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Simple method for estimating polychlorinated biphenyl concentrations on soils and sediments using subcritical water extraction coupled with solid-phase microextraction

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Abstract

A rapid method for estimating polychlorinated biphenyl (PCB) concentrations in contaminated soils and sediments has been developed by coupling static subcritical water extraction with solid-phase microextraction (SPME). Soil, water, and internal standards are placed in a sealed extraction cell, heated at 250°C for 15 to 60 min, cooled, and the PCB concentrations in the extractant water determined by SPME and GC–electron-capture detection. When PCB 103 and 169 (not found in contaminated samples) are used as internal standards to calibrate for the soil/water and water/SPME equilibria, quantitative results for individual PCB congeners typically agree within 80 to 130% of the concentrations based on Soxhlet extraction and conventional GC analysis. The reproducibility of replicate subcritical water extraction/SPME determinations is typically 10 to 15% relative standard deviation. Analysis of water extracts stored for 24 h agrees with fresh extracts, demonstrating that extracts can be stored for later SPME analysis without significant loss of the PCBs from the extractant water. The method is simple to perform, uses field-rugged and inexpensive apparatus, and generates no organic solvent waste.

Keywords: Soil; Sediments; Environmental analysis; Extraction methods; Subcritical fluid extraction; Polychlorinated biphenyls

1. Introduction

The desire to reduce the use of organic solvents and to reduce the time needed to extract organic pollutants from contaminated solids has led to new extraction methods including supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE). Similar goals have led to the development of solid-phase microextraction (SPME), a solvent-free technique for the extraction of water samples [1–10]. A recent approach for extracting organics from solids and semi-solids has utilized 'subcritical' water (hot water under enough pressure to maintain the liquid state) as the extraction solvent [11–15]. Extraction of non-polar and moderately-polar organics is based on the reduced polarity, surface tension, and viscosity of the water at higher (up to 250°C) temperatures. Under these conditions, organic compounds generally considered to be insoluble in water show dramatic increases in solubility. For example, the solubility of the pesticide chlorothalonil increases from 0.3 to 23 000 $\mu g\,l^{-1}$ (a factor of 130 000) when water is heated from ambient to 200°C [16].

Several recent reports have utilized the changes in

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water's properties to extract a variety of organic pollutants from model sorbents, contaminated soils, sludges, particulate matter, and other environmental samples [11–15]. The extracted analytes were collected 'off-line' in an organic solvent for subsequent analysis. In contrast to the dependence on pressure commonly reported for SFE with supercritical carbon dioxide, the efficiency of subcritical water extractions depends primarily on the water temperature, as long as sufficient pressure is applied to maintain the liquid state (typically <40 bar). As would be expected, more polar organics (e.g., phenols) extract efficiently at relatively low temperatures (e.g., 50 to 100°C), while non-polar organics such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) require temperatures up to 250°C for efficient extraction [11–15].

Although SPME coupled with gas chromatography (GC) is a powerful approach for the rapid extraction and analysis of non-polar and moderately-polar organics from water, its use for the analysis of organic pollutants from solid samples has been limited to compounds such as benzene that can be rapidly vaporized from solids and also show strong partitioning to the SPME phase [3,17]. Recently, we have coupled subcritical water extraction with SPME to determine the concentration of aromatic amines and PAHs in soil samples [18]. In essence, a very simple and inexpensive method for using subcritical water extraction to convert solid samples into water samples is used so that the pollutants can be determined by SPME in the extractant water. In the present study, this approach is developed for the rapid determination of PCBs from contaminated soils and sediments.

2. Experimental

2.1. Samples

Two soils contaminated with PCBs were collected from storage dumpsters at Manitoba Hydro in Winnipeg, Manitoba, Canada. Both samples were sieved through a screen with 6 mm×6 mm holes to remove rocks and other large debris. The samples were then homogenized by hand mixing for ~1 min. Since the goal of this project is to develop a simple method capable of field applications, no other sample preparation steps were performed prior to subcritical water extraction. A standard reference material, PCB-contaminated sediment (SRM 1939), was obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and used as received.

