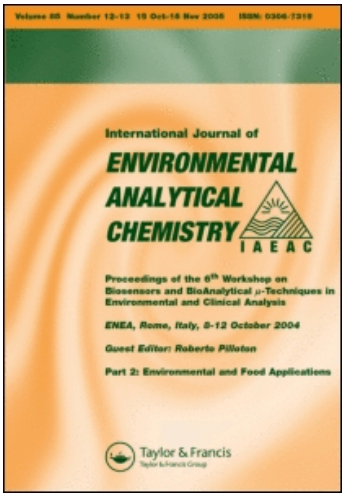

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Determination of polychlorinated biphenyls, organochlorine pesticides, chlorobenzenes in sludge and sediment samples by GC × GC-μECD†

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Gas chromatographic separation and identification of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs) and chlorobenzenes (CBz) is one of the most common analyses performed by environmental laboratories. When using comprehensive two dimensional gas chromatography (GC × GC) coupled with micro-electron capture detector (μ-ECD), within- and between-compound class separations for the target contaminants were achieved in a relatively short analysis time. With only few coelutions present, the results showed that DB-1 × Rtx-PCB is a powerful column combination providing excellent chromatographic separation for PCBs/OCs/CBz standard mix. Reference materials and 'real-life' sediments and sludges were analysed and the analytes were quantified in these samples. The results were compared to reference values and classical GC-ECD data where available. This method was shown to be precise and accurate for the standards/reference materials tested and is a feasible method for sediment and sludge sample analysis.

Keywords: GC × GC; comprehensive two dimensional gas chromatography; PCB; OC; CBz; μECD

1. Introduction

Organohalogen compounds are important environmental contaminants due to their persistence and toxicity. PCBs, OCs, and CBz, commercially produced for use in different areas, were identified in environmental samples and are generally known to bioaccumulate and biomagnify [1,2]. Classical sample analysis for these compounds employs gas chromatography (GC) coupled with electron capture detector (ECD) or mass spectrometry (MS). The electron capture detector is often the choice for PCB/OC/CBz detection due to its high sensitivity for halogenated compounds [3,4]. However, its lack of selectivity between halogenated compounds requires chromatographic separation to obtain accurate quantitative results. In a review of capillary gas chromatography of halogenated micro pollutants, de Boer [3] summarised some of the challenges that analysts encounter when analysing organochlorine pesticides (e.g. chlordane congeners tend to split among the fractions and coelute with PCBs). Cochran and Frame [4] reviewed the gas chromatography separation of PCB congeners on different GC stationary phases,

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concluding that no single column phase can resolve all the congeners even when advanced detection techniques such as mass spectrometry are involved.

Conventional GC offers good peak capacity but it fails to separate many individual constituents in complex environmental samples. The introduction of comprehensive two dimensional gas chromatography (GC × GC) provided significant increases in separating power, peak capacity and speed of analysis. GC × GC involves a serial column configuration separated by a thermal modulator [5–10]. GC × GC increases peak capacity by applying two independent separations to a sample, resulting in improved resolution of target compounds in a single analysis. There are two different approaches when selecting the columns for the GC × GC system: orthogonal and non-orthogonal [5–11]. The orthogonal separation, usually involving a non-polar and medium polar or shape selective column combination, is achieved when the separation mechanisms operate independently for the two dimensions and the synentropy across dimensions is zero [12]. Structured chromatograms are distinctly visible in GC × GC chromatograms for structurally related compounds allowing easier group-type identification [13–16]. The non-orthogonal approach, a polar and non-polar column combination, was also studied and some significant separations were reported [7].

Due to the modulation process, most GC × GC peaks are very narrow, requiring a fast detector. Time-of-flight mass spectrometers (TOFMS) are the detectors of choice due to their high scanning rate used to ensure accurate characterisation of the peaks. Also, TOFMS allows the mass spectral deconvolution of overlapping peaks when the fragmentation patterns are different [8,9,13]. The enhanced selectivity of GC × GC can enable a less selective detector such as ECD to be used for the analysis of persistent environmental contaminants. The micro electron capture detector (μECD) detector, a modification of the classical ECD, was optimised to be used with GC × GC systems [14,17–18]. The best results were obtained when working at the maximum flow of make-up gas (150 mL min^{-1}) and at temperatures above 300°C [19].

Currently, Ontario Ministry of the Environment (MOE) methods [20,21] use four different GC-ECD instruments in order to analyse PCBs, OCs, and CBz for sediment and sludge samples. Complex sample preparation such as extraction, clean-up and extract fractionation is required prior to GC analysis. For this study, pressurised liquid extraction (PLE or Accelerated Solvent Extraction – ASE – Dionex Corporation, Sunnyvale, CA, USA) was the extraction method of choice due to its advantages over traditional techniques [22–26]. The new GC × GC-μECD method presented in this paper potentially permits simultaneous analysis of the target halogenated contaminants without fractionation. The aims of the study were to efficiently separate and quantify the compounds of interest while requiring minimal extraction and clean-up. Both between- and within-compound class separations were assessed followed by the statistical evaluation of precision and accuracy of the method.

