Polychloro-*n*-alkanes in Beluga Whales from the Arctic and the St. Lawrence River Estuary.

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Introduction

Polychloro-*n*-alkanes (PCAs) are a class of industrially produced mixtures of the general formula $C_nH_{2n+2-z}Cl_z$ having carbon chain lengths from C_{10} to C_{30} and chlorine content from 30 to 70% by mass. Because they are produced *via* free radical chlorination of *n*-alkanes, a single PCA formulation consists of thousands of different compounds with a range of physical-chemical properties [1]. PCAs are generally used as high temperature lubricants in metal-working machinery and in flame retardant plasticizers; their more limited applications include use in adhesives, paints, rubber and sealants [1].

Particular attention has been given to the short chain PCAs (*i.e.*, C_{10}-C_{13}), which have the greatest potential for environmental release, exhibit the highest toxicity, and because of their environmental mobility could have adverse effects on terrestrial and aquatic organisms [1]. Fisk *et al.* (1996), from studies on juvenile rainbow trout, demonstrated that highly chlorinated short chain PCAs have the greatest potential for bioaccumulation or even biomagnification [2].

To date, there is limited information regarding the environmental levels of PCAs in aquatic biota. Even less is known about their levels in the Canadian Arctic. In the present study blubber of male beluga whales from various regions of the Canadian Arctic and the St. Lawrence River estuary have been analyzed for short chain PCAs by high resolution gas chromatography electron capture negative ion mass spectrometry (HRGC-ECNI/HRMS) as described by Tomy *et al.* (1997) [3]. The formula group abundance profiles (FGAP) of the mammals were also examined as they provided insight into the source, and mode of environmental transport of these compounds. PCA levels relative to those of other persistent organochlorines (OCs) are also reported.

Materials and Methods

Chemicals. The commercial formulation, C_{10}-C_{13}, 60% chlorine by mass (PCA-60) was supplied by Dover Chemicals Corp. (Dover, OH) and used as the external standard for this study.

Extraction. Procedures for the extraction and clean-up of blubber tissues were previously described by Muir *et al.* (1996). Fractions 2 and 3 from the Florisil column were combined, and reduced to 0.5 mL with a gentle stream of nitrogen prior to GC/MS analysis.

Gas Chromatography/Mass Spectrometry. GC/MS conditions were previously described [3].

Results and Discussion

ECNI selected ion chromatograms (SIM). Figure 1 shows the ECNI SIM of the $C_{10}H_{15}Cl_7$ formula group, based on the response of the $[M - Cl]^-$ ion, present in two beluga samples and in the PCA-60 standard. Reasons for the altered appearance of the elution profile of this species in the Pangnirtung beluga remains unclear. In may be a direct result of the PCA formulation that the mammals are exposed to in their diet or, perhaps, a difference in the food web structure. The profile of the beluga from Sanikiluaq (E. Hudson Bay) is typical of the profiles for the other belugas examined in this study.

Variation in the FGAP with sampling site. FGAPs for a few samples are shown in Figure 2. Apart from the Pangnirtung beluga, which is dominated by the $C_{10}H_{15}Cl_7$ species (its abundance accounts for 38% of the total ion signal), the FGAP for the other Arctic mammals are dominated by the lower chlorinated congeners in each homologue group. The C_{13} homologue group accounts for very little of the total abundance in all cases. The enrichment of the FGAP by the lower chlorinated congeners is consistent with the findings of Drouillard *et al.* (1998) who have shown that these congeners are the more volatile components of PCA mixtures (5). These results provide evidence for long range atmospheric transport and subsequent uptake of PCAs into remote marine foodwebs. Further evidence for atmosphere transport of these compounds is elucidated by their detection in air samples for Alert on Ellsemere Island. Mean concentrations of PCAs in air collected at Alert in 1992 were found to be 20±32 pg/m^3 (*n=4*). The FGAP for the belugas from St. Lawrence river resembles that of the commercial formulation, the sum of the less volatile C_{12} and C_{13} formula groups accounting for 45% of the total abundance. This observation suggests that local sources of PCAs, possibly from the Great Lakes may be more important inputs of PCAs into this system.

