Measurement of Drinking Water Contaminants by Solid Phase Microextraction Initially Quantified in Source Water Samples by the USGS

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Two adsorbent solid phase microextraction (SPME) fibers, 70 μm Carbowax divinylbenzene (CW/DVB) and 65 μm polydimethylsiloxane divinylbenzene (PDMS/DVB), were selected for the analysis of several target analytes (phenols, phosphates, phthalates, polycyclic aromatic hydrocarbons, and chlorinated pesticides) identified by the USGS in surface waters. Detection limits for standards ranged from 0.1 to 1 ng/mL for the CW/DVB fiber and 0.1 to 2 ng/mL for the PDMS/DVB fiber for 20 of the analytes. The remaining analytes were not extracted because their polarity precluded their partition to the solid phase of the SPME fiber. Groundwater and treated water samples collected from wells in northern New Jersey were then sampled for the USGS analytes by the SPME method as well as a modified version of EPA 525.5 using C-18 bonded solid phase extraction columns. Nine of the USGS analytes—bisphenol A, bis(2-ethylhexyl) phthalate, butylated hydroxytoluene, butlyated hydroxyanisole, diethyltoulamide, diethyl phthalate, bis(2-ethylhexyl) adipate, 1,4-dichlorobenzene, and triphenyl phosphate—were detected in groundwater samples using the CW/DVB fiber.

Introduction

There are a number of contaminants that show adverse human health effects and can enter the drinking water supply but do not have regulatory limits. Between 1999 and 2000 the United States Geological Survey (USGS) analyzed surface water samples from 139 streams in 30 states in the continental United States for such compounds (*1*). The study targeted 95 analytes that are not considered streamwater contaminants and do not have drinking water guidelines established. The analytes were classified into four different groups: vetinary and human antibiotics, prescription and nonprescription drugs, steroids and hormones, and other wastewater related compounds, which, for the most part, were plasticizers, antioxidants, or insecticides.

Five different analytical methods were selected by the USGS to analyze the samples. Antibiotics were analyzed by two different solid phase extraction−liquid chromatography/mass spectrometry electron spray ionization methods (SPE-LC/MS ESI(+)) (*2, 3*). Prescription and nonprescription drugs were analyzed using an SPE−high performance liquid chromatography (HPLC) method. Steroids and hormones were first derivatized with a silanizing agent, and then they were extracted by liquid–liquid extraction (LLE) and analyzed by gas chromatography/mass spectrometry (GC/MS). Other wastewater contaminants were also analyzed by LLE-GC/MS but without derivatization.

To date no study has been orchestrated that analyzes water samples for the "other waste water related compounds" grouped as a whole.

Plasticizers are additives to plastics designed to increase their durability and flexibility. Since plasticizers are not chemically bound to the polymer they can leach from the matrix into the environment (*4–6*). Plasticizers detected in U.S. streams by the USGS include but are not limited to the following: bis(2-ethylhexyl) adipate, bis(2-ethylhexyl) phthalate, bisphenol A, and diethyl phthalate (*1*). Phthalates are ubiquitous environmental contaminants that possess possible estrogenic properties (*6, 7*). Bisphenol A is a plasticizer so widely used that virtually everyone in the industrialized world has been exposed to it (*8*). Antioxidants, such as butylated hydroxytoluene (BHT) and butylated hydroxylanisole (BHA), are used primarily to preserve the freshness of foods. While the parent compounds do not pose adverse human health effects, the metabolites of BHT and BHA are possible cancer initiators and damage cellular DNA (*8, 9*).

Solid phase microextraction (SPME)-GC/ITMS and SPE-GC/ITMS methods were developed and optimized to determine semivolatile organic pollutants (SVOCs) in groundwater and treated drinking water in New Jersey (*10–12*). In this paper, the ability of these two methods to recover the analytes the USGS detected in surface waters was analyzed. Only the analytes from the USGS study quantified by gas chromatography without derivatization were targeted. Table 1 lists the compounds, by compound class, along with their molecular weight and octanol–water partition coefficient (log K_{ow}) values. The log K_{ow} values were calculated using the atom fragment method and are included because it drives the partitioning of the analytes to the sorbent phase of the SPME fiber (*11, 13*).

