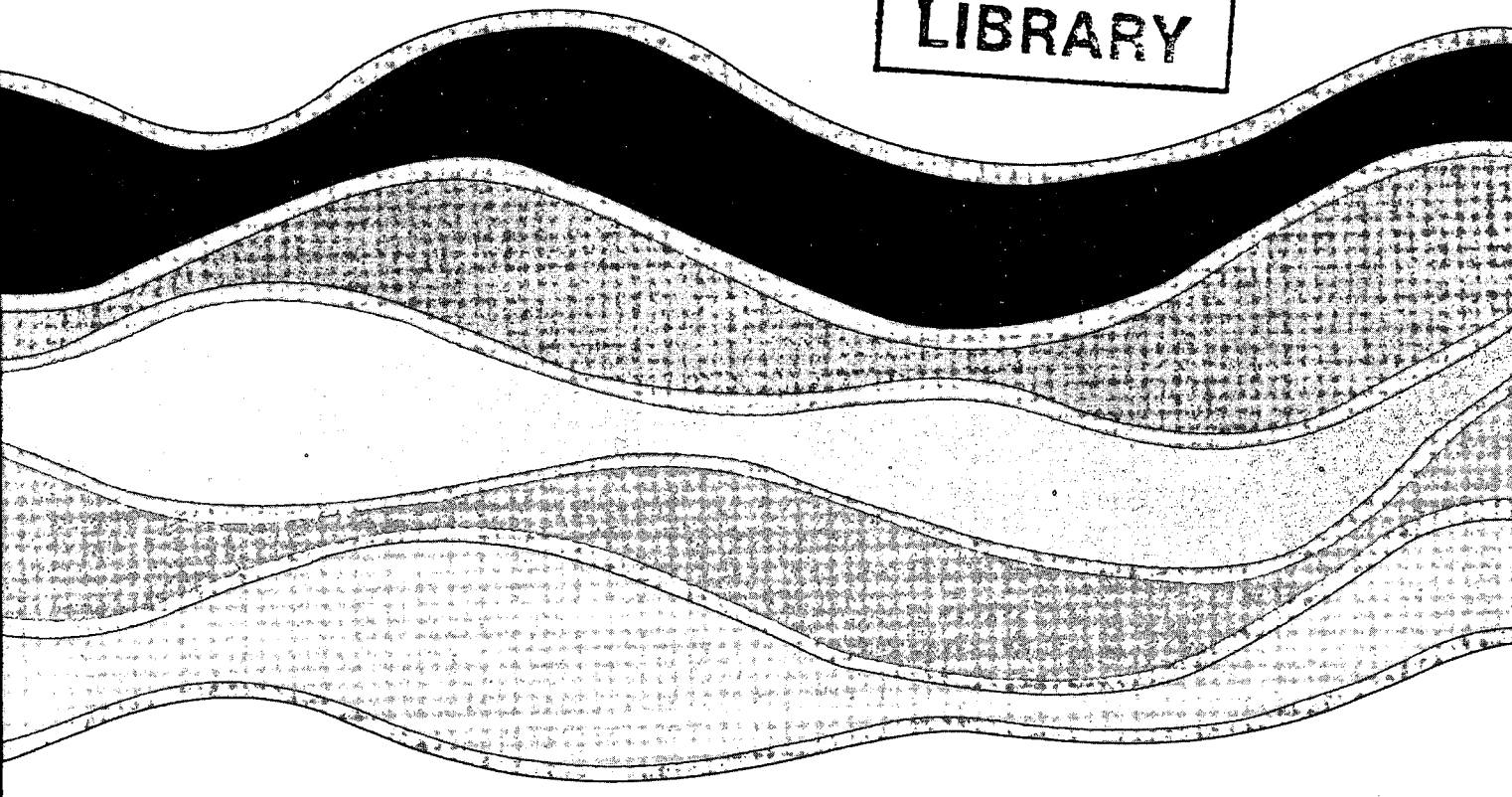
NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL de RECHERCHE sur les EAUX



OCCURRENCE OF CHLORINATED PARAFFINS IN THE ST. LAWRENCE RIVER NEAR A MANUFACTURING PLANT IN CORNWALL, ONTARIO

J.L. Metcalfe-Smith, R.J. Maguire, S.P. Batchelor and D.T. Bennie

NWRI CONTRIBUTION NO. 95-62

Occurrence of Chlorinated Paraffins in the St. Lawrence River near a Manufacturing Plant in Cornwall, Ontario

J.L. Metcalfe-Smith, R.J. Maguire, S.P. Batchelor and D.T. Bennie
Aquatic Ecosystem Protection Branch
National Water Research Institute
Department of the Environment
Canada Centre for Inland Waters
Burlington, Ontario L7R 4A6

NWRI Contribution 95-62

MANAGEMENT PERSPECTIVE

Chlorinated paraffins are mainly used as plasticizers, high-pressure lubricants and flame retardants. They were on the first Priority Substances List (PSL1) of the Canadian Environmental Protection Act (CEPA). It was not possible to assess whether these compounds were "toxic" as defined under Paragraph 11(a) of CEPA because no data were identified on their concentrations in the Canadian environment. One of the recommendations of the assessment was to acquire data on levels of chlorinated paraffins in the aquatic environment around the only manufacturing site (Imperial Chemical Industries Canada) in Canada, on the St. Lawrence River at Cornwall, Ontario. This study responds to that recommendation. The results will be communicated to the Commercial Chemicals Evaluation Branch, which is responsible for the administration of the CEPA PSL assessment program. Further work is planned to determine concentrations of chlorinated paraffins in water, sediment and biota in or near industrial centres where they are used, such as Montréal, Toronto and Hamilton.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Les paraffines chlorées sont principalement utilisées comme plastifiants, lubrifiants sous haute pression et ignifugeants. Elles figuraient sur la première liste des substances d'intérêt prioritaire (LSIP) de la Loi canadienne sur la protection de l'environnement (LCPE). Il n'a pas été possible de déterminer si ces composés étaient «toxiques» aux termes de l'article 11(a) de la LCPE, car aucune information n'a pu être obtenue sur leurs concentrations dans l'environnement. L'une des recommandations de l'évaluation a été d'obtenir des données sur les concentrations de paraffines chlorées dans le milieu aquatique situé aux environs de la seule usine (Imperial Chemical Industries Canada) fabriquant ces produits au Canada, au bord du fleuve Saint-Laurent, à Cornwall (Ontario). La présente étude fait suite à cette recommandation. Les résultats seront communiqués à la Direction de l'évaluation des produits chimiques commerciaux, chargée de l'administration du programme d'évaluation de la LSIP de la LCPE. D'autres travaux sont prévus pour déterminer les concentrations de paraffines chlorées dans l'eau, les sédiments et les biocénoses des centres industriels où elles sont utilisées, notamment Montréal, Toronto et Hamilton, ou au voisinage de ces centres.

ABSTRACT

Chlorinated paraffins are mainly used as plasticizers, high-pressure lubricants and flame retardants. They were on the first Priority Substances List (PSL1) of the Canadian Environmental Protection Act (CEPA). It was not possible to assess whether these compounds were "toxic" as defined under Paragraph 11(a) of CEPA because no data were identified on their concentrations in the Canadian environment. One of the recommendations of the assessment was to acquire data on levels of chlorinated paraffins in the aquatic environment around the only manufacturing site (Imperial Chemical Industries Forest Products [ICI]) in Canada, on the St. Lawrence River at Cornwall, Ontario. This study responds to that recommendation.

Samples of sediment, native freshwater mussels, zebra mussels and fish were collected from the St. Lawrence River in the vicinity of the combined Domtar/Cornwall Chemicals/ICI Forest Products outfall in Cornwall, Ontario, during the summer and fall of 1993. An effluent sample was collected from the ICI plant during the same period. A sample of young-of-the-year yellow perch, which had been collected immediately downstream of the combined outfall in the fall of 1992, was also obtained. These samples were all analyzed for chlorinated paraffins. The only sample that was confirmed to contain chlorinated paraffins was the effluent sample, and the total concentration was quite low, about 13 μg/L, calculated as the medium-chain chlorinated paraffin Cereclor S52 (C_{14}-C_{17}, 52% Cl).

RÉSUMÉ

Les paraffines chlorées sont principalement utilisées comme plastifiants, lubrifiants sous haute pression et ignifugeants. Elles figuraient sur la première liste des substances d'intérêt prioritaire (LSIP) de la Loi canadienne sur la protection de l'environnement (LCPE). Il n'a pas été possible de déterminer si ces composés étaient «toxiques» aux termes de l'article 11(a) de la LCPE, car aucune information n'a pu être obtenue sur leurs concentrations dans l'environnement. L'une des recommandations de l'évaluation a été d'obtenir des données sur les concentrations de paraffines chlorées dans le milieu aquatique situé aux environs de la seule usine (Imperial Chemical Industries Forest Products Canada [ICI]) fabriquant ces produits au Canada, au bord du fleuve Saint-Laurent, à Cornwall (Ontario). La présente étude fait suite à cette recommandation.