2. Experimental

2.1 *Standards and reference materials*

PCBs standards (BP-MS and BP-EC) containing 62 congeners were obtained from Wellington Laboratories (Guelph ON, Canada). A chlorobenzene standard mixture of 15 CBz, OC standard mixture of 23 compounds, decachlorobiphenyl, and 1,3,5-tribromobenzene were supplied by UltraScientific (North Kingstown, RI, USA).

Six level calibrations of PCBs/OCs/CBz standard solutions were prepared by mixing the above PCBs (BP-MS), OCs, and CBz standards in iso-octane with the final concentrations ranging from 1 ng mL^{-1} to 500 ng mL^{-1}. In addition, 4,4′-dibromo-octafluoro-biphenyl was used as internal standard for PCB congeners' quantification. Similarly, a PCBs (BP-EC)/OCs/CBz spiking solution and decachlorobiphenyl/1,3,5-tribromobenzene surrogate solution were prepared with the final concentration of 500 ng mL^{-1}.

Sediments reference material SRM 1944 was purchased from NIST (Gaithersburg, MD, USA), and sludge reference material CNS-312 from RTC (Laramie, WY, USA).

2.2 *Sample preparation*

Surrogate standards were added prior to extraction (decachlorobiphenyl and 1, 3,5-tribromobenzene) to all samples previously dried, crushed, sieved and weighed. Sediment/sludge samples were extracted with dichloromethane : hexane, 1 : 4 (v/v) using Accelerated Solvent Extraction (ASE 200, Dionex Corporation, Sunnyvale, CA, USA). The extraction conditions were as follows: one cycle extraction at 100°C, heat time 5 min, purge time 90 sec, flush volume 60%. Sample extracts were cleaned up using silica pre-packed cartridges (1 g, Varian, Mississauga, ON, Canada) and eluted with 15 mL dichloromethane : hexane, 1 : 4 (v/v). The extracts were then evaporated to 1 mL final volume in iso-octane using a Zymark Turbovap LV evaporating system (Zymark Corp., Hopkinton, MA, USA). Copper treatment was applied to all samples to remove the sulphur interferences prior to instrumental analysis. This sample preparation method is an in-house developed method based on previous data for classical GC-ECD analysis [24,27].

2.3 *GC × GC analysis*

The PCBs, OCs, CBz standard solutions along with the sediment/sludge final extracts were analysed using a GC × GC-μECD system provided by LECO Corp. (Benton Harbour, MI, USA). This system is equipped with a stationary quadruple jet dual-stage modulator, an Agilent 6890 gas chromatograph, split/splitless injector, and μECD detector.

The following chromatographic column combination was used: a 30 m, 0.25 mm i.d., 0.25 μm film thickness DB1 (100% dimethylpolysiloxane) from J&W Scientific (Folsom, CA, USA) as the first dimension column and a 1.6 m, 0.18 mm i.d., 0.18 μm film thickness Rtx-PCB from Restek Corp. (Bellefonte, PA, USA) as the second dimension column. The connections between the first dimension and second dimension columns were made using a deactivated pres-fit connector (Restek Corp). The GC × GC-μECD conditions were as follows: 1 μL splitless injection using a split/splitless injector and a 4 mm i.d. gooseneck liner (Restek Corp.). The injector was operated at a temperature of 250°C with a purge time of 90 sec. Helium gas with a purity of 99.999% was used as carrier gas with 1.5 mL min^{-1} flow rate. The modulation period was 4 sec. with a modulator temperature offset of 35°C. The primary oven temperature programming started at 80°C (hold for 2 min) to 160°C at 10°C min^{-1}, then to 280°C at 4°C min^{-1} (hold for 5 min), and the secondary oven had a 35°C temperature offset to the first dimension programme. The μECD was run at a temperature of 300°C, 5% methane in argon was used as make-up gas at a flow rate of 150 mL min^{-1}, and the data acquisition rate was set up at 50 Hz.

The total run time was 45 minutes. ChromaTof software provided by LECO Corp. was used for data analysis.

2.4 *Calibration and quantification*

In order to quantify the target analytes, six-level calibration curves were built with the analytes ranging from 1 to 500 ng mL^{-1}. The external standard method was used for OCs and CBz, while an internal standard procedure was used for PCBs quantification. Prior to injection, 10 µL of 4,4′-dibromo-octafluoro-biphenyl internal standard solution at 1 µg mL^{-1} were added to each sample. Since the quantification using ECD detector is retention time dependent and a leak can create peak shifting, the internal standard was also used to check the retention time stability between runs [28].

3. Results and discussion

3.1 *Within-class separation*

Previous studies showed that GC × GC-µECD is a very powerful technique providing excellent chromatographic separation of PCBs, OCs, CBz and orthogonal separation for all structurally related compounds [8,9,13,15,16,28,29].

