POLYCHLORINATED NAPHTHALENES IN GREAT LAKES AIR: SOURCE AND AMBIENT AIR PROFILES

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Introduction

Past and current emissions of polychlorinated naphthalenes (PCNs) have resulted in their distribution throughout environmental media from industrial regions[1,2] to remote arctic sites[3]. Potential sources are often located in urban areas leading to elevated concentrations in urban air[4,5].

This paper presents PCN levels in air collected over the Great Lakes aboard research cruises and from urban sites. A detailed congener analysis of potential source materials is done to elucidate evaporative and combustion sources of PCNs to ambient air in the Great Lakes region. PCN profiles in ambient air are compared to those found in technical PCN products, selected Aroclor PCB mixtures, and combustion fly ash from several industries.

Methods and Materials

Air samples were collected during research cruises aboard the CCGS Limnos in May 1997 (Lake Lake Superior, including transit over Lake Huron) and in July and September 1998 (Lake Ontario). Urban samples were collected in north Toronto, Ontario in October 1998 and December 1999, and in downtown at the University of Toronto in March 2000. High volume air samples (300-1500 m^3) were collected using a sampling train consisting of two polyurethane foam plugs and a glass fibre filter. PCN extraction, clean-up, and fractionation procedures are reported elsewhere[5].

PCN congener profiles were determined in source-related samples including technical PCN mixtures Halowax 1000, 1013, 1014, 1099 and 1051 (U.S. EPA Repository, Research Triangle Park, NC, USA), additional samples of Halowax 1014 and 1051, Aroclor 1254 and 1260 (Monsanto), and combustion fly ash from a medical waste incinerator, a cement kiln, a municipal solid waste incinerator, and an iron sintering plant. Trace levels of PCNs were separated from dilute solutions of the Aroclor mixtures in isooctane using mini carbon columns described by Harner and Bidleman[5]. Ash samples (~3 g, < 1 g for medical waste ash) were Soxhlet extracted with toluene for 48 h and reduced to ~1 mL by rotary evaporation. Extracts were cleaned by column chromatography using 2 g of alumina (6% water) topped with sodium sulfate and elution with 5% DCM in petroleum ether followed by volume reduction to 1 mL.

Air and source samples were analysed by gas chromatography - negative ion mass spectrometry (GC-NIMS) using an HP 5890 II GC - 5989B MS engine or an HP 6890 GC - 5973 MSD on a 60 m DB-5 column (J&W Scientific) and quantified against Halowax 1014 for tri- to octaCNs under conditions described elsewhere[5]. Coeluting penta- and hexaCNs were resolved and

quantified using a 30 m Rt-βDEXcst column and parameters described by Helm et al[6]. Mirex was used for volume correction and all air samples were recovery and blank corrected, with recoveries ranging from 70-100 %.

Results and Discussion

Figure 1 summarizes ambient air concentrations of ΣPCN collected from several regions at different times of the year. Urban levels range from 7-175 pg m^{-3} and include measurements from Chicago and Downsview in 1995[5]. Levels in Downsview in 1998 and 1999 were 7 and 89pg m^{-3}, respectively, and 22 pg m^{-3} in downtown Toronto in March 2000. Urban levels were higher than those observed over the Great Lakes, which ranged from 4-27pg m^{-3} over Lake Superior and Lake Huron in May 1997, and 3-27 pg m^{-3} over Lake Ontario in July and September 1998. The highest ΣPCN concentrations in air over Lake Ontario were measured over the western part of the lake where several industrial and urban centres are located, while the lowest levels were found over the eastern part of the lake and the upper St. Lawrence River which is largely a rural area. These results illustrate the influence of the urban air mass on regional levels of ΣPCN. For comparison, ΣPCN air concentrations from remote arctic monitoring stations at Alert, Canada and Dunai, Russia are included in Figure 1. These ranged from 0.3-8 pg m^{-3} in 1993/4[3] and <0.1-2.3 pg m^{-3} in 1994/5[6].

Although the congener distribution of PCNs in ambient air is dominated by tri- and tetraCNs (>85%), important information may be obtained from the less abundant penta- and hexaCN isomers and from minor tri- and tetraCN congeners. Resolution of CN-66 and CN-67, which are often the most abundant hexaCNs in ambient air, may provide insight into which sources influence observed air profiles[6]. These congeners have the same vapour pressure[8] and their ratio will be preserved upon evaporation from uses involving technical PCN or PCB mixtures.

Figure 2 shows the CN-66/67 amount ratio in several Halowax mixtures, two Aroclor mixtures, and combustion fly ashes, all representing possible sources. Ratios in air samples were lower than those in Halowax mixtures, but higher than in combustion flyashes, with the exception of the iron sintering ash. The ratio was lower in Aroclor 1260 than in air samples but higher in Aroclor 1254. This suggests that combustion sources and/or Aroclor 1260 may contribute to PCN levels observed in ambient air. PCB mixtures are known to contain trace levels of PCNs[9]. The ΣPCN in Aroclors 1254 and 1260 were 197 and 155 μg /g, respectively. The fly ash samples contained from 1.3-2.0 ng ΣPCN/g ash for the MSWI, cement kiln and iron sintering ash, while the medical waste ash contained 3600 ng ΣPCN/g. Variation resulting from the number of different combustion sources and their operating parameters, and differences between batches of technical mixtures needs to be investigated to fully interpret these ratios.

The influence of various sources on ambient air profiles is also apparent from the presence or absence of certain congeners or "marker compounds". Figure 3 presents the pentaCN profile for an air sample collected at Downsview in December 1999, medical waste fly ash, and Halowax 1014. CN-54 is enriched in the air sample and is indicative of combustion[10] but is a minor component of each technical product investigated. Similarly, an enrichment of tetraCN-44 was also found in urban air. Enrichment of selected congeners in air samples that are not present in technical PCN and PCB mixtures indicated that combustion sources are contributing to levels of PCNs observed in urban areas and air over Lake Ontario.