Materials and Methods

Consumables. Sodium chloride (Certified ACS), HPLC grade water, ethyl acetate (pesticide grade), methylene chloride (Optima), methanol (GC Resolv grade), hexane (pesticide grade), and acetone (HPLC grade) were obtained from Fisher Scientific (Farilawn, NJ). Hydrochloric acid (HCl, 6.0 N) was purchased from Laboratory Chem Inc. (Pittsburgh, PA).

The SPME fibers, 70 μm Carbowax/divinylbenzene (CW/DVB) and 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), and the SPE columns (Supelclean ENVI-18, 6.0 mL, 1.0 g) were purchased from Supelco (Bellefonte, PA).

Standards for acetophenone, bis(2-ethylhexyl) adipate, chlorpyrifos, tetrachloroethene, butylated hydroxytoluene, diazinon, methyl parathion, *N,N*-diethyl-*m*-toluamide, naphthalene, anthracene, benzo(*a*)pyrene, bis(2-ethylhexyl) phthalate, carbaryl, diethyl phthalate, fluoranthene, 4-methylphenol, phenanthrene, phenol, pyrene, and triphenyl

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TABLE 1. USGS Unregulated Surface Water Analytes, by Compound Class, Analyzed for in This Study[a]

analyte	molecular weight (amu)	log K_{ow}	compound class
1,4-dichlorobenzene	147	3.28	insect repellant
carbaryl	201.22	2.35	carbamate insecticide
dieldrin	409.78	5.45	chlorinated insecticide
cis-chlordane	380.91	6.26	chlorinated insecticide
lindane	290.83	4.26	chlorinated insecticide
acetophenone	120.15	1.67	ketone fragrance
N,N-diethyltoluamide	191.27	2.26	amide insect repellant
anthracene	178.23	4.35	PAH
fluoranthene	202.25	4.93	PAH
naphthalene	128.17	3.17	PAH
phenanthrene	178.23	4.35	PAH
pyrene	202.25	4.93	PAH
benzo(*a*) pyrene	252.31	6.11	PAH
butylated hydroxytoluene	220.35	5.03	phenolic food additive
bisphenol A	228.29	3.64	phenolic plasticizer
p-cresol (4-methylphenol)	108.14	2.06	phenolic disinfectant
phenol	94.11	1.51	phenolic disinfectant
chlorpyrifos	350.59	4.66	organophosphorous insecticide
diazinon	304.35	3.86	organophosphorous insecticide
methyl parathion	263.21	2.75	organophosphorous insecticide
triphenyl phosphate	326.28	4.7	organophosphorous insecticide
bis(2-ethylhexyl) adipate	370.57	8.12	phthalate plasticizer
diethyl phthalate	390.56	2.65	phthalate plasticizer
bis(2-ethylhexyl) phthalate	222.24	8.39	phthalate plasticizer
tetrachloroethylene	165.83	2.97	solvent

[a] The log K_{ow} values are calculated using the atom fragment method outlined in ref *13*. PAH refers to polycyclic aromatic hydrocarbon, USGS stands for United States Geological Survey, and log K_{ow} is the log of the octanol–water partition coefficient.

phosphate were purchased individually from Ultra Scientific (North Kingstown, RI). Bisphenol A was purchased from Cerilliant (Round Rock, TX). Standards for γ-BHC (also known as lindane), dieldrin, and *cis*-chlordane were purchased from Supelco (Bellefonte, PA) as EPA 505/525 Pesticides Mix A.

SPME Stock Solution. The stock solution was created by transferring an aliquot of all the standards, using a gas chromatographic syringe, into a 1 L amber glass I-Chem bottle with known values for impurities (Nalge Nunc International, Rockwook, TN). The solution was then brought up to 1 L using a fixed volume of HPLC grade water for a final concentration of 100 ng/mL. All analytes proved to be stable in water at these concentrations. The stock was used throughout the SPME experiments. To test the ability of the fibers to recover the analytes as well as measure detection limits, calibration curves were created. The standards for the calibration curve were created using the stock solution, HPLC grade water, and 20 mL SPME glass auto sampling vials (Varian, Microliter Analytical Supplies Inc., 22 × 75 mm, for LEAP/CTC). The final volume of each standard was 15 mL. The vials were crimped and capped using 20 mm magnetic crimp caps (Varian, Microliter Analytical Supplies Inc., Teflon/white Silicone Septa). NaCl was used to increase the salt concentration of the samples to 10% to increase recoveries by lowering the analytes aqueous solubility (*14, 15*). The calibration curve concentrations, in water, were 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 40, and 50 ng/mL.

