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Determination of Aroclor 1260 in Soil Samples by GC/MS with Solid Phase Microextraction

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Abbreviations: ECD, electron capture detector; **EI**, electron ionization; **EICs**, extracted ion chromatograms; **EPA**, the US Environmental Protection Agency; **PCB**, polychlorinated biphenyls; **PDMS**, polydimethylsiloxane; **RE**, relative error; **RSD**, relative standard deviation; **SPME**, solid phase microextraction; **TCMX**, tetrachloro-m-xylene; **TIC**, total ion current.

Keywords: Environmental samples/ GC/MS/ Polychlorinated biphenyls/ Soil /Solid phase microextraction

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Abstract

A novel fast screening method was developed for the determination of polychlorinated biphenyls (PCBs) commercial mixture, Aroclor 1260, in soil matrices by GC/MS combined with solid phase microextraction (SPME). The non-equilibrium headspace SPME with a 100 μm polydimethylsiloxane fiber was used to extract PCBs from 0.5 g soil matrices. The use of 2 mL of saturated potassium dichromate in 6 M sulfuric acid solution improved the reproducibility of the extractions and the mass transfer of PCBs from the soil matrix to the headspace and SPME fiber for extraction times of 30 min at 100 °C. The percent recoveries for the SPME method, which were evaluated using an Aroclor 1260 standard liquid injection calibration data set, were within the range of 54.9-65.7%. Extracted ion chromatogram data were used to construct the calibration curves. The accuracy was less than ±15% expressed as relative error and the precision was less than 15% expressed as relative standard deviation. The method was validated with certified soil samples and the predicted concentrations for Aroclor 1260 agreed with the certified values. The method was demonstrated to be linear from 10 ng/g to 1000 ng/g for Aroclor 1260 in dry soil.

1 Introduction

Polychlorinated biphenyls (PCBs) represent a class of organic pollutants that are characterized by biphenyl with a number of chlorine substituents that may range from 1 to 10 chlorine atoms per molecule. There are 209

possible congeners. As persistent organic pollutants, PCBs are a major environmental concern due to their ubiquity, toxicity, and persistence. In North America, commercial PCBs were produced under the trade name Aroclor by the Monsanto Company and were banned for use in 1977 [1, 2].

PCBs have been found in different matrices including soil, surface water, sediments, and air; so many approaches have been developed for the determination of PCBs and Aroclors depending on the PCB concentration in the matrices and regulatory requirements [3]. Although several bioanalytical screening methods such as multianalyte enzyme-linked immunosorbent assay [4], chemically activated luciferase gene expression assay [5] have been developed, GC coupled with an electron capture detector (ECD) or mass spectrometry (MS) are still the most widely accepted and reliable techniques for the quantification of PCBs because of their high sensitivity, good selectivity, and reproducibility [6, 7]. Traditional chemical analyses are usually very time-consuming and expensive due to the requirement of extensive extraction and cleanup procedures that are coupled to lengthy high-resolution gas chromatographic programs [8]. For soil samples, the US Environmental Protection Agency (EPA) recommends a variety of different extraction methods, including Soxhlet extraction, automated Soxhlet extraction, pressurized fluid extraction, microwave extraction, ultrasonic extraction, and supercritical fluid extraction [7]. These methods all require large volumes of organic solvent (15 ~ 200 mL) and

long extraction times (1.5 ~ 20 h) [9]. Some recent improvements to reduce the extraction time and the use of extraction solvent have been reported, such as low-pressure microwave assisted extraction [3], on-line or selective pressurized fluid extraction [10-12], and miniaturized ultrasonic solvent extraction [13]. Extraction methods with higher efficiency, shorter times, and lower costs have also been developed, including vortex assisted liquid-liquid microextraction [14], dispersive liquid–liquid microextraction [15], hollow-fiber liquid-phase microextraction [16, 17], and ultrasound assisted emulsification-microextraction [18]. However, these techniques are only applicable to liquid samples, are difficult to automate, unstable, and/or prone to cause irreversible damage to the analytes [14].

