

# NON-DIOX II

## QUANTIFYING CHLORINATED *n*-ALKANES IN ENVIRONMENTAL SAMPLES BY HIGH RESOLUTION GAS CHROMATOGRAPHY ELECTRON CAPTURE NEGATIVE ION HIGH RESOLUTION MASS SPECTROMETRY.

**Gary A. Stern, Derek C. G. Muir**, Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, Manitoba R3T 2N6, Canada, **Gregg T. Tomy, John B. Westmore**, Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada, **Aaron T. Fisk, Chris D. Cymbalisty**, Department of Soil Science, University of Manitoba, Winnipeg, Manitoba, Canada.

### 1. Introduction

Chlorinated derivatives of *n*-alkanes (CAs), also known as chlorinated paraffins, have the general formula  $C_xH_{2x+2-z}Cl_z$ . Commercially available products consist of a complex mixture of congeners and homologues having carbon chain lengths from  $C_{10}$  to  $C_{30}$  and chlorine content from 30 to 70% by mass. In laboratory studies CAs have been found to bioaccumulate and biomagnify in fish<sup>1</sup>. Since they are thought to be persistent in the environment, sensitive and specific methods for their quantitative analysis are being sought in order to assess their ecological impact.

Owing to varying carbon chain length and chlorine percentage, CAs provide a range of properties for different applications. In Canada and the US, CAs are used mainly as flame retardant plasticizers in vinyl plastics and as high-pressure lubricants in metal-working machinery. Smaller applications for CAs include use as flame retardants in rubber and paints, and as adhesives and sealants<sup>1</sup>.

Release of CAs into the environment could occur during production, storage, transportation, or industrial use; or release by leaching from landfill sites is also possible. However, the major sources of release are thought to be during production (either from spills or facility wash-down) and from industrial usage (either from improper disposal of used metal-working lubricants or carry-off from work pieces<sup>2-4</sup>). Much of this release is to the aquatic environment, either directly or via sewage treatment systems.

Environmental data on CA concentrations are lacking, mainly because their determination in environmental matrices is considered to be very difficult. However, in a recent Swedish study CAs were among the most prominent chlorinated organic contaminants in 11

representative biological samples, at concentrations ranging from 130 to 4400 ng/g lipid weight<sup>5</sup>. In waste water municipal sewer systems in southern Germany, CA concentrations in sewer films and sludges in dry matter were in the lower mg/kg range<sup>6</sup>. This is comparable to industrial sludge from the United Kingdom (10 mg/kg) and Switzerland (30 mg/kg)<sup>7,8</sup>. Present methods for quantifying CAs in environmental matrices rely on low resolution mass spectrometry<sup>4,8</sup>. A major problem associated with this method is a lack of *specificity*. Monitoring ions at nominal mass presents the problem of potential interferences from higher chlorinated PCBs, toxaphene and chlordane products which all have molecular weights similar to short and medium chain length CAs (*i.e.*, 350-500 Daltons). Other procedures using less characteristic ions, *viz.*,  $m/z$  70-73, present the problem that potentially any chlorohydrocarbon present in environmental matrices could fragment to yield such ions<sup>6</sup>.

We present here a highly selective, specific, and sensitive method for quantifying CAs in environmental matrices by HRGC-ECNI/HRMS in the SIR mode. By this method we have established the presence, and determined the levels, of CAs in fish and sediment samples from the Detroit River in the Great Lakes region.

## 2. Experimental

**Chlorinated *n*-paraffin mixture.** Paroil 1160, C<sub>10</sub>-C<sub>13</sub> chain length and ~60% chlorine, was provided by Dover Chemical Corp. (Dover, Ohio). A standard solution was prepared by weighing a known amount of the mixture, and diluting with hexane to a known concentration.

