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Quantifying C_{10}−C_{13} Polychloroalkanes in Environmental Samples by High-Resolution Gas Chromatography/Electron Capture Negative Ion High-Resolution Mass Spectrometry

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A method for quantifying C_{10}−C_{13} polychloroalkanes (PCAs) in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry in the selected ion monitoring (SIM) mode is presented. The molecular compositions of commercial PCAs and of PCA-containing extracts from environmental samples are first determined by monitoring $[M - Cl]^-$ ions of specific *m/z* value corresponding to formula groups present and by assuming that the integrated ion signals are proportional to molar concentration weighted by the number of chlorine atoms in the formula group. For quantitative measurement, one specific *m/z* peak is selected for each analyte and its SIM response is integrated. The integrated SIM responses have a linear dependence upon amount of PCA injected over the range 0.5−500 ng. An analytical protocol is then described. High-resolution (∼12 000 resolving power) mass spectrometry is shown to be desirable to eliminate self-interferences between PCAs at low resolving power (∼1000) and potential interferences from technical chlordane, toxaphene, PCBs, and other organochlorine pesticides. Extraction recoveries of PCAs from fish averaged >80%. The analytical detection limit is ∼60 pg of injected PCA, at a signal-to-noise ratio of 4:1, while the method detection limit was 23 ng/g. As illustrations of the application of the technique to "real world" problems, PCA levels in biota and sediment samples from the mouth of the Detroit River (MI) are reported to be in the 0.3−1.2 μg/g range.

Commercially produced polychloroalkanes (PCAs), of the general formula $C_nH_{2n+2-z}Cl_z$, have carbon chain lengths from C_{10} to C_{30} and chlorine content from 30 to 70% by mass.[1−3] Also known industrially as chlorinated paraffins, they are formed by direct chlorination of *n*-alkane feedstocks with molecular chlorine under forcing conditions (high temperature and/or UV/visible irradiation). These reactions, which have low positional selectivity,[4−6] yield complex mixtures of congeners (i.e., homologues and their isomers).[7] Based on the principal *n*-alkane feedstocks, which are derived from petroleum fractions, the commercial PCA mixtures fall into different categories: C_{10}−C_{13} (short), C_{14}−C_{17} (medium), and C_{20}−C_{30} (long). Owing to varying carbon chain length and chlorine percentage, PCAs provide a range of properties for different applications. The extent, and conditions, of chlorination used depend ultimately on the desired application.[8,9]

In Canada and the United States, PCAs are used mainly as flame-retardant plasticizers in vinyl plastics and as high-temperature lubricants in metal-working machinery. Their more limited applications include use as flame retardants in rubber, paints, adhesives, and sealants.[10]

Under Canada's Environmental Protection Act, PCAs have been classified as priority toxic substances; they have also been placed on the U.S. Environmental Protection Agency (EPA) Risk Reduction List. There are particular concerns about C_{10}−C_{13} PCAs because of possible adverse effects on terrestrial and aquatic organisms, and potential carcinogenicity to humans.[11−13] Their environmental concentrations are needed to estimate environmental exposure and to understand their fate. Therefore, sensitive and specific methods for their quantitative analysis are required for their exposure assessment.

Release of PCAs into the environment could occur during (1) production, (2) storage, (3) transportation, or (4) industrial use; leaching (5) from landfill sites is also possible. However, the major releases are thought to be from production, either from

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spills or facility wash-down, and from industrial usage, either from improper disposal of used metal-working lubricants or carry-off from work pieces, particularly of $C_{10}-C_{13}$ compounds.[2,11,14] Much of this release is to the aquatic environment, either directly or from sewage treatment systems.[2,11]

Knowledge of environmental levels of PCAs is limited, mainly because the determination of PCAs in environmental matrixes is considered to be very difficult. While a gas chromatography/mass spectrometry (GC/MS) method based on selected ion monitoring (SIM) of positive ions has been described,[15] the more popular methods have relied on electron capture negative ion (ECNI) low-resolution MS to monitor GC effluents.[16−24] A major problem associated with these methods is lack of *specificity*. Procedures that monitor the less characteristic *m/z* 70−73 ions,[16,17] i.e., $Cl_2^{\bullet-}$ and HCl_2^-, present the problem that potentially any chlorohydrocarbon present in environmental matrixes could fragment to yield such ions. Other methods[17−24] monitor ions at nominal mass; here there are potential interferences from higher polychlorinated biphenyls (PCBs), toxaphene, and chlordane-related compounds, which all have molecular masses similar to short- and medium-chain length PCAs (i.e., 350−500 u). We shall demonstrate that these problems can be avoided by quantifying the effluents from a high-resolution GC column by monitoring characteristic negative ions produced by ECNI MS performed at high resolving power.

We describe here the development of a selective, specific, and sensitive method for quantifying PCAs in environmental matrixes by high-resolution gas chromatography/electron capture negative ion-high-resolution mass spectrometry (HRGC/ECNI-HRMS) in the SIM mode. By this method we have established the presence, and determined the levels, of PCAs in fish and sediment samples from the Trenton Channel of the Detroit River, near its entry to Lake Erie, and in Zebra mussels from Lake Erie.

EXPERIMENTAL SECTION

Materials. Two commercial PCA products, used as analytical standards, one of $C_{10}-C_{13}$ chain length and ~60% chlorine by mass (PCA-60) and the other of $C_{10}-C_{13}$ carbon chain length and ~70% chlorine by mass (PCA-70) were graciously provided by the manufacturers (Dover Chemical Corp., Dover, OH, and Occidental Chemical Corp., Niagara Falls, NY, respectively). Isotopically labeled [$^{13}C_1$]chlordane (99% ^{13}C) and [$^{13}C_8$]mirex (99% ^{13}C) were purchased from Cambridge Isotope Laboratories Inc. (CIL) (Burlington, ON, Canada). Sources of pesticide test mixtures were as follows: toxaphene (CIL), technical chlordane (CIL), a mixture of 87 PCB congeners (Ultra Scientific, North Kingstown, RI), SRM 2261 (a chlorinated pesticide mixture, NIST, Gaithersburg, MD), and MMQA (marine mammal quality assurance, an "in house" test mixture of persistent organochlorine compounds).

Synthesis. 1,2,5,6,9,10-Hexachlorodecane was synthesized by bubbling chlorine gas, at room temperature, into neat 1,5,9-decatriene (Aldrich Chemical Co.) contained in a flask wrapped in aluminum foil to exclude light. The desired compound was the major product of the reaction, as verified by analysis of a 10% solution of the product mixture in hexane by HRGC/MS. In an attempt to prepare an analytical standard, we treated the reaction products as follows. To remove unreacted alkenes, the product mixture (0.25 mL) was mixed with 2 mL of H_2SO_4/HNO_3 (1:1) at 70 °C for 20 min and then cooled in an ice bath. After distilled water (5 mL) had been added, the mixture was extracted with hexane (3 × 3 mL). The combined extracts were concentrated to 1 mL and chromatographed on a Florisil column, as described below. Analysis by GC/MS (positive ion TIC) showed the major products to be $C_{10}H_{16}Cl_6$, $C_{10}H_{15}Cl_7$, $C_{10}H_{14}Cl_8$, and $C_{10}H_{13}Cl_9$. Additional peaks in the chromatogram accounted for 7 ± 2% of the TIC.