The technique of solid phase microextraction (SPME) was first reported by Pawliszyn and co-workers in 1989 [19], and after more than 20 years of development, has a very wide range of applications following commercialization through Supelco [20, 21]. Compared with traditional sample preparation techniques such as liquid-liquid extraction and solid phase extraction, SPME has the following advantages. First, the method is fast, simple, sensitive, and is solvent free. Second, sampling, extraction, and concentration are integrated into one step. Third, injection can be easily coupled with major separation systems such as GC, HPLC, and CE, which makes it easy to implement and automate [20]. Fourth, fibers with different selectivities [e.g., polydimethylsiloxane (PDMS), polyacrylate, carboxen,

carbowax and divinylbenzene] are commercially available. SPME has been applied to the determination of PCBs in different matrices such as water [22], soil [23], ash [24], and tissues [25]. All of these applications focused on the quantitative analysis of selected PCB congeners rather than modeling the Aroclors directly.

In this study, a fast method for the determination of Aroclor 1260 in soil matrices using headspace SPME-GC/MS was developed. The optimization of headspace SPME is discussed. The sample analysis was accomplished within 35 min by staggering the sample preparation and GC/MS analysis. The total peak areas of tetra-chlorinated biphenyls (tetra-CB, *m/z* 292), penta-chlorinated biphenyls (penta-CB, *m/z* 326), hexa-chlorinated biphenyls (hexa-CB, *m/z* 360), hepta-chlorinated biphenyls (hepta-CB, *m/z* 394), and octa-chlorinated biphenyls (octa-CB, *m/z* 430) were used to construct the calibration models for the quantification of Aroclor 1260. The method was then validated with certified soil samples. Although we do not show data for other Aroclors in this particular study, we have tested the method using different Aroclors with similar success.

2 Experimental

2.1 Reagents

An Aroclor 1260 stock solution at a concentration of 100 µg/mL in methanol was obtained from AccuStandard, Inc. (New Haven, CT). Standard solutions of Aroclor 1260 with concentrations of 0.1, 0.3, 1, 3, and 10 µg/mL were

prepared by dilutions of aliquots of the stock solution with methanol. A mixture in hexane containing 1 mg/mL of decachlorobiphenyl (deca-CB) and of tetrachloro-m-xylene (TCMX) was also obtained from AccuStandard, Inc. (New Haven, CT). Potassium permanganate, potassium dichromate, the SPME fibers coated with polydimethylsiloxane (PDMS, 7 μm or 100 μm film thickness), 20-mL headspace glass vials, and crimp seals with PTFE/silicone septa were purchased from Sigma-Aldrich Co. LLC. (St. Louis, MO). The clean soil and certified Aroclor 1260 soil samples were purchased from RT Corp (Laramie, WY).

The standard soil samples were prepared by thoroughly mixing 50 μL of standard solutions with 0.5 g clean soil and completely evaporating the solvent in a hood at room temperature. The internal standard solution containing 10 μg/mL of deca-CB and TCMX was prepared by dilution with hexane from the 1 mg/mL stock solution, but only deca-CB was used as an internal standard for the Aroclor quantification. A saturated potassium dichromate solution was prepared by dissolving an excess of potassium dichromate in 6.0 M sulfuric acid.

2.2 Instruments

All the experimental data were collected on a Thermo Finnigan PolarisQ quadrupole ion trap mass spectrometer/Trace GC system with a Triplus AS2000 autosampler (San Francisco, CA, USA). The GC/MS system was controlled by the XCalibur software version 2.0.7 provided by Thermo. The

GC separation was accomplished on a SHRXI-5MS capillary column (5% diphenyl/95% dimethylpolysiloxane cross-linked, 30 m×0.25 mm i.d., 0.1 μm film thickness) from Shimadzu Scientific Instruments Inc. (Columbia, MD). MATLAB R2012b (MathWorks Inc., Natick, MA) was used to process the data.

