

# POLYCHLORINATED PARAFFINS

## AN OVERVIEW OF THE ENVIRONMENTAL LEVELS AND DISTRIBUTION OF POLYCHLORINATED PARAFFINS

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### Introduction

Polychlorinated *n*-alkanes (PCAs), or chlorinated paraffins, consist of C<sub>10</sub>-C<sub>30</sub> *n*-alkanes with chlorine content from 30 to 70% by mass. PCAs are used as high temperature lubricants, plasticizers, flame retardants, and as additives in adhesives, paints, rubber, and sealants. Industrially, PCAs are synthesized by direct chlorination of *n*-alkanes with molecular chlorine in the presence of UV-light. Because the principal *n*-alkane feedstocks used are mixtures, their chlorinated analogues are complex formulations consisting of optical isomers and congeners<sup>1</sup>. Commercial PCA formulations fall into three categories: C<sub>10</sub>-C<sub>13</sub> (short), C<sub>14</sub>-C<sub>17</sub> (medium), and C<sub>20</sub>-C<sub>30</sub> (long).

Short chain PCAs (*s*PCAs) are of particular interest because they have been shown to have the greatest potential for environmental release, bioaccumulation, and the highest toxicity of all the PCA products<sup>1-4</sup>. Although global production of *s*PCAs has declined since the early 1980s<sup>4</sup>, because of their widespread and unrestricted use in open systems, they are now present in a range of environmental compartments. In response to these concerns, *s*PCAs have been placed on the United States Environmental Protection Agency (EPA) Toxic Release Inventory and in Canada are under consideration as Track 1 Priority Toxic Substances under Canada's Environmental Protection Act. In Europe, voluntary restrictions for *s*PCA use have been implemented by industry. However, due to the tightening of regulations on the use of *s*PCAs, it is very likely that global usage of medium chain PCAs (*m*PCA) could rise; in Europe, for example, the use of *m*PCAs has already surpassed that of *s*PCAs<sup>5</sup>.

Although *s*PCAs have similar molecular weight and physical properties (octanol-water partition coefficient, water solubility, vapor pressure) to other major persistent organochlorine contaminants such as toxaphene and PCBs, limited information is available on the fate and spatial distribution of these compounds in the environment. Even less is known about the behavior and environmental levels of *m*PCAs. The lack of environmental measurements of PCAs can be attributed to the extreme complexity of the industrial formulations and the resulting difficulties associated with their analysis. However, with the recent advances in the analysis of *s*- and *m*PCAs using high resolution negative ion mass spectrometry<sup>6,7</sup>, the volume of information on PCAs in the environment has grown considerably.

### Environmental Levels

In this section, only the more recent measurements of PCAs in environmental matrices, will be reviewed. With the many different analytical methods being used for estimating PCA residues, comparing measured environmental levels is tenuous at best. Nevertheless, comparison will be attempted because a recent inter-laboratory study shows that results were comparable within a factor of two<sup>8</sup>.

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**Abiotic Matrices:** In sediments from Germany, Ballschmiter<sup>9</sup> reported  $s\Sigma$ PCA levels ranging from  $0.017 \mu\text{g}\cdot\text{g}^{-1}$  in Hamburg Harbour to  $0.7 \mu\text{g}\cdot\text{g}^{-1}$  from the River Lech. In Canada, Muir *et al.*<sup>10</sup> reported  $s\Sigma$ PCA concentrations ranging from  $0.0073$  to  $0.29 \mu\text{g}\cdot\text{g}^{-1}$  in surface sediment samples from harbour areas along Lake Ontario. Highest concentrations were found at the most industrialised site, Windemere basin in Hamilton Harbour. In a study of  $s\Sigma$ PCAs in sediment cores from six lakes in Canada ranging from  $49^\circ\text{N}$  to  $81^\circ\text{N}$ <sup>11</sup>,  $s\Sigma$ PCA concentrations in surface sediments declined significantly from  $0.176 \mu\text{g}\cdot\text{g}^{-1}$  (dry weight) in sediments from the southern basin of Lake Winnipeg to  $0.0045 \mu\text{g}\cdot\text{g}^{-1}$  in Lake Hazen on Ellesmere Island. Corresponding surface fluxes were  $147$  and  $0.89 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ . The high flux of  $s\Sigma$ PCAs to the south basin of Lake Winnipeg suggested local contamination. This was confirmed by analysis of water collected from the Red River, a river that discharges into the southern basin of Lake Winnipeg, in which elevated levels of  $s\Sigma$ PCAs were measured to be between  $0.02$  and  $0.05 \mu\text{g}\cdot\text{L}^{-1}$ . Tomy *et al.*<sup>11</sup> also reported  $s\Sigma$ PCA concentration of  $0.018 \mu\text{g}\cdot\text{g}^{-1}$  in a surface sediment sample from Lake Nipigon, in north western Ontario. This lake is heavily populated with cottages and is used extensively for recreational purposes. In sediment collected from the mouth of the Detroit River at Lake Erie, mean  $s\Sigma$ PCA and  $m\Sigma$ PCA concentration of  $1.8$  and  $0.068 \mu\text{g}\cdot\text{g}^{-1}$ , respectively, were reported<sup>7</sup>. Surface sediment samples collected during the 1997 and 1998 Joint Ocean Ice Studies (JOIS) cruise track through the Canadian Archipelago to the Surface Heat Budget of the Arctic (SHEBA) site in the Canadian Basin interior were analyzed for  $s$ PCAs<sup>12</sup>. Sediment concentrations ranged from  $0.0048$  to  $0.0774 \mu\text{g}\cdot\text{g}^{-1}$ . A clear decreasing trend in concentrations was observed from south (Barrow Strait) to north (Peary Channel) and western Arctic (M'Clure Strait/Viscount Melville) sediment concentrations were lower than in the eastern Arctic (Nanisivik/Lancaster Sound) sediments. Lower chlorinated  $\text{C}_{10}$  and  $\text{C}_{11}$  formula groups predominate in the sediment relative to that of water from the same region and Alert air suggesting that these two groups may be less susceptible to microbial degradation.