The two dimensional chromatogram for PCBs in Figure 1 shows that orthogonal separation was achieved when using a DB-1 × Rtx-PCB column combination [10,15,19,28]. An ordered structure is observed and PCBs are seen as bands in the second dimension plane. The PCB congeners are separated according to their degree of

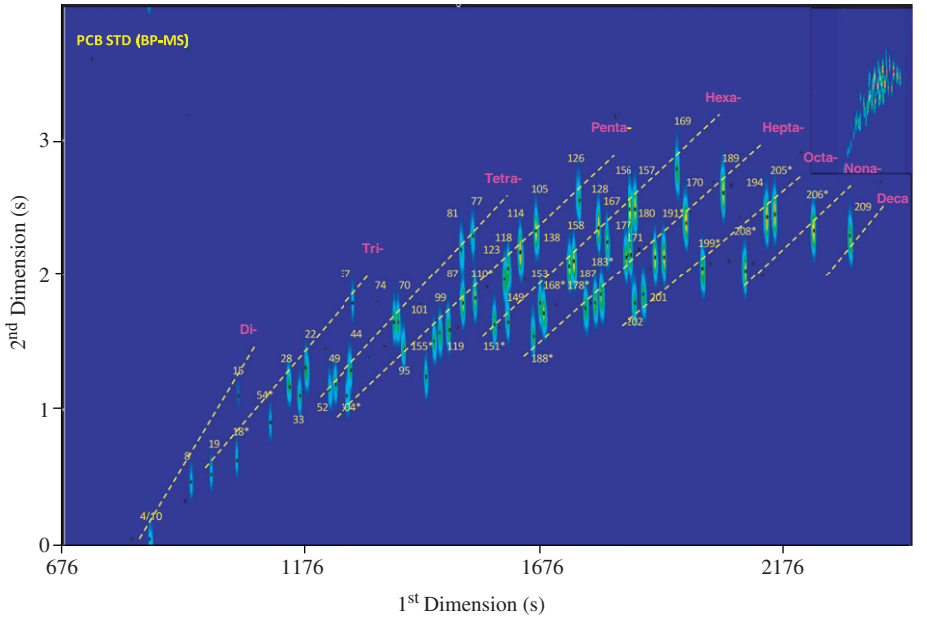

Figure 1. GC × GC-µECD two dimensional chromatogram of PCB congeners standard representing their orthogonal separation.

chlorination as well as their planar structure [13,16,29]. The dotted lines in Figure 1 represent the degree of chlorination of PCBs, from mono- to decachlorobiphenyl. The mono-ortho PCBs, and non-ortho PCBs 37, 77, 81, 126 and 169, elute later in the second dimension due to the selectivity of Rtx-PCB for the compounds that have planar configuration [16,29]. Only one coelution was present for the PCB standard analysed, PCB4 and PCB10, which was confirmed by GC × GC-TOFMS. Similar to PCBs, separation of chlorobenzenes was achieved with one coelution: 1,2,3,5-tetrachlorobenzene (1,2,3,5-TCB) and 1,2,4,5- tetrachlorobenzene (1,2,4,5-TCB) – Figure 2. These compounds also coelute in a classical GC-ECD analysis when using a DB-1 column [21] and were not resolved by GC × GC. Within-class separation was achieved without coelutions for the OC standard analysed; all 23 OC compounds were separated in one analytical run (Figure 2).

One of the advantages of using comprehensive dual gas chromatography, proven in many studies over the last few years [5–9,13,15,19,28,29], is the second dimension separation. Thus, peaks that coelute on a classical DB1 column selected as first dimension for this study [30] are further resolved by Rtx-PCB. Rtx-PCB is very selective for PCBs in the second dimension [29]. The results obtained in this study are similar to those presented by Korytar *et al.* [28] when using LC-50 as the second dimension column. The advantage of using Rtx-PCB instead of LC-50 is its stability at higher temperature oven programming (max 320°C). In addition, the method presented in this study has an overall analysis time of 45 min; a shorter run time increases sample throughput and instrument capacity.

3.2 *Between-class separation*

By applying two independent separations to the sample, the GC × GC technique enhances the separation of the different target analytes as well as increases the peak capacity [5–9]. One of the aims of the study was to simultaneously analyse all three classes of halogenated

