SUBTASK 1.20 – DEVELOPMENT OF METHODS TO DETERMINE THE ENVIRONMENTAL AVAILABILITY OF PAHs, PCBs, AND PETROLEUM HYDROCARBONS

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ABSTRACT

Three methods to determine the bioavailability of polycyclic aromatic hydrocarbons were modified and developed for application to polychlorinated biphenyls (PCBs). Water/XAD desorption and selective supercritical fluid extraction methods were developed to determine the rapidly-released fraction of PCBs from contaminated soils and sediments. A method to determine PCBs in sediment pore water based on solid-phase microextraction was also developed that is capable of determining low pg/mL concentrations with water samples as small as 1.5 mL.

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EXECUTIVE SUMMARY

Current regulatory practices are based on the default assumption that 100% of an organic pollutant on soil or sediment is available to environmental processes such as water transport and uptake by organisms. However, there is a large amount of recent evidence in the literature that demonstrates that hydrophobic organic pollutants become less available to the environment as the pollutants age on soils and sediments. The default assumption of 100% availability results in unrealistically low cleanup levels for contaminated soils and sediments, while the amount of mitigation necessary to protect the environment may be much less than current regulatory models dictate.

At present, analytical methods focus on total concentrations of organic pollutants, rather than the concentrations of pollutants that are available to cause environmental effects. We have recently developed selective analytical methods that are capable of determining the actual concentrations of polycyclic aromatic hydrocarbons (PAHs) on soils and sediments that are available for environmental processes such as desorption into water and uptake in organisms. These methods, including mild supercritical fluid extraction (SFE) and solid-phase microextraction (SPME), have been demonstrated to be useful tools to determine concentrations of PAHs in soils and sediments that actually are of environmental importance (1–6). Based on the success of these studies, we have been working to extend these methods to other hydrophobic pollutants. Although our initial focus included petroleum alkanes, because of the advice and many requests from potential commercial clients and the U.S. Navy, the focus of our investigations was shifted to polychlorinated biphenyls (PCBs). In these investigations, we adapted and tested two methods for determining the available fraction of PCBs from sediments and soil, including water/XAD desorption and selective SFE. The SPME method for ultratrace determination of PAHs in sediment pore water was automated. In addition, the Energy & Environmental Research Center developed and optimized the SPME method for determining PCBs in sediment pore water, including the testing of several SPME sorbent phases to achieve the best sensitivity (signal to noise) with mass spectral and electron capture detectors.

REFERENCES

1. Kreitinger, J.P.; Neuhauser, E.F.; Doherty, F.G.; Hawthorne, S.B. Evidence for Greatly Reduced Toxicity of PAHs to Hyalella Azteca in Sediments from Manufactured Gas Plant Sites. *Environ. Toxicol. Chem.* (accepted for publication).

2. U.S. Environmental Protection Agency. *Procedures for the Derivation of ESBs for the Protection of Benthic Organisms: PAH Mixtures*. EPA/600/R-02/013; Office of Research and Development: Washington, DC, 2003.

3. Hawthorne, S.B.; Poppendieck, D.G.; Grabanski, C.B.; Loehr, R.C. PAH Release During Water Desorption, Supercritical Carbon Dioxide Extraction, and Field Bioremediation. *Environ. Sci. Technol.* **2001**, *35*, 4577–4583.

4. Hawthorne, S.B.; Poppendieck, D.G.; Grabanski, C.B.; Loehr, R.C. Comparing PAH Availability from Manufactured Gas Plant Soils and Sediments with Chemical and Biological Tests: Part I-PAH Release During Water Desorption and Supercritical Carbon Dioxide Extraction. *Environ. Sci. Technol.* **2002**, *36*, 4795–4803.

5. Hawthorne, S.B.; Lanno, R.; Kreitinger, J.P. Reduction in Acute Toxicity of Soils to Terrestrial Oligochaetes Following the Removal of “Bioavailable” PAHs with Mild Supercritical Carbon Dioxide Extraction. *Environ. Toxicol. Chem.* **2005**, *24*, 1893–1895.

6. Hawthorne, S.B.; Grabanski, C.B.; Miller, D.J.; Kreitinger, J.P. Solid-Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values. *Environ. Sci. Technol.* **2005**, *39*, 2795–2803.

