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NEW PERSISTENT CHEMICALS IN THE ARCTIC ABIOTIC ENVIRONMENT

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Introduction

During the last five years of the Canadian Northern Contaminants Program (NCP Phase II, 1997-2002), special emphasis was placed on identifying "new" persistent chemicals in the Canadian Arctic. In some cases, the new chemicals are being currently used in Canada, the U.S. and Europe: pesticides, brominated flame retardants (BFRs) and short-chain chlorinated paraffins (SCCPs). Others considered are "legacy" substances which had not been monitored under the previous 5-year program, NCP Phase I: coplanar PCBs and polychlorinated naphthalenes (PCNs). From a national and international regulatory perspective, finding new chemicals in the Arctic implies that they are sufficiently persistent in the atmosphere and seawater to be transported long distances from their sources. Both the Canadian Toxic Substances Management Policy and the United Nations Economic Commission for Europe (UN-ECE) draft protocols on POPs include the presence of chemicals in remote environments as evidence of persistence.

This paper summarizes information on new chemicals in the arctic abiotic environment (air, water, sediment) which has been recently reported in the Canadian Arctic Contaminants Assessment Report II, Sources, Occurrence, Trends and Pathways in the Physical Environment (CACAR II - PHYS)[1].

Locations and Measurements

Archived extracts of air samples collected at monitoring stations during 1994-95 were examined for new chemicals. The stations were Alert (82°30'N, 62°20'W) and Tagish (60°20'N, 134°12'W) in the Canadian Arctic and Dunai in the Russian Arctic (74°06'N,124°30'E). Some currently used pesticides and chlorophenolic compounds (CPCs) were also measured at Alert in 1995-97 through the arctic air monitoring program[2]. Additional air samples were collected for selected chemicals in the eastern Canadian Archipelago in 1999 at Resolute Bay and from shipboard on the Swedish Tundra Northwest-99 expedition. Sediments from lakes and marine areas and seawater samples were obtained from the Archipelago. Methods are described in the primary literature referenced in CACAR II – PHYS[1].

Results and Discussion

Organohalogen Compounds in Air

Several novel organohalogen compounds were identified in air, including BFRs, PCNs, coplanar PCBs (Co-PCBs, mono- and non-ortho congeners), SCCPs, CPCs and currently used pesticides (Table 1).

Among the BFR chemicals, polybrominated diphenyl ethers (PBDEs) were the only ones of significance found in arctic air. Other BFRs (hexabromocyclododecane, HBCDD and tetrabromobisphenol A, TBBP-A) were below detection limits. PBDE concentrations in air were highest at Tagish, intermediate at Alert, and lowest at Dunai and showed a trend of higher

concentrations during the warmer months. The concentrations at Alert and Tagish were higher than air concentrations reported for the city of Chicago and the Great Lakes[3]. In the case of Tagish there is the possibility that incineration of household items in the region could contribute PBDEs to the air at the sampling site. At Alert the source has not been identified. Field blanks showed only very low levels of the PBDEs. An interesting feature of the samples collected at Alert is the presence of mono-, di- and triBDE congeners, which might be an indication of photodegradation during long-range transport.

PCNs were used in similar applications as PCBs and also produced during combustion processes such as municipal solid waste incineration[4]. ΣPCN concentrations in arctic air were strikingly variable, being highest in the eastern Arctic Ocean and from 65-75°N in the Canadian Archipelago. Concentrations in the high Arctic at Alert, the western Canadian subarctic (Tagish) and the Russian Arctic (Dunai) were an order of magnitude lower (Table 1). The ΣPCNs was 40 pg/m^3 over the Barents Sea in 1996, and related to air trajectories passing over central Europe, the U.K. and the North Sea[5]. PCNs were also elevated in U.K. air[6]. At Alert and Dunai during 1994-95, ΣPCNs were highest in winter – spring and lower in summer – fall, suggesting an association with combustion emissions. An opposite trend was found for ΣCo-PCBs, which were highest in the warmer months, especially at Dunai. The distribution of PCN homologs in air was tri = tetra > penta > hexa >hepta.

