

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins

POLYCHLORINATED (C10-C13)-ALKANES IN THE GREAT LAKES

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Introduction

Short-chain chlorinated paraffins are polychlorinated-[C₁₀-C₁₃]-n-alkanes with 50 to 70% chlorine content that are used mainly as flame retardant high temperature lubricant additives in metal working fluids [1-3]. In the United States, C₁₀-C₁₃-PCAs have been placed on the USEPA Toxic Release Inventory, and in Canada they are under consideration for classification as "Track 1", Priority Toxic Substances under the Canadian Environmental Protection Act. In Europe voluntary restrictions for short chain PCA use have been implemented by industry. C₁₀-C₁₃-PCAs are part of a larger group of chlorinated paraffins (CPs) with carbon chain lengths up to C₃₀ and chlorine content of 30-70%. The higher molecular weight products are used as flame retardant plasticizers, especially in PVC, as well as additives to improve water resistance and flame retardancy in adhesives, paints, rubber and sealants. Annual global production of all CPs is estimated to be 300 kT [1]. Approximately 25% of current production is estimated to be C₁₀-C₁₃-PCAs which is lower than in the 1970's when about 50% of CP production was in the form of C₁₀-C₁₃-PCAs [2].

The C₁₀-C₁₃-PCAs are of particular interest because they have the greatest potential for environmental release, and the highest toxicity of PCA products [4-6]. C₁₀-C₁₃ PCAs with 60-70% chlorine have similar molecular weight and physical properties (octanol-water partition coefficient, water solubility, vapor pressure) as many persistent organochlorines such as PCBs and toxaphene [3].

The limited information on the levels and fate of PCAs in the environment is due both to the difficulty associated with quantifying PCAs, because of the complexity of commercial formulations, and lack of specific methods of analysis. Tomy et al. [7] reported the use of high resolution gas chromatography- negative ion mass spectrometry (GC-HR-NIMS) for the analysis of C₁₀-C₁₃-PCAs. The use of HRMS gives the method high specificity compared to previous methods which used GC-low resolution NIMS to measure the C₁₀-C₁₃-PCA molecular ions [8] or Cl₂⁻ ions [9]. A recent interlab comparison has shown that there is agreement within a factor of 2 between low res and high res ECNIMS methods for analysis of PCAs in biological samples [10].

There are indications that PCAs are widespread environmental contaminants at ng/L levels in surface waters and ng/g (wet wt) levels in biota [7,8,11,12]. However, environmental measurements of PCAs are very limited at the present time in the USA and Canada and are only slightly more detailed in western Europe. Use of C₁₀-C₁₃-PCAs within the Great Lakes basin is likely to represent a significant fraction of total US/Canadian use due to the presence of manufacturing sites as well as to the preponderance of end users such as the auto industry (use in metals machining/stamping) and plastics industries. Tomy et al. [7] reported detectable C₁₀-C₁₃-PCAs in fish and sediment from Western Lake Erie and the Trenton Channel of the Detroit River. Murray et al. [13] found low levels of C₁₀-C₁₃ PCAs in an impounded drainage ditch containing waters which receive effluent discharge from a PCA manufacturing site in Dover, Ohio, to be

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between 0.25-0.57 µg/L. Metcalfe-Smith et al. [14] found low levels in a effluent of a manufacturing plant on the St. Lawrence river. In this study we have compared C₁₀-C₁₃-PCAs in air, water, in waste water treatment effluents, sediments, and benthic and pelagic feeding fish in western Lake Ontario and Lake Superior in order to evaluate regional differences, current and past inputs, and bioaccumulation of these products in the Great Lakes basin.

Materials and Methods

Sample collection: Samples of waste water treatment plant effluents were collected from plants serving both industrial and non-industrial areas in southern Ontario. Several of the effluents drained directly into Lake Ontario. Whole effluents were extracted as described by Metcalfe-Smith et al. [14].

Surface sediments were collected from Hamilton harbour and other five harbour areas in western Lake Ontario. A sediment core was collected from the western basin of Lake Ontario and from deep zones in Lake Superior from the limnological vessel C.S. Limnos using a box-corer. Multiple cores were obtained from each box core by pushing a 10cm dia acrylic tube into the sediment then extruding the core and slicing at 1cm intervals. The core was dated using ²¹⁰Pb. Lake water (100 L) was collected in the western end of Lake Ontario and in Lake Superior.

Water (prefiltered to 100 µm) was pumped into sealed holding tanks using a submersible pump and particles were collected using a continuous centrifuge. The centrifugate was passed (200 mL/min) through an XAD-2 column. Centrifuged particles (1-100 µm) were recovered and analysed separately.

Archived air extracts from Egbert ON were provided by Frank Froude (Atmospheric Environment Service, Environment Canada). The samples were collected in 1990 using polyurethane foam with a hi-vol sampler, as part of the preliminary work for the Integrated Atmospheric Deposition Network in the Great Lakes basin.

Extracts of whole lake trout from two locations (Niagara-on-the-Lake and Port Credit) and whole carp from Hamilton Harbour, which had been previously analysed for organochlorine pesticides were provided for analysis of C₁₀-C₁₃-PCAs.

Extraction and Isolation. Bottom sediment and suspended particulate samples were centrifuged to remove excess water, mixed with a drying agent and extracted using an Accelerated Solvent Extractor (Dionex, Oakville, ON, Canada) using dichloromethane. Sulfur was removed from the extracts using mercury and C₁₀-C₁₃-PCAs were separated from PCBs on an activated silica column. XAD columns were eluted with dichloromethane. The eluate was exchanged into hexane and chromatographed on a silica column to separate PCAs from PCBs.