Rieger and Ballschmiter<sup>13</sup>, in a study of the whole municipal waste water drainage system of a city in southern Germany, measured  $s\Sigma$ PCA concentrations ranging from  $0.5$  to  $30 \mu\text{g}\cdot\text{g}^{-1}$  and  $1$  to  $17 \mu\text{g}\cdot\text{g}^{-1}$  (dry weight), respectively, in surface films from industrial and mixed industrial/residential waste water sewer pipes (formed by deposition of organic matter). In both areas, metal-working plants where PCAs are used in high pressure additives for metal processing, were present. Concentrations in sewer films samples collected from residential areas with minimal industrial activity, ranged from  $0.5$  to  $15 \mu\text{g}\cdot\text{g}^{-1}$ . In sewage sludge sampled near the treatment plant, concentrations ranged from  $47$  to  $65 \mu\text{g}\cdot\text{g}^{-1}$ . Run-off water from the sewage plant, which is discharge into a nearby river, had a  $s\Sigma$ PCA concentration of  $0.2 \mu\text{g}\cdot\text{L}^{-1}$  while levels measured in the river water, up-stream and down stream from the purification plant were  $0.08$  and  $0.07 \mu\text{g}\cdot\text{L}^{-1}$ , respectively. A tributary river upstream of the city had  $s\Sigma$ PCA concentration of  $0.03 \mu\text{g}\cdot\text{L}^{-1}$  and was used to represent the background level in the region. Muir *et al.*<sup>10</sup> reported  $s\Sigma$ PCA concentrations ranging from  $0.06$  to  $0.448 \mu\text{g}\cdot\text{L}^{-1}$  in final effluent from sewage treatment plants in southern Ontario. Higher levels were observed in samples from treatment plants in industrialised areas such as Hamilton and St. Catherines compared to non-industrialised towns such as Niagara-on-the-Lake and Niagara Falls.

In gas phase samples of air collected at Alert (northern tip of Ellesmere Island in the high arctic) in the fall and winter of 1992,  $s\Sigma$ PCA concentrations ranged from  $<1$  to  $8.5 \text{pg}\cdot\text{m}^{-3}$ . Tomy<sup>14</sup> reported  $s\Sigma$ PCA concentrations ranging from  $65$  to  $924 \text{pg}\cdot\text{m}^{-3}$  in gas phase air samples collected every day over a four month period in the summer of 1990 at Egbert, ON, Canada, and in the UK,

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Peters *et al.*<sup>15</sup> reported a mean  $s\Sigma$ PCA concentration of  $99 \mu\text{g}\cdot\text{m}^{-3}$  in air collected from a semi-rural site in Lancaster.  $s\Sigma$ PCA concentrations in air from the latter three sites were in the order, S. Ontario > Lancaster > Alert, and most likely reflects the nearness of these sites to local source areas. Comparison between homologue distribution patterns of the latter three sites showed that the profiles from Alert and Lancaster were similar. This may reflect the fact that organochlorine contaminant content of the atmosphere in the high Arctic during winter is influenced by European sources<sup>16,17</sup> or that both sites are removed from the local source area. The Southern Ontario homologue pattern, relative to that of the Alert, Lancaster and the technical PCA-60 mixture ( $\text{C}_{10}\text{-C}_{13}$ , 60% Cl) profiles, has higher proportions of the pentachloro-*n*-decanes and -undecanes, and the hexachloro-*n*-dodecanes ( $\text{C}_{10}\text{H}_{17}\text{Cl}_5$ ,  $\text{C}_{11}\text{H}_{19}\text{Cl}_5$  and  $\text{C}_{12}\text{H}_{20}\text{Cl}_6$ , respectively). This may be attributed to the nearness of the Egbert site to local sources and the use of a variety of industrial mixtures, some of which, may have a chlorine content of <60%.