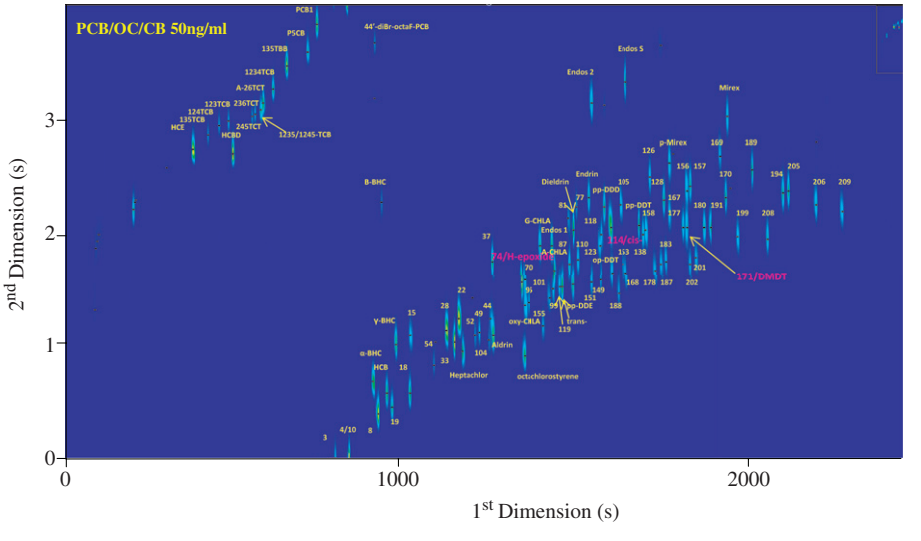

Figure 2. GC × GC-μECD two dimensional chromatogram of PCB/OC/CBz mix standard solution representing the between-class separation (see Table S1 for a list of abbreviations).

contaminants in a single analytical run. Thus, a combined standard mix containing PCBs, OCs and CBz (96 compounds in total) was prepared and injected into the GC × GC-μECD system previously described. The two dimensional chromatogram, presented in Figure 2, shows that three coelutions occurred between these target analytes: heptachlor-epoxide/PCB74, cis-nonachlor/PCB114, and methoxychlor (DMDT)/PCB171. Additionally, wrap-around was observed for CBz in this separation (Figure 2). Since the CBz do not interfere with any other analytes of interest in the chromatographic space their wrap-around is not an issue and the separation is very reproducible. A number of compounds were not baseline separated and needed manual manipulation in order to obtain a proper integration and quantification: PCB44/aldrin, PCB70/oxy-chlordane and PCB99/α-chlordane. Other peaks not baseline separated as well did not require manual manipulation by the analyst (i.e. PCB123/PCB118). Since the standard analysed does not contain all the PCBs present in the environment, there is the risk of being biased positive for specific PCBs (e.g. PCB138/163/164 not separated with this method). Compared to the classical GC-ECD where multiple columns and instruments are used, separation was achieved in a single GC × GC analytical run without the fractionation of extracts.

Besides the PCBs, OCs, and CBz standards previously discussed, other contaminant classes were evaluated for the DB1 × Rtx-PCB column combination: dioxins and furans, Toxaphene, polychlorinated naphthalenes (PCNs), polychlorinated diphenyl ethers (PCDEs) [13,14–16]. Their retention times were plotted to evaluate possible interferences with the target contaminants as well as to assess their presence in the environmental samples. These compounds did not interfere with PCBs/OCs/CBz, they were more retained in the second dimension plane and some of them exhibited wrap-around (e.g. polychlorinated dioxins/furans and Toxaphene). DB1 × Rtx-PCB also provided orthogonal separation and ordered chromatograms according to their degree of chlorination [16,29]. The coelutions within- and between- these classes of contaminants were not evaluated since it was beyond the goal for the current study.

3.3 *Precision*

The initial precision of the method was assessed by analysing 10 replicates of PCBs/OCs/CBz standard mix at 50 to 250 ng mL^{-1} level. Experimental results showed a relative standard deviation (%RSD) ranging from 0.2 to 7%.

Further, replicates of a clean sediment sample spiked with the PCBs/OCs/CBz spiking solution were extracted and analysed to assess the method performance. The within-run precision (repeatability) was calculated from the 10 replicates processed in the same analytical run while the between-run precision (reproducibility and accuracy) was calculated from eight replicates analysed in different runs. The between-run precision is an on-going process and will be continuously monitored for each set of samples analysed by GC × GC-μECD. Results, expressed as relative standard deviation (%), presented in Table 1, show that GC × GC is a very feasible technique for environmental samples analyses. The relative standard deviation falls in the accepted ±25% limits proposed for this method.

The method detection limits (MDL) were also calculated by analysing eight replicates of a clean sediment matrix spiked with the lowest level of the analytes in the calibration

curve (1 ng mL^{-1}). The MDLs varied from 0.06 to 3.5 ng g^{-1} while the estimated limits of quantification for PCBs/OCs/CBz were found to be in the range of 1 to 10 ng g^{-1}.

3.4 *Accuracy – reference materials analysis*

The accuracy of the method was assessed by analysing reference materials for two different matrices: sediment and sludge. SRM1944 sediment [23] (three replicates) and CNS312 sludge reference material (eight replicates) were processed according to the extraction, clean-up and instrumental methods described in the experimental section and the calculated analyte amounts were compared to their certified values (Figure 3a, b and c). Further, the GC × GC-μECD data for SRM1944 was also compared with previous results obtained from the classical GC-ECD analysis [20] (Figure 3c). As presented in Figure 3, PCBs and OCs data is comparable demonstrating that the method produces accurate results. However, the recoveries for some of the compounds where higher or below the

Table 1. Within-run and between-run method precision for selected PCBs/OCs/CBz compounds.

