

Environmental Chemistry

SPATIAL DISTRIBUTION OF POLYCHLORINATED NAPHTHALENES IN AIR OVER THE GREAT LAKES AND AIR–WATER GAS EXCHANGE IN LAKE ONTARIO

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Abstract—High-volume air samples were collected during research cruises of Lake Superior in August 1996 and May 1997 and of Lake Ontario (North America) in July and September 1998 and June 2000 and analyzed for polychlorinated naphthalenes (PCNs). Levels of tetra- to octachloronaphthalene (Σ PCN) varied spatially, with mean values (\pm SD) of 1.78 ± 0.74 and 1.46 ± 1.07 $\mu\text{g m}^{-3}$ for Lake Superior in 1996 and 1997, respectively, and of 5.53 ± 2.19 and 5.60 ± 2.24 $\mu\text{g m}^{-3}$ for Lake Ontario in 1998 and 2000, respectively. Evaporative sources were predominant, although combustion marker congeners such as tetrachloronaphthalenes 44 and 29 and pentachloronaphthalene 54 were present in most samples and were enhanced relative to technical PCN mixtures. The Σ PCN concentrations were higher in Lake Ontario samples collected in the western half of the lake and when winds were from the west. Greater proportions of the population and industrial areas are located around the western part of Lake Ontario. Water–air fugacity ratios, calculated from air and water samples collected in June 2000, indicate that the trichloronaphthalenes are volatilizing from Lake Ontario, whereas the tetrachloronaphthalenes are close to equilibrium and the net deposition of tetrachloronaphthalenes can occur when the urban air plume influences levels over the lake.

Keywords—Polychlorinated naphthalenes Fugacity ratio Lake Superior St. Lawrence River Combustion

INTRODUCTION

Polychlorinated naphthalenes (PCNs) are contaminants of concern that are structurally similar to chlorinated dioxins and polychlorinated biphenyls (PCBs). Like PCBs, PCNs were manufactured as complex mixtures for use in the electrical industry as dielectrics for flame-resistance and insulation in cables, transformers, and capacitors [1,2]. Peak PCN usage predates that of PCBs [3], with total global production estimated to be 10% of PCB production, or 150,000 metric tons [1]. Polychlorinated naphthalenes are found in PCB mixtures [4,5] and are produced in combustion processes such as waste incineration [6–8] and metals refining [8–10]. Polychlorinated naphthalenes are under consideration for addition to the list of compounds included in the United Nations–Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution–Protocol on Persistent Organic Pollutants [11].

Polychlorinated naphthalenes have been found in various environmental matrices of the Great Lakes region. Sediment concentrations of as much as $61 \mu\text{g g}^{-1}$ were found in highly contaminated areas of the Detroit River (USA) [12]. Polychlorinated naphthalenes were measured in fish from Lake Superior and the Detroit River and then compared to PCBs on a dioxin toxic equivalents (TEQ) basis, with PCNs contributing from 2 to 57% of the PCN+PCB TEQ [13]. In eggs of fish-eating birds collected from Michigan shores on Lake Huron and Lake Superior, PCNs formed a minor component of TEQ [14]. Human adipose tissues collected from subjects that lived in southern Ontario municipalities, mostly adjacent to the Great Lakes, contained penta- and hexachloronaphthalene

(penta- and hexaCN) in concentrations of as much as 30 ng g^{-1} [15].

Measurements of PCNs in air have focused on urban areas adjacent to the Great Lakes, with values reported for Chicago (IL, USA) adjacent to Lake Michigan [16] and for Toronto (ON, Canada) on Lake Ontario [8]. Similar mean levels of tri- to octaCN concentrations for Chicago ($68 \mu\text{g m}^{-3}$) and downtown Toronto ($51 \mu\text{g m}^{-3}$) were found. Contributions of combustion sources to PCN were noted at a sampling location in the more industrialized, northern part of Toronto [8]. In both Chicago and Toronto, PCNs contributed as much or more than the mono-/non-*ortho* PCBs to the PCN+PCB TEQ in air [8].

Polychlorinated naphthalenes are not included in ongoing air-monitoring programs in the North American Great Lakes region. This paper presents the first report, to our knowledge, of PCN concentrations over the Great Lakes and examines spatial differences both between lakes and over Lake Ontario. Congener profiles are examined to indicate which sources contribute to ambient levels, and the net direction of air–water gas exchange is estimated. These results contribute to our knowledge of the multimedia distribution of PCNs in the Great Lakes region.

MATERIALS AND METHODS

Sampling information

High-volume air samples (9–48 h, 270–1,500 m^3) were collected during five separate research cruises aboard the Canadian Coast Guard Ship *Limnos* over the Canadian and U.S. sides of the Great Lakes. Two expeditions were made to Lake Superior, one in August 1996 and one in May 1997, with samples collected over Lake Huron ($n = 4$) and Lake Erie ($n = 1$) while in transit in addition to those collected over Lake Superior ($n = 9$). Three Lake Ontario/St. Lawrence River

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cruises took place in July 1998, September 1998, and June 2000, with samples collected over the lake ($n = 9$) and the river ($n = 5$). One air sample collected near Cornwall (ON, Canada) along the St. Lawrence River in February 1999 is included with the over-river samples. Details are listed in Table 1.