PCA concentrations relative to other OCs. The concentration of PCAs relative to those of other OCs is shown in Table 1. Concentrations of PCAs in the St. Lawrence beluga were higher than in any of the Arctic mammals. Mean wet weight PCA levels in St. Lawrence beluga were 4 times higher than in belugas from W. Hudson Bay, 2.5 times higher than in belugas from Sanikiluaq, 2 times higher than in belugas from Hendrickson Island and ~1.3 times higher than in belugas from Pangnirtung.

In general, PCA concentrations were found to be lower than that of other OCs. The Henry's Law Constant (HLCs) of short chain PCAs, based on direct measurements by Drouillard *et al.* (1998), suggests that these compounds are in the range of semi-volatile organics such as HCH isomers. It is not surprising, therefore, that PCAs, like HCHs which do not biomagnify to the same extent as the other OCs, have similar environmental concentrations in the mammals investigated in this study.

References

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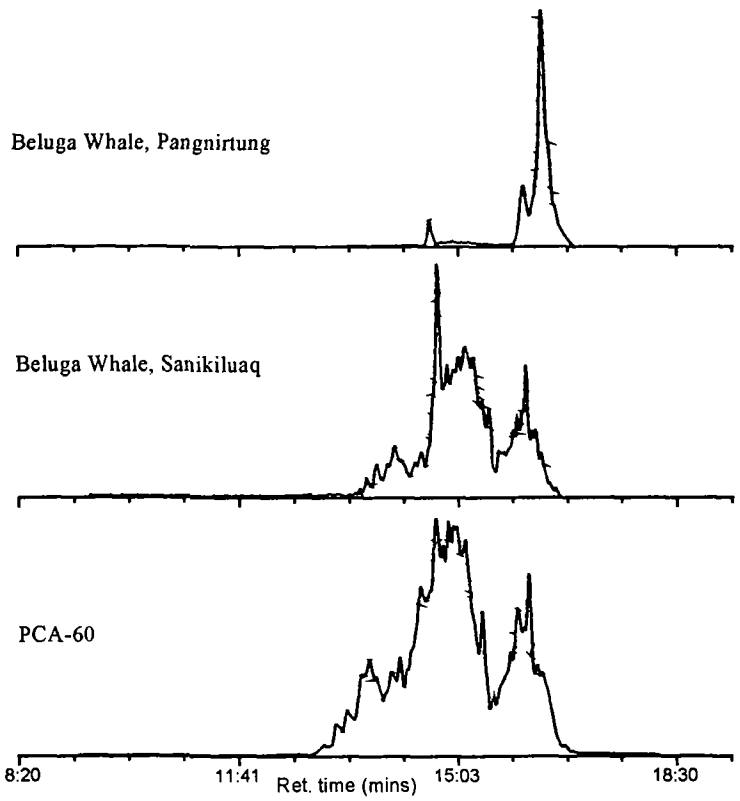

Figure 1. ECNI SIM of the $C_{10}H_{13}Cl_7$ formula group, based on the response of the $[M\text{-}Cl]^-$ ion, present in two beluga samples and in the PCA-60 standard.

Table 1. Concentration (ng/g, wet wt) and [standard deviation] of PCAs and other OCs in blubber samples from male beluga collected from the Arctic and the St. Lawrence River Estuary.

Location	Age	Lipid (%)	ΣHCH	ΣCHLOR	ΣDDT	ΣPCB	ΣCHB	ΣPCA
Hendrickson	16.6	90.9	342	2158	3388	4673	5315	626[a]
Island	[4.5]	[2.5]	[80.3]	[631]	[1090]	[1469]	[1897]	[499]
Sanikiluaq	35.6	94.8	405	4769	14738	7908	15414	323
	[13.9]	[0.7]	[84.7]	[1463]	[6854]	[1579]	[8157]	[76.2]
W. Hudson	nd	98.6	367	210	1595	2230	5537	204
Bay		[10.4]	[85.2]	[56.9]	[329]	[895]	[815]	[54.5]
Pangnirtung	8.8	90.5	233	1709	4531	3768	9273	457[b]
	[6.0]	[3.2]	[62.9]	[521]	[1835]	[1388]	[2781]	[306]
St Lawrence[d]	20.5	82.2	500	9872	124188	108583	22042	832[c]
	[7.5]	[11.1]	[189]	[6029]	[100557]	[99658]	[12986]	[500]

[a]n=17, [b]n=31, [c]n=3; nd = not determined; [d]Muir *et al.* (1996)