**Biota:** In Sweden, Jansson *et al.*<sup>18</sup> found  $s\Sigma$ PCA concentrations ranging from  $0.13 \mu\text{g}\cdot\text{g}^{-1}$  in ringed seal from Kongsfjorden to  $1.6 \mu\text{g}\cdot\text{g}^{-1}$  in herring from Skagerrak.  $s\Sigma$ PCA concentrations in whitefish (Lake Storvindeln), arctic char (Lake Vättern) and grey seal (Baltic Sea) were 1, 0.57 and  $0.28 \mu\text{g}\cdot\text{g}^{-1}$ , respectively. Herring from the Bothnian Sea and Baltic Proper were found to contain similar  $s\Sigma$ PCA concentrations of 1.4 and  $1.5 \mu\text{g}\cdot\text{g}^{-1}$ , respectively<sup>18</sup>. In the United States, yellow perch, catfish and zebra mussels from the Detroit River, MI had measured mean  $s\Sigma$ PCA concentrations of 1.1, 0.3 and  $1.2 \mu\text{g}\cdot\text{g}^{-1}$ , respectively<sup>6</sup>. Mean  $m\Sigma$ PCA levels in the perch and catfish were 0.08 and  $0.90 \mu\text{g}\cdot\text{g}^{-1}$ , respectively<sup>7</sup>. In Canada, mean  $s\Sigma$ PCAs concentrations ranged from 0.37 and  $1.4 \mu\text{g}\cdot\text{g}^{-1}$  ( $n=5$ ) in beluga blubber samples collected from St. Lawrence River<sup>19</sup>. These levels were lower than  $\Sigma$ PCB and  $\Sigma$ DDT concentrations by almost an order of magnitude<sup>19</sup>. Tomy *et al.*<sup>19</sup> also reported mean  $s\Sigma$ PCA concentrations of 0.20 ( $n=4$ ) and  $0.21 \mu\text{g}\cdot\text{g}^{-1}$  ( $n=3$ ) in beluga whale blubber from northwestern Greenland and the Mackenzie delta, NWT, respectively. In both cases, the measured  $s\Sigma$ PCA concentrations were found to be significantly lower than those of toxaphene ( $\Sigma$ CHB),  $\Sigma$ DDT and  $\Sigma$ PCB. In ringed seal from southwest Ellesmere Island, Eureka, the mean  $s\Sigma$ PCA concentrations of  $0.52 \mu\text{g}\cdot\text{g}^{-1}$  ( $n = 6$ ) exceeded those of toxaphene and was slightly lower than that of  $\Sigma$ DDT.  $\Sigma$ PCB concentrations were 2-fold higher. The mean wet weight concentration of  $s\Sigma$ PCAs in walrus blubber from animals collected in northwestern Greenland was  $0.43 \mu\text{g}\cdot\text{g}^{-1}$ .  $\Sigma$ PCB,  $\Sigma$ DDT and toxaphene concentrations were significantly lower. Stern *et al.*<sup>20</sup> reported mean  $s\Sigma$ PCAs concentrations of 0.63, 0.20, 0.32 and  $0.46 \mu\text{g}\cdot\text{g}^{-1}$  in blubber from male beluga collected in Hendrickson Island (Southern Beaufort Sea near the Mackenzie River delta), Arviat (western Hudson Bay), Sanikiluaq (Belcher Island area in southern Hudson Bay) and Pangnirtung (south eastern Baffin Island), respectively. Mean  $\Sigma$ PCA concentrations in the Pangnirtung and Hendrickson Island animals were significantly higher (t-test,  $p<0.05$ ) than those from Hudson Bay, while the Sanikiluaq animals had levels significantly higher than those from Arviat.

Stern *et al.*<sup>20</sup> noted that the Arctic animal formula group profiles showed higher proportions of the lower chlorinated congeners ( $\text{Cl}_5\text{-Cl}_7$ ), suggesting that the major source of contamination to the Arctic is *via* long range atmospheric transport. In St. Lawrence beluga, the formula group profile more closely resembles that of PCA-60 which implies that local sources of PCAs, possibly from the Great Lakes and/or the lower industrialized regions of the St. Lawrence River, predominate in the St. Lawrence River estuary.

To date, very limited information is available on  $s\Sigma$ PCA concentrations in tissues of terrestrial mammals. In Sweden, Jansson *et al.*<sup>18</sup> reported  $s\Sigma$ PCA concentrations in rabbit

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(Revingeshed, Skåne), moose (Grimsö, Västmanland), reindeer (Ottsjö, Jaäamtland) and osprey (from various regions in Sweden) to be 2.9, 4.4, 0.14 and 0.53  $\mu\text{g}\cdot\text{g}^{-1}$ , respectively. Tomy<sup>14</sup> reported a  $\Sigma$ PCA mean concentration of 0.013  $\mu\text{g}\cdot\text{g}^{-1}$  (lipid wt) in human breast milk from Inuit women living in communities on Hudson Strait in Northern Québec.

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