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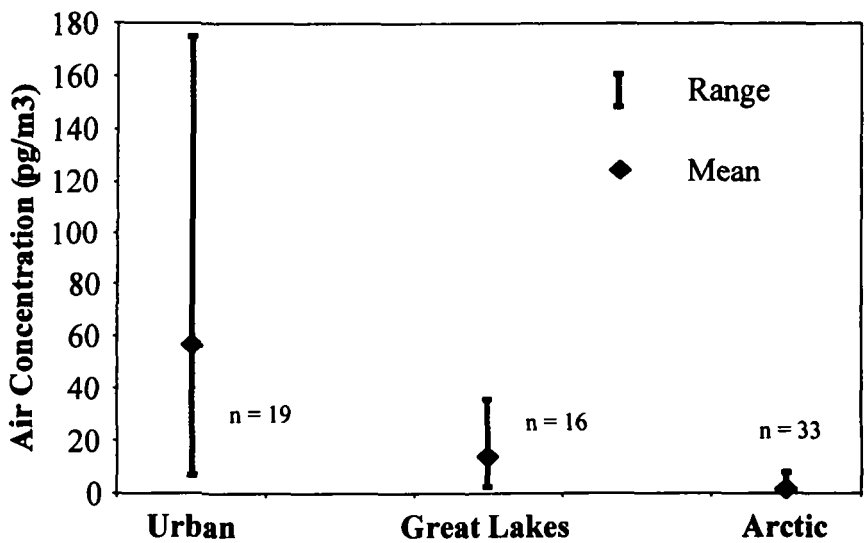

Figure 1. Mean and range of air concentrations measured in urban areas, over the Great Lakes, and at remote arctic monitoring stations.

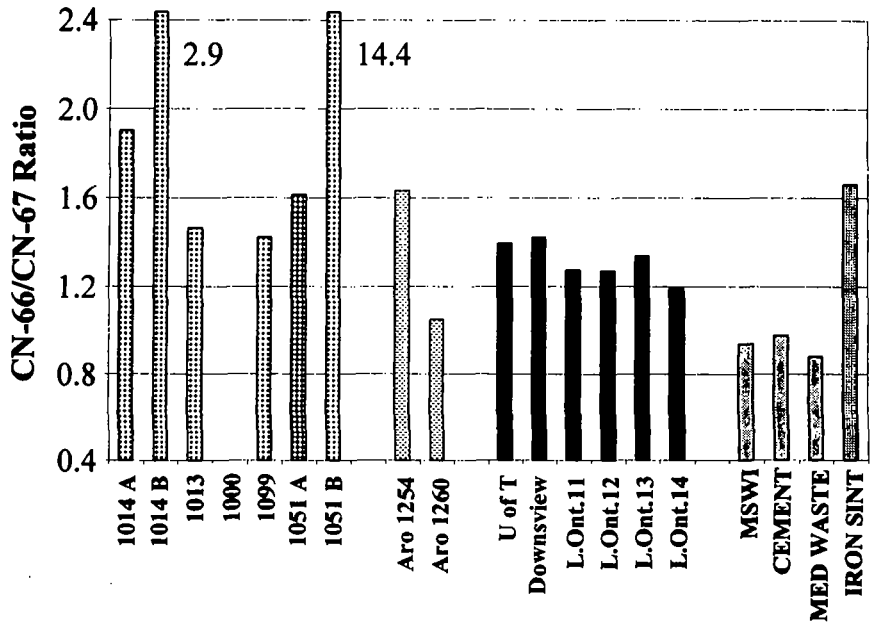

Figure 2. Ratios of the amount of CN-66 to CN-67 in several technical Halowax mixtures, Aroclor mixtures, combustion fly ashes, and air samples.

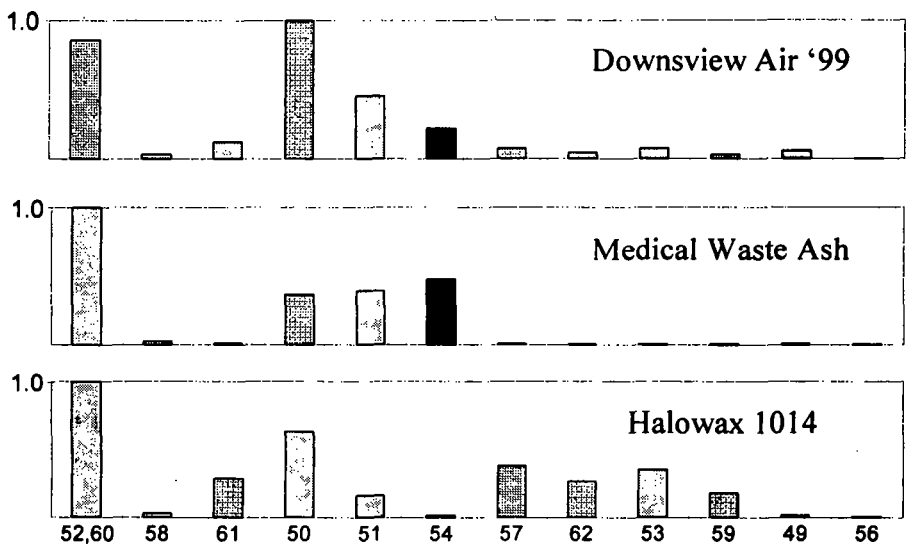

Figure 3. Normalized pentaCN profiles (GC-MS area) for representative source samples and an urban air sample.