Polychlorinated Naphthalenes in the Atmosphere of the Laurentian Great Lakes: Spatial and Temporal Trends using PUF Disk Passive Air Samplers

Tom Harner[1], Mahiba Shoeib[1], Todd Gouin[2], Pierrette Blanchard[1]

[1]Environment Canada
[2]Trent University

Introduction

Because they are persistent, toxic and bioaccumulative, PCNs have been targeted by both the international bodies (e.g. UNECE and UNEP) that identify and regulate the use of persistent organic pollutants (POPs). The main sources of PCNs to the atmosphere include emissions related to past-use (e.g. emission from landfills and old electrical equipment) as well as current sources of PCNs that are associated with combustion [1,2]. In the early nineties, Canada and the USA established the Integrated Atmospheric Deposition Network (IADN) as mandated by Annex 15 of the Great Lakes Water Quality Agreement. IADN measures POPs concentrations in air and precipitations of the Great Lakes basin to estimate atmospheric deposition [3]. In this study polyurethane foam (PUF) disk passive samplers[4] were deployed at 15 sites (including 13 IADN sites) over four consecutive, 3-month periods to investigate spatial and temporal trends of PCNs and combustion marker congeners.

Material and Methods

The uptake of air contaminants by PUF disks[4] (Fig. 1) has been described in previous studies [4,5] including the wind effect on uptake rate [6]. Sampling rates are typically ~3 m^3/day [5,7]. Recently, efforts have been made to assess the sampling rates quantitatively by using depuration compounds (DCs). These are added to the PUF disk prior to deployment and correct for potential site-to-site differences in sampling rates [7,8]. The following DCs were used in this study; 2,4,6-trichlorobiphenyl (PCB-30), deuterated γ-hexachlorocylcohexane ($d_6\gamma$-HCH), 2,3,3',4,5-pentachlorobiphenyl (PCB-107) and 2,2',3,3',4,5,5',6-octachlorobiphenyl (PCB-198). PAS were deployed throughout the Laurentian Great Lakes (Fig. 2) on a seasonal basis between July – October 2002 (period 1, i.e. summer), October – December 2002 (period 2, i.e. autumn), January – March 2003 (period 3, i.e. winter) and March – June 2003 (period 4, i.e. spring). Field blanks and replicate samplers were also deployed at selected sites.

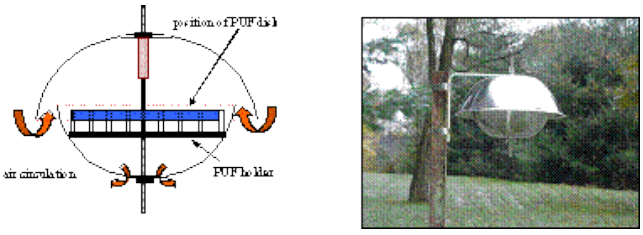

Figure 1. Schematic and photograph of PUF disk passive air sampler.

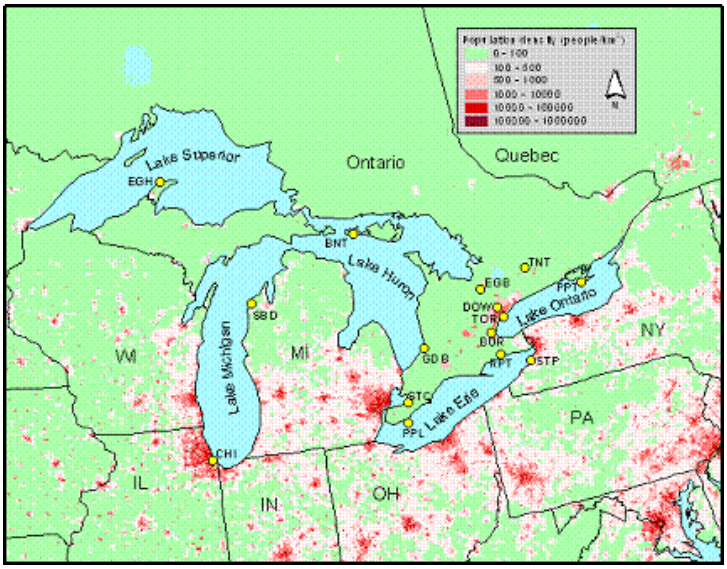

Figure 2. Location of sampling sites relative to population density. (BNT-Burnt Island; BUR-Burlington; CHI-Chicago; EGB-Egbert; EGH-Eagle Harbor; TOR-Toronto; GDB-Grand Bend; PPL-Pt. Pelee; PPT-Pt. Petre; RPT-Rock Point; SBD-Sleeping Bear Dunes; STC-St. Clair; STP-Sturgeon Point; TNT-Trent University Field Site.)

Details regarding the extraction method and sample preparation are presented elsewhere [8]. A Hewlett-Packard 6890 gas chromatograph (GC)-5973 mass spectrometer (MS) was used to quantify 27 PCN congeners using external standard solutions. Analysis was similar to a published method [9].

Results and Discussion

Quality Control/Quality Assurance

Recoveries for depuration compounds were used to calculate sampling rates for each sample. These were converted to sample volumes based on the duration of the sample. Details of this calculation are presented elsewhere [7,8]. Sampling rates were on average 2.5+/-0.9 m^3/day and sample air volumes were 100-300 m^3.