**Gas chromatography and mass spectrometry.** The industrial mixture, which is used as an external standard, was analyzed on a Hewlett-Packard 5890 Series II gas chromatograph, fitted with a high resolution 30 m x 0.25 mm i.d. DB5 column, through a heated transfer line maintained at 280°C, into a Kratos Concept high resolution mass spectrometer (EBE geometry), controlled by a Mach 3 data system. The injector port was maintained at 220°C. With helium as the carrier gas, elution was performed as follows: the initial column temperature was 80°C; held for 1 minute; it was then ramped to 260°C at a rate of 7°C min<sup>-1</sup>, held there for 8:18 min, and ramped to 280°C at a rate of 10°C min<sup>-1</sup> and held for 13 minutes. ECNI/HRMS in the SIR mode was performed at a spectrometer resolving power ~12 000. Methane was used as the moderating gas and PFK was used as the mass calibrant. Optimum sensitivity was achieved at a gas pressure of ~2x 10<sup>-4</sup> torr, recorded by a source ion gauge, an electron energy of ~180 eV, an accelerating voltage of 5.3 kV, and an ion source temperature of 120°C.

**Sample Collection and extraction.** Fish and sediment samples were collected near the mouth of the Detroit River in Lake Erie. Extraction procedures were similar to those previously used in our laboratory for determining organochlorines in sediment and biota<sup>9</sup>.

## 3. Results and Discussion

We have been able to selectively maximize the intensity of the [M-Cl]<sup>-</sup> ion with respect to other ions observed in the ECNI mass spectra of individually synthesized polychloro-*n*-alkanes at an ion source temperature of 120°C for these compounds<sup>10</sup>. Consequently, the biggest peak in the [M-Cl]<sup>-</sup> isotopic group was used for quantitation, and the second largest peak was used to confirm that the relative abundance of the quantitation ion was not spurious.

**Determining the composition of mixtures.** The relationship between composition and the molecular formulae, C<sub>x</sub>H<sub>2x-2+2</sub>Cl<sub>z</sub>, of components present in these mixtures is

# NON-DIOX II

$$Z_{\text{avg}} = m_r (14x+2) / (35.5-34.5m_r)$$

where  $Z_{\text{avg}}$  and  $m_r$  are the average number and mass fraction of chlorine, respectively<sup>11</sup>. From calculated values of  $Z_{\text{avg}}$  for the stated chlorine contents of Paroil 1160 shown in Table 1, we expect the most abundant congeners to contain  $Z_{\text{exp}}$  values bracketing the  $Z_{\text{avg}}$  values, as shown. To verify the presence of each component in the commercial mixture, SIR experiments were performed to monitor for the two largest isotopic peaks in their representative [M-Cl]<sup>-</sup> ion groups.

**Elution profiles and retention time windows.** Components listed in Table 1 are not individual congeners, but complex mixtures containing both positional and stereo isomers and, as a result, elute over a very broad retention time range. Figure 1 shows the elution profiles for the seventeen major components we found in Paroil 1160, and also the retention time windows we used to develop our analytical protocol.

**Interferences.** The analytical method outlined above has been tested on other halogenated organic compounds, known to be found in this region of the Great lakes, which could coelute with CAs and therefore interfere with our method. These compounds include PCBs, toxaphene, technical chlordane and other volatile organic compound mixtures. In the method presented here, none of these interferences were detected.

**Method of Quantitation.** The areas of the ions monitored in the standard are integrated and summed. Quantitation of CAs in samples is then achieved by comparison of the ratio of the signals for samples to that of the standard, calculated in the same manner.

## 4. Conclusions

The results shown in Table 2, represent the first data on chlorinated n-alkane levels using HRMS, and the first which reports concentrations according to homologue groups. Our future plans are to establish the linearity of the response of industrial standards, and develop methods to analyze higher chain length mixtures.

