POLYCHLORINATED ALKANES IN AMBIENT AIR FROM BEAR ISLAND

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Introduction

Polychlorinated alkanes (PCA), or chlorinated paraffins, are straight chain alkanes with varying degrees of chlorination. They have been produced since the 1930's to an extent of approximately 300 kilotons estimated for the western world[1] per year. PCA are mainly produced by direct chlorination of a petroleum fraction with molecular chlorine in the presence of UV-light[1]. PCA have been used as high temperature and pressure lubricants as well as secondary plasticisers and flame retardants in plastics and paints[2,3].

PCA are divided into three main categories, short (C_{10}-C_{13}), medium (C_{14}-C_{17}) and long chain (C_{18}-C_{30}), and further by their degree of chlorination, low (<50%) and high (>50%)[3]. Because of their relatively high assimilation and accumulation potential, the short chain and more highly chlorinated PCAs have been the most widely studied. Although PCA generally have shown low toxicity to mammals, sPCAs have a carcinogenic potential in rats and mice[3]. In addition, dose-response studies have shown that oral intake of sPCA by mice, results in an increase in liver weight, which is considerable compared to reference materials[8]. They have also shown to be toxic towards certain species in the aquatic environment[3], although at concentration levels several orders of magnitude higher than for TCDD[4].

The complexity of sPCA mixtures make it difficult to provide an analytical method for their precise and specific quantitative determination. Technical sPCA mixture consists of several thousand components, and due to the large number of isomers, complete chromatographic separation seems impossible at this point. This analytical challenge has resulted in different approaches to analysis of sPCA[1-6].

In this study ambient air samples was collected on Bear Island and sPCA analyses were performed on some selected samples.

Experimental

The air samples were collected using one glass fibre filter (GFF, Gelman type AE, No. 61635, >99 % cut-off for 0,2 mm) and two PUF plugs (100 mm diameter, 50 mm thickness and density of 25 kg/m^3) fitted in a high volume air sampler. For each sample, plugs and filter were Soxhlet extracted for 8 hours with 300 mL n-hexane:diethyl ether (9:1). The extracts were treated with concentrated sulphuric acid and fractionated on activated silica. ^{13}C-PCB 153 was used as an internal standard.

An HP5890 GC coupled to a VG AutoSpec, high resolution mass spectrometer was used for all of the analyses. The MS was operated in ECNI mode with methane at a pressure of 2×10^{-5} mbar as reagent gas. The quantifications were performed according to the method described by Tomy et al[2].

Results and Discussion

The results, shown in Table 1, are reported as the sum of C_{10}–C_{13} PCAs with 5-10 Chlorine substitutions, together with the calculated average molar mass. Calculated average molar masses are indicative of the PCA formula group profiles observed in the samples. In addition the total sPCA content of each sample, in ng, is also reported, to be able to compare the sample values with the blank values.

Table 1. ΣsPCA and calculated average molar masses in ambient air samples from Bear Island.

Sampling date (2000)	Air volume (m^3)	ΣsPCA ng/m^3	ΣsPCA ng/sample	Average molar mass g/mole
May 8th-15th	3576	7.3	26300	396
June 1st-8th	3293	10.6	34900	399
June 8th-15th	3252	8.8	28600	400
June 15th-22th	3641	7.1	25800	405
June 22th-29th	3633	1.8	6370	405
Aug 10th-27th	8160	4.3	35400	410
Nov 13th-21	4009	1.8	7300	407
Fieldblank	-	-	300	402
Fieldblank	-	-	200	399
Standard	Mix	C_{10}-C_{13}	55,5 % Cl	406

When interpreting these results, it should be taken into account that PCA is a very complex mixture. An ideal internal standard is hard to find, and the analyses are very sensitive to the performance of the mass spectrometer. Considering the complexity of these analyses, the concentrations of sPCA in the air samples from Bear Island is surprisingly high. The sPCA concentrations are two to three orders of magnitude higher than for ΣPCB and one to two orders of magnitude higher than for HCB, measured at the same location[12]. Compared to air concentrations from semi rural sites in Canada and the UK[16], the values reported here, are one to two orders of magnitude higher.

In a previous study[10], sPCA were measured in ambient air samples collected at Svalbard (79° N). The results indicated that the air at Svalbard might contain sPCA, but the values were too low compared to the fieldblanks, to draw any conclusions. Bear Island is located only 5° south of Svalbard, but still it is considered as an arctic environment. Several studies[9, 11, 12] in the past few years have shown high concentrations of POPs (persistent organic pollutants) in different medias collected at Lake Ellasjøen in the south of Bear Island. Lake Ellasjøen is located in the catchment area of large nesting colonies of seabirds, which has lead to a theory describing seabirds as the main transporters of POPs to Lake Ellasjøen. For this reason air samples were collected as close to Lake Ellasjøen as possible (16 km north).

The concentrations of sPCA found in ambient air at Bear Island were two to three orders of magnitude higher than in the ambient air samples from Svalbard. In contrast to the fieldblanks from Svalbard, the sPCA content in the fieldblanks from Bear Island are far too low for the equipment to be considered as a contributer of sPCA. The calculated average molar mass of the samples (~400) are not significantly different from the calculated average molar mass of the standard (406). This is a pattern which is expected to appear when the sampling site is close to the source. An Arctic char sample from Lake Ellasjøen, analysed in a previous study, showed a calculated average molar mass of 453[15]. If the main transport route for PCAs as well as other POPs is via birds, this indication of higher chlorinated (higher masses) PCA in the biota of Bear Island is not surprising. PCAs with lower chlorine content is reported to be more easily metabolised than the higher chlorinated PCAs[3]. Air samples collected near a source of biotransported and biotransformed PCAs could therefore result in higher calculated average masses than for air samples containing PCAs from long range transport alone.

Figure 1 shows a mass chromatogram of the octachlorododecane group for both a sample and a standard. The trace of the air sample shows a shift towards the early eluting components (the more volatile components) compared to the standard. Figure 1 shows an example of only one of the sPCA formula groups, but in general the air samples show a similar shift for all the formula groups. With only long range transport as the route for POPs to Bear Island, a shift towards earlier eluting components should intuitively be much more prominent.

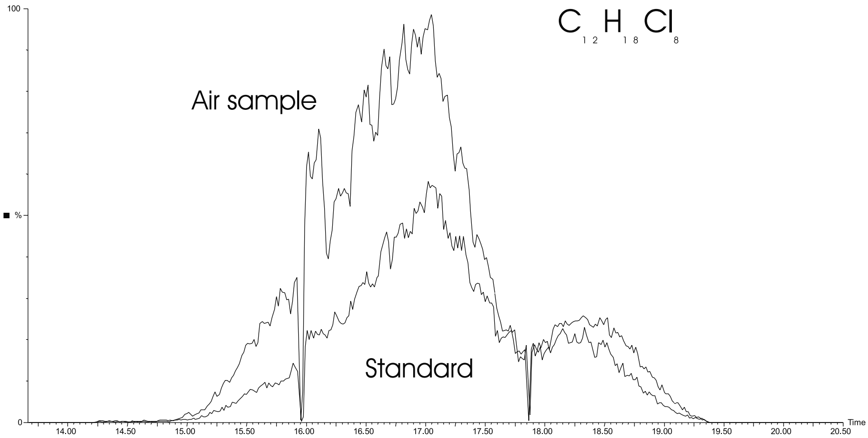

Figure 1. Mass chromatograms of the octachlorododecane group from an ambient air sample at Bear Island (upper trace), and from a standard (lower trace). The mass chromatograms are normalised to the highest point of intensity.

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