The RAW files of the two-way (retention time × mass-to-charge ratio) GC/MS data were converted to the network common document format (CDF) with the 'File Converter Tool' in the XCalibur Software. The CDF files were read directly into MATLAB using the *netcdf* functions.

2.3 Sample preparation

Soil samples of 0.5 g were added to the 20-mL SPME vial and spiked with 20 μL of internal standard solution. The samples were left in the hood at room temperature to evaporate the solvent. Then 2 mL of saturated potassium dichromate solution was added to the vial and the vial was sealed with a PTFE/silicone septum using a crimp seal. After 30 s of vortexing, the mixtures were placed in the autosampler tray for analysis. The sample vial was incubated at 100 °C for 0.5 min. A PDMS fiber was then exposed to the headspace for 30 min. The agitation was sequentially pulsed on for 10 s and then off for 10 s for the 30 min exposure.

The fiber was thermally desorbed in the GC injector at 280 °C for 5 min to prevent carryover. The analytes were separated using the following oven temperature program at a constant helium flow of 1 mL/min: 50 °C, hold for

1 min, ramp at 20 °C/min to 280 °C, hold for 10 min. The transfer line and ion source temperatures were both maintained at 280 °C. The mass spectrometer was operated in positive ion electron ionization (EI) mode at 40 eV and mass spectra were collected after a 4 min solvent delay. Full scan mode was selected for the mass spectrometer and the scan range was from mass-to-charge ratio (*m/z*) 140 to 550.

Five blank soil samples without any Aroclor and internal standard were treated in the same way. The blank soil sample data were used for correcting the baselines of the Aroclor soil samples.

3 Results and discussion

Aroclor 1260 soil samples at the concentration of 30 ng/g (ppb) were used to evaluate the optimization of SPME and instrument conditions. The peak areas of hexa-chlorinated biphenyls (hexa-CBs) were selected as references to compare the effects of different conditions because hexa-CBs are one of the major PCBs in Aroclor 1260 (46.9 weight %) [26]. Extracted ion monitoring at *m/z* 360 was used to quantify the hexa-CBs by integrating the peak areas of the extracted ion chromatogram from 12.50 to 13.78 min.

3.1 Optimization of SPME conditions

Directly exposing a PDMS fiber to the headspace of a vial containing 0.5 g of 30 ppb Aroclor 1260 soil sample demonstrated that PCBs were unable to transfer to the headspace efficiently (Supporting information Fig. S1). The low efficiency was attributed to the low boiling point and lipophilicity of PCBs,

which caused sorption of the PCBs to the surfaces of the soil particles. Elemental sulfur (S6 and S8) is another common interference in the soil matrix which could significantly decrease the extraction efficiency of the PCBs [23]. Montes et al. have demonstrated that the employment of strong oxidative conditions such as the addition of potassium permanganate solution (0.1 M in 6 M sulfuric acid) to the soil assists in the release of the PCBs from the soil and the removal of organic matter and sulfur interferences [23]. In this study, an additional two strong oxidants, potassium dichromate and chromium trioxide in 6 M sulfuric acid, were compared with potassium permanganate in 6 M sulfuric acid.

All the parameters in these initial studies were the same as section 2.3., except that the EI energy was set to 70 eV instead of 40 eV, and internal standards were not added to the samples. Three extraction solution systems were compared: 1) 2 mL $KMnO_4$ (0.1 M), 0.5 mL H_2SO_4 (6 M); 2) 2 mL 0.2 M CrO_3 in 6 M H_2SO_4; 3) 2 mL 0.2 M $K_2Cr_2O_7$ in 6 M H_2SO_4. The extraction efficiency of the $KMnO_4$ system was significantly higher (average about 2.5 times higher) than the other two extraction systems, but the repeatability was significantly worse based on four replicate extractions (Supporting information Fig. **Error! Reference source not found.**S2A). These preliminary SPME experiments were accomplished with 10-mL SPME vials and it was found that the fiber was fouled by the oxidative conditions, which may have accounted for the poor repeatability. In an attempt to mitigate the