		Within-run precision		Between-run precision	
Compound name	Expected amount (ng g^{-1})	Mean (ng g^{-1})	RSD (%)	Mean (ng g^{-1})	RSD (%)
Dioxin-like PCBs					
PCB77	50	41	12	47	10
PCB81	50	50	12	51	8.2
PCB126	50	59	12	65	9.2
PCB169	50	49	12	50	8.2
PCB105	50	49	12	48	3.3
PCB114/cis-nonachlor	100 (coelution)	110	2.2	113	8.5
PCB118	50	53	9.6	49	2.4
PCB123	50	46	11	44	4.6
PCB156	50	49	12	51	2.1
PCB157	50	46	13	50	2.4
PCB167	50	49	12	49	3.5
PCB189	50	52	13	53	3.4
EU Indicator PCBs					
PCB28	250	224	13	217	13
PCB52	50	50	13	49	2.0
PCB101	50	48	12	47	2.1
PCB118	50	53	9.6	49	2.4
PCB138	50	49	12	49	2.2
PCB153	50	48	12	50	3.4
OC Pesticides					
α-chlordane	50	52	6.1	54	16
γ-chlordane	50	54	3.1	59	13
p,p′-DDE	50	47	2.2	49	16
p,p′-DDD	50	52	2.3	57	16
p,p′-DDT	50	52	6.5	56	18
CBz					
Hexachlobenzene	50	38	3.1	39	20
1,2,4-Trichlorobenzene	50	34	13	30	16