2.2. Water extractions

All water extractions were performed using a 64 mm long×7 mm I.D. (12 mm O.D.) stainless steel pipe with national pipe thread (n.p.t.) end caps (Minnesota Valve and Fitting, Eden Prairie, MN, USA) which was rated by the supplier for a maximum pressure of 496 bar [18]. One end of the cell was closed using an end cap and a single layer of PTFE tape. The sample was then weighed into the cell and spiked with the internal standard solution containing PCB congeners 103 and 169 (chosen as internal standards because neither of these congeners is found in commercial Aroclors and, therefore, are not found in the environment). The NIST sediment was spiked with 150 ng each (in 3 μl of acetone) of the two congeners. The two soil samples were spiked with 150 ng and 200 ng of PCBs 103 and 169, respectively. The cell was then filled with HPLC-grade water (~3.5 ml) which had previously been purged with clean nitrogen for ca. 2 h to remove dissolved oxygen. The cell cap was placed on, again using a single layer of PTFE tape on the pipe threads. This procedure resulted in a ~1-ml headspace of air above the water in the cell. (*Safety note: It is imperative that there is a headspace present in the cell so that the pressure in the cell upon heating is controlled by the steam/water equilibrium. If the cap of the cell is also filled with water to eliminate the headspace, the pressure in the heated cell could exceed several thousand bar.*) The assembled cell was then placed vertically in a Hewlett–Packard (HP) Model 5890 gas chromatographic (GC) oven (Palo Alto, CA, USA) and heated without mixing. (Note that the highest pressure expected during the heating step is the steam/water equilibrium pressure of 40 bar which would occur at the highest temperature tested (250°C), a pressure much lower than the vessel rating of 496 bar. However, care must be taken to avoid the extraction of samples which may

react with water to yield higher pressures.) After heating, the cell was removed from the oven and cooled for ~2 min under tap water. The top cap was removed and 1.8 ml of the supernatant water was pipetted into a 2 ml autosampler vial containing a clean, PTFE-coated stir bar. The vial was immediately sealed with a PTFE-lined cap to avoid the loss of more volatile components [19].

2.3. SPME and GC/electron-capture detection determinations

The concentrations of the PCBs in the extractant water were determined using SPME sorption and gas chromatography–electron-capture detection (GC–ECD) with an HP Model 5890 Series II GC equipped with a split/splitless injection port. Details for optimizing the use of a split/splitless injection port for the desorption from a SPME sorbent are discussed in detail elsewhere [5,19]. Briefly, the procedure for the SPME determinations was: (1) the sorbent fiber was inserted into and exposed to the water extract for 15 min, with stirring; (2) the fiber was then withdrawn from the water sample and the analytes were recovered by inserting the fiber into the heated (300°C) split/splitless injection port (splitless mode) for 1–3 min. All determinations were performed using a 7-μm film-thickness polydimethylsiloxane (PDMS) coated fiber mounted in a manual syringe holder (Supelco, Bellefonte, PA, USA). Earlier reports demonstrated that the use of the 300°C desorption temperature did not result in degradation of the sorbent fiber or affect its performance; yet it was sufficient to quantitatively recover even non-volatile PCB congeners [5,19]. Fibers were further cleaned between samples by exposing the fiber at 300°C for 10 min in a separate GC injection port [19]. Sorbent fibers were also periodically subjected to a second desorption and GC–ECD analysis. The lack of detectable analytes demonstrated that the 3-min desorption at 300°C was sufficient to recover all of the analytes discussed in this study.

GC separations for the NIST SRM 1939 sample were performed using chromatographic conditions similar to those used by NIST during the certification process except for using a lower initial temperature to aid in focusing the analytes during the SPME desorption. These conditions included a DB-5 column (60 m×0.25 mm I.D., 0.25 μm film thickness, J&W Scientific, Rancho Cordova, CA, USA), an oven temperature of 60°C during the SPME desorption, followed by a temperature ramp at 10°C min^{-1} to 150°C (hold for 31 min), followed by a ramp of 1°C min^{-1} to 220°C, then a ramp of 3°C min^{-1} to 280°C. The NIST program started at 150°C (hold for 40 min) followed by the same temperature ramps as used for the SPME analysis. For the other two soils, a shorter column (HP5 capillary column, 25 m×0.32 mm I.D., 0.17 μm film thickness supplied by Hewlett–Packard) was used since one of the goals of the method was to provide rapid estimations of the PCB concentrations rather than high-resolution separations. The GC temperature program was 60°C during the SPME desorption step, followed by a temperature ramp at 25°C min^{-1} to 130°C, then a ramp of 8°C min^{-1} to 280°C. This resulted in a GC analysis time of ~26 min which corresponds well with the 15-min SPME sorption time.