## 5. References

- <sup>1</sup>Environment Canada, Priority Substances Program, CEPA Assessment Report, Chlorinated Paraffins. Commercial Chemicals Branch, Hull Quebec. (1993).
- <sup>2</sup>V. Zitko and E. Arsenault. Chlorinated Paraffins: Properties, uses and pollution potential. Dept. Environ., Fisheries and Marine Services, Research and Development Directorate (Tech. Rep. No. 491). 38pp. (1974).
- <sup>3</sup>Environmental Protection Agency. Office of Toxic Substances. RM1 Decision Package. Chlorinated Paraffins. Environmental risk assessment. Washington DC. (1991).
- <sup>4</sup>Swedish National Chemicals Inspectorate. KEMI Report No. 1. (1991).
- <sup>5</sup>B.Jansson, R. Andersson, L. Asplund, K. Litzen, K. Nylund, U. Sellstrom, U. Uvemo, C. Wahlberg, U. Wideqvist, T. Odsjo and M. Olsson. *Environ. Toxicol. Chem.* **12**:1163-1174. (1993)
- <sup>6</sup>R. Rieger, K. Ballschmiter. *Fresenius. J. Anal. Chem.* **352**:715-724. (1995).
- <sup>7</sup>I. Campbell, G. McConnell. *Environ. Sci. Technol.* **14**:1209-1214. (1980).
- <sup>8</sup>P. Schmid, M. Muller. *J. Assoc. Off. Anal. Chem.* **68**:427-430. (1985).
- <sup>9</sup>D.C.G. Muir, N.P. Grift, W.L. Lockhart, P. Wilkinson, B. N. Billeck and G. J. Brunskill. *Sci. Total Environ.* **160/161**:447-457. (1995).
- <sup>10</sup>G.T. Tomy, D.C.G. Muir, J.B. Westmore and G.A. Stern. 42<sup>nd</sup> Annual Conference on Mass Spectrometry and Allied Topics, Chicago, U.S.A. pp 263. June (1994).

# NON-DIOX II

<sup>11</sup>M.D. Muller and P.P. Schmid. J. High Resol. Chromat. Chromat. Commun. 7:33-37. (1984).

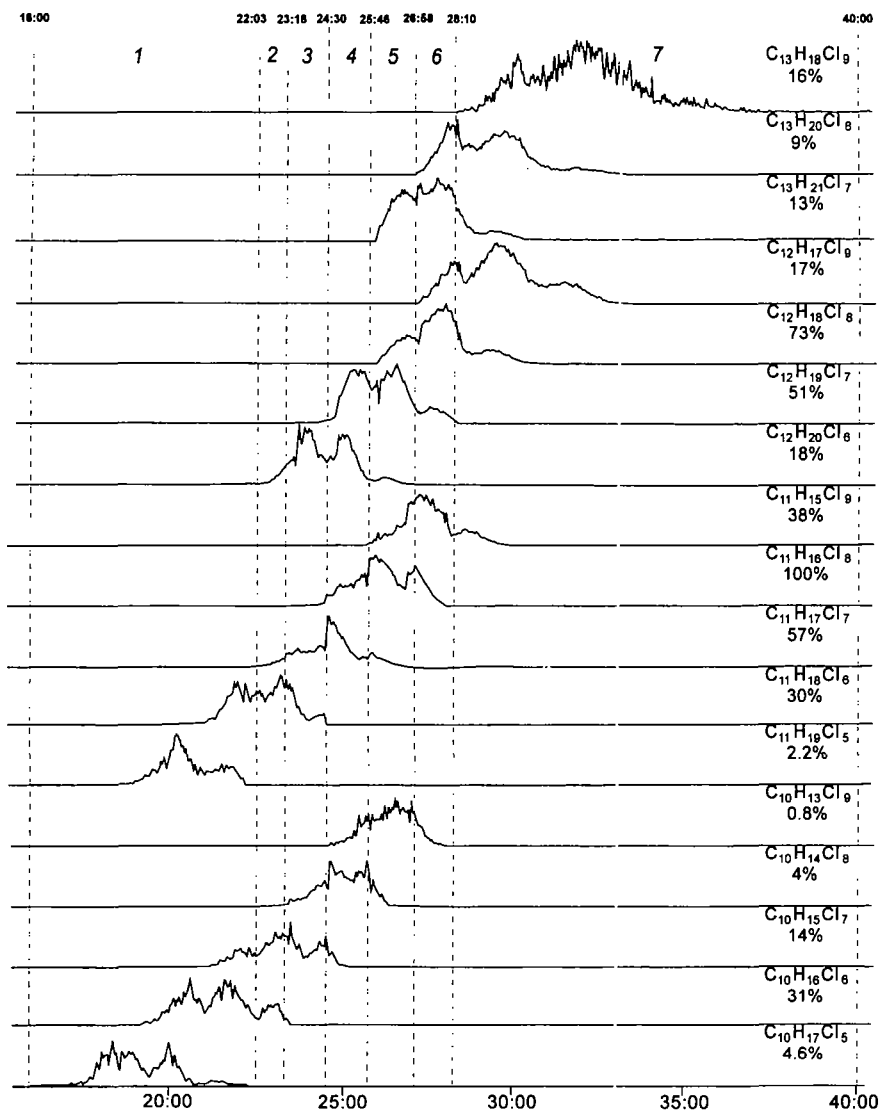
**Table 1.** Major components,  $C_xH_{2x-2z+2}Cl_z$ , expected in the commercial chlorinated paraffin mixture of specified chlorine content.