Pendant l'été et l'automne de 1993, on a prélevé des échantillons de sédiments, d'anodontes indigènes, de moules zébrées, et de poissons dans le fleuve Saint-Laurent et au voisinage de l'émissaire combiné de Domtar, Cornwall Chemicals et ICI Forest Products à Cornwall (Ontario). Un échantillon d'effluent a été prélevé à l'usine d'ICI pendant la même période. On avait également prélevé en automne de 1992 un échantillon de jeune perchaude de l'année, qui a été ramassé immédiatement en aval de l'émissaire combiné. Tous ces échantillons ont été analysés pour déterminer les concentrations des paraffines chlorées. Le seul échantillon qui en renfermait, après vérification, était celui de l'effluent; la concentration totale était assez faible, environ 13 µg/L, le calcul étant effectué avec la paraffine chlorée à chaîne moyenne, Cereclor S52 (C_{14}-C_{17}, 52 % de Cl).

INTRODUCTION

The Canadian Environmental Protection Act (CEPA) requires the Minister of the Environment and the Minister of Health to prepare and publish a Priority Substances List that identifies substances, including chemicals, groups of chemicals, effluents, and wastes that may be harmful to the environment or constitute a danger to human health (Government of Canada, 1988). The Act also requires both Ministers to assess these substances and determine whether they are "toxic" as defined under Section 11 of the Act which states:

> "...a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions
>
> (a) having or that may have an immediate or long-term harmful effect on the environment;
>
> (b) constituting or that may constitute a danger to the environment on which human life depends; or
>
> (c) constituting or that may constitute a danger in Canada to human life or health."

Substances that are assessed to be "toxic" according to this Section may be placed on Schedule I of the Act. Consideration can then be given to developing regulations, guidelines or codes of practice to control any aspect of these substances' life cycle, from the research and development stage through manufacture, use, storage, transport, and ultimate disposal.

Chlorinated paraffins (CPs) were on the first CEPA Priority Substances List (PSL)

(Environment Canada, 1989). CPs having carbon chain lengths of 10-13 are termed "short", those having 14-17 carbon atoms are considered to be "medium' and those having 18 or more are considered to be "long". Chlorine contents are in the range of 40-70% by weight. CPs are produced in, and imported into, Canada for use as plasticizers, and also as high-pressure lubricants and flame retardant additives in coatings, inks, adhesives and fabrics. They are persistent compounds and have the potential to bioaccumulate in aquatic organisms. Short-chain CPs are considered to present greater hazards to the environment than medium- or long-chain CPs. The PSL assessment (Environment Canada and Health and Welfare Canada, 1993a) did not identify data on the concentrations of CPs in any medium in the Canadian environment. However, data from other countries (including the United States) where these compounds are produced and used confirm their presence in the environment, particularly near production facilities.

The identity, properties, production, use and environmental fate and effects of CPs were extensively reviewed in the PSL assessment (Environment Canada and Health and Welfare Canada, 1993a) and in the Supporting Document for the assessment (Environment Canada and Health and Welfare Canada, 1993b). A brief summary relevant to this study follows. Due to their suitable physical and chemical properties, CPs have on many occasions replaced polychlorinated biphenyls (PCBs). This increased use has caused concern about their environmental impact. Total Canadian demand for CPs is about 4-5 kt/year. ICI Forest Products is the only manufacturer of CPs in Canada, operating a plant in Cornwall, Ontario that discharges into the St. Lawrence River. The plant's production in 1992 was approximately 4 kt. ICI produces only medium- and long-chain CPs in three grades of 42, 45 and 52 percent chlorine by weight (R.A. Helliar, Ontario Ministry of Environment and Energy, Southeastern Region, personal communication). Estimates for CP releases into the Canadian environment are not available. Releases could occur during their manufacture, use, transport and disposal. In other countries, manufacturing and lubricant applications were found to be the two points of most concentrated release into the environment.

CPs are generally considered to be persistent, and the few data that are available suggest that the potential for bioaccumulation and biomagnification could be significant. Studies in other countries, primarily the United Kingdom, U.S.A. and Sweden, have reported elevated levels of CPs in all environmental components near manufacturing sites (*e.g.,* Murray *et al.*, 1988). Particularly high concentrations have been observed in both freshwater and marine mussels. Considerable information is available on the toxicity of CPs to freshwater organisms, particularly invertebrates, under laboratory conditions. Levels in water near manufacturing sites in other countries have been found to be sufficiently high to cause adverse chronic effects in sensitive aquatic species. In Sweden, CPs are to be withdrawn from use within ten years because they do not readily degrade, they bioaccumulate and are highly toxic to crustaceans and some fish species, and they cause cancer in mammals.

Because data were not identified on the concentrations of short-, medium-, or long-chain CPs in the Canadian environment, there were no data with which to compare levels reported as causing adverse effects in biota. Consequently, it was not possible to assess whether these compounds were "toxic" as defined under Paragraph 11(a) of CEPA (Environment Canada and Health and Welfare Canada, 1993a).

A high priority recommendation for research and evaluation arising from the PSL assessment was for data on levels of short-, medium-, and long-chain CPs in the aquatic environment (particularly in biota and sediments) around the manufacturing site. This study addresses that recommendation.

MATERIALS AND METHODS

Field collections

Samples of sediment, native freshwater mussels, zebra mussels and fish were

collected from the St. Lawrence River in the vicinity of the combined Domtar/Cornwall Chemicals/ICI Forest Products outfall in Cornwall, Ontario, during the summer and fall of 1993. An effluent sample was collected from the ICI plant during the same period. A sample of young-of-the-year yellow perch, which had been collected immediately downstream of the combined outfall in the fall of 1992, was also obtained. Locations of the various sampling sites are shown in Fig. 1.

Sediment was collected by Ponar dredge from sites 4, 6 and 7 during the week of July 5-9, 1993. At each site, a subsample of surface sediment (≈ 500 mL from the top 5 cm) was scooped from the dredge into a pre-cleaned glass jar and immediately frozen on dry ice. Native freshwater mussels (F. Unionidae) were collected concurrently from sites 2, 4, 5 and 9, and zebra mussels (*Dreissena polymorpha*) from sites 2, 5 and 9, by divers. Zebra mussels were found attached to the shells of the unionids. All mussels were rinsed in river water to remove adhered sediment. Zebra mussels then were placed in pre-cleaned glass jars; unionids were wrapped in pre-fired aluminum foil and placed in food-grade plastic bags. All mussels were immediately frozen on dry ice and later transferred to a freezer in the laboratory for storage at -20 °C.

On September 1, 1993 three white suckers (*Catostomus commersoni*) and one yellow perch (*Perca flavescens*) were collected from site 1, and two white suckers and three Northern pike (*Esox lucius*) were collected from site 8, all by electroshocking. Fish were wrapped in pre-fired aluminum foil and frozen on site. Young-of-the-year yellow perch had been collected for another purpose in September 1992 from site 3. They were also wrapped in pre-fired aluminum foil, placed in whirl-pac bags and stored frozen.

A sample of ICI's effluent was collected during routine audit sampling under the Ontario Ministry of Environment and Energy's MISA (Municipal-Industrial Strategy for Abatement) program. A 24-hour composite sample was collected between 1900 hours on September 28 and 1900 hours on September 29, 1993. The sample was time-proportional, with an aliquot collected every 10 minutes. Two 20 L modified beverage

containers (Fox, 1986) were used to collect the effluent, and they were exchanged after 12 hours. Approximately 3 L of dichloromethane were added to the effluent immediately after collection, and the cans were kept cool until they were delivered to the laboratory two days later for storage at 4 °C.

Biota sample preparation

Composite samples of unionids and zebra mussels were prepared as follows: Mussels were removed from the freezer and thawed for approximately 30 minutes prior to shucking. Large numbers of zebra mussels from a given site were shucked into a 500 mL glass jar, and the total weight of the combined wet tissues was determined. Unionids were identified to species, sexed and weighed individually before being composited. Data on individual unionids are presented in Appendix I. All samples were then freeze-dried. Adult fish were weighed, measured, sexed and dissected on January 28, 1994. The liver, spleen, gonads, kidneys and gall bladder were removed in their entirety from each fish. Samples of visceral fat (where present) and dorsal muscle were also taken. Data on individual fish are presented in Appendix II. Because the highest concentrations of lipophilic organic contaminants are found in fish tissues with the highest lipid content (*e.g.*, Metcalfe-Smith *et al.*, 1995), fat (where available) and liver were chosen for analysis.

A total of 23 samples (see Table 1) were analyzed for residues of CPs. Sediment, unionids and zebra mussels were analyzed dry, whereas adult and young-of-the-year fish were analyzed wet.