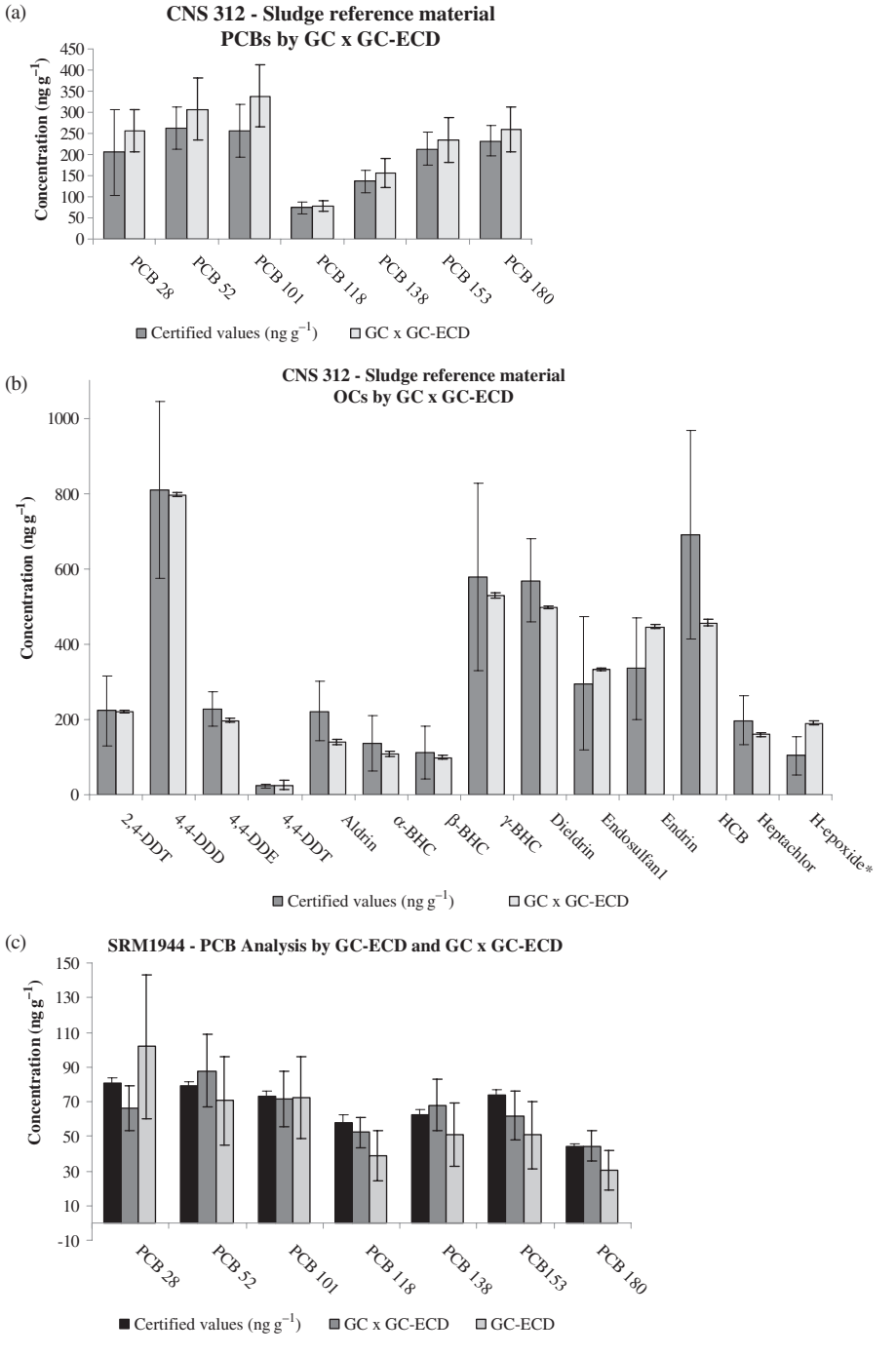

Figure 3a, b, c. Data comparison for selected PCBs and OCs analysis of CNS312 – sludge reference material and SRM1944 – sediments reference material: (a) CNS312 – PCBs by GC × GC-μECD, (b) CNS312 – OCs by GC × GC-μECD (*H-epoxide is reported as coelution with PCB74 for GC × GC), and (c) SRM1944 – PCBs by GC × GC-ECD and GC-ECD.

certified values (e.g. heptachlor epoxide reported as coelution with PCB74, PCB101 for CNS312, PCB28 for SRM1944) but still within the uncertainty limits calculated for the method, ranging from 11 to 28% for PCBs and 5 to 16% for OCs (presented as error bars in Figure 3). The GC × GC chromatograms also revealed different classes of compounds present in SRM1944 that can be identified and quantified later if required.

In addition to the reference materials tested, the accuracy of the method was also assessed through the analysis of sediments samples from an inter-laboratory study (*New York State ELAP 08-01Inter-laboratory Study for Solid Waste*). The samples were examined by both GC-ECD and GC × GC-μECD techniques for the determination of OC pesticides. The results were comparable between the classical GC, GC × GC as well as the consensus values (Figure 4, error bars are introduced as uncertainties).

3.5 *Analysis of sediment and sludge samples*

Sludge samples collected from a wastewater treatment plant in Ontario have been analysed by GC × GC-μECD and the results were compared to previous data from GC-ECD analysis. While only p,p′-DDE (8 ng g^{-1}) and very low amount of total PCBs (43 ng g^{-1}) were found by conventional analysis, GC × GC-μECD confirmed the total PCB concentration, did not find any p,p′-DDE and revealed other classes of compounds present in the samples such as polychlorinated alkanes (PCAs) [15] (Figure 5). When sludges from a different source were analysed, the PCA bands were not present. Thus, this method can be used to evaluate the presence of other classes of contaminants in the samples.

Similarly, sediment samples were analysed by both techniques and the contaminants quantified by classical GC (PCB total of 384 ng g^{-1}, p,p′-DDE 20 ng g^{-1} and Mirex 11 ng g^{-1}) were comparable to GC × GC results (PCB total of 347 ng g^{-1}, p,p′-DDE

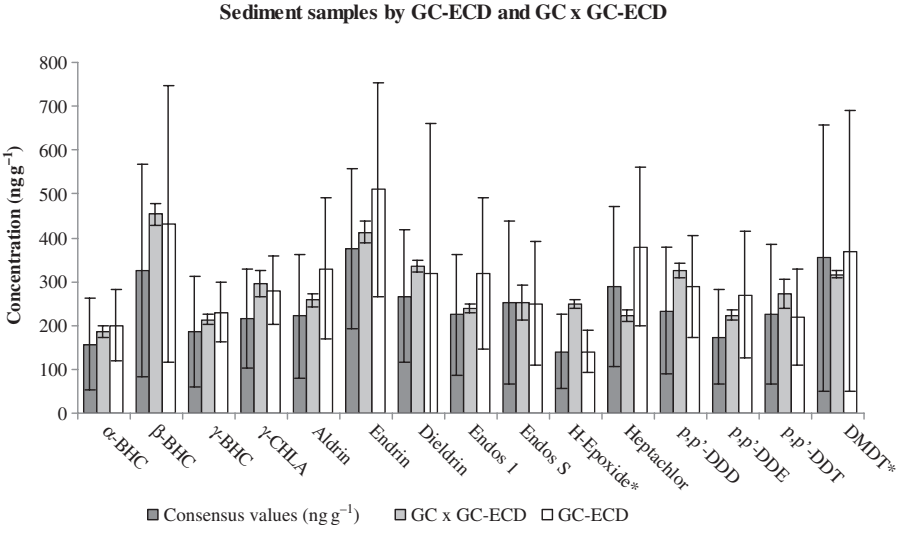

Figure 4. Data comparison of GC-ECD and GC × GC-μECD results for the analysis of OC pesticides in sediment samples – *New York State ELAP 08-01Inter-laboratory Study for Solid Waste*. *H-epoxide is reported as coelution with PCB74 for GC × GC and DMDT coelution with PCB171.