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INTRODUCTION AND BACKGROUND

There is increasing weight of evidence that hydrophobic organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and petroleum hydrocarbons, become less available to organisms as the pollutants age on soils and sediments. In the past, potential environmental effects of such pollutants were based on the total concentrations of these pollutants, rather than the concentrations of these pollutants that are actually available to cause environmental effects. The awareness that environmentally relevant concentrations are often much lower than the total pollutant concentrations is starting to be considered by regulatory agencies in the criteria for site regulation and mitigation. However, there is a critical need for rapid analytical tools that are capable of determining the chemical and biological availability of such pollutants on soils and sediments.

Recently, the Energy & Environmental Research Center (EERC) developed a method to determine the bioavailability of PAHs on soils and sediments that is based on a mild extraction with supercritical carbon dioxide. This supercritical fluid extraction (SFE) method developed for PAHs under commercial and U.S. Department of Energy (DOE) Joint Venture support is now under serious consideration by regulators in New York state and California for use in developing site remediation criteria. To the best of our knowledge, this would be the very first use of a lab bioavailability test in the United States for supporting contaminated site mitigation requirements by government regulators. For some sites, this could reduce the quantity of soil "trucked and dumped" to a tiny fraction of the quantity required by present regulatory practices that are based on total PAH concentrations rather than available PAH concentrations.

Most recently, the EERC investigated the use of both SFE and sediment pore (interstitial) water PAH concentrations to predict the toxicity of PAHs to the aquatic organism, *Hyalella azteca* (1). The determination of pore water PAH concentrations required the development of an ultratrace method based on solid-phase microextraction (SPME). This method is capable of measuring individual PAH concentrations as low as pg/mL (as required by the U.S. Environmental Protection Agency [EPA's] regulatory narcosis model [2]) using samples as small as 1.5 mL. In these studies, both SFE and SPME methods developed at the EERC correctly predicted that 6 out of the 35 test sediments would be toxic. In contrast, the EPA's model incorrectly predicted that 32 out of the 35 sediments would be toxic. Clearly, both the SFE and SPME methods are large improvements over the existing EPA narcosis model (2) in measuring the PAH concentrations that are actually important to protecting the environment.

These initial sediment toxicity studies have been receiving increased attention from several commercial companies who have legacy PAH-contaminated sites. Our SFE and SPME methods were used in 2005 and 2006 to determine the bioavailability of PAHs on six different sites involving more than 200 sediment and pore water samples. Although the data reduction on theses sites is in progress, the results show that the SPME and SFE methods improve the prediction of toxicity for PAH-contaminated sediments.

During 2005 and 2006, multiple discussions were held with industry representatives including those from the oil and gas industry, the steel industry, the aluminum industry, environmental consulting groups, and academic colleagues, and there was complete agreement that PCBs are the most important focus for future development and application of our SFE and SPME methods. Therefore, the EERC has subsequently developed selective SFE and water/XAD desorption methods to determine the rapidly released fraction of PCBs from soils and sediments. Both of these methods are depletive, which means that they measure the total mass of available PCBs in a soil or sediment sample. In contrast, SPME measurement of sediment pore water concentrations is nondepletive, i.e., it measures the equilibrium concentrations of PCBs in the pore water. Both depletive and nondepletive methods have previously been shown to increase the ability to predict toxicity of hydrophobic pollutants (1, 3–6).

EXPERIMENTAL

Selective SFE and Water/XAD methods

SFE was performed using an ISCO model 210 extractor as described in References 3 and 4. One to 4 gram soil or sediment samples were extracted using carbon dioxide at a flow rate of 1.0 mL (measured as compressed carbon dioxide at the pump). Extracted PCBs were collected by bubbling the carbon dioxide effluent through ca. 15 mL of acetone. Two PCB internal standards that are not found in commercial PCB formulations were added (congeners 103 and 169, which are 2,2',4,5',6-pentachlorobiphenyl and 3,3',4,4',5,5' hexachlorobiphenyl, respectively), and the extracts were analyzed by capillary gas chromatography (GC) using either mass spectrometry (MS) or electron capture detector (ECD) detection. All chromatographic separations were performed with a 60 m, 250 µm i.d. HP-5 MS column (or equivalent). PCB quantitations and identifications were based on authentic PCB standard solutions.