Sample Collection, Extraction, and Isolation. A review of procedures used for extraction and isolation of PCAs from environmental matrixes revealed that methods for determination of persistent organochlorines should be suitable for recovery of PCAs.[19] Extraction and isolation of PCAs from sediments and fish were therefore performed by standard procedures used in our laboratory for determining organochlorine compounds in sediments and biota, with small modifications.[25,26] Frozen whole fish and Zebra mussels were ground cryogenically (dry ice). Samples (~10 g of wet weight) were mixed with anhydrous Na_2SO_4 to yield a flowable powder, spiked with a recovery standard, namely, [$^{13}C_1$]-chlordane, and then Soxhlet extracted (glass thimble) with 350 mL of 1:1 dichloromethane (DCM)/hexane for 4 h. Ten percent of the extract was used to determine lipid levels gravimetrically; the remaining extract was used for PCA determination. Lipids were first removed from the samples by gel permeation chromatography[27] (GPC). The GPC columns (29.5 mm i.d. × 400 mm) were packed with 60 g (dry weight) of 200−400 mesh S-X3 Bio-Beads (Bio-Rad Laboratories, Hercules, CA) that had been soaked in DCM/hexane (1:1) overnight. The column was eluted with 325 mL of DCM/hexane; the first 150 mL contained lipids and was discarded. The remainder was evaporated to 1 mL for cleanup on Florisil. Fractionation on 8 g of reagent grade 60−100 mesh Florisil was achieved with the solvent sequence 38 mL of hexane (F1), 42 mL of 15:85 DCM/hexane (F2), and 52 mL of 1:1 DCM/hexane (F3). Fraction F1 contained all the PCBs, chlorinated benzenes, DDT and its metabolites, and other chlorinated aromatics, but no PCAs. Fractions F2 and F3 contained PCAs, along with the [$^{13}C_1$]chlordane, while F3 contained more polar organochlorines such as heptachlor epoxide and dieldrin. For PCA analysis, F2 and F3 were combined and diluted with

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hexane, and then the solvent volume was reduced to 0.5 mL by a gentle stream of nitrogen prior to GC/MS analysis. A known amount of [$^{13}C_8$]mirex, to be used as an internal standard for SIM, was added to the residual solutions at this stage.

The sediment samples were freeze-dried, and subsamples (~10 g of dry weight) were spiked with the same recovery standards as the fish samples and then Soxhlet extracted with 250 mL of 1:1 DCM/hexane for 24 h. After removal of sulfur-containing compounds by treatment of the extracts with copper powder (nitric acid washed) for 15 min at room temperature, the extracts were fractionated on Florisil, as described above for the fish samples. The extract was diluted with hexane, and then the solvent volume was reduced to 0.25 mL. A known amount of [$^{13}C_8$]mirex was then added.

Recovery Efficiencies. To estimate the efficiency of PCA extraction from Detroit River biota, we determined the recovery efficiencies from spiked samples of fish from a lake in the Canadian Arctic, which we assumed would have low levels of PCAs. Lake trout muscle tissue homogenates (each ~10 g), collected from Maguse Lake, NWT, Canada, were spiked with 1 and 10 μg doses of PCA-60 (six samples at low dose, six at high dose). Another, nonspiked sample, was used as a blank. [$^{13}C_1$]-Chlordane (8 ng) was also added to each sample. Extraction, workup, and analytical procedures were identical to those used for fish and Zebra mussel samples.

PCA recovery efficiencies from sodium sulfate were estimated by spiking 10 g samples of Na_2SO_4 with 1 and 10 μg doses of PCA-60 (six samples at low dose, six at high dose). Another nonspiked sample of Na_2SO_4 was used as a blank. [$^{13}C_1$]chlordane (8 ng) was also added to each sample. Extraction, workup, and analytical procedures were identical to those used for the Detroit River sediment samples.

Gas Chromatography and Mass Spectrometry. All analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph, fitted with a high-resolution 30 m × 0.25 mm i.d. DB-5ms fused-silica column (Chromatographic Specialities, Brockville, ON, Canada), connected through a heated transfer line maintained at 280 °C, to a Kratos Concept high-resolution mass spectrometer (EBE geometry) controlled by a Mach 3 data system. All sample injections, as solutions in hexane, were made by a CTC A200SE autosampler under data system control. The injector port temperature was 220 °C, and a helium carrier gas flow rate of 0.75 mL/min was maintained by an electronic pressure program. The column temperature program was as follows: initial 150 °C; hold for 1 min; ramp to 260 °C at 7 °C min^{-1}; hold for 8:18 min; ramp to 280 °C at 10 °C min^{-1}; hold for 13 min.

EI mass spectra of GC effluents were scanned from *m/z* 400 to 40 at a rate of 0.7 s/decade, at an ion source temperature of 220 °C, electron beam current of 500 μA, and ion acceleration voltage of 8 kV. The electron beam energy was adjusted to maximize the response for the *m/z* 231 ion of perfluorokerosene (PFK) (~55 eV). ECNI mass spectra were scanned at 1 s/decade over the range *m/z* 600 to 65, with methane as the moderating gas and PFK as the mass calibrant. Ion source temperatures were 120 and 220 °C for 1,2,5,6,9,10-hexachloro-*n*-decane and 120 °C for selected ion monitoring. Optimum sensitivity was achieved at an ion source temperature of 120 °C (see Results and Discussion section), an ambient methane gas pressure of ~2×10^{-4} Torr, as recorded by the source ion gauge, an initial electron beam energy of ~180 eV, and an ion accelerating voltage of 5.3 kV. In the SIM mode, performed at a resolving power ~12 000, the cycle time for each window was 1 s, with equal dwell times for each monitored ion.

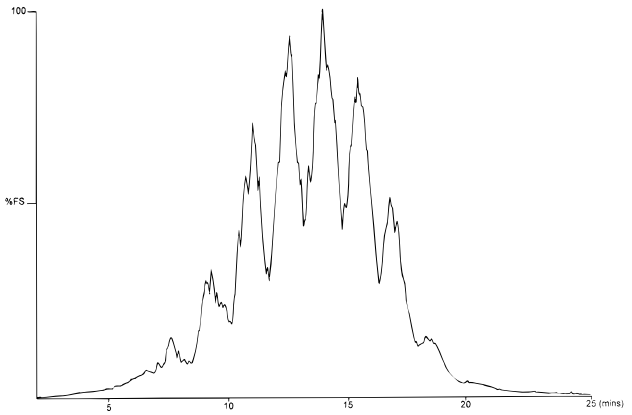

Figure 1. HRGC/ECNI-MS total ion chromatogram (*m/z* 65−600) of PCA-60 (C_{10}−C_{13}, 60% Cl by mass) at an ion source temperature of 120 °C, with methane as reagent gas, and 1 s/decade scan rate.

Environmental Sample Collection and Analysis. Fish were netted at the mouth of the Detroit River at Lake Erie in August 1995. One yellow perch (~300 g) and one channel catfish (~1000 g) were selected for analysis. Zebra mussels were obtained from Middle Sister Island in western Lake Erie. Sediment was collected at the same location as the fishes. Three ponar grabs of sediment were homogenized in a stainless steel bucket; a portion was placed in an amber glass jar and frozen until needed.