SCCPs are used as extreme pressure additives in lubricants. Maximum usage of SCCPs occurred between 1978 and 1985[7]. The ΣSCCPs (C_{10} – C_{13}) in archived 1993-94 samples from Alert ranged from <0.4 to 7.3 (mean 2.0) pg/m^3.

The currently used organochlorine pesticides trifluralin, methoxychlor, endosulfan and lindane were determined in 1994-95 archived air samples and/or in 1995-97 samples from Alert (Table 1). Lindane (γ-HCH) was the most abundant pesticide, followed by methoxychlor and trifluralin. Current use of lindane in Canada and Europe, and use/re-emission of technical HCH in Asia probably account for its major sources. Endosulfan is widely used in Canada, the U.S. and Europe. Methoxychlor has limited use in Canada and the U.S. on fruit crops and home gardening products. More than 5000 tonnes/y of trifluralin was applied annually in western Canada and the U.S. during the 1990s. The presence of trifluralin in arctic air is surprising, since its reported atmospheric half life is only 21-74 minutes[8]

Other chemicals identified were octachlorostyrene (OCS) and the chlorophenolic compounds (CPCs) pentachloroanisole, trichloroveratrole and tetrachloroveratrole (Table 1). OCS is a byproduct of chlorine manufacturing, while the CPCs are methylation products of chlorophenols, possibly originating from pulp bleaching and chlorination of wastewater.

Organohalogen Compounds in Sediments

ΣPBDEs in three marine sediment samples were 107, 122 and 297 pg/g dw. PBDE 47, the most abundant congener, occurred at 40, 46, and 107 pg/g dw.

ΣSCCPs in marine sediments from the Archipelago ranged from 4.8 to 77 ng/g dw and generally decreased from the south to north (Figure 1). A ΣSCCP concentration of 4.5 ng/g dw was found in the surface slice of a sediment core collected from Lake Hazen on Ellesmere Island[9]. Relative to the commercial PCA 60 formulation (C_{10} -C_{13} , 60% Cl) the shorter carbon chain length and lower chlorinated C_{10} and C_{11} formula groups were predominant in sediments. This result is consistent with the trend of increasing vapour pressures with shorter carbon chain length and lower degree of chlorination Analysis of a laminated sediment core from a lake on Devon Island in the Archipelago revealed trends in ΣSCCPs that were similar to historical use patterns, with about a 10-y lag time between commercial introduction and arrival at the lake's sediments.

Chloroanisoles and free chlorophenols were found in a sediment core from Coal Lake, a small sub-alpine headwater lake in Yukon, Canada. The ΣCPCs started to increase in the 1940s, coincident with the introduction of pentachlorophenol (PCP) as a wood preservative. Peak concentrations of 2.5 pg/g dw occurred in 1952, and gradually declined to 1.6 pg/g dw in the 1997

layer. The onset of chloroanisoles occurred about 12 years later than chlorophenols. Chloroanisole concentrations were approximately the same as those of the chlorophenols, but peaked in 1992 with a secondary peak in 1963.

Organohalogen Compounds in Seawater

A search was made for a large number of modern pesticides in seawater. Lindane and endosulfan were the only compounds found; others were below the detection limit. Although lindane is still used in Canada and was recently deregistered in other circumpolar countries, it is likely that historical atmospheric and oceanic transport of technical HCH, as well as lindane, from Eurasia are largely responsible for the present-day concentrations in arctic seawater. Concentrations of lindane measured during the 1990s are generally highest in the Beaufort Sea and western Archipelago (0.35-0.95 ng/L), somewhat lower in the Bering-Chukchi seas (0.18-0.46 ng/L), northern Canada Basin (0.47 ng/L) and the White Sea (0.16-0.41 ng/L) and lowest in the Barents Sea and eastern Arctic Ocean (0.16–0.29 ng/L). Concentrations of endosulfan I in Canadian arctic waters ranged from <0.5-10 pg/L, with averages of 2.0 pg/L in the northern Canada Basin in 1994[10] and 6.3 pg/L in the eastern Archipelago in 1999.