oxidative fouling problem, 20-mL vials were used to create a larger volume for headspace for the extractions. However, after approximately 20 analyses, the PDMS fiber still turned black, which indicated that even the larger headspace volume was not able to prevent the fiber from being contaminated by the $KMnO_4$ (Supporting information Fig. S2B).

The use of CrO_3 and $K_2Cr_2O_7$ offered stable extraction efficiencies and less degradation of the SPME fibers. Other treatments such as with a strong basic solution (10 M NaOH) or a strong acidic solution (10 M H_2SO_4) or single addition of water were investigated, but failed to effectively release the PCBs from the soil to the headspace (Supporting information Fig. S1).

The effect of CrO_3 versus $K_2Cr_2O_7$, the effect of concentration of $K_2Cr_2O_7$ in 6 M H_2SO_4, and the effect of solution volume on absolute recoveries were also studied. The responses obtained from different solutions with a 0.5 g soil sample are given in Supporting information Fig. S3. There was no significant difference between different extraction systems (p = 0.15 by one-way analysis of variance). Therefore, $K_2Cr_2O_7$ was chosen as the extraction solution because of its availability. The concentrations and amounts of $K_2Cr_2O_7$ solution added to the sample had no significant effect on the extraction efficiency. Saturated $K_2Cr_2O_7$ in 6 M H_2SO_4 was chosen to oxidize organic matter to the largest extent and the amount of solution was set to 2 mL instead of 4 mL to create more headspace and prevent SPME fiber degradation by the extraction solution.

The coatings of SPME fiber were selected between 7 μm PDMS and 100 μm PDMS because PDMS had a higher affinity for PCBs than the other coatings in previous studies [22, 23, 27, 28]. To evaluate the influence of the fiber thickness, both fibers were exposed to the headspace at 100 °C for 30 min, and the 100 μm PDMS fiber was chosen for further study because the signals were approximately three times better (Supporting information Fig. S4).

After SPME extraction, the desorption of the fiber was accomplished in the GC injection port at 280 °C (the maximum operation temperature for 100 μm PDMS fiber) for 5 min to avoid the carryover effect. The absence of carryover was also validated by a system blank injection after each sample analysis.

The effects of extraction temperature and extraction time on the hexa-CBs extracted by headspace SPME with 100 μm PDMS fiber were investigated. Soil samples of 0.5 g were extracted by 2 mL saturated $K_2Cr_2O_7$ in 6 M H_2SO_4 for 30 min at 25, 60, and 100 °C and responses obtained plotted with respect to temperature as given in Fig. 1A. The mobility of the PCBs through liquid and gas phases was significantly improved with the increase in extraction temperature, so the responses obtained at 100 °C were much larger than the responses at the other two lower temperatures. Finally, 100 °C was selected as the extraction temperature. Equilibrium was not achieved, so even higher temperatures

may increase mass transport, but could exceed the pressure safety limits of the SPME vial. The extraction time profiles for 5, 15, 30, and 60 min at 100 °C are given in Fig. 1B. The adsorption of PCBs to the fiber had not equilibrated after a 30 min extraction. To keep the analysis within a reasonable time, the extraction time was fixed at 30 min.

3.2 GC/MS analysis

To develop an efficient method, a full separation of all 209 possible PCB congeners was not attempted. A 22 min GC temperature program was used in this study which was reported earlier [29]. About 40 total ion current (TIC) chromatographic peaks can be separated for Aroclor 1260 (Fig. 2A). Each chromatographic peak may contain multiple co-eluted PCBs.