Analytical methods

(a) Materials

Three CP standards (Cereclors C42, S45 and S52) were obtained from ICI (Cornwall, Ont.). Cereclor C42 is a long-chain CP (C_{20}-C_{30}, 42% Cl average, average

molecular formula $C_{24}H_{44}Cl_6$). Cereclor S45 is a medium-chain CP (C_{14}-C_{17}, 45% Cl average, average molecular formula $C_{15}H_{27}Cl_5$). Cereclor S52 is a medium-chain CP (C_{14}-C_{17}, 52% Cl average, average molecular formula $C_{15}H_{26}Cl_6$) (Hollies *et al.*, 1979; Environment Canada and Health and Welfare Canada, 1993b). Table 2 gives some additional product information. Pesticide grade dichloromethane (Burdick and Jackson, Muskegon, MI) and toluene (BDH, Toronto, Ont.) were obtained and their purities (at 250X and 1X concentration, respectively) were checked before use. Both the concentrated sulfuric acid used for tissue lipid cleanup, and the mercury used for sulfur removal from the sediments, were reagent grade from BDH (Toronto, Ont.). The concentrated sulfuric acid was washed with dichloromethane to remove contaminants. The sodium sulfate was heated to 500 °C for 24 hours before use. Celite (BDH, Toronto, Ont.) was Soxhlet-extracted with dichloromethane prior to use. All glassware and sodium sulfate were solvent-rinsed before use.

(b) Extraction and cleanup of samples

Effluent -

The effluent samples in the two collection vessels were transferred, along with the 3 L of dichloromethane added at the time of collection, to a modified 40 L stainless steel beverage container (Fox, 1986), and the sample was stirred for 30 minutes. The pH (unadjusted) was about 7. Approximately 2200 mL of dichloromethane were recovered after phase separation. The extraction was repeated twice, with 500 mL of dichloromethane added each time. The combined dichloromethane extracts were dried by passage through anhydrous sodium sulfate. Toluene was added to the extract prior to concentration by rotary evaporator and evaporation under a stream of nitrogen. The 2 mL final toluene extract was analyzed without cleanup by gas chromatography with an electron capture detector (GC-ECD), and by gas chromatography - mass spectrometry (GC-MS) as described below.

Sediment -

Three sediment samples were freeze-dried, ground and passed through a 20 mesh sieve. A 25 g subsample of each was placed in a thimble with sodium sulfate and Soxhlet-extracted with dichloromethane for 8 hours. The extracts were concentrated by rotary evaporation, then dried by passage through sodium sulfate, and transferred into toluene. The extracts were treated with mercury, stirred, and centrifuged to remove sulfur. It was necessary to repeat this procedure at least twice with approximately 0.5 mL of mercury each time until the mercury stayed in beads and no black residue was left. The extracts were then cleaned up on alumina by the method of Murray *et al.* (1988) before analysis by GC-ECD and GC-MS as described below.

Mussels -

Composite samples of unionids and zebra mussels were freeze-dried and ground in a blender to a fine powder. This was combined with Celite and sodium sulfate and Soxhlet-extracted with dichloromethane for 8 hours. The extracts were evaporated to dryness by rotary evaporation to determine lipid weights. Samples were redissolved in hexane (1 mL hexane/0.1 g lipid [Jansson *et al.*, 1991]), and concentrated sulfuric acid was added to the extracts to destroy the lipids. After phase separation, the acid phase was back-extracted with hexane, and the hexane fractions were combined and cleaned up on alumina (Murray *et al.*, 1988). After concentration and solvent-exchange into toluene, the final extracts were analyzed by GC-ECD and GC-MS as described below.

Fish tissues -

Liver and fat tissues, as well as a composite sample of 78 juvenile perch (whole) were ground in a mortar and pestle with sodium sulfate until the tissues were dry. The samples were wrapped in aluminum foil and returned to the freezer until extracted. The Soxhlet extraction and lipid and alumina cleanup procedures were the

same as those used for mussel tissues.

Recoveries from various matrices -

Recoveries of CPs from water, sediment and various biota by standard extraction techniques are generally > 90% (*e.g.*, Hollies *et al.*, 1979), thus they were not tested in this study. However, various spike recovery experiments were performed with Cereclor S45, testing for losses upon evaporation of extracts to dryness (using nitrogen "blow-down" or rotary evaporation), and the effect of the sulfuric acid treatment to destroy lipids. In another experiment, an archived freeze-dried mussel sample was Soxhlet-extracted, spiked with 2 mg of Cereclor S45, and treated with concentrated sulfuric acid to destroy lipids. In all experiments the recoveries of Cereclor S45 were greater than 90%. It was assumed that the recoveries of Cereclors C42 and S52 from mussel tissues, and their stability to sulfuric acid, were similar to that of Cereclor S45.

(c) Analysis

GC-ECD -

GC-ECD was used for preliminary characterization of Cereclor standards, for spike recovery experiments, and for initial screening of the sample extracts. However, it is well known that GC-ECD is relatively insensitive for CPs because of low electron densities in CP molecules (*e.g.*, Muller and Schmid, 1984). Consequently, the GC-MS technique described below was used for the quantitation of CPs in the extracts of environmental samples.

GC-ECD analyses were done with a Hewlett-Packard 5890A Series II GC with a single splitless injector - dual capillary column - dual detector technique using a 7673A autosampler (1 μL injection). A DB-5 and a DB-1701 column (J&W Scientific) were used. Column dimensions were 30 m x 0.25 mm i.d., with 0.25 μm film thickness. Injector and

detector temperatures were 200 and 300 °C, respectively. The initial column temperature was 90 °C (1 min hold) and the program rate was 4 °/min to 300 °C (with only a 1 min hold in order to prolong column life). The column temperature was then decreased to 280 °C at 20 °C/min (15 min final hold). The hydrogen carrier gas and nitrogen make-up flow rates (at 90 °C) were 1.5 and 40 mL/min, respectively. A toluene injection at elevated injector, detector and column temperatures was made after every injection of a standard or sample. Stock solutions of the three Cereclor solutions, C42 (1108 ng/μL), S45 (1016 ng/μL), and S52 (1002 ng/μL), were prepared in toluene. Because of the low response of the ECD to these compounds, these solutions were used as external standards without further dilution.

Figure 2 shows GC-ECD chromatograms of 1 μL injections of the C42, S45 and S52 standards at approximately the same concentrations (1000 ng/μL). The appearance of the chromatograms is typical of chlorinated paraffins (Muller and Schmid, 1984; Schmid and Muller, 1985; Kraemar and Ballschmiter, 1987; Murray *et al.*, 1988; Tomy *et al.*, 1993). The broad hill-like shape of the chromatogram is due to the large number of congeners and isomers present in such mixtures. Congeners and isomers present in low concentrations cause the rise in the baseline, while congeners and isomers present in higher concentrations give rise to the peaks (Tomy *et al.*, 1993). The ECD response of the Cereclors (S52 > S45 >> C42) is in accordance with their average molecular weights and chlorine contents. Quantitation of the Cereclor standards was based on the total area of the "hills" in the chromatograms. Instrument detection limits were approximately 1100 ng, 40 ng and 20 ng for Cereclors C42, S45 and S52, respectively.

GC-MS -

As indicated above, GC-ECD is relatively insensitive for CPs. Consequently, the method chosen for the analysis of CPs in environmental samples was on-column injection with negative ion chemical ionization, a technique that has been used with some success

before (*e.g.*, Gjos and Gustavsen, 1982; Muller and Schmid, 1984; Schmid and Muller, 1985; Jansson *et al.*, 1991, 1993). The analysis of CPs is fairly complex, and no chromatographic method published to date is entirely satisfactory because no standards exist for the many individual chlorinated paraffin homologs and congeners. Consequently the approach taken in the analysis of environmental samples has been to quantitate the CPs against available standards, which may or may not be suitable for the analysis. A complicating factor may be the weathering of CPs in the environment, producing a CP profile that does not match available standards. Kraemar and Ballschmiter (1987) quantitated CPs with reference only to a commercial Hordaflex LC 60. Jansson *et al.* (1991) used several unidentified CPs as reference standards, and the one that gave a chromatographic pattern and/or mass spectra most similar to the one obtained from the sample was used for their quantitation. Schmidt and Muller (1985) chose only two signals from a composite (short-, medium- and long-chain CPs) NCI-GC-MS ion chromatogram, and from the mass spectra of these two signals they chose the two most abundant masses from each. They then compared environmental extracts by comparing summed abundances of the two dominant ion masses for the appropriate peaks with summed abundances for the standards. The explicit assumption was that the masses chosen were representative for both the standard CP mixture and for the CP composition of the samples analyzed. CP concentrations in the environmental extracts were then calculated by comparing NCI-GC-MS reconstructed ion chromatographic peak areas. Murray *et al.* (1988) studied the occurrence of CPs in effluents of, and downstream from, a CP manufacturing plant in Ohio. They used standards of three CPs that were manufactured by the plant (Paroil 1160 [C_{10}-C_{12}, 50-60% Cl]; Paroil 152 [C_{14}-C_{17}, 50-60% Cl]; and Paroil 142 [C_{20}-C_{30}, 40-50% Cl]. In a refinement of the technique of Muller and Schmid (1984), they quantitated the CPs by cumulative mass ranges: C_{10}-C_{12} (323-329; 357-363; 365-399), C_{14}-C_{17} (399-419; 439-453; 475-487), C_{20}-C_{30} (496-506; 512-517), and recognized that their quantitation procedure may have led to errors by including other CPs not explicitly sought.