Because the SFE conditions (temperature and pressure) that best mimic bioavailability are best based on comparison with biological tests (which were beyond the scope of the present project), we developed a “stair-step” set of SFE conditions with increasingly strong SFE conditions to show various levels of bioavailability that can be compared to biological tests applied to the same samples in the future. These conditions (in order of the mildest to strongest extraction conditions) were 200 bar 50°C, 400 bar 100°C, and 400 bar 150°C. Each of these SFE conditions was applied sequentially to a sample. Finally, the extracted residue was subjected to 18 hours of Soxhlet extraction to recover any PCBs not extracted by the sequential SFE procedure.

The water/XAD method previously reported for PAHs (3, 4) was performed in an analogous manner for PCBs. In short, 1 gram of sediment was mixed with 20 mL of water and 2 grams of clean XAD sorbent resin. After mixing for several days (typically 12 days), the XAD and sediment samples were recovered separately from the water and extracted overnight with a

1:1 mix of acetone/hexane. The same internal standards and analysis methods were used to determine PCB concentrations as described above for the SFE experiments.

SPME Pore Water PCB Measurements

The major effort in these developmental investigations was to optimize each step of the method in relationship to subsequent steps, with a target of obtaining the best sensitivity (signal to noise) from small (1.5 mL) samples. Our previous SPME method for PAHs (6) can obtain sensitivities as good as (or even better than) competitive methods, but our SPME method has the very important advantage that only 1.5 mL pore water samples are required, while other approaches require a liter of water to get the same detection limits that we obtain from 1.5 mL samples. This advantage is crucial to widespread use of pore water methods, since conventional approaches require that ca. 1-gallon buckets of each sediment be collected, homogenized, and shipped to the laboratory, while our SPME method routinely operates with 200 mL sediment samples. The advantages for field site surveys requiring pore water determinations on 20 to 40 sediments are substantial.

Development of the SPME method for PCBs included the selection of the sorbent fiber that 1) yielded the best collection efficiencies of the PCBs in the water samples, 2) had the least carryover between highly contaminated samples, 3) had the least artifacts that interfered with the GC detector, and 4) maintained sensitivity over many uses. Therefore, all commercially available SPME sorbent fibers that are applicable for hydrophobic organics (such as PCBs) were evaluated for these characteristics. Fiber materials included polydimethylsiloxane (PDMS) in both 7 and 100 µm film-thicknesses, 60 µm PDMS/divinylbenzene (DVB), 65 µm Carbowax/ DVB, and 30 µm DVB/Carboxen/PDMS.

The fibers were evaluated using both MS and ECD detectors, since artifacts that affected detector response would be different. In addition to comparing ECD and MS detection using conventional electron impact (EI) ionization, the relative sensitivity of positive ion EI and negative ion chemical ionization (CI) were compared, again to determine the best signal-to-noise ratio it was possible to obtain for the range of PCB congeners typically found in environmental samples.

RESULTS AND DISCUSSION

Selective SFE and Water/XAD methods

The relative solvent strength of supercritical carbon dioxide for hydrophobic organics such as PCBs can be controlled over a broad range by the temperature and pressure used for the extraction. Therefore, by sequentially increasing the solvent strength of the extraction conditions, the EERC hoped to be able to determine a range of PCB availability from easily available, to very tightly bound to the sediment surface. In our original work with PAHs, we had a biological endpoint (bioremediation results from a field study) which was used to optimize the ability of selective SFE to measure the bioavailable fraction of PAHs. In the present study of PCBs, no biological endpoint was available, so multiple selective SFE conditions were used to generate a stair-step plot of different degrees of loosely bound to tightly bound PCBs. Future studies with biological endpoints can then be compared to the stair-step extractions to find the SFE conditions that best mimic the test biological system. The individual SFE conditions included (in order of the mildest to strongest extraction conditions) 200 bar 50°C (for the most loosely bound PCBs), 400 bar 100°C, and 400 bar 150°C (for the most tightly bound PCBs).

Each of these SFE conditions were applied sequentially to different sediment samples to yield extraction profiles like those shown for a harbor sediment (National Institute of Standards and Technology [NIST] standard reference material 1939) shown in Figure 1. Each PCB congener shows selective behavior with the fraction of rapidly available molecules (those extracted at the mildest condition between 0 and 60 min) ranging from ca. 20% to 60%, and the remaining molecules being extracted at the moderate (60 to 120 min) and strongest (120 to 180 min) SFE conditions, results that indicate wide ranges of bioavailability for different fractions of each PCB congener. It is also interesting to note that, similar to many PAH-contaminated sediments, the lower molecular weight PCBs show more difficult extraction (indicating tighter binding to the sediment matrix and less bioavailability) than the higher molecular weight congeners. Since the solubility of the lower molecular weight PCBs is higher in supercritical carbon dioxide than the solubility of higher molecular weight PCBs, the fact that higher molecular weight PCBs extract at the milder SFE conditions clearly demonstrates that the lower molecular weight PCBs are more tightly bound (and therefore less bioavailable) than higher molecular weight PCBs.