To test the repeatability of the method, three 20 ng/mL samples ($N = 3$) were extracted by each fiber. The coefficient of variance (CV) was then calculated. The coefficient of variance was defined as the standard deviation, based on three replicate extractions, of the area under curve for each analyte, divided by the average area under curve with the result being multiplied by 100%. A CV of 20% or below was defined as acceptable variance.

SPME Extraction Conditions. A Varian CP-3800 gas chromatograph coupled to a Saturn 2200 GC/MS ion trap mass spectrometer (Walnut Creek, CA) was used for analysis. A CTC Analytics Combi PAL injector with SPME agitator attachment (Zwingen, Switzerland) was used for agitation and heating of samples as well as injection into the GC/MS. A SPME fiber holder for Leap Combi PAL autosampler was used to hold the SPME fiber during extraction and injection.

A septum programmable split/splitless injector was used in the splitless mode. The gas chromatograph was equipped with a 30 m 5% phenyl/95% dimethylsilicone fused silica DB-XLB capillary column with a 0.25 mm ID and 0.25 μm film thickness (JW Scientific, Folsom, CA). Helium was used as the carrier gas with a flow rate of 33 cm/s.

The Combi PAL injection/sample preparation program for direct injection was as follows: extraction time of 50 min, desorption time of 5 min, preinjection time of 1 min, incubation temperature of 45 °C, agitation speed of 500 rpm, vial penetration 31.0 mm, and injection penetration of 54.0 mm. All parameters were the same for headspace except the incubation temperature and vial penetration depth, which were 55 °C and 25.0 mm, respectively.

The column oven program was as follows: inject at 60 °C and hold in splitless mode for 5 min, 60–130 at 7 °C/min, 130–200 at 5 °C/min, 200–260 at 6 °C/min, 260–310 at 7.5 °C/min, and hold for 9.33 min for a final run time of 55 min.

The ion trap mass spectrometer (ITMS) was operated in EI positive mode and tuned with perfluorotributlyamine (FC-43). The electron multiplier voltage, emission current, multiplier offset, and modulation amplitude were set at 1800–2100 V, 40 μA, +/− 200, and 7.5 V, respectively. The transfer line and ion trap manifold were 270 and 225 °C, respectively. The mass range scanned was from 45 to 450 m/z at 0.66 s/scan. Data acquisition was started at 6.8 min. Data were acquired using Saturn GC/MS workstation Version 5.51 Software.

Sample Collection. Fifty-eight groundwater and treated water samples were collected, using 1 L amber glass I-Chem bottles with known values for impurities (Nalge Nunc International, Rockwook, TN), from 31 wells in the Piedmont and Highlands regions of Northern New Jersey. One water blank was analyzed for every 10 water samples, to test for impurities and background levels. For each well two raw and two treated water samples were collected so replicates could be run. Samples were stored at 4 °C until time for analysis. Samples were analyzed by SPME or loaded onto SPE columns within 48 h of sample collection to limit analyte breakdown or volatilization.

SPME Analysis of Samples. Of the 1L water sample, 15 mL were transferred to SPME auto sampler vials for direct SPME and an additional 12.5 mL to a separate vial for headspace SPME analysis. Since no sample enrichment occurs, analytes had the same concentration in the water

samples as in the allotted SPME sample volume. The same vials were used for headspace analysis as direct analysis, but the crimp caps used for headspace analysis were specifically designed for sampling headspace (Varian, Microliter Analytical Supplies Inc., 5 mm opening, Teflon/white silicone septa).

Analysis of Samples Using Modified EPA 525.2. SPE columns were conditioned using an optimized EPA 525.2 method. The following solvent scheme was used to condition the columns: 4 mL of ethyl acetate (pesticide grade), 4 mL of methylene chloride (Optima), 2 mL of 1:1 ethyl acetate: methylene chloride, 2 mL of 3:2 acetone (HPLC grade):hexane (pesticide grade), 6 mL of methanol (GC Resolv grade), and 6 mL of HPLC grade water. The columns were not allowed to dry once methanol was added.

