

## **Polychlorinated Alkanes in the Atmosphere of the United Kingdom and Canada - Analytical Methodology and Evidence of the Potential for Long-range Transport**

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### **Introduction**

Polychlorinated alkanes (PCAs) are a class of chemicals comprising of chlorinated straight chain hydrocarbons. They are sold commercially as "chlorinated paraffins" in mixtures based on chain length (short: C10-C13, medium: C14-C17, long: C18-C30) and degree of chlorination (40 - 70% chlorine w/w). They have a wide range of application: the main uses being as extreme pressure lubricant additives, plasticisers, flame retardants and paint additives. They are not known to occur naturally (1).

PCAs have been classified as priority toxic substances under the Canadian Government's Environmental Protection Act and also placed on the U.S. Environmental Protection Agency's Risk Reduction List. Short-chain PCAs are of concern owing to their toxicological properties and their capacity to bioaccumulate (1,2).

Owing to their widespread and unrestricted use in predominantly open systems, PCAs are now present in a wide range of environmental compartments, including: water (3); sediments (4); terrestrial and aquatic biota (5); sewage sludge (6); and human tissue (7). Limited data are available for PCAs in air (2). Data on the physical and chemical properties of PCAs under ambient environmental conditions and also on their environmental behaviour and fate are limited.

This study details the findings of the analysis of air samples from a semi-rural site in the United Kingdom (UK) and 2 locations in Canada: a semi-rural site in Southern Ontario and a remote site in the Canadian Arctic.

## Materials and Methods

*Sampling and Extraction* - Air was sampled using Graseby-Anderson PS1 and PM10 high volume air samplers. Sampling was conducted at Lancaster University, UK (54°2'N, 2°47'W), and also near Egbert, S.Ontario (44°14'N, 79°47'W) and Alert, NWT (82°20'N, 62°20'W), both in Canada. Particulates were retained with a glass fibre filter (GFF), and vapour phase organic chemicals were trapped on 2 polyurethane foam (PUF) plugs. GFFs were pre-treated by combusting at 450°C for 4 hours and PUF plugs were pre-extracted with dichloromethane (DCM) for 24 hours by Soxhlet extraction. The volume of air sampled ranged from ~ 1500 m<sup>3</sup> in the UK to ~ 15000 m<sup>3</sup> at Alert in the Canadian Arctic. Sampling was undertaken in summer 1990 at S.Ontario; between September and December 1992 at Alert; and between May 1997 and January 1998 at Lancaster. For the initial stage of this investigation it was decided not to examine the particle-vapour phase partitioning of PCAs. Therefore, the GFFs and PUF plugs were extracted together for 12 hours with DCM/hexane (50:50). Future work will focus on determining phase partitioning of PCAs in the atmosphere.

*Gas Chromatography/Mass Spectrometry* - Analyses were performed on a Hewlett-Packard (HP) 5890 Series II gas chromatograph, fitted with a high resolution DB-5 fused silica column (30 m x 0.25 mm i.d., 0.25 µm film thickness) and ECNI/MS was performed on a Kratos Concept high resolution mass spectrometer. GC/MS conditions and the method of quantitation were previously described (8).

## Results and Discussion

Mean concentrations reported relate to the sum of short-chain PCAs from penta- to nona-chloro substitution patterns (ie. C-10 to C-13 and Cl-5 to Cl-9), denoted by ΣPCA. Table 1 shows the mean concentrations of ΣPCA in air from the 3 locations studied. Figures 1a to 1e illustrate the PCA homolog patterns of typical North American and UK commercial short-chain PCA products and typical homolog patterns in air from the 3 study sites.

The absolute amounts of ΣPCA indicate concentrations of PCAs in air in the order: S.Ontario < UK < Alert. However, these data are from a limited sample size and were collected at different times. Therefore, comparison between sites should be made with caution. In particular, sampling was conducted in S.Ontario to target periods of warm weather and periods when atmospheric transport was highest from likely source areas (9).

In relation to other atmospheric contaminants, the concentrations of ΣPCA at S.Ontario and Alert (543±318 and 20±32 pg.m<sup>-3</sup>, respectively) are similar in magnitude to total PCB concentrations (S.Ontario: range = 74-682; Alert: mean = 20 pg.m<sup>-3</sup>) measured over the same period (9,10). Similarly, at Lancaster, the ΣPCA concentration (99±101 pg.m<sup>-3</sup>) is also comparable to total PCB concentrations (mean = 160; range = 50-375 pg.m<sup>-3</sup>) in 1994-95 (11).

Comparison of homolog distribution patterns for the three sites (Figure 1c to 1e) shows that the profiles from Alert and Lancaster are similar. This may reflect the fact that the organochlorine

contaminant content of the atmosphere in the high Arctic during winter is influenced by European sources (12) or that both sites are removed from local source areas.

The fact that the homolog pattern for S.Ontario is different might be a reflection of differences in the commercial products. Figure 1a and 1b shows that there are some differences between the PCA homolog distribution pattern of two commercial short-chain PCA products. The North American 60% chlorinated short-chain PCA product has higher relative amounts of hexa- and hepta-chlorinated PCAs whereas the UK product has a slightly higher degree of chlorination (63%) and is dominated by hepta- and octa-chlorinated PCA congeners.

The results of this study indicate that PCAs are a significant class of organochlorine contaminants in the atmosphere. The detection of PCAs in the atmosphere of the remote high Arctic indicates that PCAs are available for long-range transport. Further work is planned to provide more complete spatial and temporal resolution of atmospheric PCA loadings and also to investigate processes of partitioning and fractionation which may affect PCAs in the atmosphere.

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**Table 1:** Concentrations of PCA in ambient air at the three study sites.

Location	Mean concentration pg.m <sup>-3</sup> (± 1 std. devn.)
Lancaster, UK	99 (± 101)
S. Ontario, Canada	543 (± 318)
Alert, Canada	20 (± 32)

**Figure 1a to 1e:** PCA homolog patterns for commercial products and in ambient air at the three study sites.