Calibration standards for SPME determinations of individual PCB congeners were prepared by diluting a commercial mixture of 21 PCB congeners (100 μg ml^{-1} each in acetone) ranging from di- to decachlorobiphenyls (AccuStandard, New Haven, CT, USA). Appropriate volumes (5 to 50 μL) were spiked into 1.8 ml water samples (in GC autosampler vials) along with the two internal standards (PCBs 103 and 169) used for the soil samples. The quantities of internal standards added to the calibration standard water samples was 1% of the quantities added to the soil samples to adjust for the water/soil partitioning which occurs upon cooling the extraction cell (discussed below).

2.4. Conventional extractions

Concentrations of the PCBs in the two industrial soils (triplicate 5-g samples mixed with an equal mass of anhydrous sodium sulfate) were determined using Soxhlet extraction with 150 ml of hexane–acetone (1:1) for 18 h with a cycle time of ~15 min. The same internal standards used for the quantitation of the organics in the sonication and Soxhlet extracts were used for the SPME determinations. After extractions were completed, the solvent volume was

concentrated by 20-fold under a gentle stream of nitrogen and analyzed using the same GC–ECD conditions as described above for the SPME determinations.

2.5. Determining soil/water partitioning

Based on previous reports, the conditions used for the PCB extraction should be capable of quantitatively transferring the PCBs from the soil into the extractant water [12,15]. However, when the cell and its contents are cooled after the subcritical water extraction, the solvated PCBs can repartition back to the soil before the water aliquot is removed for SPME analysis. As discussed below, the two internal standards were added to the soil in the hope that they could be used to adjust for this repartitioning. In order to determine the fraction of each PCB congener that is found in the soil and in the extractant water (after the heating and cooling steps), replicate Soil 'A' samples were extracted in an identical manner as described above, except that no internal standard was added prior to the heating step. After the heating (15 min at 250°C) and cooling steps were completed, the soil/water slurry was centrifuged to separate the solid and liquid phases. The internal standards were added to each fraction. The soil was then mixed with sodium sulfate and extracted by sonication overnight with *n*-hexane–acetone (1:1), and the water was extracted with three 2-ml aliquots of *n*-hexane. In addition, the sample cell was rinsed three times with 2 ml aliquots of *n*-hexane–acetone (1:1) (containing the internal standards). The concentrations of the PCBs in each fraction were then determined as described above.

3. Results and discussion

Initial comparisons of the subcritical water extraction/SPME approach with conventional Soxhlet extraction were performed using Soil 'A' which had been contaminated 20 years earlier with low ppm levels of PCBs. Fig. 1 shows the chromatograms resulting from a Soxhlet extraction (5 g), and from the subcritical water exaction/SPME analysis (0.5 g) using a 1-h water extraction at 250°C. The short GC analysis time gives reasonably good separation of the