RESULTS AND DISCUSSION

1. Method Development. The difficulties of quantifying PCAs in environmental matrixes arise from the extreme complexity of industrial preparations. For example, a short-chain PCA mixture (C_{10}−C_{13}), with 60% by mass of chlorine, when analyzed by HRGC/ECNI-MS, yielded the total ion chromatogram shown in Figure 1. Its general appearance is typical of results previously reported for PCA mixtures.[21−23,28] The mixture elutes over a wide retention time range, and components are not resolved to baseline even with the high-resolution GC column. The underlying broad hill results from the large number of congeners present in low concentrations, while congeners present in higher concentrations give rise to the broad unresolved peaks because of coelution.[28] To emphasize the complexity of the PCA mixtures, we have calculated the number of positional isomers possible for C_{10}−C_{13} polychloro-*n*-alkanes having no more than one chlorine atom bound to any carbon atom. The restriction of no more than one chlorine atom bound to any carbon atom was imposed because, although free-radical chlorination has low positional selectivity,[4−6] a second chlorine atom does not readily substitute for hydrogen at a carbon already bound to chlorine. Even though chlorine for hydrogen substitution at adjacent carbons is discriminated against, we have included this possibility in the calculations because the discrimination is not severe, as confirmed by the ability to make PCAs with high chlorine contents in which vicinal chlorines *must* be present. Table 1 shows the results of these calculations, restricted to formulas observed to be actually present. The complexity is really at least 1 order of magnitude greater than

(28) Tomy, G. T.; Muir, D. C. G.; Westmore, J. B.; Stern, G. A. Proceedings of the 41st Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, May 30−June 4, 1993.

Table 1. Number of Positional Isomers Calculated for n-$C_nH_{2n+2-z}Cl_z$ by Assuming No More Than One Bound Cl Atom on Any C Atom[a]

	n			
z	10	11	12	13
5	126	236	396	651
6	110	236	472	868
7	60	170	396	868
8	25	85	255	651
9	5	30	110	365
10	1	6	36	146
totals	327	763	1665	3549
totals	PCA-60, PCA-70 = 6304			

[a] Given by $N = {}^1/_2[\{n!/z!(n-z)!\} + s]$, where s is the number of symmetrical isomers. Four different cases arise: (a) n even, z even, $s = \{{}^1/_2 n\}!/\{{}^1/_2 z\}!\{{}^1/_2 n - {}^1/_2 z\}!$; (b) n even, z odd, $s = 0$; (c) n odd, z even, $s = \{{}^1/_2(n-1)\}!/\{{}^1/_2 z\}!\{{}^1/_2(n-1) - {}^1/_2 z\}!$; (d) n odd, z odd, $s = \{{}^1/_2(n-1)\}!/\{{}^1/_2(z-1)\}!\{{}^1/_2(n-1) - 1/2(z-1)\}!$

the numbers in Table 1 indicate because chlorine substitution at a secondary carbon atom usually produces a chiral carbon atom so that enantiomers and diastereomers will be generated. Furthermore, although the hydrocarbon feedstocks used to prepare the PCAs are primarily *n*-alkanes, they do contain branched alkanes and, probably, other hydrocarbons which would also add to the complexity of the mixtures. Even if only small percentages of the theoretically possible number of chloroalkanes are readily formed, the data in Table 1 demonstrate that even the short-chain-length C_{10}–C_{13} commercial PCA mixtures contain many thousands of compounds.

The mass spectra of fractions eluting from the GC column were extremely complex and impossible to interpret, because they contained many components. Even so, in the development of the protocol it was necessary to learn the *composition* of the analyte mixtures. To do this, we first had to establish a limited, and sufficient, number of abundant representative ion m/z values to monitor. If too many values are chosen, sensitivity is reduced because the percentage of the duty cycle spent monitoring each ion is decreased. Thus, the ECNI mass spectra of individual synthesized polychloro-*n*-decanes were examined to determine the characteristic ions produced in high yield. (Even though our synthesized compounds will undoubtedly be minor components of the commercial mixtures and environmental samples, the implicit assumption is that the form of their spectra will be representative of those of compounds present in the PCA mixtures.) Next, for PCA-60 and PCA-70, to be used as test cases, and, ultimately, as standards for quantification, the molecular formulas likely to be present in high concentration were estimated and the exact masses of their abundant characteristic ions were calculated. For each commercial PCA mixture, elution profiles of high-concentration species were recorded by SIM of their characteristic negative ions. Because the elution times were long, the efficiency of SIM was improved by dividing the total recording time into a number of windows during which a small number of ions was monitored. Next, the elution profiles of characteristic ions in the ECNI mass spectra of the extracts from the sediment and fish samples from the Detroit River were generated in the same way. The extensive information obtained from these profiles was invaluable for developing a simplified procedure for quantifying PCAs in environmental samples. Further details of these steps are now described.

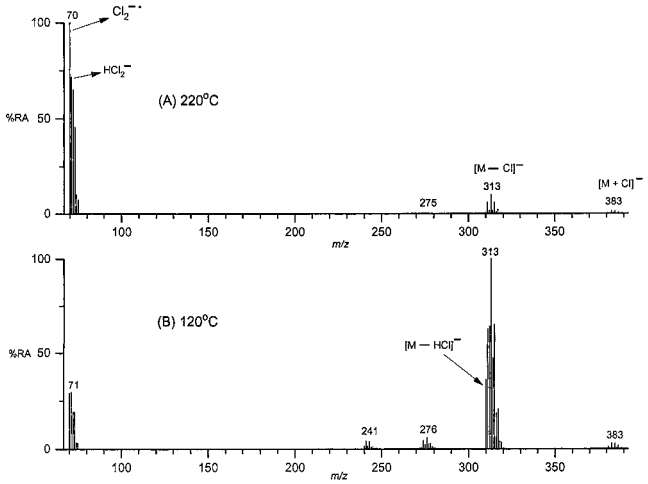

Figure 2. ECNI mass spectra of 1,2,5,6,9,10-hexachloro-*n*-decane at ion source temperatures of (a) 220 and (b) 120 °C.

2. ECNI Mass Spectrometry of Synthesized Polychloro-*n*-alkanes. The ECNI mass spectra of synthesized 1,2,5,6,9,10-hexachlorodecane at two ion source temperatures are shown in Figure 2. At 220 °C, the spectrum is dominated by low-mass ions corresponding to $Cl_2^{\bullet-}$ (m/z 70/72/74) and HCl_2^- (m/z 71/73/75); the molecular ion, m/z 346, is not detected but the $[M - Cl]^-$ ion, m/z 311, is observed clearly. [For poly(chlorine)-containing ions, the m/z values quoted are for the all ^{35}Cl isotope combination]. Small quantities of $[M - HCl]^{\bullet-}$ (m/z 310) and of $[M + Cl]^-$ (m/z 381) are also present. The domination by $Cl_2^{\bullet-}$ and HCl_2^- ions, at the usual ion source temperature of 220 °C, is observed not only for the example shown in Figure 2a but also for all of the several individual polychloro-*n*-alkanes we have synthesized.[29] For analytical purposes there are two problems with monitoring these ions: first, they are not characteristic of any one polychloro-*n*-alkane, and second, they could arise in the spectra of other chlorinated compounds. However, we were able to *selectively maximize*, at an ion source temperature of 120 °C (as illustrated in Figure 2b), the abundance of the characteristic $[M - Cl]^-$ ion with respect to the abundances of the structurally noninformative $Cl_2^{\bullet-}$ and HCl_2^- ions, for all of our synthesized polychloro-*n*-alkanes. In this spectrum, the abundance of the $[M - HCl]^{\bullet-}$ ion has increased to ~60% of that of the $[M - Cl]^-$ ion, and there are also groups of small peaks corresponding to further successive losses of HCl and/or $Cl^{\bullet}$. The chloride adduct is still observed; it arises by gas phase ion chemistry in the ion source.[30–32] Its abundance is sensitive to ion source conditions and also to the extent and position of chlorination in individual polychloroalkanes.