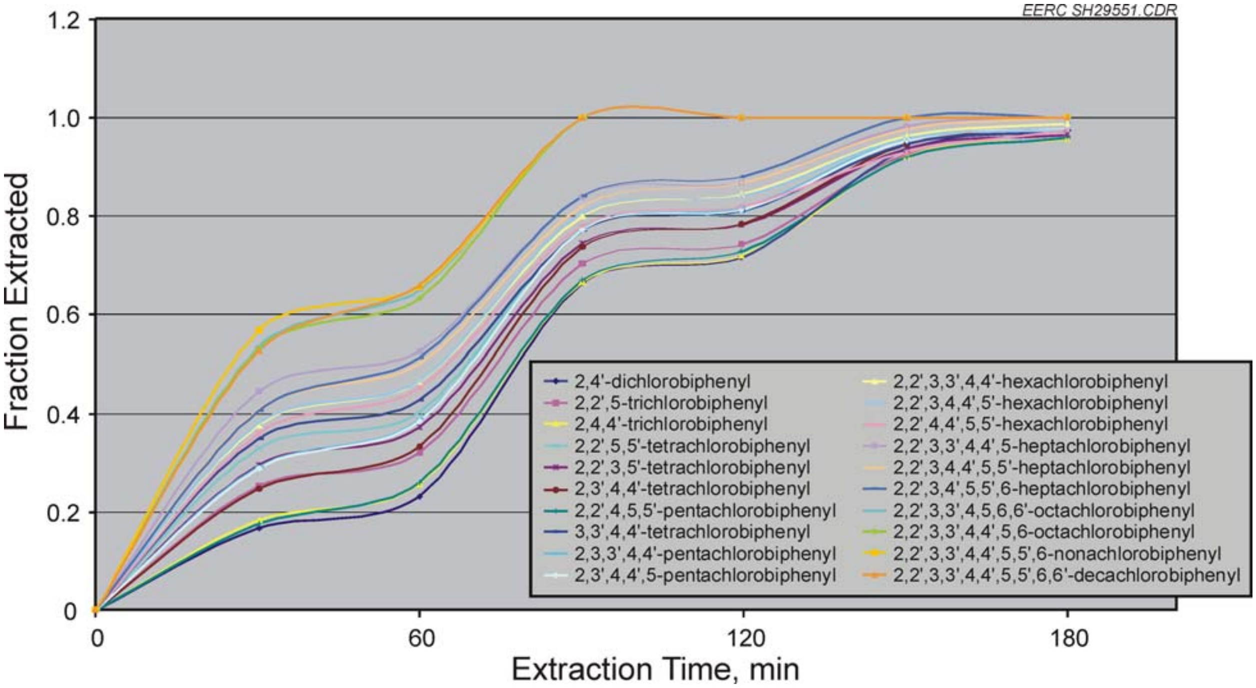

Figure 1. Selective stair-step SFE of PCBs from sediment (NIST SRM 1939). The solvent strength was increased every 60 min as described in the text.

Our implementation of the water/XAD method for measuring the bioavailable fractions was first verified by determining the available fractions for PAHs on samples previously measured by the developer of the technique, Professor Ray Loehr (University of Texas, Austin) (3, 4). Results from Professor Loehr's lab and from the EERC showed good agreement for each PAH for two soils with different degrees of rapidly available fractions, thus demonstrating successful implementation of the technique. Next, the EERC applied the same approach for several PCB-contaminated soils and sediments. Table 1 shows the rapidly available fraction for representative congeners from four soils and sediments, and the results clearly demonstrate the different degrees of bioavailability that can exist for PCBs on different soils and sediments.