Air was drawn through a train consisting of a glass-fiber filter (GFF; 20.3×25.4 cm) and two polyurethane foam plugs (PUF; length, 7.5 cm; diameter, 8 cm). Procedures for cleaning the PUF and GFF before sampling have been published elsewhere [17], and collected samples were stored in a freezer until extraction.

Water samples (~ 100 L) were collected at five stations during the June 2000 cruise on Lake Ontario (Table 1) by submersible pump into stainless-steel pressure cans. Labeled organochlorine pesticide and PCB surrogates were added, and the water was passed through a GFF (diameter, 14.2 cm) and then approximately 50 ml of XAD-2 resin (Supelco, Bellefonte, PA, USA). The resin was stored in water and refrigerated until extraction. Sample collection and processing procedures as well as precleaning methods for the XAD-2 resin have been published previously [18].

Extraction and fractionation

Polyurethane foam plugs were extracted overnight by Soxhlet using petroleum ether. The XAD-2 was eluted with 325 ml of dichloromethane (DCM). The DCM was separated from the residual water, and the water was extracted twice with 50 ml of DCM. The DCM portions were combined and dried with anhydrous sodium sulfate.

Extracts were reduced to approximately 1 ml, exchanged into isoctane, and then fractionated on silicic acid (SA) columns containing 3.0 g of 3% (w/w) deactivated SA overlaid with 2.0 g of neutral alumina (6% [w/w] water deactivated) and 0.5 g of anhydrous Na_2SO_4 . Both PCNs and PCBs eluted in fraction 1 (F1) with 20 to 30 ml of petroleum ether. Fraction 1 was reduced to 1 ml and then fractionated on minicarbon columns containing 100 mg of 20:1 SA:AX-21 activated carbon between two 50-mg SA layers as described by Harner and Bidleman [16]. Multi- and mono-*ortho* PCBs were eluted with 5 ml of 30% (v/v) DCM in cyclohexane in fraction 1 (F1-1; not analyzed). The PCNs were eluted in fraction 2 (F1-2) with 5 to 6 ml of toluene. Fractions 1 and 2 were each reduced to approximately 1 ml or 200 μl for analysis.

Chemical analysis

Polychlorinated naphthalenes were quantified by gas chromatography electron capture–negative-ion mass spectrometry using an HP 5890 Series II Plus GC-5989B mass spectrometer engine or an HP 6890 GC-5973 mass selective detector (Hewlett-Packard, Avondale, PA, USA) in selected ion-monitoring mode with methane as the reagent gas. Analytes were separated on a 60-m, DB-5 gas chromatography column (inner diameter, 0.25 mm; film thickness, 0.25 μm) and quantified against a Halowax 1014 technical PCN mixture (U.S. Environmental Protection Agency, Research Triangle Park, NC, USA) containing known amounts of tri- to octaCNs [16,19]. Congeners absent in Halowax 1014 but present in some air samples (triCNs 20, 21, 26, and 13 and tetraCNs 44 and 29) were quantified using electron capture–negative-ion mass spectrometry response factors determined from source samples containing these congeners and the mass selective detector in electron-impact mode [8]. Mirex was added as an internal standard for volume correction. Monitored ions, temperature programs,

and mass selective detector conditions are as listed by Helm et al. [20]. The same temperature program was used for analyses on the HP 5890 II gas chromatography 5989B mass spectrometer engine. However, the transfer line temperature was 250°C, whereas the ion source and quadrupole temperatures were 150 and 100°C, respectively.

Quality control

Peaks were identified based on retention time and ion ratios compared to the Halowax standard, and peaks were quantified if target:qualifier ion ratios were within $\pm 20\%$ of standard values. Average extraction and fractionation process spike recoveries of Halowax 1014 ranged from 78 to 114% for individual PCN congeners, with relative standard deviations of 4 to 21%. The PCN concentrations were adjusted for recovery factors because recovery efficiencies were related to the degree of chlorination.

Polyurethane foam blanks ($n = 9$) were collected by placing PUF plugs into the sampling train but not drawing air. These blanks were then treated as samples through the extraction and fractionation procedures. The method detection limit (MDL) was calculated as the mean blank values plus three standard deviations for each PCN congener. Measurements exceeding the MDL were blank-corrected and included in the reported ΣPCN concentrations and in further calculations. Individual PCN MDLs ranged from 1 to 340 fg m^{-3} (assuming 700 m^3 of air).

Glass-fiber filters were not analyzed for PCNs in this study, except for the sample collected near Cornwall in February 1999. Less than 4% of ΣPCN was found on filters during the summer months for urban samples collected in Toronto [8]. Although higher proportions of hepta- and octaCNs may occur on filters and their values may be underestimated, these congeners are minor contributors to ΣPCN . Only tetra- to octaCNs are included in the ΣPCN values, because excessive breakthrough (PUF2:PUF1, >0.33) of the triCNs occurred in many of the samples. Hepta- to octaCNs were above the MDL in only two samples. Breakthrough did not occur in the samples from June 2000 over Lake Ontario because lower air volumes were sampled (272–400 m^3).