Water samples were loaded using a Simon Varistaltic pump (Manostat, Co., Barrington, IL) and a continuous flow (CF) liner system. After the samples were loaded, the SPE columns were stored at −20 °C, for no longer than 72 h, until elution. Analytes were eluted from the columns using a Visiprep-DL solid phase extraction vacuum manifold (Supelco, Bellefonte, PA) and the following solvent scheme: 4 mL of ethyl acetate, 4 mL of methylene chloride, 2 mL of 1:1 ethyl acetate:methylene chloride, 2 mL of 3:2 acetone:hexane, and 2 mL of methanol. The eluate was concentrated, under vacuum, until a final volume of approximately 1 mL was obtained. The samples were then transferred to GC auto sampler vials (National Scientific Company, Duluth, GA). One microliter of sample was injected.

The injector temperature program was as follows: 100 °C held for 0.5 min, increased at 150 °C/min to 280 °C and held for 20.31 min. The GC oven program for liquid injections was as follows: inject at 35 °C and hold for 4 min, 35–130 at 7 °C/min, 130–200 at 5 °C/min, 200–260 at 6 °C/min, and 260–340 at 8 °C/min with a hold time of 8.43 min for a final runtime of 60 min. The mass spectrometric parameters were the same as for the SPME experiment except that the emission current and multiplier offset were set at 10 μA and +/− 0 V, respectively. Data acquisition was started at 10 min.

Results and Discussion

Detection Limits. Table 2 lists the linear measurement range of the method that includes method detection limits for each fiber as well as the reporting limits published by the USGS. The method detection limit for this work was defined as the lowest analyte concentration measured that maintained linearly of the calibration curve after all sample preparation steps had been completed. The method detection limit is the lowest value of the linear measurement range in the column. Linearity was defined as the concentration range over which the calibration curve for the analytes had a linear response, as measured by R^2 values greater than 0.8.

A concentration was calculated assuming linearity if an R^2 greater than 0.8 was obtained from the calibration curve, based on extraction of nine concentration levels (0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 40, and 50 ng/mL). The USGS reported levels are determined per each analytical method they used. Reported levels were determined by the USGS by either instrument response, calculating the detection limit, or by obtaining the data from the previously published procedures (*1*). The method detection limits (MDLs) for the CW/DVB fiber were at 1 ng/mL or lower for all compounds except carbaryl. Carbaryl, a carbamate, is thermally labile making analysis by gas chromatography difficult (*16, 17*). Carbaryl is one of five carbamates that the SPME-GC/ITMS method does remove effectively from the sample (*11*). The carbamates that are recovered are those with the highest octanol–water partition coefficients (log K_{ow}) illustrating a relationship between SPME and log K_{ow} (*18*). The higher carbaryl detection limit may arise from it being thermally labile. Chlorinated pesticides, dieldrin, *cis*-chlordane, and lindane, had the lowest MDLs (0.1 ng/mL) of all the analyte classes. Data demonstrated that the CW/DVB fiber is the best commercially available fiber for extracting organochlorine pesticides from water (*11, 18*).

TABLE 2. Linear Measurement Range Including Method Detection Limits (MDLs) Obtained for Two Different SPME Fibers Along with USGS "Reported Limits" (RLs)[a]

analyte	CW/DVB (ng/mL)	PDMS/DVB (ng/mL)	USGS (ng/mL)
1,4-dichlorobenzene	0.5–50	0.1–50	30
carbaryl	10–50	1–20	60
dieldrin	0.1–50	1–40	80
cis-chlordane	0.1–50	1–40	40
lindane	0.1–50	1–40	50
acetophenone	nd	nd	150
N,N-diethyltoluamide	1–10	1–20	40
anthracene	0.5–50	1–50	50
fluoranthene	0.5–50	1–50	30
naphthalene	0.5–50	0.2–50	20
phenanthrene	0.5–50	1–50	60
pyrene	0.5–50	1–50	30
benzo(*a*)pyrene	0.5–50	40–50	50
butylated hydroxytoluene	1–20	1–10	80
bisphenol A	1–20	1	90
p-cresol (4-methylphenol)	0.5–50	0.2–1	40
phenol	nd	nd	250
chlorpyrifos	1–40	1–40	20
diazinon	1–40	1–50	30
methyl parathion	nd	nd	60
triphenyl phosphate	1–40	1–40	100
bis(2-ethylhexyl) adipate	1–40	1–40	2000
diethyl phthalate	0.5–50	0.2–50	250
bis(2-ethylhexyl) phthalate	0.5–50	1–50	2500
tetrachloroethylene	nd	nd	30

[a] MDLs are defined as the lowest concentration measured linearly. A linear response range is defined as the concentration range over which the calibration curve has an R_2 value greater than 0.8. RLs are defined in ref *1* as either an instrument response, a calculated detection limit, or data obtained from the previously published procedures. An "nd" entry represents an analyte that was not detected. CW/DVB stands for Carbowax/divinylbenzene, PDMS/DVB stands for polydimethylsiloxane/divinylbenzene, and USGS stands for United States Geological Survey.

