-Cl to 8-Cl PCNs. PCBs were quantified against a mixture of non-ortho and mono-ortho PCBs. Multi-ortho PCBs in fraction F1-1 were quantified using a Hewlett Packard GC equipped with an electron capture detector (GC-ECD) against a mixture of 56 individual congeners.

Prior to soxhlet extraction, PUF plugs were fortified with a surrogate mixture containing $^{13}C_{12}$ PCB. Recoveries of these surrogates were used to correct for non-ortho PCB losses. To correct for PCN and mono-/multi-ortho PCB losses, four clean PUFs were spiked with Halowax 1014 and a PCB mixture containing 56 congeners.

Alert and Dunai

At both locations, weekly air samples were collected at a flow rate of approximately 1.1 m^3 min^{-1} using a high volume train consisting of a 20 cm diameter glass fiber filter followed by two 20 cm diameter, 4 cm thick PUF plugs. Each weekly sample represented an air volume of about 11 400 m^3. Monthly PUF blanks were collected by handling a clean PUF as a sample but not drawing air through it. For this study, we were able to obtain a limited set of archived weekly PUF and GFF extracts representing approximately 2500 m^3 (Alert) and 3000 m^3 (Dunai) air. All extracts were fortified with $^{13}C_{12}$-PCBs and analyzed by the same method described for the eastern Arctic samples.

Results and Discussion

PCNs and PCBs in Air

Concentrations of PCNs (pg m^{-3}) averaged 38 (n=2) for the Barents Sea and 8.8 ± 3.6 (n=12) for the north east Arctic Ocean. Values at the monitoring stations were: Alert - 3.7 ± 2.6 (n=5) and Dunai Island - 0.95 ± 0.44 (n=3) (pg m^{-3}) *(9)*. These are approximately an order of magnitude lower than levels reported in urban areas. The average concentration of PCNs in Chicago during the winter (February-March, 1995) was 68 pg m^{-3}. The arctic samples also have a homolog mass distribution dominated by the lighter (3 and 4-Cl) congeners (Figure 1). This may be due to preferential volatilization of the lighter PCN congeners. i.e. global fractionation or may be attributed to different source signatures.

Concentrations of total PCBs (approximately 100 congeners) at Alert and Dunai were taken from Stern et al. *(9)*. When compared to values of ΣPCB reported for the warm months (May-Aug.) at Alert (38 pg m^{-3}) in 1994, levels in the Barents Sea (126 pg m^{-3}) were approximately 3.5 times greater, while levels in the north east Arctic were in good agreement

(37 pg m^{-3}). Concentrations of non-ortho (coplanar) and mono-ortho PCB congeners were measured and are summarized elsewhere*(11)*.

Implications regarding Toxicity

Toxic equivalent factors (TEFs) have been determined for PCBs *(12)* and several 6-7 chlorinated PCN congeners *(4)*. TEQs (TCDD toxic equivalents) were calculated by multiplying the air concentration of the particular compound by its TEF value. The relative TEQ contributions for non- and mono-ortho PCBs and several dioxin-like PCNs are summarized in Figure 2. In all cases the highest TEQ contribution is attributed to the coplanar PCBs, mostly congener 126. The PCNs also make an important contribution - accounting for 13-20% of the TEQ at the arctic sites (except at Dunai where the relative contribution was only ~2%) and ~30% in Chicago.

Conclusions

PCNs and non-/mono-ortho PCBs have been quantified for the first time in arctic air samples. The relative dioxin-type toxicity contribution (TEQ) of PCBs and PCNs indicates that PCNs account for 2-20% of TEQ in arctic air - compared to 30% in urban Chicago. More work is merited to investigate concentrations of coplanar PCBs and PCNs in arctic samples, since these compounds may elicit significant human and animal toxicities.

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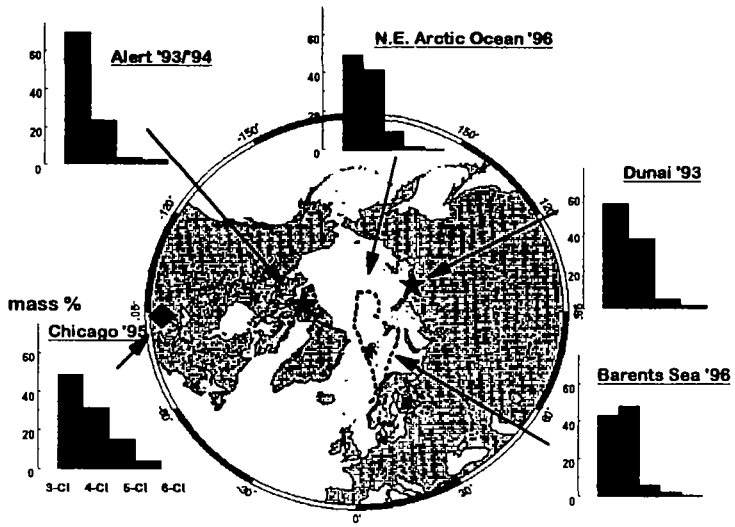

Figure 1. Map showing cruise track and PCN homolog profiles at the sampling locations.

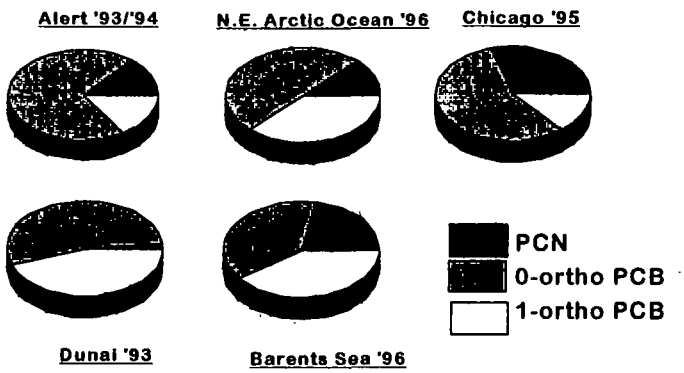

Figure 2. Percent TCDD TEQ contributions of PCNs, coplanar PCBs (congeners 77 and 126), and mono-ortho (congeners 105, 114, 118 and 156) in air samples from arctic and urban air.