Two XAD blanks were prepared aboard the ship in June 2000 by passing 1 L of deionized water through the sample apparatus and subsequently treating as samples. An additional extraction/fractionation blank was carried out to monitor for interferences. Extraction and fractionation process spikes of Halowax 1014 ($n = 3$) yielded average recoveries of 69 to 100% (relative standard deviations, 1–24%) for individual PCN congeners. Additional XAD extractions with 100 ml of DCM showed that all PCNs eluted in the original extraction volume (325 ml). Because of high blank values for several pentaCN and higher congeners, only tri- and tetraCN water concentrations were blank/recovery-corrected and reported.

RESULTS AND DISCUSSION

PCN concentrations in Great Lakes air and water

Air concentrations are summarized in Figure 1 and Table 1. Average ΣPCN (tetra- through octaCN) concentrations over Lake Superior in August 1996 and May 1997 were 1.78 ± 0.74 and 1.46 ± 1.07 pg m^{-3} , respectively. On the combined July and September 1998 sampling cruises, ΣPCN levels averaged 5.53 ± 2.19 pg m^{-3} over Lake Ontario and 2.71 ± 1.79 pg m^{-3} over the St. Lawrence River, whereas concentrations

Table 1. Locations, temperatures, and polychlorinated naphthalene (PCN) concentrations for North American Great Lakes and upper St. Lawrence River samples

Sample ^a	Latitude (N)/longitude (W)		Air/water temperature (°C)	Concentrations (pg m ⁻³ or pg L ⁻¹)					
	Sample on ^b	Sample off		TriCN ^c	TetraCN	PentaCN	HexaCN	ΣPCN ^d	
Lake Superior August 1996 (air)									
LMN001 (LH)	42°59'/82°42'	46°30'/84°19'	18.7		2.46	0.415	0.164	3.04	
LMN002	46°28'/84°27'	47°34'/86°57'	13.4		1.79	0.288	0.080	2.16	
LMN003	48°22'/87°32'	48°15'/89°10'	9.3		1.25	0.211	0.066	1.53	
LMN004	48°15'/89°10'	47°12'/89°40'	15.0		0.83	0.040	0.008	0.87	
LMN005	47°12'/89°40'	46°31'/87°20'	17.0		2.25	0.288	0.026	2.57	
LMN006 (LH)	46°31'/87°20'	43°00'/82°42'	16.0		0.89	0.136	0.015	1.04	
LMN007 (LE)	43°00'/82°42'	42°37'/79°53'	22.7		8.97 ^e	1.908	0.407	11.51	
Lake Superior May 1997 (air)									
LMN008 (LH)	42°59'/82°42'	46°28'/84°27'	3.1		2.78	0.597	0.036	3.41	
LMN009	46°28'/84°27'	48°15'/89°11'	2.4		2.27	0.325	0.029	2.63	
LMN010	48°15'/89°11'	46°47'/92°03'	3.1		2.38	0.233	0.015	2.63	
LMN011	46°47'/92°03'	47°36'/89°00'	3.8		0.55	0.136	0.010	0.70	
LMN012	47°36'/89°00'	48°15'/89°11'	3.7		0.41	0.107	0.003	0.52	
LMN013	48°15'/89°11'	46°28'/84°27'	4.8		0.72	0.130	ND ^f	0.85	
LMN014 (LH)	46°28'/84°27'	42°59'/82°42'	5.6		1.80	0.183	0.037	2.02	
Lake Ontario July 1998 (air) ^g									
ONT001/2			22.8		6.50	1.05	0.18	7.74	
ONT003/4			22.1		2.53	0.45	0.08	3.07	
ONT005/6 (St.L.)			22.1		1.47	0.18	0.03	1.68	
ONT007/8 (St.L.)			20.8		1.14	0.11	0.01	1.26	
ONT009/10			17.8		6.62	1.14	0.18	7.94	
Lake Ontario September 1998 (air) ^h									
ONT011 (N)			19.8		3.42	0.669	0.143	4.23	
ONT012 (N; St.L.)			14.4		2.12	0.460	0.089	2.67	
ONT013 (D; St.L.)			18.6		3.90	1.162	0.176	5.24	
ONT014(D)			19.1		3.50	0.979	0.188	4.67	
Cornwall February 1999 (air)									
CWALL (St.L.)				2.96	2.67	0.619	0.131	3.51	
Lake Ontario June 2000 (air)									
LONT00 Burl	43°17'/79°48'	43°17'/79°48'		7.35	4.62	0.778	0.056	5.45	
LONT00 1A	43°18'/79°46'	43°44'/78°08'	14.1	6.74	2.78	0.425	0.011	3.22	
LONT00 2A	43°43'/78°01'	44°05'/76°24'	12.9	4.06	3.44	0.832	0.209	4.48	
LONT00 7A	44°08'/76°20'	43°23'/77°53'	15.7	6.69	4.32	1.084	0.198	5.60	
LONT00 8A	43°23'/78°01'	43°18'/79°45'	19.7	8.55	7.13	1.883	0.216	9.22	
Lake Ontario June 2000 (water) ⁱ									
LONT00 HV 1 A/B	43°25'/79°23'		11.5	13.4	7.68				
LONT00 HV 2 A/B	43°43'/78°01'		9.5	12.1	4.25				
LONT00 HV 3 A/B	43°47'/77°10'		11.5	17.7	6.44				
LONT00 HV 5	44°31'/75°47'		13.5	16.0	6.06				
LONT00 HV 12 A	43°29'/77°02'		14.4	19.0	5.48				

^a LH = Lake Huron; LE = Lake Erie; St.L. = upper St. Lawrence River.