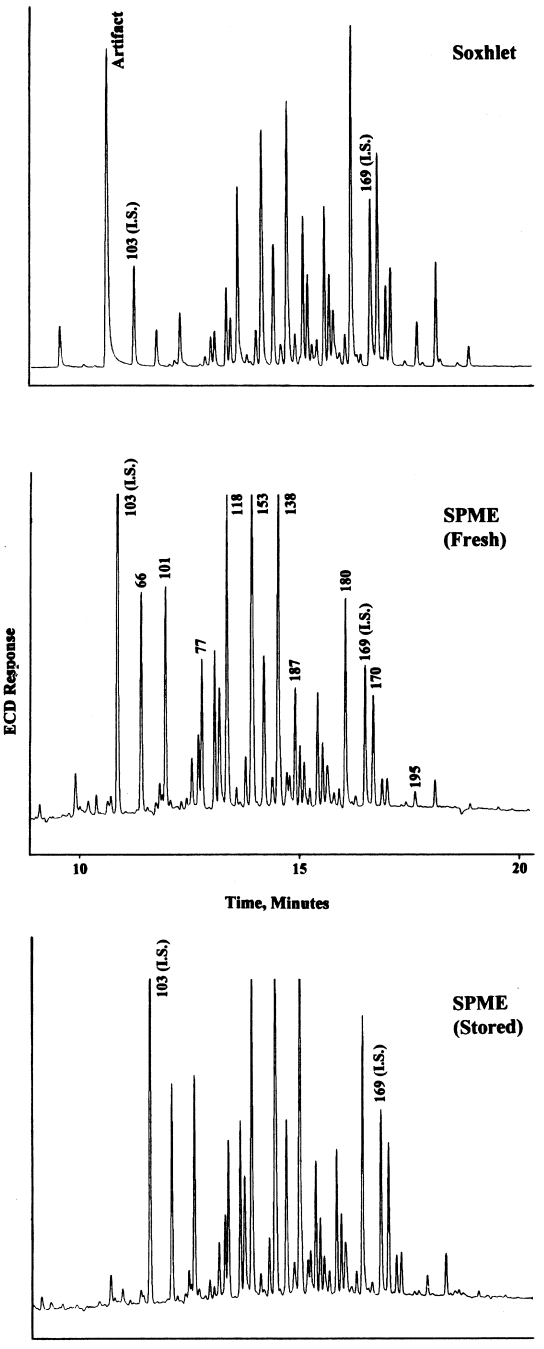

Fig. 1. GC–ECD chromatograms of Soil A extracts. The 18-h Soxhlet extract (top) was concentrated 20-fold prior to analysis. The subcritical water extracts (60 min at 250°C) were analyzed by SPME and GC–ECD either immediately after cooling (middle) or after storing the extract water in a silanized autosampler vial for 24 h (bottom).

PCB congeners. The chromatograms from the Soxhlet extractions and the subcritical water/SPME procedure are similar, except that the water/SPME chromatograms show somewhat higher peaks for the earlier-eluting congeners, and the Soxhlet extract has a large artifact peak which is not present in the water/SPME chromatogram.

3.1. Quantitative determinations

3.1.1. Calibration

The coupled subcritical water extraction/SPME procedure involves two processes: the extraction of the solutes from the soil into the water, and the sorption of the analytes from the extractant water to the SPME sorbent (discussed in more detail below). Both steps are not necessarily exhaustive, and are controlled by the soil/water equilibria and the water/SPME equilibria, respectively. More polar analytes (e.g., aromatic amines) remain in the water phase after the extraction, which allows quantitative calibration by determining the response of the analytes in a standard water solution using SPME as previously described [18]. In contrast, hydrophobic analytes such as PAHs show substantial partitioning back to the soil when the cell is cooled after the extraction. In our previous report, this step was calibrated by adding deuterated PAHs to the sample prior to extraction and assuming that the water/soil and the water/SPME partitioning was the same for the deuterated PAH standards and the PAHs present in the original soil sample. Good quantitative agreement with conventional methods was obtained [18].

Since PCBs show similar subcritical water extraction behavior and SPME partitioning behavior as shown by PAHs [9,11,12,18,19], the analogous use of isotopically-labeled PCB congeners for in-situ calibration would appear feasible. Unfortunately, deuterated PCBs show too much overlap in their mass spectra with their non-deuterated analogs (because of the chlorine isotope pattern). Therefore, in the present study, two PCB congeners (PCB 103 and PCB 169, both of which are not present in commercial Aroclor preparations) were added to the samples prior to extraction in the hope that they could be used to compensate both for the soil/water and the SPME/water partitioning of the various PCB congeners found in the samples.

3.2. Subcritical water/SPME versus Soxhlet extractions

Conditions for the subcritical water extractions were chosen based on previous reports using dynamic (flowing) subcritical water to extract PCBs from soils and sediments [12,15] which demonstrated that 250°C extraction for 60 min gave good recovery of PCBs. Therefore, subcritical water/SPME determinations of PCBs in two soils were performed by placing the loaded cells (including 0.5 g of soil, 3.5 ml of water, and the internal standards) in the GC oven for 60 min at 250°C. After cooling the cell, the extractant water was analyzed using SPME as described above.