3. Determining the *m/z* Values of Ions To Be Used for Selected Ion Monitoring. In the light of the foregoing observations it is apparent that we need to monitor the $[M - Cl]^-$ ions of the abundant components of the commercial PCA mixtures. (The effects of ignoring the contributions of the $[M - HCl]^{\bullet-}$ ions are minor and will be assessed later.) A guideline for prediction of

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Table 2. Average Chlorine Number, z_{av}, in PCAs, $C_nH_{2n+2-z}Cl_z$, of 50−70% Chlorine Content, by Mass[a]

C_{10}−C_{13}			C_{14}−C_{17}		
n	z_{av} (60% Cl)	z_{av} (70% Cl)	n	z_{av} (50% Cl)	z_{av} (60% Cl)
10	5.8	8.8	14	5.4	8.0
11	6.3	9.6	15	5.8	8.6
12	6.9	10.5	16	6.2	9.2
13	7.5	11.4	17	6.6	9.7

[a] For each carbon number, n, the chlorine content is assumed to be the same as the overall chlorine content. Values are cited for a widely used C_{14}−C_{17} PCA even though we did not detect significant C_{14} levels in our samples.

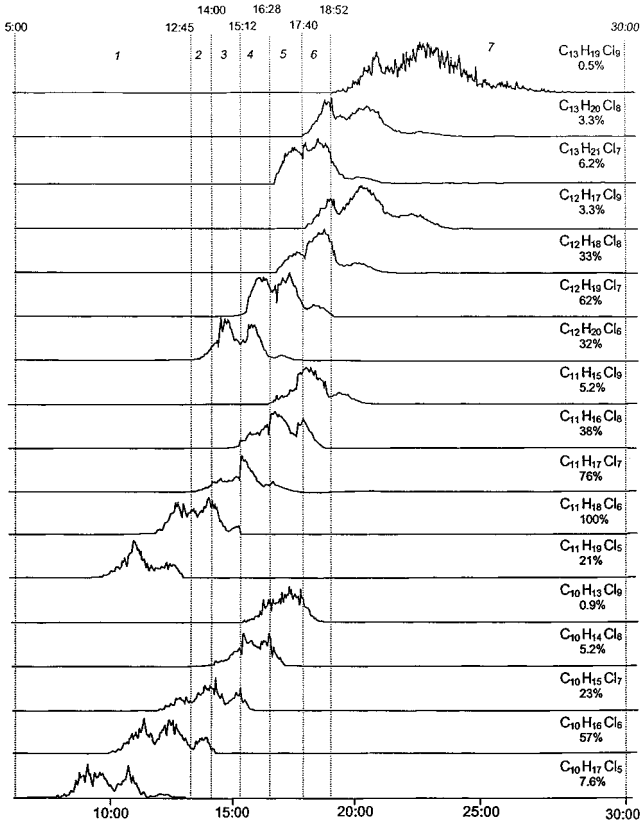

Figure 3. HRGC/ECNI-HRMS elution profiles of monitored ions in PCA-60 aligned to show the seven time windows used.

the formulas of the most abundant molecules present was obtained from the relationship[20] between the average number of chlorine atoms, z_{av}, and the mass fraction, m_f, of chlorine in congeners of formula $C_nH_{2n+2-z}Cl_z$ which, for a given carbon number n, is

$$z_{av} = m_f(14n + 2)/(35.5 - 34.5m_f)$$

For the specified chlorine contents of PCA-60 and PCA-70, we calculated values of z_{av} for each significant carbon number reported by the manufacturers to be present, by assuming that for congeners with a specific carbon number the chlorine mass fraction was the same as the overall, or bulk, reported chlorine mass fraction. These values are shown in Table 2 and can be used as a guide for initial selections of ions to be monitored. For molecular formulas close to the average formula, which are expected to dominate, we selected the two most abundant isotopic combinations in their $[M - Cl]^-$ ion groups. The exact masses and abundances (as a percentage of the total in the ion formula) are given in Table 3, but only for ions actually found to be present in significant amounts. The most abundant m/z value (i.e., most abundant isotopic combination) was used as a quantitation ion for SIM and the next most abundant as a confirmation ion. The abundance of the $[M - Cl]^-$ ion is thus given by the response for the monitored peak divided by the abundance of the monitored peak. The resolving power, 12 000, used for these measurements was as high as practical in order to keep the monitored mass acceptance window as small as possible in order to avoid, or to minimize, contributions from interfering ions (at 12 000 resolving power the peaks are 33 mmu wide at m/z 400). The possibility of interfering ions, and their influence on the analysis, is addressed later.

4. Elution Profiles and Retention Time Windows. As previously noted, any specific molecular formula for a PCA corresponds to a very complex mixture of compounds containing both positional and stereo isomers, and as a result, the compounds present elute over a very broad retention time range. Since elution time ranges can extend over approximately 3−6 min, coelution of components becomes an issue and can make establishment of the SIM retention time windows more complicated. Thus, for PCA-60, the characteristic ions of compounds corresponding to significant molecular formulas (i.e., ion signals ∼>0.5% relative to the largest ion signal) were monitored to establish the elution profiles shown in Figure 3. Under our conditions we found seven windows, as indicated in Figure 3, to be convenient and practical for determining these profiles, but with different resources and circumstances other choices of windows might be preferred. The intensity scales of these profiles have been normalized by the data system and hence do not reflect the relative amounts of the respective congeners corresponding to a particular formula in the sample. For PCA-70, owing to the shift to higher chlorine content, the elution profiles differed, indicating changes in isomeric composition, and somewhat different species were monitored (Table 3). The problem of quantification will be addressed in the next section.

5. Quantitative Measurements. The elution profiles show that PCA samples from differing origins do not have exactly the same compositions, and this must be taken into account in the development of any analytical procedure. Since standards for quantitative analysis should preferably be closely related to the analyte, it appears that PCA-60 or PCA-70 would be an almost ideal primary standard, particularly because preliminary analysis of environmental samples showed that they contain mainly the same formula groups. (A disadvantage of using such materials as standards is that commercial preparations may not be pure or well-characterized or may contain unstated additives.) It thus becomes necessary to relate the measured SIM signals to the bulk concentrations of the standard(s) and analytes, which we performed as follows.