14 ng g^{-1} and Mirex 10 ng g^{-1}). In addition, the two dimensional technique revealed other classes of contaminants present in the sample which were not previously detected by GC-ECD (Figure 6). After a preliminary assessment of the 'unknown' compounds the samples can be directed to a more sensitive or selective method for analysis.

One of the challenges encountered when analysing sludge and sediment extracts was the presence of PCA bands that interfered with some of the higher chlorinated PCBs (i.e. PCB170, PCB180) making quantification difficult. At low concentrations their bias was insignificant; however, if PCAs are present at high concentrations different extraction and clean-up procedures should be employed [21].

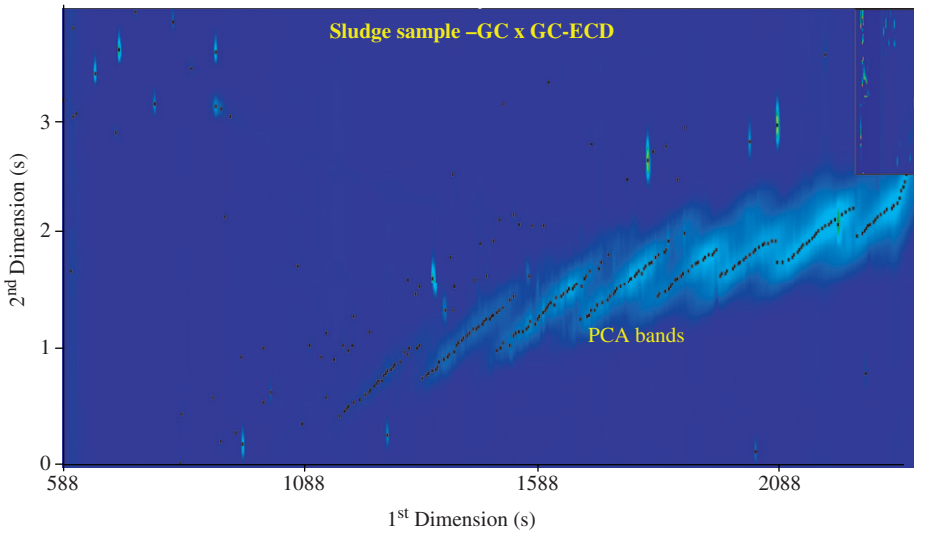

Figure 5. Contour plot of GC × GC-μECD analysis for sludge sample.

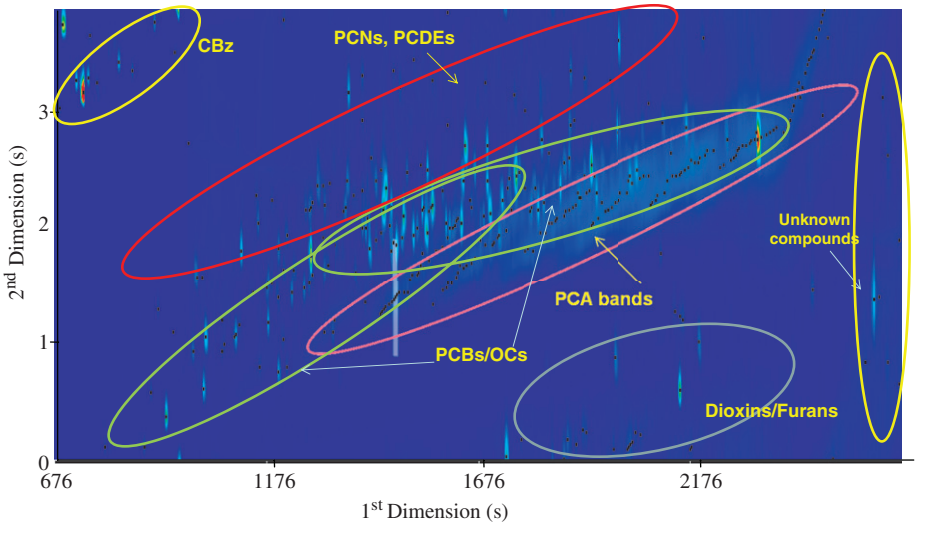

Figure 6. Contour plot of GC × GC-μECD analysis for sediment sample.

Another issue was the interference of an unknown compound, later identified as triclosan by GC × GC-TOFMS, with gamma-chlordane (γ-chlordane) (Figure 7). A possible source is the detergent used for washing the glassware where triclosan is one of its constituents. Different more rigorous washing procedures (multiple rinses with different solvents followed by sonication steps) were tried but triclosan was not removed completely. Depending of the background interference, γ-chlordane was properly quantified and chromatographically separated from triclosan. In a 'real' sample, the analyst should pay careful attention to γ-chlordane's retention time and compare it with a control sample, such as matrix spike when using ECD as the detection of choice. It was observed that manual integration was required to accurately quantify γ-chlordane.

