POLYCHLORINATED NAPHTHALENES IN ARCTIC AIR AND BIOTA

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Introduction

The use of polychlorinated naphthalenes (PCNs) in past industrial applications and emissions from current combustion sources have resulted in their widespread environmental presence. These compounds are of concern in the arctic environment due to their persistence, ability to accumulate[1] and their dioxin-like toxicity[2]. PCNs have been detected in ambient air at remote arctic monitoring stations[3].

This paper presents ΣPCN levels and trends measured at Alert, Canada and Dunai Island, Russia over 1994. Particle-gas partitioning is assessed as a mechanism for long range transport of PCNs. To provide an indication of their presence the Canadian arctic food chain, PCN results from analysis of selected ringed seal and beluga whale blubber samples are presented.

Methods and Materials

Ambient air samples were collected as part of a multi-year monitoring program at remote arctic sites at Alert, Canada and Dunai Island, Russia for which experimental details have been reported[4]. Portions of archived weekly extracts (PUF and filters) from each monitoring station were combined into 4 week composites (13 in a year) for 1994 and the first 4 weeks of 1995. Extracts were received in DCM, exchanged into isooctane then reduced in volume.

Beluga whale and ringed seal blubber samples were collected near Pangnirtung, NT, Canada in an ongoing sampling and stock identity program supported by the Nunavut Wildlife Management Board (NWMB) and Department of Fisheries and Oceans (DFO). Blubber and other tissues were collected by hunters using standardized kits during subsistence hunts and shipped frozen and stored at -40°C until analysis. Two grams of blubber was partially thawed, combined with anhydrous Na_2SO_4, and extracted twice in hexane in a small ball mill, centrifuging and decanting the hexane between extractions. Portions of the extract (1/10) were used for gravimetric lipid analysis while portions representing 0.66 g and 0.44 g of blubber for ringed seal and beluga, respectively, were used for PCN analysis. Animals were aged by thin sectioning a canine tooth from the lower jaw and counting growth layer groups in the dentine using transmitted light.

Air and biota extracts were fractionated as described elsewhere[3] and 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 previously reported conditions[3].

Coeluting penta- and hexaCNs were resolved and quantified using a 30 m Rt-βDEXcst column and parameters described by Helm et al[5]. Mirex was used for volume correction and all air samples were recovery and blank corrected, with fractionation/clean-up recoveries ranging from 70-100 %.

Results and Discussion

Figure 1 summarizes ΣPCN concentrations at Alert and Dunai in 1994/95. Levels ranged from <0.1 - 1.0 pg m^{-3} at Alert and <0.1 - 2.3 pg m^{-3} at Dunai. Similar levels were reported from the same sites in 1993, ranging from 0.91-8.0 pg m^{-3} at Alert and 0.31-1.2 pg m^{-3} at Dunai[3]. Concentrations at Alert and Dunai were lower than levels observed in arctic air at lower latitudes over the Eastern Arctic Ocean, Norwegian Sea, and Barents Sea[3]. Seasonal variations in ΣPCN levels were observed at both Alert and Dunai, with higher concentrations during colder months. A similar observation was made for PAHs at these sites[6] although PCBs did not exhibit a seasonal trend[7]. Association of PCNs with arctic haze during winter may account for these variations as ΣPCN and TSP concentrations were positively correlated.

During the colder months, a higher proportion of PCNs was associated with the particle phase. Particle-gas partitioning of PCNs may be described by $K_p = F/A(TSP)$, where F and A are the particle and gas phase concentrations, respectively (ng/m^3) and TSP is the total suspended particle concentration (ng/m^3). TSP was assumed equal to SO_4^{2-} concentrations at Arctic sites[6]. Figure 2 illustrates the relationship between log K_p and log K_{OA} (the octanol-air partition coefficient[8]) of the PCN congeners for 1994 winter composite samples (n=7) at Alert. K_{OA} values were adjusted to average air temperatures during the time samples were collected[9]. The strong correlation supports the use of K_{OA} as a descriptor of particle-gas exchange.

PCN levels found in ringed seal and beluga blubber are summarized in Table 1. ΣPCN concentrations ranged from 53-372 pg/g in beluga and 46-66 pg/g in ring seal on a blubber wet weight basis (approx. 90% lipid). These levels are a factor of 10-100 times lower than those found in Baltic Sea harbour porpoises[10] and 2-10 times lower than in harbour porpoises from the west coast of Sweden[11]. The levels in ringed seal were similar to the 38 pg/g lipid (tetra- and pentaCNs) found in a ringed seal from near Svalbard, Norway[12]. The PCN homolog distribution differed between species with tetraCNs followed by pentaCNs dominating in ringed seal while a more even distribution was evident in beluga. This likely results from differences in metabolic processes.

In the beluga, pentaCNs-52/60, -50, and -61 and hexaCNs-66/67 were the dominant higher chlorinated congeners. These congeners have been found to bioaccumulate in several species[1]. Separation of CN-52/60 and CN-66/67 is necessary to fully assess toxicity as the coeluting congeners have different toxic equivalence factors[2], and especially if one congener has a higher bioaccumulation potential. CN-66/67 ratios were determined in the beluga samples and ranged from 0.83-1.34. Similar values of 1.03-1.16 were found in selected winter air samples from Alert and Dunai, suggesting that neither CN-66 nor CN-67 is more accumulative than the other in beluga whales.