^b Water samples collected at the latitude/longitude listed.

^c Trichloronaphthalenes in air only reported for June 2000 because of significant breakthrough to back polyurethane foam plug (PUF2/PUF1 > 0.33) in other samples.

^d Sum of tetra- through octaCNs.

^e Breakthrough of some tetraCNs.

^f No hexaCNs exceeded their method detection limit.

^g Duplicate samples with ΣPCN differences of 5–57%.

^h Collected as day (D) or night (N) samples over several days.

ⁱ Duplicate high-volume (HV) samples collected for each of samples 1–3, with percentage differences listed in the text.

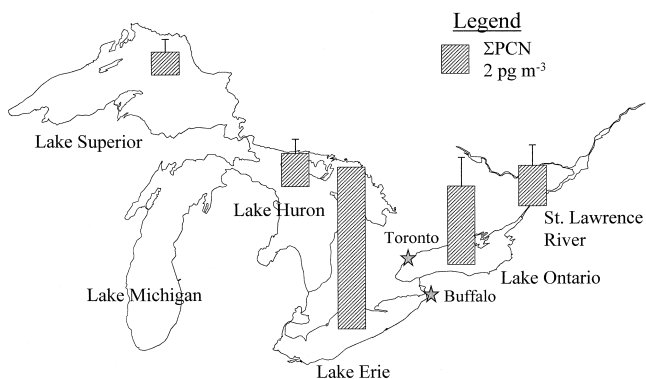


Fig. 1. Map showing the Great Lakes and the average (+ one standard deviation) polychlorinated naphthalene (PCN) concentrations (sum of tetra- to octachloronaphthalenes; pg m^{-3}) in ambient air over the lakes and the upper St. Lawrence River (Canadian and U.S. sides).

averaged $5.60 \pm 2.24 \text{ pg m}^{-3}$ over Lake Ontario in June 2000. A ΣPCN concentration of 3.51 pg m^{-3} was found in the air collected near Cornwall in February 1999. To our knowledge, these are the first reported PCN concentrations over the Great Lakes.

Ambient air PCN levels were measured in urban areas in Chicago and Toronto in 1995 [16] and in Toronto again in 1998 to 2001 [8]. The triCNs were the dominant homologue group in the Chicago air samples, whereas tri- and tetraCNs had similar concentrations in Toronto. The triCNs were approximately equal to the sum of the tetra- to octaCNs over Lake Ontario in 2000 (Table 1). Recalculated values for tetra- to octaCNs ranged from 16 to 80 pg m^{-3} in Chicago (excluding one outlier) [16]. Tetra- through octaCNs ranged from 18 to 59 pg m^{-3} in downtown Toronto in 2000 to 2001 but were lower in northern Toronto in 1998 to 2001, with concentrations of 5 to 27 pg m^{-3} , except for one high sample of 49 pg m^{-3} . Polychlorinated naphthalene levels in urban air are typically higher than those in more rural areas [21,22].

Concentrations of tri- and tetraCNs in water collected from Lake Ontario are listed in Table 1. Duplicate samples, collected in three cases, showed good agreement with the percentage differences of 1 to 7% for triCNs and of 0.3 to 24% for tetraCNs. Concentrations varied little across the lake, with triCNs ranging from 11.9 to 19.0 pg L^{-1} and tetraCNs from 4.3 to 8.4 pg L^{-1} . Few reports of PCNs in water have appeared in the literature. Järnberg et al. [23] found 0.89 ng L^{-1} of tetra- through heptaCNs in a PCB-contaminated lake and 2.6 ng L^{-1} in percolating landfill runoff. Concentrations of PCN in groundwater at $\mu\text{g L}^{-1}$ levels were found near a landfill in Spain [24].

Spatial trends

Spatial differences were observed for PCN concentrations between lakes in the region (Fig. 1). Analysis of variance revealed that mean ΣPCN concentrations varied significantly by location ($p < 0.0001$; Lakes Superior, Huron or Ontario, and the St. Lawrence River). A Bonferroni multiple mean comparison showed that mean ΣPCN concentrations (mean \pm standard deviation) were significantly higher ($p < 0.05$) over Lake Ontario ($5.56 \pm 2.09 \text{ pg m}^{-3}$) than over Lake Superior ($1.60 \pm 0.90 \text{ pg m}^{-3}$), Lake Huron ($2.38 \pm 1.07 \text{ pg m}^{-3}$), and the upper St. Lawrence River ($2.87 \pm 1.59 \text{ pg m}^{-3}$). No significant differences were found between concentrations over any of the other water bodies ($p > 0.05$). The highest concentration was