Full scan mode was used for MS and the mass scan range was from *m/z* 140 to 550 because most of the ions for the PCB mass spectra are larger than *m/z* 145. The effects of EI energy on signal response were evaluated at electron energies of 15, 40, and 70 eV. Very low responses were obtained by using an EI energy of 15 eV, and an EI energy at 40 eV gave a factor of two times better response than using an EI energy of 70 eV (Fig. 1C). Therefore, the EI energy was set at 40 eV for further work in this study.

3.3 Analytical method performance

The data sets were pretreated by orthogonal baseline correction (using bases of 10 components) for which the GC/MS baseline/background was

reconstructed from a best fitting orthonormal bases constructed from one of the blank SPME runs. The full details of baseline correction are described in a previous study [29]. Using this approach, the artifact peaks (e.g., PDMS peaks) and baseline were thereby significantly reduced in the TIC chromatograms (Fig. 2B). The correction method was less effective for extracted ion chromatograms (EICs), because the EICs are relatively indifferent to PDMS fragment ions from column bleed and the SPME fiber.

Although the internal standard solution contained both TCMX at 9.5 min and deca-CB at 19.5 min, only deca-CB was used as internal standard because of its closer structure and chemistry to the PCBs of interest, and because TCMX eluted early and overlapped with some of the matrix peaks. The molecular ion of deca-CB (*m/z* 498) was extracted from TIC and the peak area was integrated at retention time window between 19.3 to 19.6 min. Each chromatogram was normalized to the peak area of deca-CB respectively.

EICs at retention time windows between 11.0 to 16.0 min were used to construct smaller two-way GC/MS data sets which were selective for the PCBs. The molecular ions of tetra-chlorinated biphenyls (tetra-CB, *m/z* 292), penta-chlorinated biphenyls (penta-CB, *m/z* 326), hexa-CB (*m/z* 360), hepta-chlorinated biphenyls (hepta-CB, *m/z* 394), and octa-chlorinated biphenyls (octa-CB, *m/z* 430) were used to create EIC two-way data (Fig.

2C). All five PCBs mentioned above represent more than 99% of the PCBs in Aroclor 1260 [26].

The proposed method resulted in a linear dynamic range of 10-1000 ng/g of Aroclor 1260 with a regression equation y = 73.38x + 0.94 (R^2 = 0.9992). The accuracy and precision of the method were evaluated by the prepared soil samples at three different concentrations with three replicates at each concentration. As reported in Table 1, the accuracy is in the range of 0 to 0.9% expressed by the relative error (RE, %) and the precision is in the range of 4.6 to 12.6%, expressed by relative standard deviation (RSD).

In this study, the limit of detection (LOD) was calculated from three times the standard deviation of the blank signal [30]. Five blank soil samples with internal standard were treated the same as described in section *2.3.* The predicted concentrations for blank samples were calculated. Then three times the standard deviation of predicted concentrations was taken as the LOD, which yielded a value of 5.2 ng/g.

3.4 Recovery evaluation of SPME-GC/MS method

To evaluate the recovery of the SPME method, another calibration data set using standard liquid injection was collected. All the instrumental parameters were the same as those described in section *3.2.,* except that the injection mode was changed from SPME mode to splitless liquid injection mode. A set of 0.5 g Aroclor 1260 soil samples at the concentrations of 10, 30, 100, and 300 ng/g in five replicates were collected using the SPME-

GC/MS method. The calibration mode was constructed using EIC data and the mass of Aroclor 1260 extracted by SPME was determined. The SPME peak areas were compared to those of the liquid injection calibration curve to assess the mass loading on the column. The percent recovery was calculated using the calculated mass on-column of the SPME-extracted sample relative to the absolute mass contained within the vial before SPME extraction. The results are listed in Table 2. The recoveries ranged between 55-66% for the SPME samples at the four concentrations studied. The results are not surprising if one considers that the adsorption equilibrium between PCBs and the SPME fiber was not properly established within 30 min (Fig. 1B). However, the low recoveries did not affect the accuracy of the method because they were reproducible.