The method chosen for our work was NCI-GC-MS with full scan, because the

method of Murray *et al.* (1988) using single ion monitoring parameters was not feasible with our instrument. However, the gas chromatographic operating parameters were similar to those used by Murray *et al.* (1988). The GC separation was performed on a Hewlett-Packard 5890 Series II GC with a temperature-programmable on-column injector and a 7673 autosampler. A 30 m x 0.25 mm i.d. (0.25 μm film thickness) J&W DB-5MS fused silica capillary column was used, coupled to a 1 m x 0.53 mm i.d. Hewlett-Packard uncoated, deactivated retention gap. The initial column temperature was 80 °C (2 min hold) and the program rate was 10 °/min to 280 °C (15 min final hold). The on-column injector was programmed to track the oven temperature. The helium carrier gas was electronically pressure-programmed to maintain a constant flow of 1 mL/min throughout the entire run. The gas chromatograph was coupled to a Hewlett-Packard 5989A MS Engine *via* a heated transfer line at 250 °C. The reagent gas was methane which was optimized to 1.4 torr in the ion source. The ion source and quadrupole analyzer were kept at 125 °C and 100 °C, respectively. Identification of CPs was done by selected ion monitoring (SIM) mode with a cycle time of 0.45 seconds, and confirmations were obtained with full scan mass spectra in the mass range m/e 300-550, with a scan time of 1.06 seconds. The mass spectrometer was equipped with a HP-UNIX data system. Quantitation was done by summing the areas of all bands of peaks in the total ion chromatogram corresponding to the CPs, and comparing the total area with the total area of a Cereclor S-52 standard. The limits of quantitation (10X signal/noise ratio) of Cereclor S52 were 1 μg/L in water (40 L), 3.5 mg/kg dry weight for sediment (25 g), and 3.5 mg/kg wet weight for tissues (10 g).

RESULTS AND DISCUSSION

CPs were only found in the plant effluent, and not in any other sample. Figure 3 shows that the extract of plant effluent exhibited a chromatogram characteristic of CPs. Figure 3 also shows a chromatogram of the Cereclor S52 standard for comparison. Although the chromatograms are not identical, they are similar enough to justify quantitating the CPs in the plant effluent on the basis of the Cereclor S52 standard. CPs

were not found in any other sample analyzed, although many of the other samples were found to contain penta-, hexa- and heptachlorobiphenyls as well as hepta- and octachlorodibenzofurans. All of these other compounds have ion fragments that interfere with CP analysis by selected ion monitoring mode NCI GC-MS, but full-scan NCI GC-MS distinguished the CPs from these interferents. Typical mass spectral data are given in Figure 4, which shows a negative ion mass spectrum of one of the peaks in Cereclor S52. As discussed before (*e.g.,* Muller and Schmid, 1984), the mass spectrum of a single chromatographic signal of CPs shows perturbed patterns due to overlapping of molecular ions with fragments of those molecular ions formed by dechlorination and dehydrochlorination. For example, the cluster at m/e 436 is indicative of seven chlorine atoms and corresponds to the molecular ion for the compound $C_{14}H_{23}Cl_7$. The dehydrochlorination product corresponding to the m/e 436 cluster is shown at m/e 400, which is representative of a Cl_6 pattern. The same cluster at m/e 400 also represents the molecular ion for the compound $C_{14}H_{24}Cl_6$, which has a molecular weight of 402. The dehydrochlorination of the ion at m/e 402 results in the cluster shown at m/e 366.

The concentration of the CPs in the effluent was estimated to be 12.7 µg/L, calculated as Cereclor S52. This concentration is in the range reported by Murray *et al.* (1988) for CPs in effluents from a CP manufacturing plant in Ohio.

ACKNOWLEDGEMENTS

We thank K. Hill, NWRI and J. Biberhofer, Environment Canada, Ontario Region for assistance in the field, and C.A. Sullivan for the alumina cleanup of some of the sample extracts. We also thank M. Eckersley, Ontario Ministry of Natural Resources, Cornwall District, for providing the adult fish, Dr. K. Suns, Ontario Ministry of Environment and Energy (MOEE), Rexdale Laboratory, for providing the juvenile perch, and P. Taylor, MOEE, Southeastern Region, for collecting the effluent sample. We thank ICI Forest Products for permitting us to collect a sample of effluent from their Cornwall plant.

REFERENCES

Environment Canada (1989). Priority Substances List. In: *The Canada Gazette, Part 1*, Ottawa, Ont., Feb. 11, pp. 543-545.

Environment Canada and Health and Welfare Canada (1993a). Canadian Environmental Protection Act priority substances list assessment report: chlorinated paraffins. Minister of Supply and Services Canada, 32+ pp. (ISBN 0-662-20515-4).

Environment Canada and Health and Welfare Canada (1993b). Canadian Environmental Protection Act priority substances list supporting document: chlorinated paraffins. Commercial Chemicals Evaluation Branch, Hull, Québec K1A 0H3, 66 pp.

Fox, M.E. (1986). A practical sampling and extraction system for the quantitative analysis of sub-ng/L organochlorine contaminants in filtered water and suspended solids. In *Methods for Analysis of Organic Compounds in the Great Lakes, Vol. II*, eds. W.C. Sonzogni and D.J. Dube, Univ. Wisconsin Sea Grant Institute publ. WIS-SG-86-244, Madison, WI, pp. 27-34.

Gjos, N. and Gustavsen, K.O. (1982). Determination of chlorinated paraffins by negative ion chemical ionization mass spectrometry. Anal. Chem. **54**, 1316-1318.

Government of Canada (1988). An act respecting the protection of the environment and of human life and health. In *Hansard*, Chapter 22, pp. 1-96, Queen's Printer, Ottawa, Ont.

Hollies, J.I., Pinnington, D.F., Handley, A.J., Baldwin, M.K. and Bennett, D. (1979). The determination of chlorinated long-chain paraffins in water, sediment and biological samples. Anal. Chim. Acta **111**, 201-213.

Jansson, B., Andersson, R., Asplund, L., Bergman, A., Litzen, K., Nylund, K., Reutergardh, L., Sellstrom, U., Uvemo, U.-B., Wahlberg, C. and Wideqvist, U. (1991). Multiresidue method for the gas chromatographic analysis of some polychlorinated and polybrominated pollutants in biological samples. Fresenius J. Anal. Chem. **340**, 439-445.

Jansson, B., Andersson, R., Asplund, L., Litzen, K., Nylund, K., Sellstrom, U., Uvemo, U.-B., Wahlberg, C., Wideqvist, U., Odsjo, T. and Olsson, M. (1993). Chlorinated and brominated persistent organic compounds in biological samples from the environment. Environ. Toxicol. Chem. **12**, 1163-1174.

Kraemer, W. and Ballschmiter, K. (1987). Detection of a new class of organochlorine compounds in the marine environment: the chlorinated paraffins. Fresenius Z. Anal. Chem. **327**, 47-48.

Metcalfe-Smith, J.L., Maguire, R.J. and Batchelor, S.P. (1995). Polychlorinated biphenyl congeners and chlorinated pesticides in fish from the Yamaska River basin, Québec. Water Qual. Res. J. Canada **30**, 179-204.

Muller, M.D. and Schmid, P.P. (1984). GC/MS analysis of chlorinated paraffins with negative chemical ionization. J. High Resol. Chromatogr. Chromatogr. Commun. **7**, 33-37.

Murray, T., Frankenberry, M., Steele, D.H. and Heath, R.G. (1988). Chlorinated paraffins: a report on the findings from two field studies, Sugar Creek, Ohio and Tinkers Creek, Ohio. Vol. 1. Technical Report. U.S. Environmental Protection Agency Report 560/5-87-012, Office of Toxic Substances, Exposure Evaluation Division, 401 M St. S.W., Washington, DC 20460, U.S.A., 65+ pp.

Schmid, P.P. and Muller, M.D. (1985). Trace level detection of chlorinated paraffins in biological and environmental samples, using gas chromatography/mass spectrometry with negative-ion chemical ionization. J. Assoc. Offic. Anal. Chem. **68**, 427-430.

Tomy, G.T., Muir, D.C.G., Westmore, J.B. and Stern, G.A. (1993). Liquid chromatography/plasmaspray mass spectrometry for characterization of a commercial chlorinated n-paraffin mixture. Abstracts 41st Amer. Soc. Mass Spectrom. Conf., San Francisco, CA, U.S.A., June 1993, pp. 143a-143b.

Table 1. Samples of effluent, sediment and biota analyzed for residues of chlorinated paraffins.