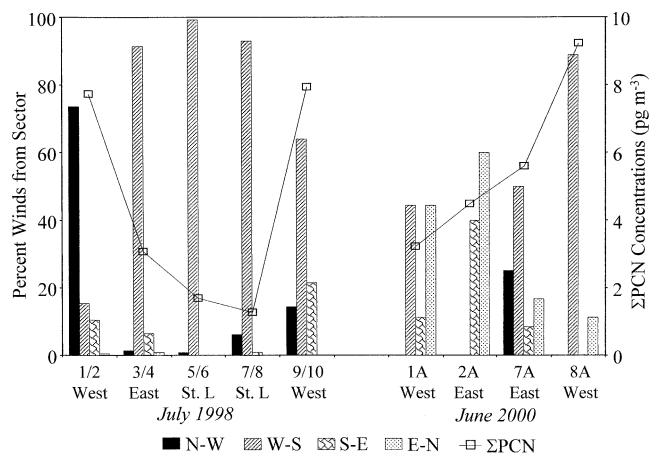


Fig. 2. Percentage of wind measurements from the north-to-west (N-W), west-to-south (W-S), south-to-east (S-E), and east-to-north (E-N) sectors and polychlorinated naphthalene (ΣPCN) concentrations for air collected above the western and eastern parts of Lake Ontario and the upper St. Lawrence River (St. L.) during the July 1998 and June 2000 cruises. Concentrations were higher with westerly winds and when air was collected at the western part of Lake Ontario, demonstrating the importance of proximity to source areas and the occurrence of prevailing westerly winds on observed PCN concentrations.

found over Lake Erie (11.5 pg m^{-3}), but only one sample was collected above this lake. Population and industrial density is greater around Lake Ontario than around Lakes Superior and Huron and the upper St. Lawrence River area, leading to a greater number of diffuse and point sources near Lake Ontario. Levels of tetra- through hexaCNs in background air averaged 5.1 pg m^{-3} in southern Sweden, which is closer to more populated areas, and 1.6 pg m^{-3} in northern Sweden [25]. These levels are comparable to those over Lake Ontario and Lake Superior, respectively.

A trend in concentration was apparent over Lake Ontario in July 1998 and June 2000 in relation to sampling locations and wind directions. September 1998 samples were collected intermittently over several days as lake-day and lake-night samples and could not be included in this analysis. Wind directions were recorded every 5 min in July 1998 and every hour in June 2000. These recordings were grouped into four quadrants, expressed as the percentage of the time the winds were from that quadrant, and were compared to observed PCN concentrations (Fig. 2).

In July 1998, winds were predominantly from the north-to-west and west-to-south quadrants throughout the cruise. The ΣPCN concentrations were highest for samples collected in the western end of Lake Ontario with urban/industrial areas to the northwest of Toronto, west (Hamilton, ON, Canada), and southwest along the Niagara River (St. Catherine's, ON, Canada; Niagara Falls ON, Canada/NY, USA; and Buffalo, NY, USA). Samples collected farther away from these areas in the eastern portion of the lake and in the upper St. Lawrence River had lower concentrations. Wind directions were more varied during the June 2000 cruise, with a greater proportion coming from the easterly directions (south-to-east and east-to-north) for samples LONT00 1A and 2A (Fig. 2). The ΣPCN concentrations were lower in these samples, then increased when the winds shifted, originating from westerly directions. The highest air-sample concentration during this cruise was collected in western Lake Ontario when the winds were predominantly from the southwest. Both cruises illustrate the effects of urban and industrial airsheds on ΣPCN levels over

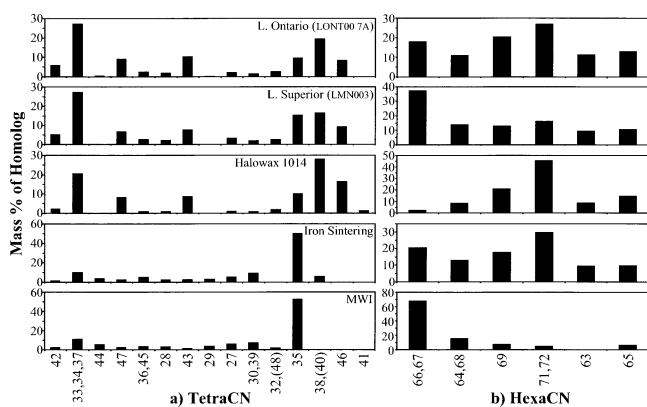


Fig. 3. Homologue normalized mass distributions of (a) tetrachloronaphthalenes (tetraCN) and (b) hexachloronaphthalenes (hexaCN) in representative air samples from Lake Ontario and Lake Superior and in source samples, including technical Halowax 1014, iron-sintering fly ash, and municipal waste incinerator (MWI) fly ash [8].

Lake Ontario. The influence of urban areas on concentrations in air over water bodies has been similarly noted for PCBs and polycyclic aromatic hydrocarbons near Chicago [26–30]. No trends were discernable for PCN concentrations in air over Lake Superior associated with wind directions.