(a) Determination of Total $[M - Cl]^-$ Ion Response. The first step involves the integration of the ion signal profiles such as those shown in Figure 3. In Table 3 these integrated signals, for ions generated from PCA-60 and PCA-70, are listed as a percentage of the largest signal for each compound. Since these are based on specific m/z values monitored, they were converted to the true relative integrated signal for each ion formula by dividing these signals by the fractional abundance of the specific m/z value monitored (as described above), and then renormalizing, to give relative adjusted ion signals (not tabulated).

Table 3. Calculated *m/z* Values of $[M - Cl]^-$ Ions Monitored and Their Percent Abundances in the Ion Formulas, Together with Experimental Percent Relative Responses, for $C_nH_{2n+2-z}Cl_z$ Isomers Present in PCA-60 and PCA-70

isomer formula (n, z)	*m/z* value (% abundance)[a]		% rel response[b]		window no.[c]
	quantitation ion	confirmation ion	PCA-60	PCA-70	
10, 5	279.0055 (37.8) (ocm)	277.0084 (29.0) (ocm)	7.6		1
10, 6	312.9665 (35.7)	314.9636 (23.2)	57	5.3	1, 2
10, 7	346.9275 (32.3) (ch, tox)	348.9246 (26.3) (ch, tox)	23	14	1−4
10, 8	380.8886 (28.5)	382.8856 (27.8)	5.2	24	2−5
10, 9	416.8467 (27.9) (tox)	414.8496 (24.6) (tox)	0.9	7.0	4−6
10, 10	450.8077 (27.1)	448.8106 (20.9)		0.43	5−7
11, 5	293.0211 (37.4)	291.0241 (28,7)	21		1
11, 6	326.9822 (35.3)	328.9792 (23.0)	100	2.8	1−3
11, 7	360.9432 (32.0) (pcb)	362.9402 (26.0) (pcb)	76	49	2−5
11, 8	394.9042 (28.1) (pcb)	396.9013 (27.5) (pcb)	38	100	3−6
11, 9	430.8623 (27.6) (pcb)	428.8656 (24.3) (pcb)	5.2	57	5−7
11, 10	464.8233 (26.8)	462.8263 (20.6)		8.0	6, 7
12, 6	340.9978 (34.9)	342.9949 (22.8)	32		2−5
12, 7	374.9588 (31.6)	376.9559 (25.8) (tox)	62	15	3−6
12, 8	408.9199 (27.8)	410.9169 (27.2)	33	47	5−7
12, 9	444.8779 (27.4)	442.8809 (24.0)	3.3	52	6, 7
12, 10	478.8390 (26.6)	476.8491 (20.4)		11.3	6, 7
13, 7	388.9745 (31.3)	390.9715 (25.5)	6.2		5−7
13, 8	422.9355 (27.5)	424.9326 (26.9)	3.3	4.9	6, 7
13, 9	458.8936 (27.1)	456.8966 (23.8)	0.5	6.6	6, 7
$[^{13}C_8]$mirex[d]	409.7747	411.7718			6

[a] The peak of highest abundance in the $[M - Cl]^-$ ion group (as percent of total of all isotopic combinations) was used for quantification; the next most abundant ion was also monitored to confirm that the relative response of the quantification ion was not spurious. Interferences detected at a resolving power of 1000, but not at 12 000 (see text), are noted in parentheses: (ocm) organochlorine mixture; (ch) chlordane; (tox) toxaphene; (pcb) PCBs. [b] As percent of greatest response. A missing entry indicates that the response was not detectably above the noise level. Also not detected were species with carbon or chlorine numbers outside the listed ranges. [c] Retention time (min) windows (Figure 3): 1, 5:00−12:45; 2, 12:46−14:00; 3, 14:01−15:12; 4, 15:13−16:28; 5, 16:29−17:40; 6, 17:41−18:52; 7, 18:53−30:00. [d] The monitored ions were the $^{13}C_8{}^{12}C_2{}^{37}Cl^{35}Cl_7{}^{\bullet -}$ and $^{13}C_8{}^{12}C_2{}^{37}Cl_2{}^{35}Cl_6{}^{\bullet -}$ ions from $[^{13}C_8]$mirex, $^{13}C_8{}^{12}C_2Cl_{12}$.

(b) Determination of Relative Concentrations of Molecular Components. The dependence of the adjusted ion signals upon concentrations is certain to be complicated and cannot be known; at a minimum, the factors involved include the relative probabilities of negative ion formation and, also, the relative extents to which losses of $Cl^{\bullet}$ occur. However, because unsubstituted alkanes do not readily form negative ions, it is apparent that negative ion formation is dominated by the chlorine content of the molecule. Therefore, we ignored the hydrocarbon part and made two alternative assumptions regarding the influence of the chlorine atoms in the molecules. It will be shown that the resulting quantitative measurements are remarkably insensitive to the difference between the assumptions. In the first assumption, the relative adjusted ion signals are taken to depend directly on the molar (because the contribution of hydrocarbon part is ignored) concentrations of the species present, irrespective of their chlorine content; i.e., the responses of all chlorine-containing molecules are equal. This assumption undoubtedly progressively overestimates the relative concentrations of species as their chlorine content increases. In the second assumption, which is probably more realistic, the adjusted ion signals are taken to be proportional to the number of chlorine atoms in a parent molecule, as well as to its molar concentration; i.e., the relative concentrations are calculated from the adjusted ion signals divided by the number of chlorine atoms in the molecule. The relative molar concentrations of the various significant formula groups present in PCA-60 are plotted in bar graph form in Figure 4a, based upon the first assumption, such that the total relative concentration of all species equals 100%. A similar plot is shown in Figure 4b, based on the second assumption. In Figure 4b, therefore, relative to Figure 4a, the apparent concentration of molecules with higher chlorine content is reduced with respect to those with lower chlorine content, reflecting the overestimation of these species in Figure 4a. However, the change in the apparent relative concentration of the most abundant species, $C_{11}H_{18}Cl_6$, is small, i.e., 19.0 → 21.1%, from the first to the second assumption. For each carbon number the relative concentrations have been totaled and expressed as a percentage of the overall total; panels a and b of Figure 4 show that these values are also insensitive to differences between our assumptions.

For a reason to be stated later, the average molar mass of the PCA is needed. (The average molar mass is $\sum M_i A_i$, where M_i and A_i are the molar mass and sum of fractional abundances of compounds of formula i.) It has therefore been calculated for the compositions in Figure 4b and included in this and other figures.

The elution profile signals for PCA-70 have been treated in a similar way (Figure 4c,d) and similar conclusions can be drawn. Because of the higher overall chlorine content (i.e., smaller relative percentage changes in chlorine content between molecular formulas), the difference between the two assumptions is even smaller. The change in the apparent relative concentration of the most abundant species, $C_{11}H_{16}Cl_8$, is 25.1 → 25.5%, from the first to the second assumption. The relative concentration of each carbon number group is quite similar to that of PCA-60 indicating, probably, the use of a similar hydrocarbon feedstock for the manufacture of both commercial products.

The similarity of the results based on the two assumptions gives confidence to our method of quantification of the signals and suggests that errors associated with either assumption will be small. In the remaining discussion we have used the second assumption, i.e., the SIM signals are proportional to molar concentration weighted by chlorine number, because it is intuitively more satisfying.