Sample Type	Sample #	Description	Volume extracted (L)	Wet weight extracted (g)	Dry weight extracted (g)	% Moisture	% Lipid	% LOI*
Water	Effluent	24-hr comp.	27.22					
Sediment	4-S	sediment			25.69	77.2		19.57
	6-S	sediment			26.01	51.7		5.32
	7-S	sediment			25.19	42.0		4.38
Unionids	2-M	6 *Elliptio complanata*			12.27	88.3	5.10**	
	4-M	2 *E. complanata* & 1 *Anodonta grandis*			5.57	92.5	5.80**	
	5-M	7 *E. complanata*			12.37	89.6	7.25**	
	9-M	9 *E. complanata*			12.26	89.5	8.90**	
Zebra	2-ZM	84 individuals			9.76	89.7	14.07**	
mussels	5-ZM	158 individuals			3.33	87.4	13.46**	
	9-ZM	82 individuals			10.33	89.9	15.00**	
YOY perch	3-YOY	78 individuals		254.9			5.49	
Adult fish	1-1L	*P. flavescens* (liver)		1.89			2.71	
	1-1F	*P. flavescens* (fat)		2.20			83.29	
	1-2L	*C. commersoni* (liver)		6.97			8.61	
	1-2F	*C. commersoni* (fat)		6.32			76.70	
	1-3L	*C. commersoni* (liver)		13.92			3.25	
	1-4L	*C. commersoni* (liver)		14.81			5.27	
	8-1L	*C. commersoni* (liver)		0.61			2.94	
	8-2L	*C. commersoni* (liver)		0.69			2.90	
	8-3L	*E. lucius* (liver)		5.53			7.50	
	8-4L	*E. lucius* (liver)		9.26			10.61	
	8-5L	*E. lucius* (liver)		28.44			6.07	

* LOI = loss on ignition; ** lipid content determined on a dry weight basis.

Table 2. Some properties of the "Cereclor" chlorinated paraffins used in this study.*

Grade	% Cl	Average MW	Appearance	Colour (Hazen Units)	Density (g/mL, 25 °C)	Viscosity (poise, 25 °C)
C42	42	600	clear very pale yellow liquid	250	1.16	25
S45	45	390	clear, water white mobile liquid	80	1.16	2
S52	52	440	clear, water white liquid	100	1.25	15

*From ICI Mond Division, The Heath, Runcorn, Cheshire WA7 4QD, England; MW, molecular weight.

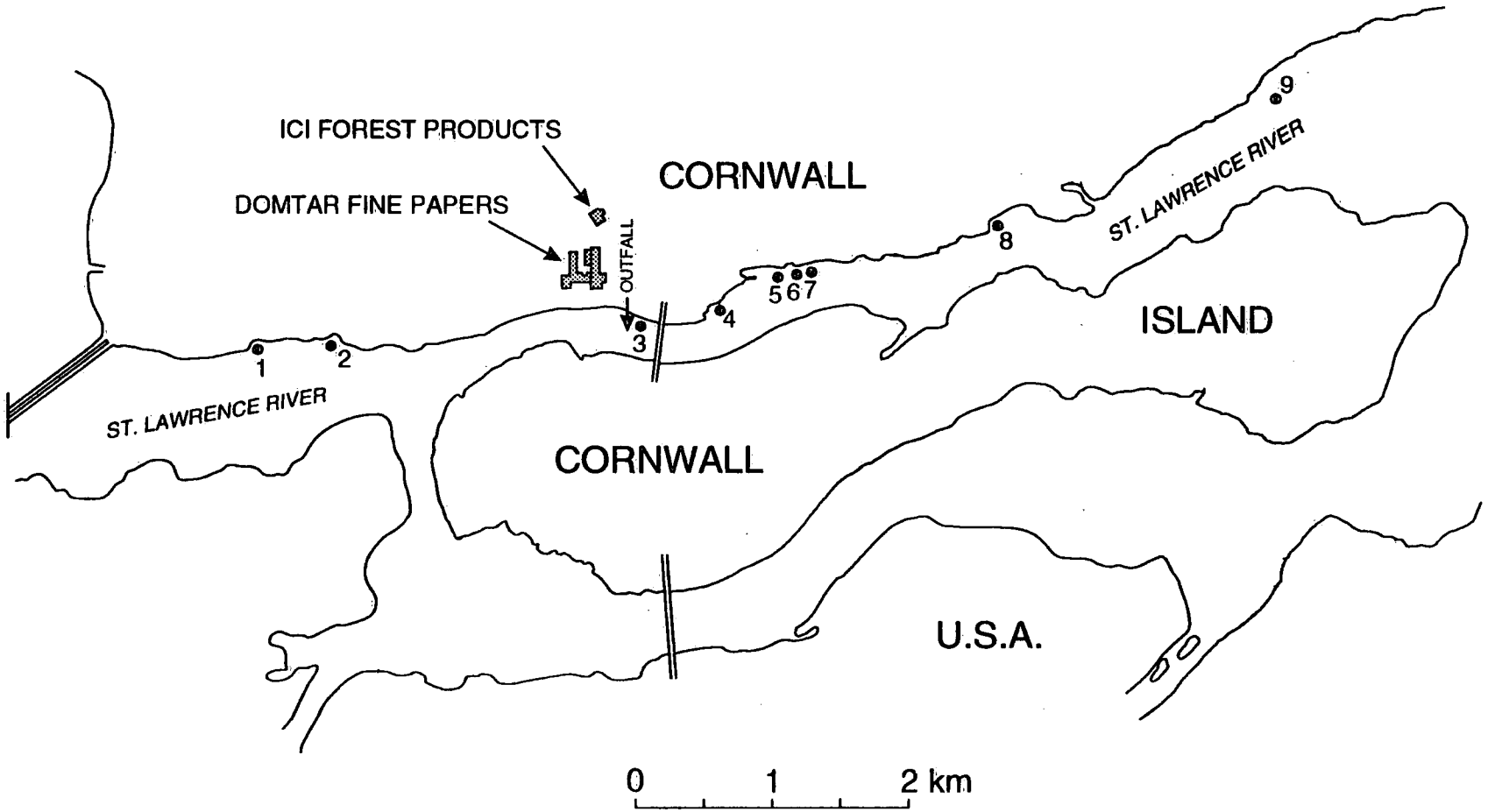
Figure Captions

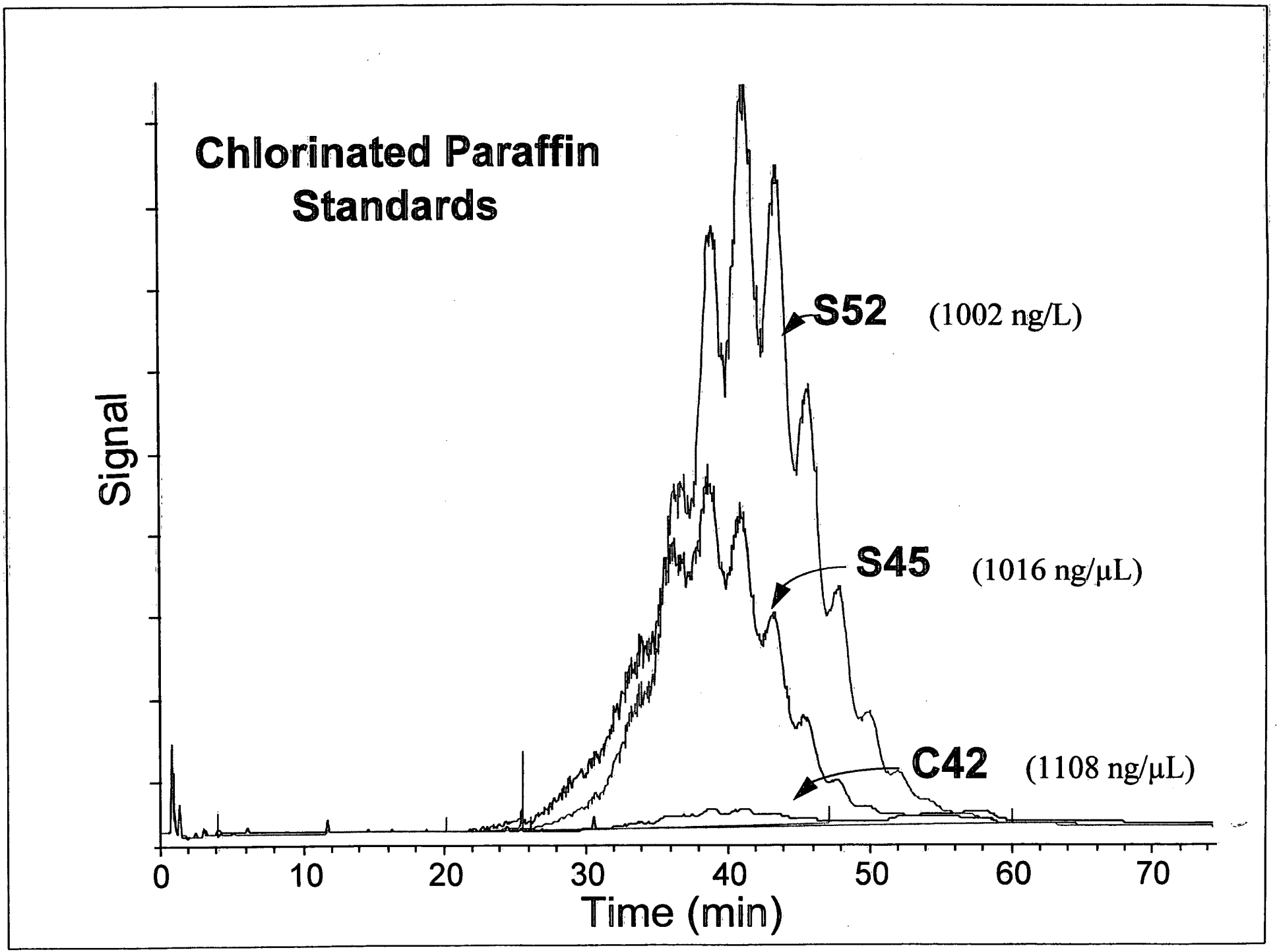
Figure 1. Locations of sampling sites.