The CW/DVB fiber did not extract four (acetophenone, methyl parathion, phenol, and tetrachloroethylene) of the 25 analytes examined. The recovery of phenol was poor because it eluted with air and water impurities before 6.80 min (*18*). The mass spectrometer was started at 6.80 min to lessen the effect of air and water on the filament and to prolong the filaments lifetime. Acetophenone was probably not recovered because of its hydrophillicity, log K_{ow} value of 1.67, and its low molecular weight, 120.5. Data has shown that the CW/DVB fiber has molecular weight and log K_{ow} based operational ranges. The ability of the fiber to extract analytes with molecular weights or log K_{ow} values above or below this operational range decreases the further you get from the range (*18*). Tetrachloroethylene is a volatile organic compound (VOC). The SPME method was optimized for semivolatile compounds so it is probable that one or more of the analytical parameters were not optimal for the extraction of this volatile analyte. It is unknown why methyl parathion was not seen as an analyte in the chromatogram since it is not thermally labile. Methyl parathion is an organophosphorous pesticide; a class previously not exam-

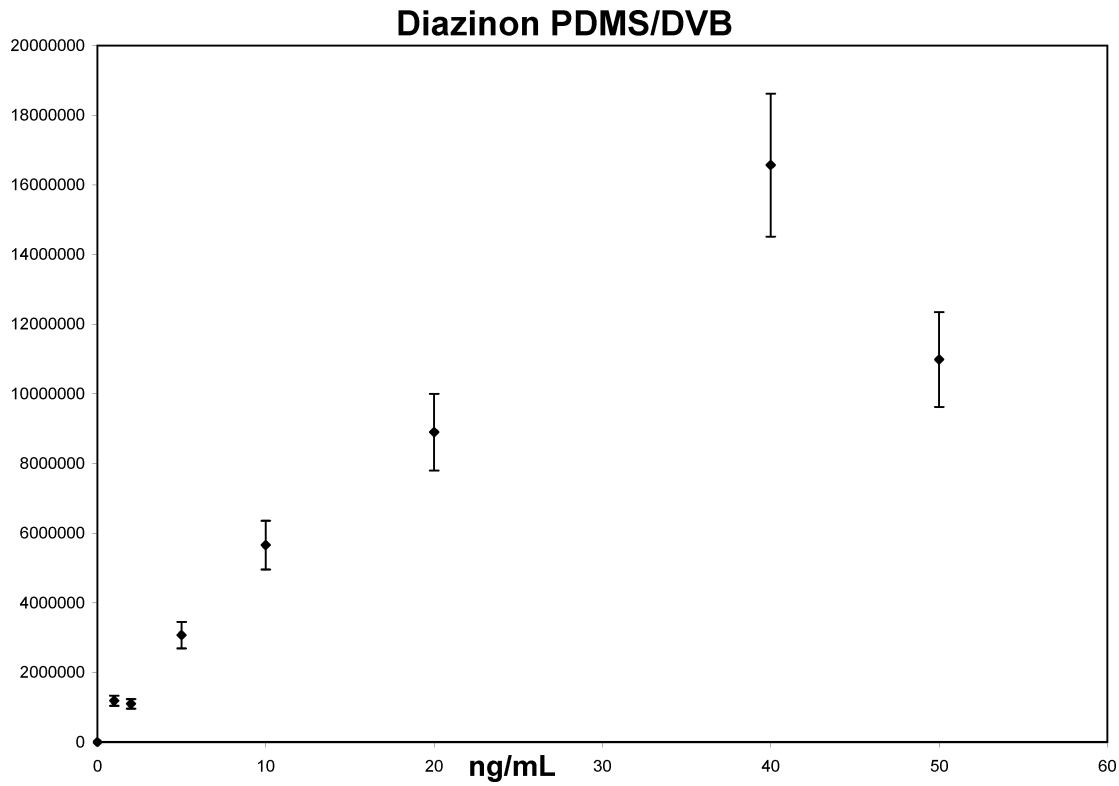

FIGURE 1. Calibration curve for diazinon with extraction by PDMS/DVB fiber. The nonlinear curve shape at higher concentrations indicates competition effects (*21*). PDMS/DVB stands for polydimethylsiloxane/divinyl benzene.