SPME Pore Water PCB Measurements

During this study, the EERC had several discussions with representatives from the utilities, aluminum, steel, and petroleum industries as well as with EPA scientists that focused on the need for a simple and practical method for measuring PCBs in sediment pore water that had the characteristics of the SPME method we previously developed for PAHs, i.e., low detection limits with small sample volumes and applicable to routine determinations of pore water PCBs in a large number of sediment samples. Therefore, a major effort in this project was to optimize SPME measurement of pore water PCBs, while maintaining the sensitivity and robustness of our PAH method. As noted in the experimental section, this included selection of the optimal SPME stationary phase (both for it's ability to efficiently extract PCBs from water as well as providing low background for the subsequent chromatographic analyses) as well as determining the best gas chromatographic detector for PCBs, both in terms of sensitivity and lack of interferences.

Selection of Fiber Stationary Phase

The five SPME stationary phases listed in the Experimental section were first tested with a solution of 20 PCB congeners (dichloro to decachloro) on both ECD and MS detectors. These initial experiments showed that the 65 µm Carbowax/DVB and 30 µm DVB/Carboxen/PDMS phases were unsuited for PCB analyses because of low extraction efficiencies and/or unreasonably high background peaks in the ECD and MS chromatograms. The remaining three fibers were more extensively tested, and found to have reasonable extraction efficiencies, with ca. 30% to 70% of each PCB congener being extracted in 30 min from a 1.5 mL water sample. (Note that the extraction efficiency does not need to be 100% for quantitative analyses by the SPME method, since the use of suitable internal standards in each water sample accounts for varying SPME extraction efficiencies as described earlier for our PAH method in Reference 6.) Based on extraction efficiencies, similarly low detection limits could be obtained from either of the three fibers. However, the 60 µm PDMS/DVB showed higher background peaks (especially for the ECD detector), and thus was not as useful for PCB determinations as the 7 or 100 µm PDMS fibers. Overall, with the 30 min sorption period used, the 7 µm fiber was slightly more sensitive for higher molecular weight PCBs than the 100 µm fiber, but the opposite case was true for lower molecular weight PCB congeners. However, the 100 µm fiber had slightly higher background with both MS and ECD detectors. In addition, our previous experience with PAHs showed that carryover from highly contaminated water samples was significantly worse with the 100 µm fiber than the 7 µm fiber, and we expected that the same would be true for PCBs. Therefore, we chose the 7 µm PDMS fiber as the optimal SPME sorbent. This result is also

Table 1. Rapidly Desorbing (“Available”) Fractions of Individual PCB Congeners Determined by the Water/XAD Desorption Method

	Sediment “A”			Sediment “B”			Soil “C”			Sediment “D”		
	Total Mean Conc., ng/g	Mean Fast Fraction	Std. Dev. Fast Fraction	Total Mean Conc., ng/g	Mean Fast Fraction	Std. Dev. Fast Fraction	Total Mean Conc., ng/g	Mean Fast Fraction	Std. Dev. Fast Fraction	Total Mean Conc., ng/g	Mean Fast Fraction	Std. Dev. Fast Fraction
2,4'-dichlorobiphenyl	ND[1]	ND	ND	2332	0.21	0.02	ND	ND	ND	13	0.51	0.08
2,2',5-trichlorobiphenyl	ND	ND	ND	747	0.39	0.03	ND	ND	ND	29	0.71	0.04
2,4,4'-trichlorobiphenyl	ND	ND	ND	971	0.17	0.03	ND	ND	ND	53	0.48	0.03
2,2',5,5'-tetrachlorobiphenyl	ND	ND	ND	1335	0.39	0.04	54	0.77	0.06	61	0.48	0.10
2,2',3,5'-tetrachlorobiphenyl	ND	ND	ND	322	0.35	0.03	8	0.78	0.03	59	0.36	0.07
2,3',4,4'-tetrachlorobiphenyl	ND	ND	ND	320	0.21	0.04	57	0.82	0.04	39	0.46	0.04
2,2',4,5,5'-pentachlorobiphenyl	11	0.72	0.06	188	0.10	0.02	212	0.90	0.02	9	0.31	0.07
3,3',4,4'-tetrachlorobiphenyl	193	0.90	0.03	360	0.36	0.04	1844	0.80	0.05	39	0.64	0.05
2,3,3',4,4'-pentachlorobiphenyl	88	0.87	0.03	221	0.22	0.04	713	0.74	0.05	34	0.42	0.05
2,3',4,4',5-pentachlorobiphenyl	22	0.94	0.01	116	0.21	0.03	182	0.73	0.04	11	0.48	0.02
2,2',3,3',4,4'-hexachlorobiphenyl	1000	0.90	0.03	129	0.35	0.05	8345	0.76	0.05	36	0.43	0.03
2,2',3,4,4',5'-hexachlorobiphenyl	986	0.90	0.03	232	0.33	0.05	8503	0.76	0.05	44	0.37	0.05
2,2',4,4',5,5'-hexachlorobiphenyl	63	0.89	0.03	40	0.29	0.02	510	0.75	0.04	ND	ND	ND
2,2',3,3',4,4',5-heptachlorobiphenyl	514	0.88	0.04	82	0.27	0.03	4276	0.68	0.05	12	0.35	0.06
2,2',3,4,4',5,5'-heptachlorobiphenyl	921	0.85	0.06	87	0.28	0.06	8851	0.64	0.06	22	0.30	0.05
2,2',3,4',5,5',6-heptachlorobiphenyl	491	0.84	0.06	46	0.23	0.03	4634	0.64	0.06	10	0.28	0.03
2,2',3,3',4,5,6,6'-octachlorobiphenyl	884	0.49	0.16	NR	NR	NR	561	0.50	0.04	ND	ND	ND
2,2',3,3',4,4',5,6-octachlorobiphenyl	1079	0.49	0.13	NR	NR	NR	643	0.49	0.03	ND	ND	ND
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	ND	ND	ND	ND	ND	ND	259	0.34	0.06	ND	ND	ND