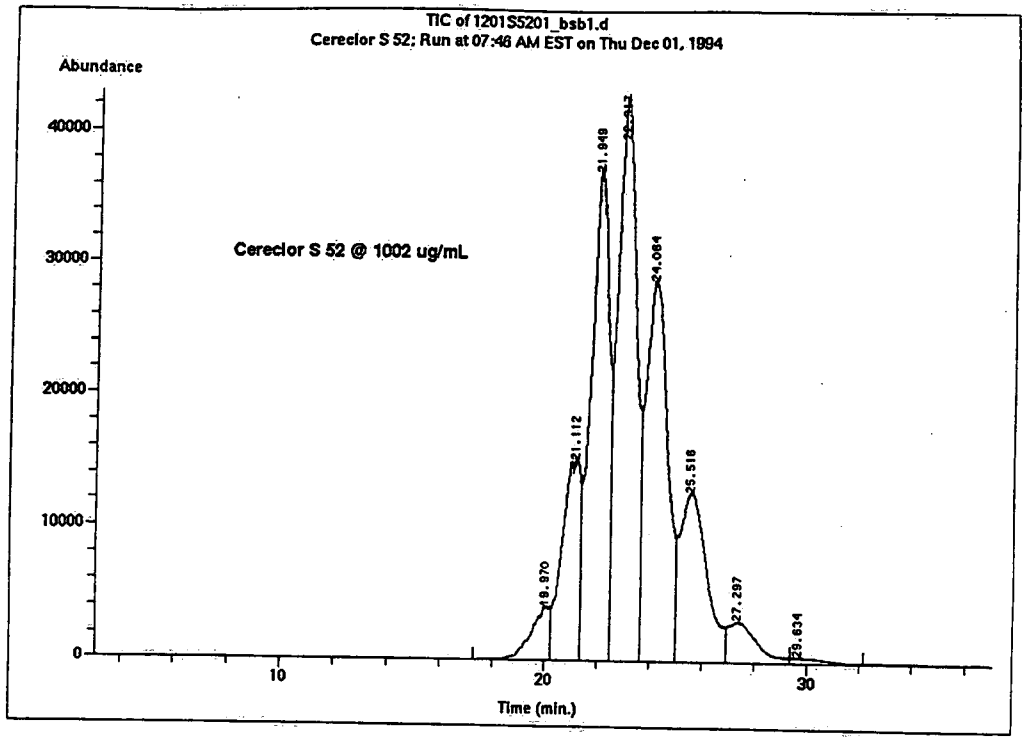
Figure 2. GC-ECD chromatograms of 1 μg/L injections of Cereclor C42, S45 and S52 standards at approximately the same concentrations (1000 ng/μL).

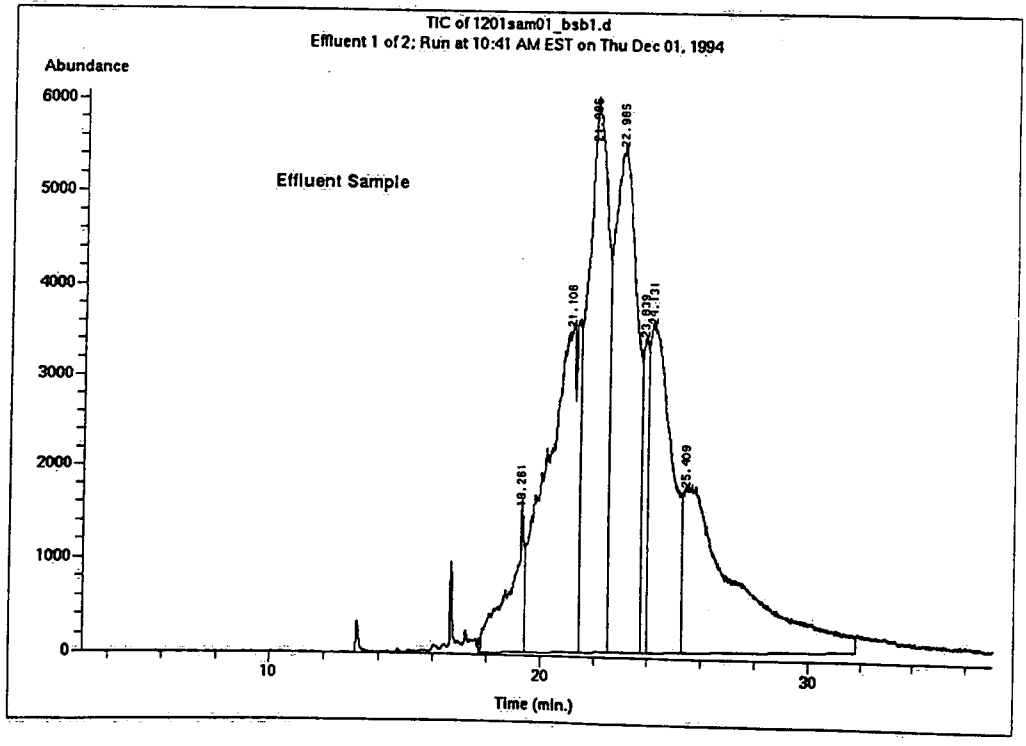
Figure 3. NCI-GC-MS reconstructed ion chromatograms for a Cereclor S52 standard (top) and an extract of the ICI plant effluent (bottom).

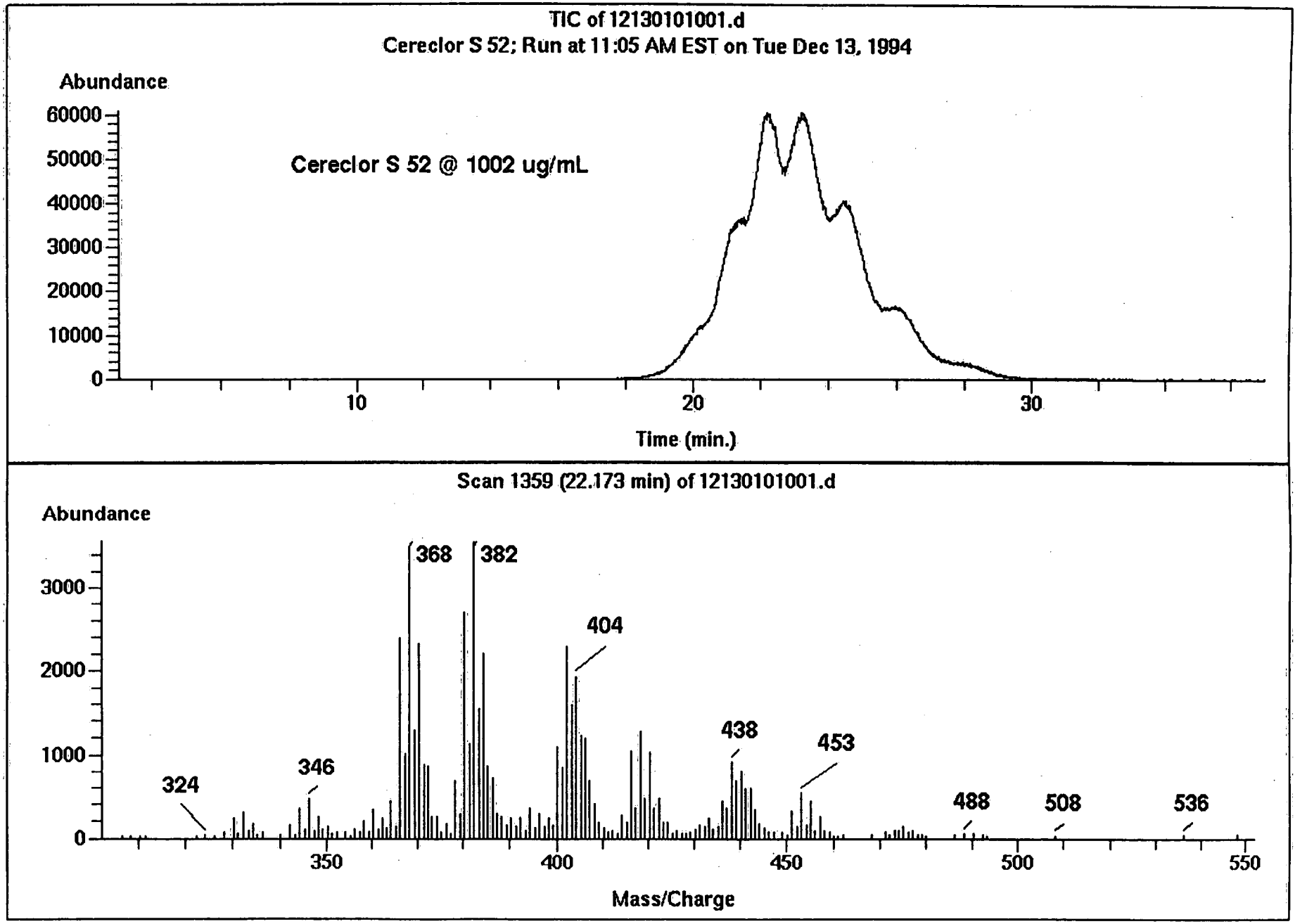
Figure 4. Total ion chromatogram (NCI-GC-MS) of Cereclor S52, and negative ion mass spectrum of peak at 22.173 minutes retention time.