3.5 Validation of method by certified soil samples

Certified soil samples originally contaminated with Aroclor 1260 at 1.50 μg/g (prediction interval 0.65-2.34 μg/g) were measured using the previously optimized conditions. The certified soil samples were diluted with certified clean soils to the concentrations at 50 ng/g and 500 ng/g. Each soil sample was analyzed by SPME-GC/MS in four replicate trials. As given in Table 3, the estimated concentrations are inside of the certified prediction intervals.

4 Conclusions

A fast Aroclor-based quantitative method for PCBs in soil samples by SPME-GC/MS has been proposed in this study. The combination of potassium

dichromate and sulfuric acid solution was used to extract PCB from soil for the first time, and the parameters for the non-equilibrium headspace SPME were optimized. The extracted ion two-way (EIC) data sets were used to construct calibration curves and the method has been validated by commercial certified soil samples. The predicted concentrations of Aroclor 1260 were all in the prediction intervals for the certified soil samples. The proposed method has the advantage of the high sample throughput, with a soil sample being prepared and analyzed staggeringly about every 35 min. The headspace SPME method is easy to perform and has the potential to be adapted for onsite analysis. Other preliminary studies have demonstrated its application to the field study combined with a portable GC/MS instrument [31]. The method required a low sample amount (0.5 g) which can benefit applications for which sample availability is a limiting factor.

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Department of Energy Office of Environmental Management Portsmouth/Paducah Project Office, or of the Voinovich School of Leadership and Public Affairs at Ohio University.

The authors have declared no conflict of interest.

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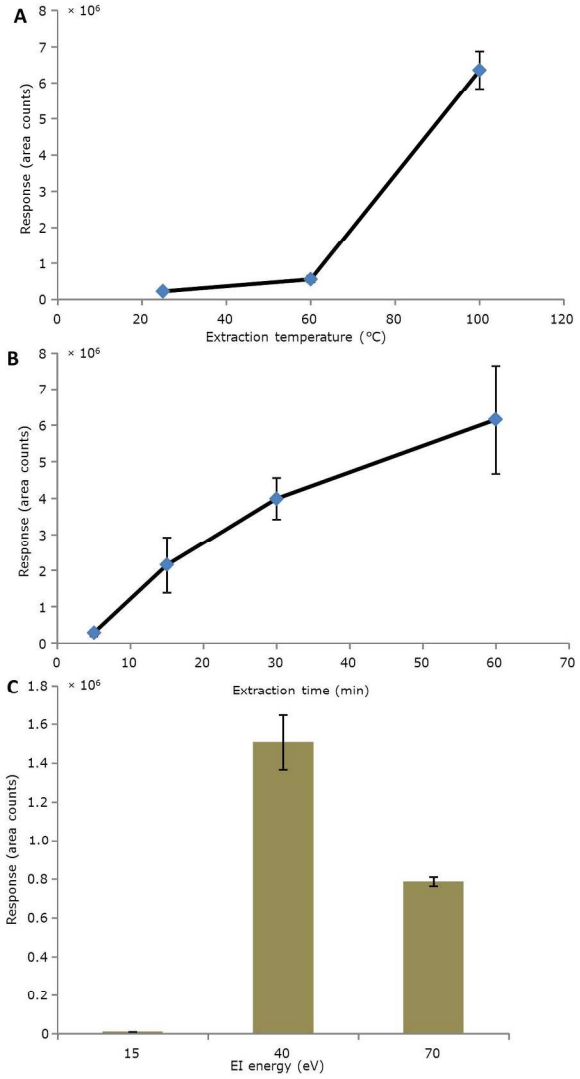
Legends of figures:

Figure 1. The effect of extraction temperature (A), extraction time (B), and electron ionization energy (C) on the extraction efficiency of PCBs from soil samples spiked with Aroclor 1260. (n = 3)

Figure 2. GC/MS TIC chromatograms of Aroclor 1260 before (A) and after (B) baseline/background correction for 30 ng/g soil sample after headspace SPME extraction. On the right (C) are EICs for tetra-, penta-, hexa-, hepta-, and octa-CBs at zoom-in retention time window.