Paroil 1160 (C <sub>10</sub> -C <sub>13</sub> , 60%)			
X	Zavg	Zexp	MF
		5	C <sub>10</sub> H <sub>17</sub> Cl <sub>5</sub>
10	5.8	6	C <sub>10</sub> H <sub>16</sub> Cl <sub>6</sub>
		7	C <sub>10</sub> H <sub>15</sub> Cl <sub>7</sub>
		8	C <sub>10</sub> H <sub>14</sub> Cl <sub>8</sub>
11	6.3	5	C <sub>11</sub> H <sub>19</sub> Cl <sub>5</sub>
		6	C <sub>11</sub> H <sub>18</sub> Cl <sub>6</sub>
		7	C <sub>11</sub> H <sub>17</sub> Cl <sub>7</sub>
		8	C <sub>11</sub> H <sub>16</sub> Cl <sub>8</sub>
12	6.9	6	C <sub>12</sub> H <sub>20</sub> Cl <sub>6</sub>
		7	C <sub>12</sub> H <sub>19</sub> Cl <sub>7</sub>
		8	C <sub>12</sub> H <sub>18</sub> Cl <sub>8</sub>
		9	C <sub>12</sub> H <sub>17</sub> Cl <sub>9</sub>
		13	C <sub>12</sub> H <sub>16</sub> Cl <sub>10</sub>
13	7.5	7	C <sub>13</sub> H <sub>21</sub> Cl <sub>7</sub>
		8	C <sub>13</sub> H <sub>20</sub> Cl <sub>8</sub>
		9	C <sub>13</sub> H <sub>19</sub> Cl <sub>9</sub>

**Table 2.** CA (C<sub>10</sub>-C<sub>13</sub>, 60%) levels in sediment (ng/g dry wt) and fish (ng/g wet wt) in samples from the Detroit River.

Sample	N	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	Total CAs
<i>Yellow Perch</i>	1	520	1490	990	150	3150
<i>Sediment</i>	1	80	370	470	140	1060
<i>Zebra Mussel</i>	1	150	690	800	180	1820

# NON-DIOX II



**Figure 1.** Elution profiles, retention time windows and relative response (%) for the major components (monitored as  $[M-Cl]^-$  ions) found in Paroil 1160.

## Acknowledgements

The authors would like to thank Dr. D. Haffner (Great Lakes Institute, University of Windsor) for providing the environmental samples. We also thank Environment Canada (Commercial Chemicals Evaluation Branch) and NSERC for their financial assistance.