[1] Not detected.

[2] Not reported.

fortuitous, since the same fiber was the best for our PAH method, and we plan to combine the two methods in the future so that PAHs and PCBs can both be determined by a single analysis in pore water samples.

Selection of Gas Chromatographic Detectors

Because of its selectivity, MS is the detector of choice when complex environmental samples are analyzed. For halogenated organics like PCBs, there are two useful ways in which to operate the MS detector, i.e., conventional MS (which uses EI ionization and positive ion detection and is used for virtually all standard GC/MS methods for organic compounds) and negative ion chemical ionization (NICI) MS. For highly halogenated compounds, NICI is more sensitive than conventional positive ion EI, but the opposite is true for less halogenated compounds. Therefore, we compared the sensitivity of both modes of ionization with PCBs ranging from dichlorobiphenyl to decachlorobiphenyl congeners. In essence, NICI and positive ion EI had similar sensitivities for the tetrachloro congeners, but NICI was much more sensitive for the more highly chlorinated congeners. Unfortunately, the sensitivity of NICI for lower molecular weight PCBs was increasingly poor as the degree of chlorination dropped. Thus the detection limits for NICI for lower molecular weight PCB congeners were orders of magnitude poorer than positive ion EI, although NICI was more sensitive for the higher molecular weight PCBs. For pore water determinations of PCBs, we decided that conventional positive ion EI was the method of choice for four reasons: 1) the sensitivity is similar for all PCB congeners, making calibration and routine operation more robust and simpler; 2) most PCBs found in pore water will be the lower molecular weight congeners, for which NICI has much poorer sensitivity; 3) positive ion EI has a greater range of detector linearity than NICI; and 4) many more labs are familiar with positive ion EI than NICI. However, it should be noted that, if the goal for a particular sediment pore water is to get ultratrace determinations of the more highly chlorinated PCB congeners, than NICI would be the ionization method of choice.

The second decision in selecting detectors required comparing MS and ECD. ECD is more sensitive than conventional MS (using EI ionization and positive ion detection) for PCBs. Typically, injected quantities of 100 fg can be detected by ECD, while ca. 1 pg is needed for MS detection in the conventional positive ion mode. However, as discussed above, the SPME stationary phase (as well as sediment pore water samples) can yield chromatographic peaks that interfere with the detection of PCB peaks in the chromatogram. Unfortunately, this was found to be a significant problem for the ECD detector even with the best of the fibers (the 7 µm PDMS fiber), presumably a result of PDMS bleed from the sorbent fiber. Because of these interferences, the final detection limits for MS and ECD were similar. Therefore, since MS is a much more selective detector than ECD, MS was chosen as the detector of choice for the SPME pore water PCB method.

Typical results of the SPME method for pore water from three sediments are shown in Table 2. Reproducibility of the method is reasonably good for a trace method at moderate concentration waters, but becomes poorer as the detection limit of ca. 1 pg/mL is approached. However, the reproducibility of the method and its detection limits using only 1.5 mL water samples easily rivals conventional methods that are typically dependent upon liter samples of pore water.