Congener profiles and source indicators

Homologue mass percentage distributions (tetra- to octaCNs) for all samples collected ranged from 74 to 95% for tetraCNs (with only three samples >90%), 5 to 22% for pentaCNs, and <MDL to 5% for hexaCNs. The average mass percentage of tetraCN was significantly lower ($p < 0.05$, Student's t test) over Lake Ontario ($80.2 \pm 4.1\%$) than Lake Superior ($85.2 \pm 5.2\%$), whereas penta- and hexaCNs were higher ($p < 0.01$), with $17.0 \pm 3.1\%$ and $2.8 \pm 1.3\%$, respectively, for Lake Ontario and $13.3 \pm 5.0\%$ and $1.5 \pm 1.5\%$ for Lake Superior. This is consistent with a greater number of sources in closer proximity to Lake Ontario and a greater influence of transport of the lighter tetraCN congeners to the Lake Superior region.

Differences in homologue distributions were not as apparent on individual cruises given the limited number of samples that were collected. However, in the air above Lake Superior during August 1996, the sample with the lowest concentration (LMN004) had the highest proportion of tetraCNs and coincided with winds from the north. Tetrachloronaphthalenes are more volatile than the penta- and hexaCNs and, thus, are more subject to revolatilization and transport. In July 1998, samples collected in the upper St. Lawrence River exhibited higher proportions of tetraCNs (88–91% of Σ PCN) than over-lake samples (82–83%). The over-lake samples, collected closer to urban source areas, had greater contributions from penta- and hexaCNs, which have lower vapor pressures and are not transported to the same extent as the tetraCNs. Air samples from downtown Toronto showed even lower contributions of tetraCNs to Σ PCN (70–79%) [8].

Congener profiles for representative samples are illustrated in Figure 3 for the tetra- and hexaCN homologue groups and include air samples from Lakes Ontario and Superior, a typical technical Halowax mixture, and industrial-source fly ashes from an iron-sintering plant and a municipal waste incinerator, both located within the Lake Ontario region. Tetrachloronaphthalene profiles for all air samples were similar to the Halowax

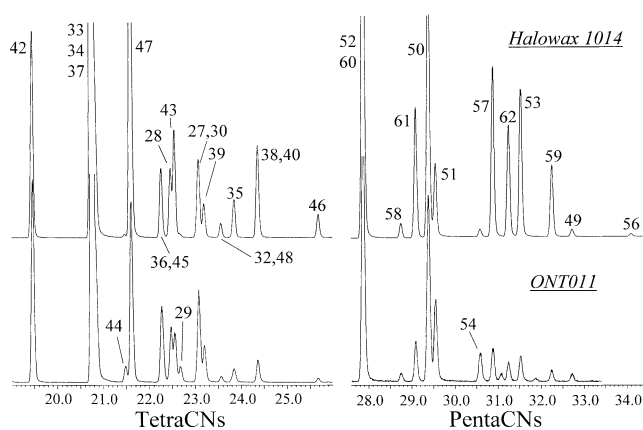


Fig. 4. Chromatogram illustrating the presence of the combustion marker congeners tetrachloronaphthalenes (tetraCNs) 44 and 29, and pentachloronaphthalene (pentaCNs) 54 in an air sample (ONT011) collected over Lake Ontario compared to a Halowax 1014 technical PCN mixture.

profile, suggesting the predominance of evaporative sources to Great Lakes air. The percentage contributions of CN 42 and of CNs 33, 34, and 37 to total tetraCNs were greater in air samples than in the Halowax mixtures (Fig. 3), which is expected, because these congeners have higher vapor pressures among the tetraCNs [31] and will become relatively enriched during atmospheric transport from sources. Hexachloronaphthalene patterns in air differed from the Halowax mixture and other evaporative sources such as PCB mixtures [5], showing an increase in the relative contribution of CNs 66 and 67 (Fig. 3). A similar profile was found in the iron-sintering fly ash, suggesting that such a source may contribute, to some extent, to hexaCN levels. Steel industries are located adjacent to the lakes, an example being in Hamilton (ON, Canada), which is at the western end of Lake Ontario. Chloronaphthalenes 66 and 67 are also the most abundant hexaCN congeners in other combustion sources such as municipal waste incineration (Fig. 3) [7,8,23]. However, these congeners are more volatile than the other hexaCNs [31]; thus, such an enrichment may result from their preferential evaporation and transport as well as from the influence of combustion sources. The CN 66 and 67 congeners were the most abundant PCNs in lake trout found in Lake Siskiwit on Isle Royale in Lake Superior [13]. These congeners are the most toxic [32] and among the more bioaccumulative PCNs [1].