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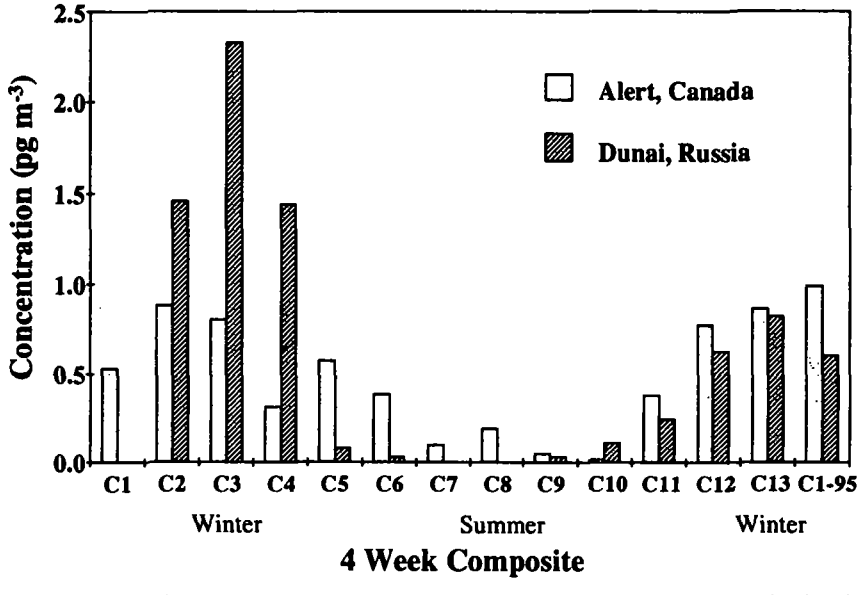

Figure 1. ΣPCN concentrations (PUF and filter) at Alert, NT and Dunai Island, Russia in 1994-1995 for 4 week composite samples.

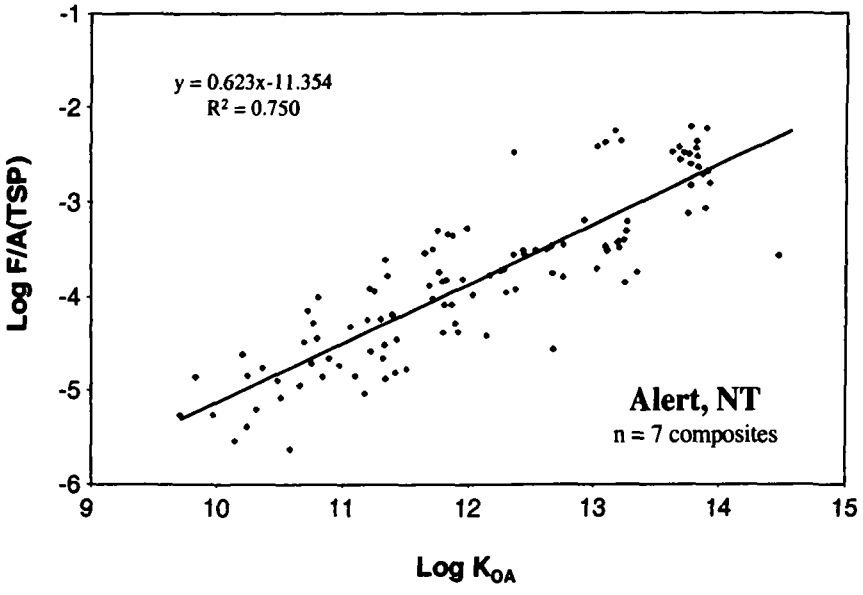

Figure 2. Particle-gas partitioning as a function of Log K_{OA} at Alert, NT in 1994-95. F and A represent particle- and gas-phase concentrations of PCN congeners (ng/m^3) and TSP is taken as the particulate sulfate concentration (ng/m^3).

Table 1. Sex, age and PCN concentrations (pg/g wet weight) for beluga whale and ringed seal blubber samples.

				PCN Concentrations (pg/g)				
Sample	Species	Sex	Age	TriCNs	TetraCNs	PentaCNs	HexaCN	ΣPCN
B94-151	Beluga	F	13	3.7	53.9	117.2	50.6	225.5
B94-163	Beluga	F	41+	ND	12.5	29.6	10.5	52.6
B94-142	Beluga	F	12	2.0	58.9	123.8	56.4	241.1
B94-118	Beluga	M	13	5.78	146.6	144.5	75.6	372.4
B94-120	Beluga	M	3	8.4	75.9	114.5	93.5	292.8
B94-122	Beluga	M	3	1.0	75.8	111.2	143.3	331.4
93-54	R. Seal	F	10	8.4	37.9	13.8	2.3	62.4
93-56	R. Seal	M	8	5.8	30.2	14.3	0.3	50.5
93-57	R. Seal	M	7	4.6	30.2	15.6	1.8	52.2
93-59	R. Seal	M	9	4.9	32.2	21.2	0.8	59.0
93-60	R. Seal	F	13+	5.7	26.3	14.2	ND	46.3
93-61	R. Seal	F	8+	11.2	38.2	17.0	ND	66.4

ND - not detected