SOURCES OF POLYCHLORINATED NAPHTHALENES IN URBAN AIR AND OCCURRENCE IN THE ARCTIC ENVIRONMENT

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Introduction

Polychlorinated naphthalenes (PCNs), manufactured as complex mixtures for use in the electrical industry[1], are also found in PCB mixtures[2] and waste incinerator emissions[3,4]. Recent studies of their toxicological properties[5], occurrence in biota[6-8] and humans[9], and presence in remote regions[10,11] support their proposed addition to the UN-ECE LRTAP - POPs Protocol.

This paper reports contributions of combustion and evaporative emissions of PCNs and non-/mono-*ortho*-substituted PCBs (n/m-*o*-PCBs) to urban air and illustrates the influence of urban and industrial areas on air concentrations over the Great Lakes. Seasonal trends in arctic air are highlighted and discussed in terms of long range transport from source regions and their presence in arctic marine mammals investigated. PCNs are compared to PCBs on a toxicity basis and shown to be a compound class of concern.

Materials and Methods

Air samples (24-48 hour; 700-1800 m^3) were collected using glass fibre filters (GFF) and polyurethane foam plugs (PUF) in urban Toronto, Canada, over the Great Lakes, and at Resolute Bay, Canada. Archived weekly sample extracts collected at remote arctic sites at Alert and Tagish, Canada and Dunai Island, Russia were obtained, for which experimental details have been reported[12], and portions were combined into 4 week composites for 1994 and the first 4 weeks of 1995 representing 1900-3600 m^3 of air. Blubber from beluga whale and ringed seal collected near Baffin Island were extracted by ball mill and lipids removed[11]. Air samples were Soxhlet extracted then air and blubber extracts were fractionated by column chromatography on silicic acid then mini-carbon columns using published methods[10,13]. Combustion fly ashes from a municipal waste incinerator, cement kiln, iron sintering plant and medical waste incinerator, and technical PCN (Halowaxes 1014, 1013, 1099, 1000, 1051) and PCB (Aroclors 1254, 1260) mixtures were examined for PCN source congener patterns. Sample details and extraction methods are reported elsewhere[13].

Samples were analysed by gas chromatography-negative ion mass spectrometry (GC-NIMS) using 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 and an 8-congener n/m-*o*-PCBs solution with published parameters[11]. Coeluting penta- and hexaCNs were resolved using a 30 m Rt-ßDEXcst column and conditions listed in Helm et al[14]. Mirex was used for volume correction and all air samples were recovery and blank corrected, with fractionation/clean-up recoveries ranging from 60-120 %.

Table 1. Mean, Minimum and Maximum Concentrations (pg m^{-3}) of PCNs and mono-/non-*ortho* PCBs in Urban, Lake Ontario / Cornwall, and Ambient Arctic Air.

	ΣPCN[a]			ΣMono-/Non-ortho PCBs[b]		
Location	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Toronto						
UT	51	31	78	17	6.4	30
MSC	28	7.3	84	5.5	1.2	16
Lake Ontario	18	9.2	34	7.2	2.9	17
Lake Superior	4.6	0.8	16			
St. Lawrence River	7.9	3.2	17	4.3	1.6	13
Arctic						
Alert, NT	0.54	0.006	1.0	0.09	0.03	0.19
Dunai, Russia	0.82	0.005	2.9	0.41	0.18	0.80
Tagish, YK	0.33	ND[c]	1.7	0.002	0.11	0.04
Resolute, NT	4.2	1.6	12	0.61	0.26	1.3

[a] Sum of tri- to octaCNs; breakthrough of triCNs occurred in some samples. [b] Sum of m-*o*-PCBs 118, 114, 105, 156 and n-*o*-PCBs 81, 77, 126, 169. [c] Below the method limit of detection.

Results and Discussion

Table 1 summarizes ΣPCN and Σn/m-*o*-PCB ambient air concentrations at various locations. In Toronto air, PCNs averaged 51 pg m^{-3} at a downtown site (UT) which was higher than in the city's north (MSC) and were similar to levels in other urban areas[15,16]. Congener distributions varied between the sites with the MSC profile reflecting greater combustion-related inputs as indicated by profile comparisons between air and source samples. An enrichment of combustion congeners is illustrated by the normalized mass percent distribution (UT/MSC)[13], except for July when the pattern was related to vapour pressures (Figure 1). This suggests that evaporative emissions dominate at during the summer, but MSC is further removed from downtown emissions, or fewer evaporative sources influence MSC air. In cooler months, evaporation is less important and combustion contributions of up to 55 % of total PCNs at MSC are observed[13]. Non-*ortho* PCBs, also formed in combustion processes, were enriched in air near MSC relative to UT.

ΣPCN and Σn/m-*o*-PCBs in Great Lakes air were lower than in urban air, but concentrations were elevated over Lake Ontario relative to Lake Superior and the St. Lawrence River. The Lake Ontario shoreline is more urban/industrialized than Lake Superior or the St. Lawrence River with more sources contributing to the air. A trend was observed over Lake Ontario with higher PCN levels coinciding with winds from the west which pass over the more populated regions. A similar trend was not observed for the n/m-*o*-PCBs. Combustion markers were present and enhanced in PCN profiles relative to technical mixtures.