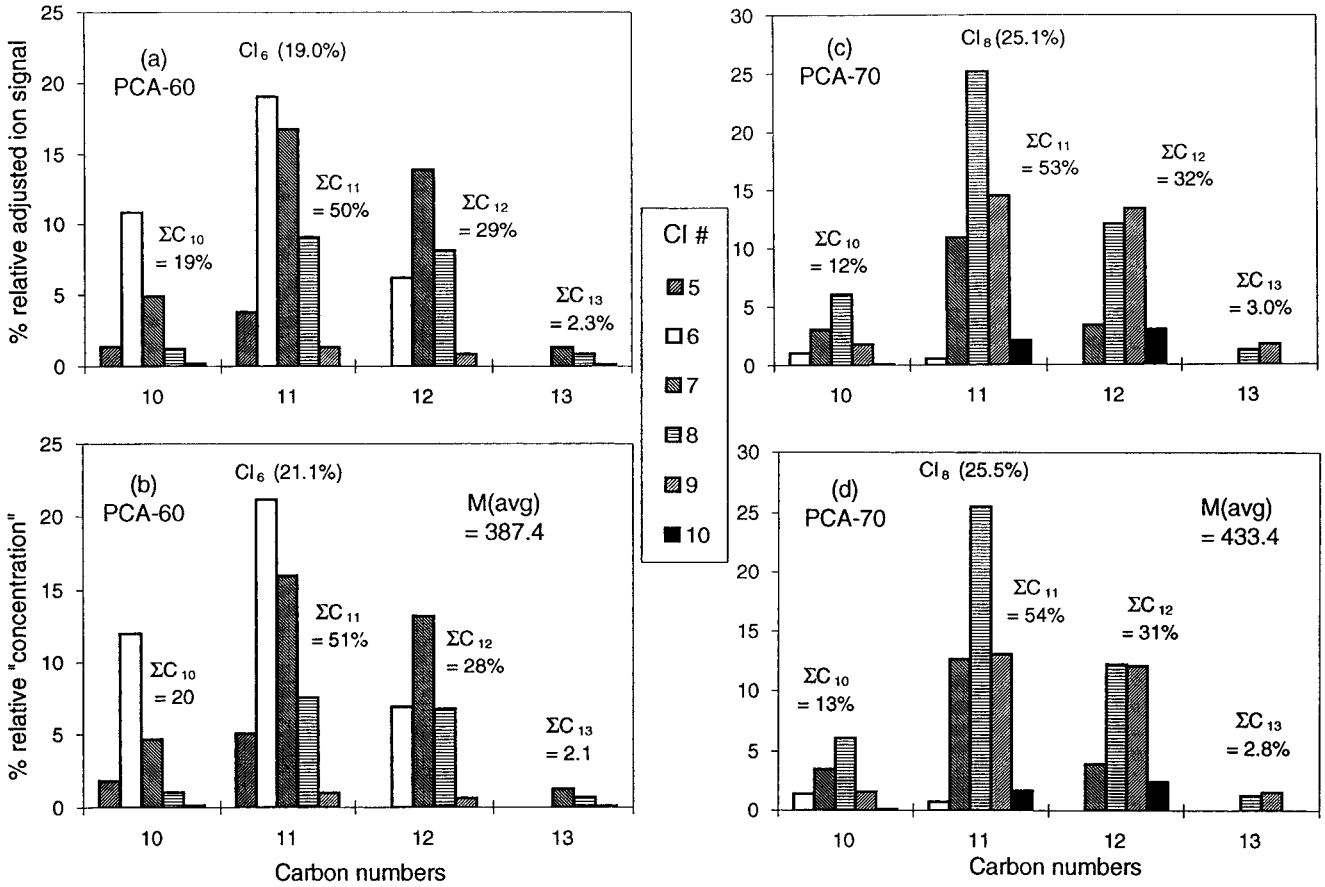

Figure 4. Molar "compositions" of PCA-60 and PCA-70 (C_{10}–C_{13}, 70% Cl by mass), based on the assumption that the SIM signal of a formula group is proportional (a, c) to molar concentration and (b, d) to molar concentration weighted by chlorine number. The totals may not equal 100% owing to rounding approximations. Uncertainties in estimating molar composition have been discussed in the text.

Qualitative Analysis of PCA-Containing Environmental Samples. PCAs were detected in several samples collected from the Detroit River. Elution profiles of monitored ions of components detected in the extracts resemble, but show differences from, the profiles observed for the commercial PCAs. In addition, as illustrated by the following examples, the relative amounts of components having specific formulas do not exactly correspond to the amounts of components observed in the commercial samples.

The elution profiles for the PCA extract from a perch (whole fish), manipulated in the same way, yield the bar graph shown in Figure 5a. Although there may be many inputs of PCAs into the Detroit River, it is apparent that the bar graph pattern resembles those of the commercial PCAs. The pattern shown is intermediate between those of the 60% Cl and 70% Cl commercial products but is closer to that of the latter. This view is supported by the calculated average molar mass, which is closer to that of the 70% Cl PCA. In fact, the average molar mass can provide a semiquantitative comparison index of the similarity between PCAs. The relative concentration of $C_{10}H_{16}Cl_6$ seems to be anomalously high in this sample indicating, perhaps, an additional input for compounds of this formula other than the commercial PCAs we have so far considered.

In a similar way, several samples from other biota and sediments from the Detroit River were examined. Representative results, also summarized in bar graph form in Figure 5, indicate that, in every case, C_{11} and C_{12} compounds were the major species, with smaller quantities of C_{10} and C_{13} compounds. Species with carbon numbers of 14 were not detected above the chemical background signal. The chlorine content of PCAs in perch and sediment appears to be higher than in catfish and Zebra mussels.

6. Final Analytical Procedure. After the compositions of the commercial PCA mixtures and of the environmental samples (as shown in Figures 4 and 5) have been established, it now becomes possible to recommend a simplified, and less time-consuming, analytical procedure based on monitoring a prominent ion of the environmental sample (e.g., for the perch extract the integrated *m/z* 394.9042 peak signal of the $C_{11}H_{16}Cl_7^-$ ion could be measured) and comparing this to that of a suitable integrated signal from PCA-60 or PCA-70, acting as primary quantitative standards. However, because these products can only be used as external standards, an internal (or secondary) standard is needed in both standard and analyte solutions to relate the relative SIM responses of the GC/MS system for these two injections to each other. The internal standard should be a compound closely related to the primary standard and to the analyte but which does not give ions that will interfere with their monitored ions. There are probably many suitable choices. We used [$^{13}C_8$]mirex, which has been used in our laboratory in analysis of another complex organochlorine mixture, namely, toxaphene, and monitored the two most abundant isotopic species, of the prominent $[M - 4Cl]^{\bullet -}$ ion (Table 3). Thus, standard solutions of PCA-60 or PCA-70, together with the internal mirex standard, in hexane were prepared. An aliquot of this solution, sufficient to give acceptable ion signals for the sample and internal standard, was then injected and the appropriate ion signals were monitored. Recalling that