ICI FOREST PRODUCTS
DOMTAR FINE PAPERS
OUTFALL
CORNWALL
ST. LAWRENCE RIVER
ISLAND
ST. LAWRENCE RIVER
CORNWALL
U.S.A.
1
2
3
4
5 6 7
8
9
0
1
2 km


Chlorinated Paraffin Standards
S52 (1002 ng/L)
S45 (1016 ng/µL)
C42 (1108 ng/µL)
Signal
0
10
20
30
40
50
60
70
Time (min)


TIC of 1201S5201_bsb1.d
Cereclor S 52; Run at 07:46 AM EST on Thu Dec 01, 1994
Abundance
Cereclor S 52 @ 1002 ug/mL
18.870
21.112
21.848
24.064
25.518
27.297
29.634
Time (min.)


TIC of 1201sam01_bsb1.d
Effluent 1 of 2; Run at 10:41 AM EST on Thu Dec 01, 1994
Abundance
Effluent Sample
18.261
21.108
22.985
24.131
25.409
Time (min.)


TIC of 12130101001.d
Cereclor S 52; Run at 11:05 AM EST on Tue Dec 13, 1994
Abundance
60000
50000
40000
30000
20000
10000
0
Cereclor S 52 @ 1002 ug/mL
10
20
30
Time (min.)
Scan 1359 (22.173 min) of 12130101001.d
Abundance
3000
2000
1000
0
368
382
404
438
453
324
346
488
508
536
350
400
450
500
550
Mass/Charge

Appendix 1. Biological measurements on individual unionids used to prepare composite samples. All specimens are *Elliptio complanata* except where otherwise noted.

Site	Composite	Sex	Wet weight (g)	Shell length (mm)
2	2-M	M	33.88	91.00
		M	23.53	93.90
		F	28.98	87.95
		F	36.50	90.55
		F	53.58	109.95
		F	57.58	110.80
4	4-M	M	31.25	91.95
		M*	39.45	85.70
		M	18.03	80.95
5	5-M	M	25.06	83.85
		F	36.27	98.80
		M	23.96	87.55
		F	21.87	81.45
		F	24.33	83.45
		M	18.91	79.25
		F	20.13	79.85
9	9-M	M	29.09	93.70
		M	22.11	82.85
		M	14.54	75.25
		F	18.58	80.30
		M	23.73	86.30
		F	27.35	90.35
		M	20.99	84.85
		F	21.05	81.65
		F	32.92	95.30

*_Anodonta grandis_; F = female and M = male.

Appendix II. Biological measurements on individual adult fish.*

Site & Fish #	Species	Sex	Fork length (cm)	Whole weight (g)	Liver	Spleen	Gonads	Kidneys	Gall Bladder	Dorsal Muscle	Visceral Fat
1-1	*P. flavescens*	F	24.1	187.3	1.89	0.13	1.34			27.02	2.20
1-2	*C. commersoni*	F	43.2	1126.0	6.97	1.91	46.11	7.01	6.32	23.78	6.32
1-3	*C. commersoni*	F	43.2	1185.2	13.92	3.13	34.75	11.63	7.89	34.59	
1-4	*C. commersoni*	F	45.1	1326.5	14.81	2.59	44.10	11.09	9.28	46.05	
8-1	*C. commersoni*	I	22.5	155.0	0.61	0.27		0.76		12.22	
8-2	*C. commersoni*	I	21.6	142.0	0.69	0.14		1.20	0.21	14.09	
8-3	*E. lucius*	F	39.4	453.7	5.53	0.19		4.03	0.24	20.94	
8-4	*E. lucius*	F	47.0	583.0	9.26	0.55	2.91	7.00	0.60	27.10	
8-5	*E. lucius*	F	61.0	1497.0	28.44	1.81	14.94	15.79	1.23	36.15	

*F = female; I = immature; missing values indicate insufficient material to sample.

All Chlorinated Paraffin References (Including Those Used in This Report)

Bengtsson, B.-E., Svanberg, O., Linden, E., Lunde, G. and Baumann Ofstad, E. (1979). Structure related uptake of chlorinated paraffins in bleaks (*Alburnus Alburnus* L). Ambio **8**, 121-122.

Bergman, A., Blomkvist, G. and Orn, U. (1988). Tri- and tetrachlorophenyl methyl sulphones identified in lettuce, potatoes and soil. Chemosphere **17**, 717-725.

Birtley, R.D.N., Conning, D.M., Daniel, J.W., Ferguson, D.M., Longstaff, E. and Swan, A.A.B. (1980). The toxicological effects of chlorinated paraffins in mammals. Toxicol. Appl. Pharmacol. **54**, 514-525.

Campbell, I. and McConnell, G. (1980). Chlorinated paraffins and the environment. 1. Environmental occurrence. Environ. Sci. Technol. **14**, 1209-1214.

Chan, P.K.L. and Meek, M.E. 91994). Chlorinated paraffins: evaluation of risks to health from environmental exposure in Canada. Environ. Carcinogen. Ecotoxicol. Rev. **C12**, 219-229.

Environment Canada (1989). Priority Substances List. In: *The Canada Gazette, Part 1*, Ottawa, Ont., Feb. 11, pp. 543-545.

Environment Canada and Health and Welfare Canada (1993a). Canadian Environmental Protection Act priority substances list assessment report: chlorinated paraffins. Minister of Supply and Services Canada, 32+ pp. (ISBN 0-662-20515-4).

Environment Canada and Health and Welfare Canada (1993b). Canadian Environmental Protection Act priority substances list supporting document: chlorinated paraffins. Commercial Chemicals Evaluation Branch, Hull, Québec K1A 0H3, 66 pp.

Friedman, D. and Lombardo, P. (1975). Photochemical technique for the elimination of chlorinated aromatic interferences in the gas-liquid chromatographic analysis for chlorinated paraffins. J. Assoc. Offic. Anal. Chem. **58**, 703-706.

Gjos, N. and Gustavsen, K.O. (1982). Determination of chlorinated paraffins by negative ion chemical ionization mass spectrometry. Anal. Chem. **54**, 1316-1318.

Haglund, P., Asplund, L., Jarnberg, U. and Jansson, B. (1990). Isolation of toxic polychlorinated biphenyls by electron donor-acceptor high performance liquid chromatography on a 2-(1-pyrenyl)ethyldimethylsilylated silica column. J. Chromatogr. **507**, 389-398.

Hollies, J.I., Pinnington, D.F., Handley, A.J., Baldwin, M.K. and Bennett, D. (1979). The determination of chlorinated long-chain paraffins in water, sediment and biological samples. Anal. Chim. Acta **111**, 201-213.

Howard, P.H., Santodonato, J. and Saxena, J. (1975). Investigation of selected potential environmental contaminants: chlorinated paraffins. U.S. Environmental Protection Agency Report EPA-560/2-75-007, Office of Toxic Substances, Washington, DC 20460, 109+ pp.

Jansson, B., Andersson, R., Asplund, L., Bergman, A., Litzen, K., Nylund, K., Reutergardh, L., Sellstrom, U., Uvemo, U.-B., Wahlberg, C. and Wideqvist, U. (1991). Multiresidue method for the gas chromatographic analysis of some polychlorinated and polybrominated pollutants in biological samples. Fresenius J. Anal. Chem. **340**, 439-445.

Jansson, B., Andersson, R., Asplund, L., Litzen, K., Nylund, K., Sellstrom, U., Uvemo, U.-B., Wahlberg, C., Wideqvist, U., Odsjo, T. and Olsson, M. (1993). Chlorinated and brominated persistent organic compounds in biological samples from the environment. Environ. Toxicol. Chem. **12**, 1163-1174.

Jansson, B., Asplund, L. and Olsson, M. (1984). Analysis of polychlorinated naphthalenes in environmental samples. Chemosphere **13**, 33-41.