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273x464mm (300 x 300 DPI)

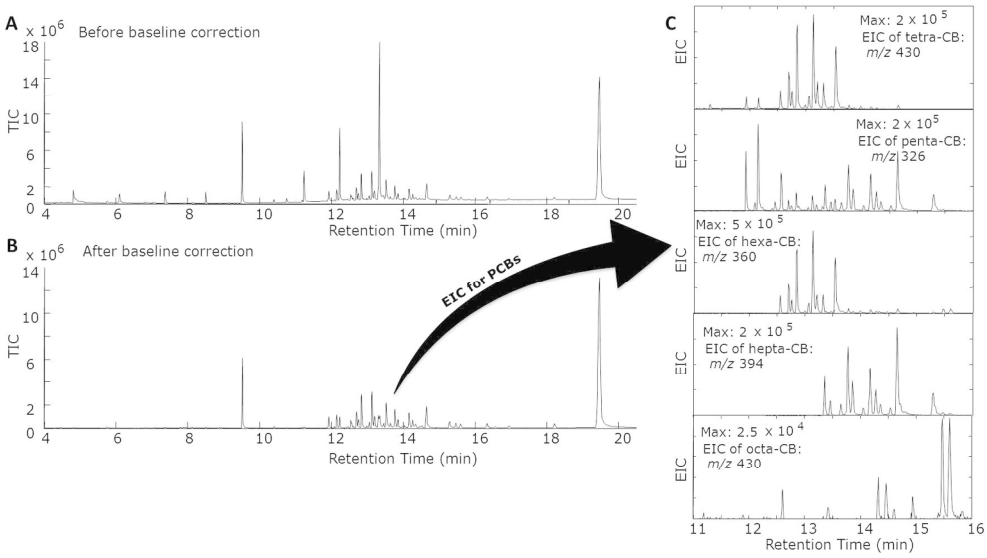

Figure 2. GC/MS TIC chromatograms of Aroclor 1260 before (A) and after (B) baseline/background correction for 30 ng/g soil sample after headspace SPME extraction. On the right (C) are EICs for tetra-, penta-, hexa-, hepta-, and octa-CBs at zoom-in retention time window.
304x170mm (300 x 300 DPI)

Table 1. Accuracy and precision of developed method

Aroclor 1260 concentration (ppb)	Measured concentration (ppb)	Mean concentration (ppb)	Accuracy (RE, %)	Precision (RSD, %)
30	26.8			
30	29.7	30	0	11.2
30	33.5			
300	309			
300	285	301	0.3	4.6
300	309			
1000	1078			
1000	1085	1009	0.9	12.6
1000	864			

Table 2. The percentage recoveries of Aroclor 1260 by SPME-GC/MS.

Aroclor1260 concentration (ppb)	Aroclor1260 in the vial (ng)	Aroclor1260 on column (ng)	Mean recovery (%)	RSD (%)
10	5	2.9		
10	5	2.6		
10	5	2.9	61.4	11.9
10	5	2.8		
10	5	4.1		
30	15	10.3		
30	15	9.8		
30	15	9.4	65.7	6.1
30	15	8.6		
30	15	11.1		
100	50	33.8		
100	50	31.2		
100	50	31.3	64.5	5.0
100	50	29.2		
100	50	35.7		
300	150	82.9		
300	150	82.8		
300	150	82.5	54.9	0.8
300	150	80.2		
300	150	83.4		

Table 3. Application of the method to certified soil samples (n = 4).

Prediction interval (certified reference value) (ppb)	Concentration found (ppb)
217-780 (500)	545±91
22-78 (50)	64±15