At the remote arctic stations, ΣPCN concentrations were highest at Dunai, Russia, and lowest at Tagish, YK, and varied seasonally with higher concentrations during winter (Figure 2) when air masses entering the Arctic originate over Eurasia. No trend was found for Σn/m-*o*-PCBs except at Dunai where concentrations increased in the warmer months, likely from more localized PCB emissions. Stern et al.[12] found enrichment of penta- and hexaCBs to total PCBs at Dunai during the summer months. Summer 1999 concentrations at Resolute, NT were elevated relative to the high arctic stations and

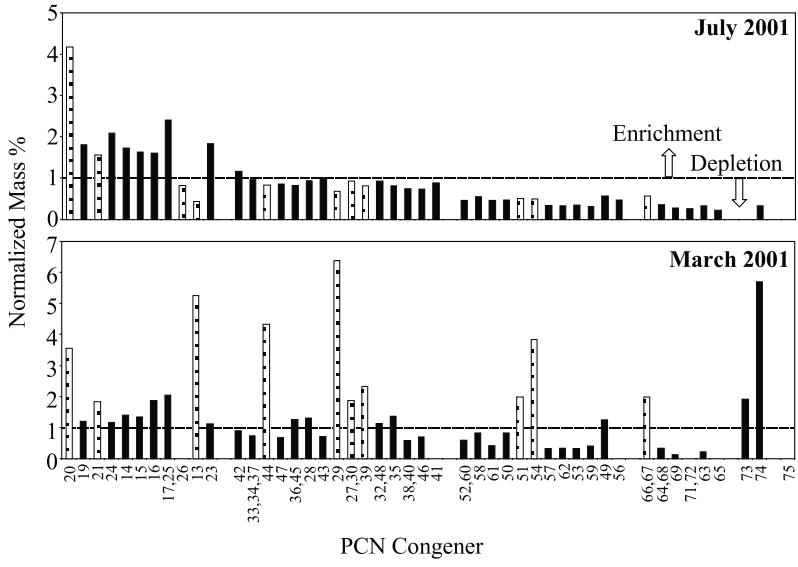

Figure 1. Normalized PCN mass percent distribution (MSC divided by UT distributions) for samples collected during the same period. Combustion-related congeners are lightly shaded.

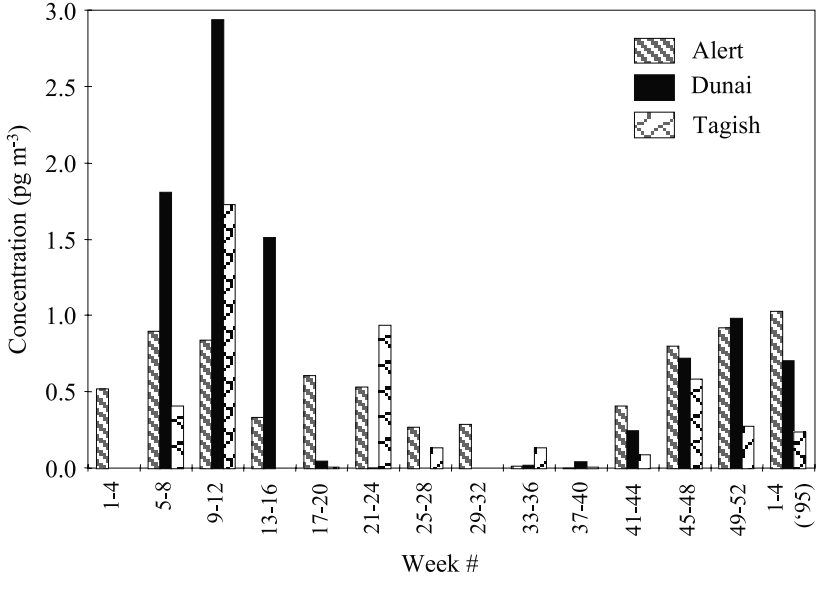

Figure 2. Seasonal ΣPCN concentration trend in air at remote arctic monitoring stations at Alert, NT, Dunai, Russia, and Tagish, YK in 1994/95.

Clausius-Clapeyron plots suggest that evaporation from local surfaces or sources contribute to these levels in addition to advective transport. ΣPCN concentrations ranged 36-383 and 35-71 pg g^{-1} in beluga and ringed seal, respectively, and Σn/m-*o*-PCBs ranged 15-317 and 16-41 ng g^{-1}.

PCNs and n/m-*o*-PCBs were compared on a toxicity basis relative to 2,3,7,8-TCDD using equivalency factors listed by Kannan et al.[7]. In urban air, 64, 33, and 3 % of total PCN+PCB toxic equivalents (TEQ) on average were contributed by PCNs, non-, and mono-*ortho* PCBs, respectively, at MSC and 48, 50, and 2 % at UT[13]. In arctic air, PCNs contributed >70 % to PCN+PCB TEQ in the winter months at Alert and Dunai but non-*ortho* PCBs dominated during the summer months and at Tagish year round. PCNs contributed an average of 11 % to PCN+PCB TEQ in beluga whale blubber even though Σn/m-*o*-PCB concentrations were ~500 times higher than SPCNs[11].

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