4. Conclusions

As already demonstrated by many published studies, comprehensive two dimensional gas chromatography coupled with a micro electron capture detector allows the analysis of PCBs, OCs, and CBz in a single analytical run. No fractionation of the extracts was required prior to instrumental analysis which resulted in significant savings of time and analysis costs with subsequent increase in data quality. The DB1 × Rtx-PCB column combination selected for the GC × GC system yield excellent within- and between-class separations. This method was shown to be precise and accurate for the standards and reference materials tested. To further emphasise the significance of this technique, the data

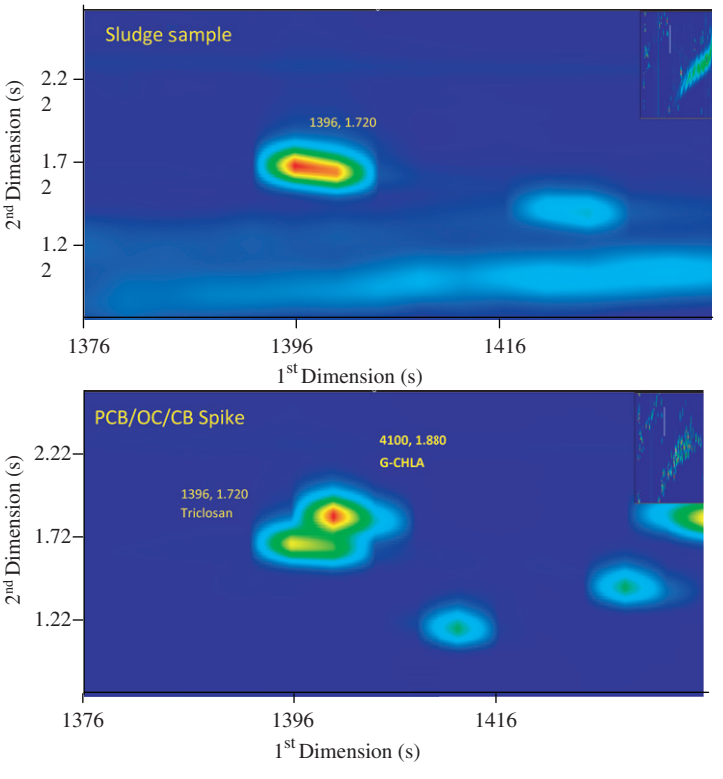

Figure 7. Two dimensional chromatograms representing the triclosan peak (marked as unknown) interfere with γ-chlordane for sludge and a quality control sample (PCB/OC/CBz spike).

obtained by GC × GC was compared to the classical GC method. The results were similar for both techniques, yet the GC × GC has many advantages over the classical approach. While the GC × GC can analyse all the target compounds in a 45 minute analytical run, the classical GC-ECD uses multiple columns and instruments that analyse each different class of interest separately in four analytical runs [20,21]. The sediment and sludge extracts are very complex, and many unidentified compounds were observed in the two dimensional chromatograms obtained. Some of the groups or compounds might interfere with the target analytes and improvements need to be considered to avoid any unnecessary contamination or background interferences. Other compounds could be identified by using available data previously published as well as data pointed out in this study and the technique could be used as initial assessment of additional or non-routine compounds, analytical triage and forensic fingerprinting to match specific source patterns. Previously acquired data can be reinterpreted for the undetermined compounds present in the samples and historical trends can be determined.

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Table S1. List of abbreviations used in the figures.

Name of compound	Abbreviations
Photo-mirex	*p*-Mirex
alpha-Hexachlorocyclohexane	α-BHC
beta-Hexachlorocyclohexane	β-BHC
gamma-Hexachlorocyclohexane	γ-BHC
alpha-Chlordane	α-CHLA
gamma-Chlordane	γ-CHLA
cis-Nonachlor	cis-
trans-Nonachlor	trans-
Heptachlor epoxide	H-epox
Methoxychlor	DMDT
Endosulfan I	Endos 1
Endosulfan II	Endos 2
Endosulfan sulfate	Endos S
Hexachloroethane	HCE
1,3,5-Trichlorobenzene	1,3,5-TCB
1,2,4-Trichlorobenzene	1,3,5-TCB
1,2,3-Trichlorobenzene	1,3,5-TCB
Hexachlorobutadiene	HCBD
2,4,5-Trichlorotoluene	2,4,5-TCT
2,3,6-Trichlorotoluene	2,3,6-TCT
1,2,3,5-Tetrachlorobenzene	1,2,3,5-TCB
1,2,4,5-Tetrachlorobenzene	1,2,4,5-TCB
1,2,3,4-Tetrachlorobenzene	1,2,3,4-TCB
2,6,α-Trichlorotoluene	2,6,α-TCT
Pentachlorobenzene	P5CB
Octachlorostyrene	ocstyr
Hexachlorobenzene	HCBD