The concentrations determined depend heavily on which internal standard is used as demonstrated in Table 1. When the concentrations are based on PCB 103 (2,2′,4,5′,6-pentachlorobiphenyl), the values determined using subcritical water/SPME analysis range from ~130 to 25% (for low- and high-molecular-mass congeners, respectively) of the Soxhlet values. In contrast, the values based on PCB 169 (3,3′,4,4′,5,5′-hexachlorobiphenyl) as the internal standard range from ~450 to 80% (for low- and high-molecular-mass congeners, respectively) compared to Soxhlet. Note that the values calculated based on PCB 169 are ~3-fold higher than those calculated based on PCB 103 as the internal standard for all of the congeners extracted. This demonstrates that the higher-molecular-mass congeners show more partitioning back to the soil (when the extraction cell is cooled) than the lower-molecular-mass congeners, as would be expected based on partitioning experiments discussed below.

As might be expected, the internal standard which is closer in molecular mass to the target PCB congener gives the concentration which corresponds best with the value determined for the same soil based on Soxhlet extraction and conventional GC–ECD analysis. Thus, the lower-molecular-mass congeners (tetra- and pentachlorobiphenyls) generally agree best with the Soxhlet values when their concentrations are based on the pentachlorobiphenyl internal standard PCB 103. Similarly, the higher-

Table 1
Dependence on internal standard of PCB concentrations determined using subcritical water extraction/SPME analysis for soil A

PCB congener	Cl substitution	Soxhlet conc. ($\mu g\ g^{-1}$) (%R.S.D.)[a]	Water/SPME, % recovery (%R.S.D.)[b]	
			vs. PCB 103	vs. PCB 169
66	2,3′,4,4′	0.061 (8)	130 (9)	450 (14)
77	3,3′,4,4′	0.11 (11)	120 (13)	420 (18)
101	2,2′,4,5,5′	0.13 (11)	92 (13)	310 (18)
118	2,3′,4,4′,5	0.26 (13)	82 (9)	280 (14)
138	2,2′,3,4,4′,5′	0.50 (10)	44 (10)	150 (15)
153	2,2′,4,4′,5,5′	0.47 (11)	61 (9)	210 (14)
170	2,2′,3,3′,4,4′,5	0.22 (9)	33 (10)	110 (15)
180	2,2′,3,4,4′,5,5′	0.62 (23)	23 (9)	81 (14)
187	2,2′,3,4′,5,5′,6	0.20 (14)	39 (9)	130 (14)
195	2,2′,3,3′,4,4′,5,6	0.042 (8)	24 (5)	80 (10)

[a]Concentration and relative standard deviations (%R.S.D.) are based on triplicate 18-h Soxhlet extractions and conventional GC–ECD analyses.
[b]% recoveries compared to Soxhlet extraction based on PCB 103 and PCB 169 as internal standards for the subcritical water extraction/SPME determinations.

molecular-mass congeners (hexa-, hepta-, and octachlorobiphenyls) agree best when their concentrations are based on the hexachlorobiphenyl PCB 169 (Table 1).

When the values based on PCB 103 are used for the tetra- and pentachlorobiphenyls, and when those based on PCB 169 are used for the hexa- to octachlorobiphenyls, agreement with the Soxhlet values is reasonably good for both soil samples, i.e., the recoveries for the subcritical water/SPME method are generally within 80 to 130% of the Soxhlet values for both samples (Table 2). In addition, the quantitative reproducibility of the subcritical water/SPME method is relatively good, with typical R.S.D.s ranging from 10 to 15% (similar to those found by replicate Soxhlet extractions, as shown in Table 1).

PCB concentrations are frequently determined as 'total Aroclor' by comparing the total GC–ECD chromatographic peak areas to those of a commercial Aroclor preparation. Table 3 shows the agreement between Soxhlet extraction and the subcritical water/SPME method when the PCB concentrations are determined as total Aroclor 1254 (the Aroclor whose GC–ECD chromatogram most closely resembles the PCBs extracted from these two soils). When the values are calculated based on PCB 103 as the internal standard, agreement is poor-i.e., the resultant values are several times lower than those determined for the Soxhlet extracts. However, when the total Aroclor concentrations are calculated based on PCB 169, the agreement with the Soxhlet values is reasonably good for both soils (Table 3). The better agreement based on PCB 169 as the internal standard would be expected based on the chromatographic results (Fig. 1), since the majority of the total GC–ECD peak areas (>80% for both samples) result from the hexa- and higher-molecular-mass congeners.