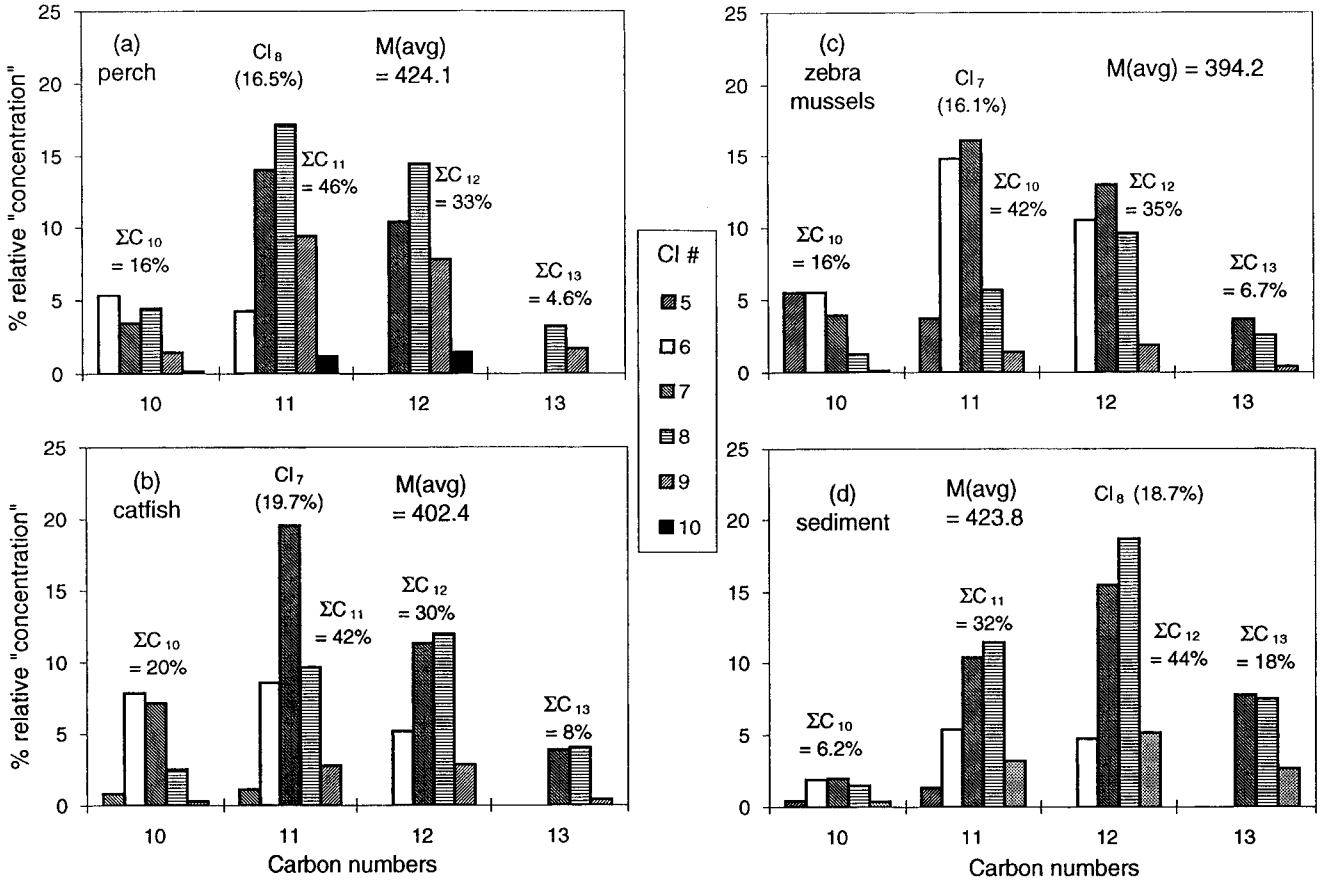

Figure 5. Molar "composition" of PCAs in various samples from the Detroit River, based on the assumption that the SIM signal of a formula group is proportional to molar concentration weighted by chlorine number: (a) perch, (b) catfish, (c) zebra mussels, (d) sediment. (See Figure 4 caption.)

the SIM response is taken to be proportional to the molar (or weighted molar) concentration then

$$\text{inj mol PCA} = C\frac{\text{SIM}}{(m/z\ \text{ab})(\text{form ab})}$$

where C is a constant, SIM is the integrated ion signal of the monitored m/z peak, m/z ab is the fractional relative abundance of the monitored m/z species in the ion formula (Table 3), and form ab is the fractional relative abundance of the molecular formula in the PCA (as obtained from bar graphs such as those in Figures 4 and 5). Similarly, an aliquot of a solution of the PCA extract from an environmental sample, containing the internal standard (in known concentration *ratio* to that in the primary standard solution) was analyzed in the same way. By assuming that the ion source conditions do not change over the short time interval between injections, the ratio of the number of moles of injected PCA in the analyte and primary standard is given by

$$\frac{\text{inj mol PCA(analyte)}}{\text{inj mol PCA(stand)}} = \frac{\text{SIM(analyte)}}{\text{SIM(stand)}}\frac{m/z\ \text{ab(stand)}}{m/z\ \text{ab(analyte)}}\frac{\text{form ab(stand)}}{\text{form ab(analyte)}}$$

To determine the injected mass of PCA in a sample, we now multiply the injected moles by the average molar mass of the PCA present. (This value has been included on each bar graph plot.)

The procedure described can be illustrated by estimating the mass of PCA in the perch extract. On the basis of monitoring the most abundant peak in the analyte and PCA-60 primary standard, we therefore use m/z ab(stand) = 0.353 (for m/z 326.9822) and m/z ab(analyte) = 0.281 (for m/z 394.9042) (see Table 3). From Figures 4b and 5a we obtain form ab(stand) = 0.211 and form ab(analyte) = 0.165, while the respective average molar masses of standard and analyte are 387.4 and 424.1. Thus

$$\frac{\text{inj mass PCA(analyte)}}{\text{inj mass PCA(stand)}} = \frac{\text{SIM(analyte)}}{\text{SIM(stand)}}\frac{0.353}{0.281}\frac{0.211}{0.165}\frac{424.1}{387.4}$$

Finally, the concentration of PCA in the injected analyte solution can be calculated from the relative volumes (nominally 1 μL by autoinjection) of injected analyte and primary standard solutions by multiplying by R, the ratio of the integrated SIM signal of the monitored ion of the internal standard in the primary standard solution to its integrated SIM signal in the analyte solution. Therefore, in the current example

$$\frac{\text{PCA(analyte)(ng}/\mu\text{L)}}{\text{PCA(stand)(ng}/\mu\text{L)}} = \frac{\text{SIM(analyte)}}{\text{SIM(stand)}} \times 1.76R$$

Thus, if the correction terms are ignored, the errors from this cause are relatively small, i.e., less than a factor of 2.

Linearity of Response and the Detection Limit. Tests for linear dependence of the SIM response upon the amount of PCA

injected were carried out for PCA-60 and PCA-70. Two series of solutions were prepared (one series for each PCA), each series containing 0.5−500 ng/μL PCA and a constant amount of the mirex internal standard. For each injection, 1 μL of solution was used and the integrated SIM signals were measured for the $[M - Cl]^-$ ion (of the $C_{11}H_{18}Cl_6$ species for PCA-60 and of the $C_{11}H_{16}Cl_8$ species for PCA-70), while the SIM signal of the monitored ion of mirex gave precise volume determination. Very good linear plots, passing through the origin, with correlation coefficients (r^2) of 0.997 and 0.998, respectively, obtained.