Spatial and Temporal Trends of PCN air concentrations

Air concentrations (pg/m^3) for SPCN (Figure 3) ranged from less than a few pg/m^3 at the background sites to as high as 46 pg/m^3 for Chicago. High concentrations were also observed in Toronto (18-35 pg/m^3) and similar to values reported previously for the same location by Helm et al. [1]. PCN air concentrations for Toronto and Chicago were about 5-10 times higher than for background rural sites. This is of similar magnitude to the gradient observed for PCBs along an urban rural-transect extending ~75km north of Toronto [4], however, PCB concentrations were about an order of magnitude higher.

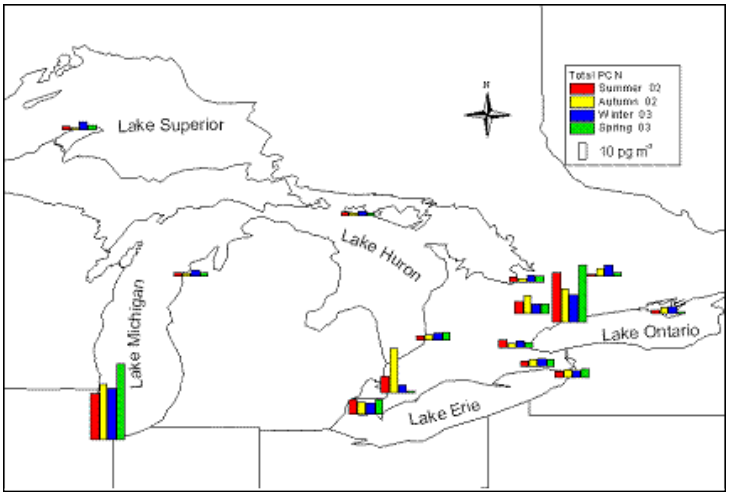

Figure 3. Spatial and temporal trends for PCN air concentrations (pg/m^3) in the Laurentian Great lakes.

Moderately high PCN air concentrations were reported for sites: DOW, STC and PPL. All three sites are downwind of major urban/industrial centers where PCNs would have been historically used – Toronto in the case of DOW and Detroit in the case of STC and PPL. The average PCN congener composition did not vary much between sites and seasons - 31%, 34%, 29% and 5% for 3-Cl, 4-Cl, 5-Cl and 6-Cl congeners respectively.

There were a few noteworthy seasonal differences in PCN levels. First, concentrations were consistently higher at the background sites during the winter period (Figure 3) suggesting again the importance of combustion type sources. Conversely, concentrations of PCNs at urban sites (TOR especially) were low during the winter, perhaps associated with reduced emissions from sources of technical PCN during this time of the year (i.e. landfill, electrical equipment).

Various combustion processes (e.g. wood and coal burning, incineration) have been shown to produce a PCN profile that is enriched in some congeners relative to their contribution in technical PCN formulations. The presence of these congeners can therefore be used to assess the input of combustion sources. Figure 4 shows enrichment factors (EFs) for three combustion marker PCNs that were detected in almost all samples. EFs were calculated for each congener and were normalized to the average value for that congener for all sites during each integration season. Lee et al.[2] have shown that PCNs 24 and 50 are enriched during coal and wood combustion. Co-eluting congeners 66/67 are associated with incineration sources [1].

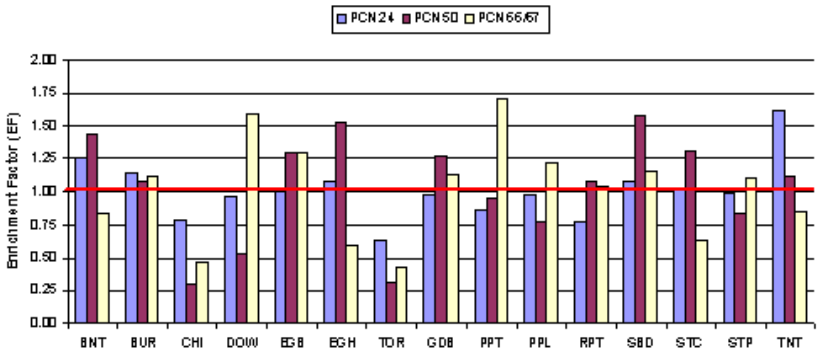

Figure 4. Enrichment factors (EF) for combustion marker PCNs.

The two urban sites (CHI and TOR) that exhibited the highest PCN concentrations have the lowest contribution of combustion marker PCNs. This is probably because the contribution of past-use PCN technical formulations continues to dominate emissions to the atmosphere. In fact, highest contributions of combustion marker PCNs (especially congeners 24 and 50) occur at background sites (e.g. BNT, EGB, EGH, SBD and TNT) where technical PCN inputs are expected to be low. The high contribution of PCN 66/67 at DOW is consistent with previous measurements at this site [1]. This study is a good example of the utility of passive air samples for providing quantitative and qualitative information that can be used to assess levels and sources of contaminants in the atmosphere.

Acknowledgements

This project was partially funded by Existing Substances Branch, Environment Canada. We also thank Celine Audette for deploying samples and IADN site operators for assistance with sample collection.

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