ined using this method. Of the organophosphorous pesticides examined, methyl parathion has the lowest molecular weight and log K_{ow} value. It is possible that the thresholds for this compound class are above the values for methyl parathion.

MDLs ranged from 0.1 to 2 ng/mL for 20 of the 25 analytes using the PDMS/DVB fiber. Four analytes—carbaryl, diethyl phthalate, 1,4-dichlorobenzene, and naphthalene—had lower MDLs, 2 ng/mL, 0.2 ng/mL, 0.1 ng/mL, and 0.3 ng/mL, respectively, when the PDMS/DVB fiber was used, compared to the CW/DVB fiber. The CW/DVB fiber had MDLs of 10 ng/mL, 0.5 ng/mL, 0.5 ng/mL, and 0.5 ng/mL, respectively, for these compounds. Naphthalene and 1,4-dichlorobenzene are nonpolar and should be more efficiently extracted by the nonpolar PDMS phase of the fiber than by Carbowax, an extremely polar phase less likely to extract nonpolar analytes. Benzo(*a*)pyrene (B(*a*)P) had the highest MDL, 40 ng/mL. Previous studies demonstrate that higher molecular weight PAHs (MW > 229), such as B(*a*)P, require extraction times over 60 h long in order to reach equilibrium (*19, 20*). The extraction time for direct immersion SPME was 50 min long, not long enough for the fiber to reach equilibrium with B(*a*)P. An extraction time of over 50 min was not used in this study because it would be too long and impractical. The PDMS/DVB fiber was also not able to extract acetophenone, phenol, methyl parathion, and tetrachloroethylene from water, possibly for the same reason.

The MDLs for both SPME fibers were considerably lower than those published by the USGS. The most dramatic effects were seen for phthalates. Using the CW/DVB fiber, detection limits were roughly 2000 times lower for bis(2-ethylhexyl) adipate, 2500 times lower for diethyl phthalate and 25000 times lower for bis(2-ethylhexyl) phthalate. The SPME method was an ideal alternative for the analysis of these compounds due to its increased sensitivity.

The longest linear range (0.1−50 ng/mL) using the CW/DVB fiber was demonstrated for chlorinated pesticides. Previously, the CW/DVB fiber was demonstrated to be the most sensitive fiber for extraction of organochlorine pesticides (*11, 18*). Ten of the remaining 16 analytes were linear in the response range of 0.5−50 ng/mL. Although the fiber was able to detect below 0.5 ng/mL, the calibration curve becomes nonlinear at these concentrations. Diethyltoulamide had the smallest linear response range, 1−10 ng/mL.

Diethyl phthalate (0.2−50 ng/mL), 1,4-dichlorobenzene (0.1−50 ng/mL), and naphthalene (0.2−50 ng/mL) had the longest linear ranges using the PDMS/DVB fiber. The shortest linear response range was for 4-methylphenol, 0.2−1 ng/mL. Eight other analytes, bis(2-ethylhexyl) adipate, diethyltoulamide, lindane, *cis*-chlordane, dieldrin, triphenyl phosphate, diazinon, and chlorpyrifos, also became nonlinear at higher concentrations. This was most likely the result of competition effects. At higher concentrations, the adsorption sites on the fiber are saturated and thus cannot extract any more analyte (*21*). It is at this point that analytes compete for the adsorption sites on the fiber. This competition for adsorption sites can occur not only when multiple analytes are present but also when one analyte or concomitant compound is present in high concentrations. The calibration curve for diazinon illustrating competition effects at higher concentrations, along with error bars, is shown in Figure 1.

PDMS/DVB is an adsorbent fiber, and at higher concentrations—if competition for adsorption sites is occurring—the calibration curve will take on the curvilinear shape, illustrated in Figure 1. The effect of analyte competition for the fibers adsorption sites has been previously studied for compound classes other than those studied here (*21*). In order to obtain a linear response for these analytes, the sample would have to be diluted.