Recommendations

Several recommendations were made in CACAR 2-PHYS concerning new chemicals:

- Recognizing that the presence in the Arctic and other remote regions is a key point in evaluating chemicals for persistence, surveillance of the chemicals discussed here should be continued and the search expanded for additional contaminants.
- The ability of currently used chemicals to undergo long-range transport should be assessed.
- Photochemical products of contaminants should be identified and evaluated with respect to their potential for atmospheric formation and transport.

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Table 1. Novel Halogenated Organic Compounds in Arctic Air, pg/m^3

Compound	Date	Alert, Canada	Tagish, Canada	Dunai, Russia	Canadian Archipelago	Eastern Arctic Ocean	Ref.

ΣPCNs	1993-94	2.5		0.84		11.6	5
	1994-95	0.50	0.33	0.65			1
	1999				5.7		11
ΣCo-PCBs[a]	1993-94	0.46		1.9		0.98	5
	1994-95	0.084		0.44			1
	1999				1.2		11
ΣPBDEs[b]	1994-95	240	424	18			1
ΣSCCPs	1993-94	2.0					1
ΣCPCs[c]	1993-94	4.2	5.5	4.8			1
	1995-97	4.7					2
OCS	1993-94	0.79	0.67	0.60			1
Endosulfan	1993-94	4.2	7.1	3.0			1
	1995-97	4.4					2
	1999				4.0		
Methoxychlor	1993-94	0.27	0.36	0.41			1
	1995-97	0.16					2
Trifluralin	1993-94	0.12	0.16	0.18			1
	1995-97	0.09					2
Lindane	1995-97	6.4				17	2,12
	1999				10		

a) Sum of mono-CBs 105, 114, 118, 156, and non-ortho CBs 77, 81, 126, 169

b) Sum of BDEs 47, 99, 100, 153, 154

c) Sum of chlorophenolic compounds pentachloroanisole, trichloroveratrole, tetrachloroveratrole

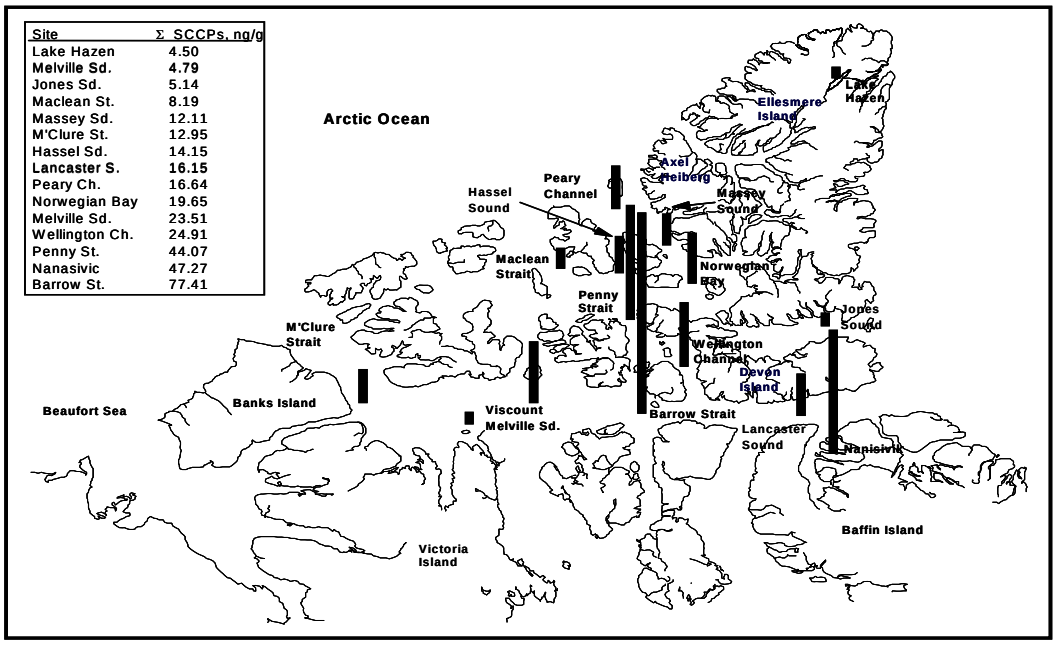

Figure 1. ΣSCCP concentrations (ng/g dw) in surface sediments from the Canadian Arctic.