3.3. Effect of storing the water extracts

A major goal of this work is to develop a method that can easily be used in the field. By far the most complicated (and least field-portable) instrumentation required for the subcritical water/SPME method is the gas chromatograph. In addition, transporting an ECD system to the field is problematic in many countries because of regulations controlling the radioactive ECD source. Thus, a field survey for PCB contamination might be most easily accomplished by performing the static subcritical water extraction in the field and transporting the autosampler vials containing the water extracts back to the laboratory. Since no organic solvent waste is generated by the subcritical water extraction, and

Table 2
Comparison of Soxhlet extraction and subcritical water extraction/SPME determinations of PCBs in historically-contaminated soils

PCB congener	Cl substitution	PCB concentration, μg g^{-1} ± S.D.[a]		
		Soxhlet	Water/SPME	
			Fresh	Stored 24 h[b]
Soil A				
66	2,3′,4,4′	0.06±0.01	0.08±0.01	0.09±0.01
77	3,3′,4,4′	0.11±0.01	0.14±0.02	0.17±0.02
101	2,2′,4,5,5′	0.13±0.01	0.12±0.02	0.14±0.01
118	2,3′,4,4′,5	0.26±0.03	0.21±0.02	0.26±0.06
138	2,2′,3,4,4′,5′	0.50±0.05	0.75±0.11	0.67±0.12
153	2,2′,4,4′,5,5′	0.47±0.05	0.64±0.06	0.61±0.11
170	2,2′,3,3′,4,4′,5	0.22±0.02	0.25±0.04	0.25±0.03
180	2,2′,3,4,4′,5,5′	0.62±0.14	0.50±0.07	0.47±0.05
187	2,2′,3,4′,5,5′,6	0.20±0.03	0.27±0.04	0.25±0.02
195	2,2′,3,3′,4,4′,5,6	0.042±0.003	0.033±0.003	0.033±0.008
Total[c]		2.6	3.0	2.9
Soil B				
66	2,3′,4,4′	0.061±0.001	0.087±0.004	0.085±0.005
77	3,3′,4,4′	0.079±0.003	0.10±0.01	0.10±0.01
101	2,2′,4,5,5′	0.10±0.01	0.10±0.01	0.10±0.01
118	2,3′,4,4′,5	0.16±0.01	0.14±0.05	0.13±0.05
138	2,2′,3,4,4′,5′	0.29±0.01	0.48±0.01	0.49±0.09
153	2,2′,4,4′,5,5′	0.28±0.003	0.42±0.07	0.43±0.06
170	2,2′,3,3′,4,4′,5	0.13±0.01	0.14±0.02	0.15±0.01
180	2,2′,3,4,4′,5,5′	0.30±0.01	0.28±0.03	0.28±0.01
187	2,2′,3,4′,5,5′,6	0.12±0.003	0.16±0.01	0.16±0.01
195	2,2′,3,3′,4,4′,5,6	0.028±0.004	0.023±0.004	0.021±0.004
Total[c]		1.5	1.9	1.9

[a]Concentrations and relative standard deviations (%R.S.D.) are based on triplicate 18-h Soxhlet extractions, and quadruplicate 60-min subcritical water extraction/SPME determinations for each soil. Concentrations were based on PCB 103 (2,2′,4,5′,6-pentachloro-biphenyl) as the internal standard for all tetra- and pentachlorobiphenyl congeners, and were based on PCB 169 (3,3′,4,4′,5,5′-hexachlorobiphenyl) as the internal standard for all hexa-, hepta-, and octachlorobiphenyl isomers.
[b]Water extracts were analyzed by SPME immediately after subcritical water extraction (fresh) or stored for 24 h in autosampler vials prior to analysis.
[c]Total concentration of PCB congeners listed in the table.

only 2-ml autosampler vials need to be shipped for each sample, extraction and transport of a large number of samples would be practical. However, for this approach to be useful, the SPME analysis of the subcritical water extracts must give the same results after storage as for the fresh extract.