MS quantification of C₁₀-C₁₃-PCAs. Extracts were analysed by GC-Electron capture negative ion high resolution mass spectrometry (ECNI/HRMS) using a Kratos Concept MS as described by Tomy et al [7]. SIM was performed at a resolving power of ~12 000 (sufficient to exclude potential interferences from other organochlorines), with a cycle time of 1 sec for each window, and equal dwell times for each ion monitored.

Method detection limits (MDL) were approximately 10 ng/g dw for sediment and fish samples. Reagent blanks analysed with sediment samples had PCAs < 2x lower than the MDL.

Results and Discussion

Waste water treatment effluents: C₁₀-C₁₃-PCAs were detected in all sewage treatment plant final effluents from the western Lake Ontario area at ng/L concentrations. Higher concentrations were found in samples from treatment plants in industrialized areas, e.g. Hamilton and St. Catharines,

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compared to non-industrial towns, e.g. Niagara-on-the-Lake (Table 1). These concentrations appear to be typical of waste waters. Reiger and Ballschmiter [8] reported C₁₀-C₁₃ (62% Cl) PCA concentrations of 70 to 120 ng/L in water upstream and downstream of a

Table 1. C₁₀-C₁₃-PCAs in final effluent of sewage treatment plants on Lake Ontario (ng/L)¹

Location	C10	C11	C12	C13	ΣPCAs
Woodward Ave. STP, Hamilton, ON	128	155	153	11.5	448
Halton Skyway STP, Burlington, ON	38	19	12	<1	68
Stanford WPCP, Niagara Falls, ON	11	34	36	1	82
Port Dalhousie WPCP, St. Catherines, ON	19	39	47	5	110
Port Weller WPCP, St. Catherines, ON	22	27	28	4	80
Niagara-on-the-Lake, WPCP	13	18	27	1	60

¹C10 to C13 headings refer to concentrations of all chlorodecanes to chlorotridecanes, respectively. ΣPCAs are the sum of all C₁₀-C₁₃-PCAs.

sewage treatment plant in Germany. In the United States, Murray et al. [13] reported C₁₀-C₁₃ (60% Cl) PCA concentrations of <150 to 3300 ng/L in water from an impoundment drainage ditch that received effluent from a CP production plant in Dover OH.

Lake sediments: A sediment core collected from the west basin of Lake Ontario had total C₁₀-C₁₃-PCA concentrations of 410 ng/g (dry wt) in the surface slice (0-1 cm). This compared with 115 ng/g of total PCBs (sum of 100 congeners) in the same sample. A subsurface maximum of PCA was observed in slices with median age of 1971 (800 ng/g dw) indicating larger inputs of the short chain CPs to Lake Ontario in the past. A pre-1900 slice analysed as a matrix blank had levels of C₁₀-C₁₃-PCA near the method detection limit. Surficial sediments from six harbour sites in Western Lake Ontario including Hamilton Harbour and Toronto harbour had lower C₁₀-C₁₃-PCA concentrations than the sediment core (7-285 ng/g dw). Highest levels were observed in Hamilton harbour and lowest in Toronto harbour.

Air: PCA (C₁₀-C₁₃, 60-70% Cl) concentrations ranged from 65 to 924 pg/m³ in gas phase air samples collected every day over a four month period in the summer of 1990 at Egbert (ON), a rural site northwest of Toronto. This compares with a mean concentration of 99 pg/m³ (C₁₀-C₁₃, 60-70% Cl) in air collected from a semi-rural site in Lancaster, UK [15]. The homologue pattern in air at Egbert, had higher proportions of the pentachloro-n-decanes and -undecanes, and the hexachloro-n-dodecanes relative to that of Lancaster. This may be attributable to the nearness of the Egbert site to local sources within the Great Lakes basin and the use of a variety of industrial mixtures, some of which, may have a chlorine content of <60%.

Lake Ontario fishes: C₁₀-C₁₃-PCAs were detectable in all samples of carp and rainbow trout (Table 2). Concentrations in carp from Hamilton harbour were higher than observed in catfish and perch from western Lake Erie [7]. Lower concentrations in rainbow trout than carp were surprising given that they would be expected to feed at a higher trophic level. It is possible that trout have greater capacity to degrade C₁₀-C₁₃-PCAs than carp. Levels of PCBs in the Lake trout were 55 to 76x higher than C₁₀-C₁₃-PCAs in the same fish samples (Table 2).

Table 2. C₁₀-C₁₃-PCA concentrations (ng/g ww) in whole fish samples from western Lake Ontario

Species/location	N	C10	C11	C12	C13	ΣPCAs	ΣPCBs
Carp, Hamilton Harbour	3	14.2	355	1090	1170	2630	- ¹
Lake trout, Niagara-on-the-Lake	5	3.1	16.4	30.1	9.3	58.8	3200

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Lake trout, Port Credit	4	3.8	20.2	37.1	11.4	72.6	5150
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¹Not analysed for PCBs

Conclusions

The data for C₁₀-C₁₃-PCAs in sediment, air, and fishes are the first environmental measurements in Lake Ontario. Combined with previous work on the Detroit River/Western lake Erie [7] and recent studies of PCAs in lake sediments including Lake Nipigon (upstream of Lake Superior) [16] it appears that C₁₀-C₁₃-PCAs contamination is widespread in the Great Lakes. However levels are relatively low in fish compared to PCBs. To fully assess the extent of persistence and bioaccumulation of PCAs more information is needed on current emissions and on half-lives in sediment, surface waters and the atmosphere.

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