The influence of combustion sources on PCN levels over the Great Lakes was further considered by examining combustion marker congeners such as tetraCNs 44 and 29 and pentaCN 54. These congeners are absent from or are trace components in Halowax [8,33] and Aroclor PCB [5] mixtures but are present in the fly ash of several combustion-related industries in the region [8]. Meijer et al. [34] found higher proportions of combustion-related PCNs, including CN 54, in more recent soil samples from the United Kingdom. Chloronaphthalenes 44, 29, and 54 were present in most samples, although at low levels (Fig. 4). By expressing their amounts as fractions of the marker congener and a more abundant congener in the homologue group, the markers were found to be enriched relative to the Halowax 1014 standard. For example, when CN 44 was detected, its isomer fraction relative to CN 42 ($44/[44+42]$) ranged from 0.034 to 0.10 in air over Lakes Ontario and Superior. This compares to values of 0.013 to 0.020 in Halowax 1014. Both CN 44 and 42 fraction values

Table 2. Calculation of tri- and tetrachloronaphthalene homologue Henry's Law constant from octanol-air (K_{OA}) and octanol-water (K_{OW}) partition coefficients

Octanol-air			Octanol-water			Air-water		
Congener	Log K_{OA} ^a	K_{OA}	Congener	Log K_{OW} ^b	K_{OW}	K_{AW} ^c	H ^d	H ^e
Trichloronaphthalenes								
19	7.88	7.63E + 07	21	5.35	2.24E + 05			
24/14	7.82	6.60E + 07	21	5.59 ^f	3.89E + 05			
23	8.14	1.37E + 08	26	5.12	1.32E + 05			
Mean		9.3E + 07			2.5E + 05	2.7E - 03	6.3	9.4
Standard deviation		3.9E + 07			1.3E + 05	1.8E - 03	4.2	
Tetrachloronaphthalenes								
33/34/37	8.68	4.82E + 08	27	5.75	5.62E + 05			
32	9.21	1.64E + 09	27	5.50 ^f	3.16E + 05			
35	9.04	1.11E + 09	27	6.34 ^g	2.19E + 06			
38	9.04	1.09E + 09	27	5.94 ^h	8.71E + 05			
46	9.08	1.22E + 09	28	5.77	5.89E + 05			
47	8.74	5.49E + 08	42	6.19	1.55E + 06			
			42	6.38 ^f	2.40E + 06			
			43	5.76	5.75E + 05			
			43	5.96 ^f	9.12E + 05			
			47	5.81	6.46E + 05			
Mean		1.01E + 09			1.06E + 06	1.0E - 03	2.5	7.0
Standard deviation		4.35E + 08			7.30E + 05	8.5E - 04	2.0	

^a Calculated from Harner and Bidleman [45] at 12.1°C.

^b Opperhuizen [46], unless noted.

^c Air-water partition coefficient = $K_{AW} = K_{OW}/K_{OA}$.

^d H (Henry's Law constant) = $K_{AW}RT$ at 12.1°C.

^e Estimated H (temperature adjusted) from HenryWin estimation software (U.S. Environmental Protection Agency; bond method, detailed in Meylan and Howard [39]).

^f Isnard and Lambert [47].

^g Lei et al. [38].

^h Opperhuizen et al. [48].

ranged from 0.040 to 0.092 in the air of downtown Toronto, an area influenced more by evaporative sources, compared to 0.036 to 0.56 in the air of northern Toronto, where combustion sources also contribute [8]. Similarly, fractions of CN 29 relative to CN 36 (29/[29+36]) and of CN 54 relative to CN 61 (54/[54+61]) reflected downtown Toronto values. The marker congeners, although present, were not enriched to the extent found in the northern part of Toronto, and together with the congener profiles in the air and source samples (Fig. 3), they indicate that although combustion sources do contribute, that evaporative sources are the dominant contributors to Σ PCN levels over the lakes.

Fugacity fractions and air-water exchange

Air-water gas exchange is an important environmental fate process for semivolatiles organic compounds such as organochlorine pesticides and polychlorinated biphenyls (PCBs) in the Great Lakes [35,36]. The net direction of gas exchange (sorption and volatilization) for PCNs may be estimated from air and water samples and literature values for physicochemical properties using a fugacity-based, two-film model [37]:

$$f_w = 10^{-12} C_w H / M \quad (1)$$

$$f_A = 10^{-12} C_A R T_A / M \quad (2)$$

$$f_w / f_A = C_w H / C_A R T_A \quad (3)$$

where f_w and f_A are the fugacities of the compound of interest in water and air (Pa), C_w and C_A are the dissolved water and vapor-phase concentrations (pg m^{-3}), H is the Henry's Law constant adjusted to the water temperature ($\text{Pa m}^3 \text{mol}^{-1}$), R

is the gas constant ($8.314 \text{ Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$), T_A is air temperature (K), and M is the molecular weight (g mol^{-1}). The water-air fugacity ratio (f_w/f_A) indicates the net direction of air-water exchange, where $f_w/f_A > 1$ is net volatilization, $f_w/f_A < 1$ is net sorption, and $f_w/f_A \approx 1$ indicates equilibrium.

Congener-specific Henry's Law constants have not been measured; thus, values were estimated on a homologue basis from measured octanol-air partition coefficients (K_{OA}), adjusted to the average water temperature for collected samples (12.1°C), and from measured octanol-water partition coefficients (K_{OW}) (Table 2). The partition coefficients were averaged for each homologue (tri- and tetraCNs), and the standard error was propagated through the calculations. The K_{OW} values were not adjusted for temperature, because they were expected to increase by only 0.2 log units by decreasing the temperature from the reference temperature (25°C) to 12.1°C [38], which is within the standard error of the average of measured values. For comparison, temperature-adjusted Henry's Law constants were also calculated using HenryWin software (EPI Suite[®]; U.S. Environmental Protection Agency, Washington, DC; detailed in Meylan and Howard [39]). The estimated H values used in fugacity calculations are included in Table 2.