Table 3
Comparison of total PCBs (vs. Aroclor 1254) determined using Soxhlet extraction and subcritical water/SPME analysis

	Soxhlet conc. (μg g^{-1}	Water/SPME conc. (μg g^{-1})			
		Fresh[a]		Stored 24 h	
		vs. 103	vs. 169	vs. 103	vs. 169
Sample A	8.0±1.3	1.7±0.2	8.0±0.5	2.2±0.5	7.4±1.1
Sample B	13.3±1.2	2.6±0.2	12.0±1.6	2.5±0.4	12.1±1.4

[a]Water extracts were analyzed by SPME immediately after subcritical water extraction (fresh) or stored for 24 h in autosampler vials prior to analysis.

To simulate transport from the field, subcritical water extracts of both soils were prepared exactly as before, except that the water extracts were stored in the autosampler vials at room temperature for 24 h before SPME analysis. Quantitative comparisons were then performed using freshly-prepared water standards as before for the fresh samples.

As shown in Tables 2 and 3, the samples which were stored for 24 h before analysis generally showed excellent agreement with samples that were subjected to SPME analysis immediately after subcritical water extraction. These results indicate that shipping samples should be practical for this technique. In addition, the results clearly demonstrate that a large number of samples can be extracted in a batch mode by the static subcritical water technique, then the individual water extracts can be analyzed later as convenient (e.g., by commercially-available GC instrumentation equipped for automated SPME determinations).

3.4. Determination of PCB concentrations in NIST SRM 1939

Additional validation of the method was performed using the NIST PCB-contaminated sediment (SRM 1939) with subcritical water extractions performed for both 15 and 60 min at 250°C. Quantitations were based on PCB 103 for tri-, tetra-, and pentachloro congeners, and PCB 169 for hexa- and heptachloro congeners.

As shown in Table 4, generally good agreement was achieved with the NIST values (based on two sequential 16-h Soxhlet extractions) using the subcritical water extraction/SPME approach with either 15- or 60-min extractions. However, the recoveries were somewhat higher using a 60-min extraction, especially for the higher-molecular-mass congeners. The disagreement between the subcritical water/SPME approach and the NIST values was the worst for PCB 28 and 52 (tri- and tetrachloro-congeners), presumably because the pentachlorobiphenyl PCB 103 internal standard did not accurately reflect the sediment/water and water/SPME partitioning steps as well for these lower-molecular-mass congeners as for the congeners with a more similar molecular mass. Since the remaining congeners are best represented by an internal standard of similar molecular weight, perhaps the accuracy of the results for PCB 28 and 52 could be improved by using a tri- or tetrachloro- congener as an internal standard. The

Table 4
Subcritical water extraction/SPME determination of PCBs in NIST river sediment (SRM 1939)

Congener	Concentration, $\mu g\ g^{-1} \pm$ S.D.[a]		
	NIST	15 min water/SPME	60 min water/SPME
18	3.46±0.08	3.1±0.5	4.1±0.2
28[b]	2.21±0.10	2.9±0.5	4.2±0.6
44[b]	1.07±0.12	0.61±0.06	0.85±0.07
52	4.48±0.14	1.5±0.2	2.2±0.4
66	0.93±0.01	1.3±0.1	1.4±0.04
101	0.82±0.01	0.46±0.08	0.50±0.04
118	0.51±0.01	0.44±0.09	0.36±0.13
128	0.10±0.01	0.11±0.07	0.19±0.10
138	0.57±0.01	0.38±0.09	0.44±0.10
170	0.11±0.01	0.07±0.05	0.13±0.06
180	0.16±0.01	0.09±0.04	0.15±0.04
187	0.18±0.01	0.16±0.06	0.30±0.06
Total[c]	14.6	11.1	14.8

[a]NIST concentrations are based on two sequential 16-h Soxhlet extractions. Subcritical water extraction/SPME values are based on triplicate extractions and analyses using either 15- or 60-min subcritical water extraction followed by a 15-min SPME sorption step.
[b]Concentration values certified by NIST. All other values are reported by NIST as method-dependent informational values.
[c]Total concentrations of the PCB congeners reported in this table.

results shown in Table 4 also indicate that the errors in concentrations tend to average out. For example, the total concentration of the PCB congeners reported by NIST is 14.6 $\mu g\ g^{-1}$ (Table 4), while the total concentrations determined by the subcritical water/SPME method is 11.1 and 14.8 $\mu g\ g^{-1}$ for the 15- and 60-min extractions, respectively.