Jensen, S. and Jansson, B. (1976). Anthropogenic substances in seal from the Baltic: methyl sulfone metabolites of PCB and DDE. Ambio **5**, 257-260.

Kannan, N., Tanabe, S., Wakimoto, T. and Tatsukawa, R. (1987). Coplanar polychlorinated biphenyls in Aroclor and Kanechlor mixtures. J. Assoc. Offic. Anal. Chem. **70**, 451-454.

Kraemer, W. and Ballschmiter, K. (1987). Detection of a new class of organochlorine compounds in the marine environment: the chlorinated paraffins. Fresenius Z. Anal. Chem. **327**, 47-48.

Lahaniatis, E.S., Parlar, H., Klein, W. and Korte, F. (1975). Contributions to ecological chemistry XCIV: analysis and photochemistry of polychlorinated paraffins. Chemosphere **2**, 83-88.

Lloyd, K., Brownlee, L., Zitko, V. and Chan, P. (1993). Canadian Environmental Protection Act priority substances program assessment report: chlorinated paraffin waxes. Confidential draft report containing only the environmental sections.

Lombardo, P., Dennison, J.L. and Johnson, W.W. (1975). Bioaccumulation of chlorinated paraffin residues in fish fed Chlorowax 500C. J. Assoc. Offic. Anal. Chem. **58**, 707-710.

Madeley, J.R. and Birtley, R.D.N. (1980). Chlorinated paraffins and the environment. 2. Aquatic and avian toxicology. Environ. Sci. Technol. **14**, 1215-1221.

Muller, M.D. and Schmid, P.P. (1984). GC/MS analysis of chlorinated paraffins with negative ion chemical ionization. J. High Resol. Chromatogr. Chromatogr. Commun. **7**, 33-37.

Murphy, P.G. (1972). Sulfuric acid for the cleanup of animal tissues for analysis of acid-stable chlorinated hydrocarbon residues. J. Assoc. Offic. Anal. Chem. **55**, 1360-1362.

Murray, T., Frankenberry, M., Steele, D.H. and Heath, R.G. (1988). Chlorinated paraffins: a report on the findings from two field studies, Sugar Creek, Ohio and Tinkers Creek, Ohio. Vol. 1. Technical Report. U.S. Environmental Protection Agency Report 560/5-87-012, Office of Toxic Substances, Exposure Evaluation Division, 401 M St. S.W., Washington, DC 20460, U.S.A., 65+ pp.

Schmid, P.P. and Muller, M.D. (1985). Trace level detection of chlorinated paraffins in biological and environmental samples, using gas chromatography/mass spectrometry with negative-ion chemical ionization. J. Assoc. Offic. Anal. Chem. **68**, 427-430.

Svanberg, O., Bengtsson, B.-E., Linden, E., Lunde, G. and Baumann Ofstad, E. (1978). Chlorinated paraffins - a case of accumulation and toxicity to fish. Ambio **7**, 64-65.

Svanberg, O. and Linden, E. (1979). Chlorinated paraffins - an environmental hazard? Ambio **8**, 206-209.

Tomy, G.T., Muir, D.C.G., Westmore, J.B. and Stern, G.A. (1993). Liquid chromatography/plasmaspray mass spectrometry for characterization of a commercial chlorinated n-paraffin mixture. Extended abstract of a presentation at 41st Amer. Soc. Mass Spectrom. Conf., San Francisco, CA, U.S.A., June 1993. Abstract: pp. 143a-143b.

U.S. Environmental Protection Agency (1993). RM2 exit briefing on chlorinated paraffins and olefins. Draft report, December 1, 42 pp.

Wells, D.E., Cowan, A.A. and Christie, A.E.G. (1985). Separation of organochlorine residues by absorption chromatography prior to capillary gas chromatography. J. Chromatogr. **328**, 372-377.

Zitko, V. (1972). Problems in the determination of polychlorinated biphenyls. Inter. J. Environ. Anal. Chem. **1**, 221-231.

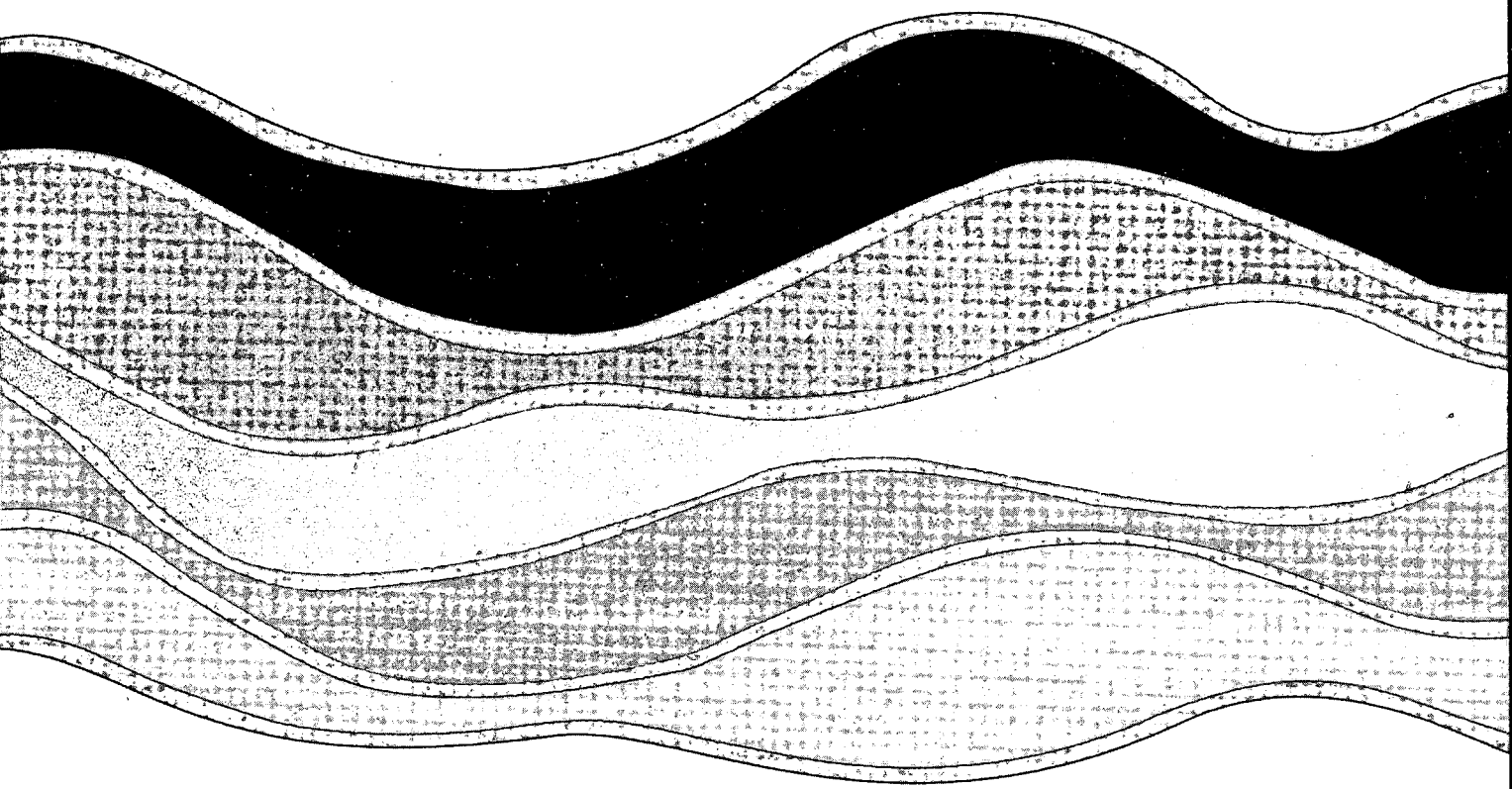
Zitko, V. (1973). Chromatography of chlorinated paraffins on alumina and silica columns. J. Chromatogr. **81**, 152-155.

Zitko, V. (1974). Confirmation of chlorinated paraffins by dechlorination. J. Assoc. Offic. Anal. Chem. **57**, 1253-1259.

Zitko, V. (1980). Chlorinated alkylbenzenes in C_{12} chlorinated paraffins. Chemosphere **9**, 139-142.

Zitko, V. (1980). Chlorinated paraffins. In "Handbook of Environmental Chemistry, Vol. 3, Part A, Anthropogenic Compounds", ed. O. Hutzinger, Springer-Verlag, New York, ISBN 3-540-09690-6, pp. 149-156.

Zitko, V. and Arsenault, E. (1974). Chlorinated paraffins: properties, uses and pollution potential. Environment Canada, Fisheries and Marine Service Tech. Rep. 491, St. Andrews, N.B., 38+ pp.



NATIONAL WATER RESEARCH INSTITUTE
P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

Environment Canada Environnement Canada

Canada

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX
C.P. 5050, BURLINGTON (ONTARIO) L7R 4A6

Think Recycling!

Pensez à recycler !