Fugacity ratios calculated from average water concentrations and individual air samples collected during June 2000 on Lake Ontario are listed in Table 3. TriCN f_w/f_A ratios were >1 in all cases, indicating net volatilization. For the tetraCNs, f_w/f_A ratios were >1 , except for one sample, and were generally closer to equilibrium values, especially using H calculated from K_{OW} and K_{OA} . Polychlorinated biphenyls, which are compounds similar to PCNs, have been shown to be undergoing

Table 3. Tri- and tetrachloronaphthalene (triCN and tetraCN) fugacity ratios calculated for Lake Ontario in June 2000

Air sample	f_w/f_A^a		f_w/f_A^b	
	TriCN	TetraCN	TriCN	TetraCN
LONT00 1A	6.1	2.2	9.2	6.3
LONT00 2A	10.2	1.8	15.3	5.1
LONT00 7A	6.1	1.4	9.2	4.0
LONT00 8A	4.7	0.9	7.1	2.4

^a H calculated from octanol–air partition coefficient (K_{OA}) and octanol–water partition coefficient (K_{OW}) values.

^b H calculated by HenryWin software (bond method; U.S. Environmental Protection Agency).

net loss from the lakes because of gas exchange but also to be approaching equilibrium [35,36,40].

The lowest tetraCN fugacity ratio (0.9) occurred for an air sample collected closer to urban sources in the western end of Lake Ontario when winds were from the southwest, indicating that urban sources influence air–water exchange over the lake and, possibly, result in deposition. Indeed, if average tri- and tetraCN air concentrations observed in downtown Toronto were used [8], f_w/f_A values of 3.8 and 0.7, respectively (H from K_{OA} and K_{OW}), would result, showing net volatilization of triCNs but net deposition of tetraCNs. Net absorption of the sum of PCBs to southern Lake Michigan was found for model estimates based on elevated PCB concentrations over water resulting from the air plume from the Chicago area [28]. A similar observation was made for PCBs in precipitation with concentrations 2- to 400-fold higher over southern Lake Michigan than at a background station on the eastern shore, illustrating the influence of the urban Chicago air plume on wet deposition to the lake [26]. Green et al. [29] suggested that the PCB elevated concentration zone caused by the Chicago air plume reached 40 km over Lake Michigan. Polychlorinated biphenyl concentrations in surface films of urban, suburban, and rural areas in and near Toronto decreased by two-thirds within 12 to 14 km of the urban center for hexa- to decachlorinated biphenyls and within 50 km for mono- and dichlorinated biphenyls [41]. Loading of PCNs to the Great Lakes likely is influenced by urban airsheds, similar to PCBs, because PCNs are present in PCBs [4,5] and urban air concentrations are elevated [8,22] in comparison to rural locations. The city of Toronto will influence loadings to the western end of Lake Ontario, especially when winds are from the northwest.

Net volatilization of triCNs will result if significant loadings occur from sources such as urban runoff [42] or incoming tributaries or if transformations occur in the water column. Järnberg et al. [43] found a shift to lower-chlorinated PCN congeners when Halowax 1014 in methanol was irradiated in sunlight. More comprehensive sampling and experimental work is required to assess the fate of PCNs in the water column.

High relative standard deviations (up to 80%) resulted from calculation of a homologue value of H from measured K_{OA} and K_{OW} values. The H values calculated by the HenryWin software are estimated from fragment constants. The two calculations considered here are estimates, and as such, variation exists between the two values. Even direct H measurement methods can result in significant variation by factors of two to three, as is the case for many PCB congeners [44 and references cited therein]. Obtaining congener-specific and temperature-dependent Henry's Law constants may reduce this variation. A more detailed analysis of air–water exchange con-

sidering individual congeners is warranted to determine if net loading or loss is occurring, especially for the more toxic and higher-molecular-weight congeners. Combustion-related congeners may also exhibit f_w/f_A of differing magnitudes than congeners that are typical of evaporation sources. Meijer et al. [34] found that the lowest soil–air fugacity fractions in United Kingdom soils were for combustion-related congeners.

CONCLUSIONS

Analysis of air samples from several research cruises over the Great Lakes and the upper St. Lawrence River reveal spatial variations in the concentrations of PCNs. Higher levels occurred over Lake Ontario than over Lakes Huron and Superior and the St. Lawrence River. Population density is higher near Lake Ontario, likely resulting in a higher proportion of diffuse and point PCN sources. Urban and industrial areas adjacent to Lake Ontario influence air concentrations, especially when winds are from the west. Congener profiles indicate that evaporative sources of PCNs predominate, but some contributions of combustion sources were apparent. Air–water gas-exchange calculations show that the triCNs are volatilizing from Lake Ontario and that the tetraCNs are closer to equilibrium but are also volatilizing. Deposition of tetraCNs may occur when urban air plumes reach over the lake. Direct measurements of H are required to improve estimates of air–water gas exchange and to make flux calculations for specific PCN congeners of importance.

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