3.5. Soil/water and water/SPME partitioning

SPME determinations of organics in water samples is based on an equilibrium (rather than exhaustive) extraction between the SPME sorbent phase and the water sample. Earlier reports have shown that unknown concentrations of PCBs in water can be reliably determined by calibrating the SPME and GC steps using water-based PCB standards as long as proper precautions to avoid carryover on stir bars and the SPME sorbent are used [19]. The sensitivity of the technique will, of course, be based on the fraction of PCB molecules which partition to the fiber sorbent during the SPME step. Based on sequential extractions of a single water sample, ~20 to 50% of the PCBs molecules in the 1.8 ml water samples partition to the 7-μm fiber during the SPME step, and are thus introduced into the GC for analysis. These experimental results agree with calculated values based on published SPME/water distribution coefficients (K_{dv}) of the PCB congeners used in the present study [20].

In addition to the water/SPME partitioning, the subcritical water extraction and cooling step in a closed vial adds the possibility that PCBs which are solvated during the extraction step may repartition to the soil upon cooling to room temperature. To determine the extent of repartitioning that may occur, 0.5-g samples of Soil 'A' were each extracted in triplicate (60 min at 250°C), the cell was cooled, and the quantity of the individual PCB congeners in the soil, water, and cell rinsings were determined as described above. These partitioning studies demonstrated that ~1–3% of each congener was found in the water extract after cooling, and the remainder was found in the soil or sediment residue (no significant quantities of PCBs were found in the cell rinsings). As would be expected based on their lower solubility in water [21], the higher-molecular-mass PCBs remained ~1–2% in the water, while the lower-molecular-mass congeners remained ~3% in the water.

In summary, even though the subcritical water/SPME method includes two partitioning steps, these steps can be accounted for by proper selection of internal standards. As discussed above, the SPME step extracts ~20 to 50% of the total quantity of each PCB congener from the extractant water, and 1 to 3% of extracted PCBs remain in the water solution after cooling for SPME sorption. Therefore, the entire procedure results in ~1% of the PCB molecules present on the soil to ultimately be transferred to the GC injection port. Thus, the use of a 0.5-g sample for subcritical water/SPME determinations will yield the same ultimate analytical sensitivity as would be obtained by performing a Soxhlet extraction on a 5-g sample, concentrating the extract to 1 ml, and injecting 1 μl of the concentrated extract by on-column injection.

3.6. Practical characteristics of the method

The ultimate goal of these studies is to develop very simple, field-portable, and inexpensive approaches for the determination of organic pollutants on soils and sediments. Subcritical water extraction/SPME has several attractive characteristics to meet this goal. First, the apparatus are simple and inexpensive. Our laboratory-built extraction cells are ca. $6 (US) each, and typically are used for more than 20 extractions. The cost of the extraction fluid (HPLC-grade water) is negligible, and no organic solvent waste is generated. Each SPME fiber costs about $40 US, and is typically used for ~40 determinations. The extraction system itself is reliable and extremely easy to operate, simply because there is no pump, no flow control devices (e.g., such as the restrictors needed for SFE), and no collection device. In contrast to organic solvent extractions, no sample drying steps are required since water is the extraction fluid. Pressure safety is an issue, but as long as the static extraction cells ALWAYS contain sufficient gas headspace, the maximum pressure possible is the steam/liquid equilibrium, which is only 40 bar for the 250°C extraction used in this study.

Finally, the method is reasonably fast, since only

15- to 60-min extraction times are required, followed by ~5 min for cooling and transferring the extractant water to an autosampler vial, 15 min for SPME sorption, and 20 min for GC analysis. Thus, with a 15-min subcritical water extraction, data is available are approximately one hour from sample collection.

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