Table 2. Triplicate Determinations of PCBs in 1.5 mL Samples of Pore Water Using SPME

	Pore Water "A" Concentration, pg/mL		Pore Water "B" Concentration, pg/mL	
	Mean	SD	Mean	SD
2,4'-dichlorobiphenyl	3.1	1.9	1.9	0.9
2,2',5-trichlorobiphenyl	1.1	0.5	2.4	1.2
2,4,4'-trichlorobiphenyl	3.9	0.5	3.9	1.2
2,2',3,5'-tetrachlorobiphenyl	1.9	0.2	9.9	0.7
2,2',5,5'-tetrachlorobiphenyl	0.7	0.3	1.4	0.2
2,3',4,4'-tetrachlorobiphenyl	1.5	0.0	4.4	0.6
3,3',4,4'-tetrachlorobiphenyl	1.9	0.3	4.7	1.0
2,2',4,5,5'-pentachlorobiphenyl	23.6	2.3	57.3	6.5
2,3,3',4,4'-pentachlorobiphenyl	4.5	0.3	8.7	3.1
2,3',4,4',5-pentachlorobiphenyl	7.6	1.3	6.5	2.5
2,2',3,3',4,4'-hexachlorobiphenyl	25.5	2.4	49.0	1.0
2,2',3,4,4',5'-hexachlorobiphenyl	23.8	1.9	49.1	2.5
2,2',3,3',4,4',5-heptachlorobiphenyl	12.8	2.7	15.2	1.6
2,2',3,4,4',5,5'-heptachlorobiphenyl	31.7	1.6	48.9	16.5
2,2',3,4',5,5',6-heptachlorobiphenyl	21.2	9.2	19.4	1.9

CONCLUSIONS

Methods were developed and tested for three different bioavailability assays for PCBs including two depletive methods (water/XAD desorption and selective SFE) and one equilibrium (nondepletive) method to measure sediment pore water concentrations of PCBs using SPME. During these investigations, we have received multiple requests from industry and government clients to develop the pore water method to have the same capabilities as our PAH method. It has been very clear from several discussions that both commercial and governmental personnel think that development of a robust and reliable method for determining pore water PCBs is the most important topic of this project. Therefore, the development of the SPME method for PCBs was a major focus of these investigations. This method is now sufficiently ready to begin field trials, which are tentatively planned in conjunction with RETEC Corporation and the U.S. Navy to begin in late April 2006. We anticipate that any further refinement of the method in response to the realities of and results from large-scale field sampling studies will be performed under separate funding in conjunction with those studies.

REFERENCES

1. Kreitinger, J.P.; Neuhauser, E.F.; Doherty, F.G.; Hawthorne, S.B. Evidence for Greatly Reduced Toxicity of PAHs to Hyalella Azteca in Sediments from Manufactured Gas Plant Sites. *Environ. Toxicol. Chem.* (accepted for publication).

2. U.S. Environmental Protection Agency. *Procedures for the Derivation of ESBs for the Protection of Benthic Organisms: PAH Mixtures*. EPA/600/R-02/013; Office of Research and Development: Washington, DC, 2003.

3. Hawthorne, S.B.; Poppendieck, D.G.; Grabanski, C.B.; Loehr, R.C. PAH Release During Water Desorption, Supercritical Carbon Dioxide Extraction, and Field Bioremediation. *Environ. Sci. Technol.* **2001**, *35*, 4577–4583.

4. Hawthorne, S.B.; Poppendieck, D.G.; Grabanski, C.B.; Loehr, R.C. Comparing PAH Availability from Manufactured Gas Plant Soils and Sediments with Chemical and Biological Tests: Part I-PAH Release During Water Desorption and Supercritical Carbon Dioxide Extraction. *Environ. Sci. Technol.* **2002**, *36*, 4795–4803.

5. Hawthorne, S.B.; Lanno, R.; Kreitinger, J.P. Reduction in Acute Toxicity of Soils to Terrestrial Oligochaetes Following the Removal of “Bioavailable” PAHs with Mild Supercritical Carbon Dioxide Extraction. *Environ. Toxicol. Chem.* **2005**, *24*, 1893–1895.

6. Hawthorne, S.B.; Grabanski, C.B.; Miller, D.J.; Kreitinger, J.P. Solid-Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values. *Environ. Sci. Technol.* **2005**, *39*, 2795–2803.