The analytical detection limit for both PCAs was estimated to be ~60 pg, at a signal-to-noise ratio of 4:1. Method detection limits (MDL) were determined by measuring the mean of the background signals from extracted sodium sulfate samples, and are reported as this mean plus 3 times the standard deviation.[33] The MDL was 23 ng/g (n = 5 samples).

Potential Interferences. The most obvious sources of interference are the PCAs themselves because the workup procedures, HRGC, and ECNI together discriminate strongly against other compounds. The $[M - HCl]^{\bullet -}$ ion will interfere with the $[M - Cl]^-$ ion of the same formula group monitored, as could $[M - Cl]^-$ and $[M - HCl]^{\bullet -}$ ions of other formula groups that elute at some time during the SIM period of the selected ion. The effects of these interferences can be assessed.

The $[M - HCl]^{\bullet -}$ ion will interfere with the $[M - Cl]^-$ ion owing to its natural ^{13}C content; the mass of ^{13}C is 4.5 mmu less than that of ^{12}CH. At 400 u, at a resolving power of 12 000, the mass spectral peaks are 33 mmu wide at 5% of their height; therefore, most of the $[M - HCl]^{\bullet -}$ peak area will be included in the area recorded for the $[M - Cl]^-$ isotopic combination of the same nominal mass. By assuming, in the worst case, that 100% of the peak area of $[M - HCl]^{\bullet -}$ is included, and that the relative abundance of the $[M - HCl]^{\bullet -}$ ion is 60% of that of the $[M - Cl]^-$ ion (as in Figure 2), then the maximum contribution to the signal for the monitored ion of a C_{11} PCA is $60 \times 11 \times 0.011 = 7.3\%$, where the natural $^{13}C/^{12}C$ ratio is taken as 1.1%. Of course, similar contributions will apply to the signals for all other $[M - Cl]^-$ ions monitored, and the small errors arising for this reason tend to be self-correcting; therefore, it is not worthwhile to attempt to apply factors to correct for the formation of the $[M - HCl]^{\bullet -}$ ion.

It is possible for the $[M - Cl]^-$ ions of other formula groups to interfere with the monitored ion. For example, when monitoring the $C_{11}H_{16}{}^{37}Cl^{35}Cl_6^-$ ion of the $C_{11}H_{16}Cl_8$ formula group a potential interference is the $C_{13}H_{21}{}^{37}Cl_4{}^{35}Cl_2^-$ ion of the $C_{13}H_{21}Cl_7$ formula group. Since the mass difference is 61 mmu, these ions are well separated at a resolving power of 12 000 but would partially overlap at a resolving power of 1000; this example, which is typical for these species, illustrates why high-resolution mass spectrometry is beneficial for making reliable quantitative measurements.

We also checked to see whether a number of common environmental contaminants, including toxaphene, chlordane, PCBs, and mirex, would interfere with the analytical method; although they are discriminated against by the workup procedure, coelution during gas chromatography remains a problem if residual interferences escape the cleanup procedures. Thus, separate injections of toxaphene, a technical chlordane mixture, a mixture of 87 PCB congeners, and a mixture of organochlorine pesticides (SRM 2261 and MMQA) were made. The ions listed in Table 3 were monitored in the same way as for the PCA mixtures. At a resolving power of 12 000, no interferences were detected above the signal baseline noise, but the interferences noted in Table 3 occurred at a resolving power of 1000.

(33) Long, G. L.; Winefordner, J. D. *Anal. Chem.* **1983**, *55*, 712A−724A.

Table 4. Mean Percent Recoveries of PCA-60 and Chlordane from Spiked Fish Muscle (Arctic Lake Trout) and Sodium Sulfate

sample	PCA-60	$[^{13}C_1]$chlordane
fish[a]	97 ± 3	97 ± 2
fish[b]	73 ± 3	88 ± 2
ss[a]	90 ± 3	91 ± 6
ss[b]	81 ± 3	87 ± 2

[a] 1 μg total PCA spiked in 10 g of tissue or sodium sulfate (six samples of each). [b] 10 μg total PCA spiked in 10 g of tissue or sodium sulfate (six samples of each).

Accuracy of the Analytical Method and Choice of Standard for Quantitative Studies. As noted above, we used PCA-60 as a standard for quantitative work. This material has the advantage that it closely resembles the analytes of interest, but it should not be regarded as a well-characterized standard. Our attempts to clarify this problem met with mixed success. By the method described above, and assuming that PCA-60 was 100% pure, we determined the response of PCA-70, after correction for the presence of ~15% of additives that its manufacturer indicated we would not detect, to be 80 ± 5% of the theoretical value. We considered this to be an acceptable result. However, attempts to prepare a well-characterized standard have not yet been successful. Despite our best efforts to date, the "purified" products of addition chlorination of 1,5,9-decatriene gave a response of only ~25% of the theoretical value. In addition to purity concerns, there is the possibility that response factors differ significantly between the synthesized material and PCA-60. Thus, because of the consistency between the results for the PCA-60 and PCA-70 materials we have, for now, based our quantitative results on the PCA-60 material.

Recovery Efficiencies. To apply the protocol to environmental samples, we first checked recovery efficiencies of PCA-60 and chlordane from arctic lake trout muscle, known to have low levels of organochlorine residues, and from sodium sulfate (in place of a sediment) as already mentioned, with the results shown in Table 4. Consistent, acceptably high, percentage recoveries of PCA-60 and chlordane from multiple samples of fish and sodium sulfate were obtained.

Results for Environmental Samples. Recoveries of $[^{13}C_1]$-chlordane from biota and sediment from the Detroit River are also high, but not for Zebra mussel samples from Lake Erie (Table 5). This table presents the mean (of two) levels of PCAs detected in these samples. These are therefore lower limits to the PCA levels actually present. On the assumption that PCA recoveries are the same as those of chlordane, we have also estimated in Table 5 the PCA levels that would be present in these samples.

CONCLUSIONS

In conclusion, PCAs represent a difficult analytical problem because of the complexity inherent to industrial mixtures. The analytical protocol we describe includes the first report of the application of high-resolution ECNI mass spectrometry to this problem. It has advantages over previously reported methods

Table 5. Mean Percent Recovery of Chlordane from Spiked Samples and Mean PCA Levels Recovered from Biota (ng/g of Wet Weight) and Sediment (ng/g of Dry Weight) from the Detroit River and Lake Erie[a]

sample	chlordane rec (%)	PCA recovered					total PCA[b]
		$\sum C_{10}$	$\sum C_{11}$	$\sum C_{12}$	$\sum C_{13}$	total	
perch	88	162	465	333	46	1010	1148
catfish	79	48	101	72	19	241	305
zebra mussels	54	104	273	228	44	651	1205
sediment	86	15	79	109	45	248	288

[a] Duplicate samples of each. [b] Estimated by assuming PCA percent recoveries are the same as those of chlordane.

because it determines individual formula groups, allowing correction for differences in patterns between analyte and standard, and avoids interferences from other PCAs, and other persistent organochlorine compounds. In principle, the protocol can be extended to PCAs of lower and higher carbon number.

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