The CW/DVB fiber had longer linear ranges than the PDMS/DVB fiber for 14 of the 21 analytes. This was probably because the phases of the CW/DVB fiber are more polar than the PDMS/DVB fibers phases. Both fibers have a DVB phase, but the Carbowax phase is extremely polar, while the PDMS phase is nonpolar. The analytes are mostly polar in nature and were extracted more efficiently by the polar Carbowax phase. The results demonstrated that the CW/

TABLE 3. Coefficient of Variance (CV, %) for Analytes Based on Three Replicate Injections[a]

analyte	CW/DVB CV (%)	PDMS/DVB CV (%)
1,4-dichlorobenzene	5.3	4.6
carbaryl	6.3	nd
dieldrin	8.7	9.6
cis-chlordane	10.4	16.5
α-lindane	2.9	24.1
N,*N*-diethyltoluamide	9.6	13.9
anthracene	4.9	6.3
fluoranthene	2.5	12.0
naphthalene	3.0	2.3
phenanthrene	3.2	3.6
pyrene	4.1	2.7
benzo(*a*)pyrene	33.1	nd
butylated hydroxytoluene	11.8	25.9
bisphenol A	8.3	58.3
p-cresol (4-methylphenol)	8.9	36.3
diazinon	12.4	18.4
chlorpyrifos	8.4	29.2
triphenyl phosphate	18.2	17.0
bis(2-ethylhexyl) adipate	41.4	35.9
diethyl phthalate	10.1	27.2
bis(2-ethylhexyl) phthalate	24.2	7.5
pooled CV	35.4	67.5

[a] An "nd" entry indicates that the analyte was not detected. Included is the pooled coefficient of variance (CV) for each fiber. CW/DVB stands for Carbowax/divinylbenzene, and PDMS/DVB stands for polydimethylsiloxane/divinylbenzene.

DVB fiber was more sensitive and had a greater affinity for these analytes over a broader concentration range.

Fiber Repeatability. To test the repeatability of the method, three 20 ng/mL ($N = 3$) spikes were analyzed by each fiber. Table 3 shows the coefficient of variance (CV) for each compound along with the pooled coefficient of variance for each fiber. An acceptable CV was defined as less than 20%.

Three of the 21 analytes recovered had CVs higher than 20% for the CW/DVB fiber: B(*a*)P, bis(2-ethylhexyl) adipate, and bis(2-ethylhexyl) phthalate. B(*a*)P had a CV of 33.1%, possibly because it did not reach equilibrium with the SPME fiber (*19, 20*). For the higher molecular weight PAHs to reach equilibrium, the fiber must be sampling the solution for 60 h. To avoid analyte breakdown, the field samples were analyzed within 48 h of collection. In order to process the samples in the required time limit, the repeatability of the higher molecular weight PAHs was sacrificed. A general rule of thumb is that the extraction time should be similar in length to the GC run time (*22*). Bis(2-ethylhexyl) phthalate and bis(2-ethylhexyl) adipate have molecular weights of 390.56 and 370.57, respectively. These analytes also have large log K_{ow} values, 8.12 for bis(2-ethylhexyl) adipate, and 8.39 for bis(2-ethylhexyl) phthalate. In another study, it was determined that the response of the CW/DVB fiber to phthalates falls off due in part to the analytes being too hydrophobic and having a high molecular weight (*18*). This decrease in the efficiency of the CW/DVB fiber to extract these hydrophobic analytes led to higher method variability.

The CW/DVB fiber method had, on average, the lowest CVs, all under 5.0%, for the PAHs, excluding B(*a*)P. This shows that despite the CW/DVB fiber being extremely polar and the PAHs being nonpolar the compounds have a high affinity for the fiber.

Seven of the analytes—bis(2-ethylhexyl) adipate, diethyl phthalate, BHT, bisphenol A, 4-methylphenol, lindane, and chlorpyrifos—had CVs over 20% using the PDMS/DVB fiber. The phenolic compounds had the highest CVs, ranging from 25.9 to 58.3%. The PDMS/DVB fiber is not as polar as the CW/DVB fiber so it did not have the affinity for polar phenols that the Carbowax phase did. The lack of affinity may prevent the compounds from reaching equilibrium with the fiber, increasing the variance. Excluding benzo(*a*)pyrene, which the fiber did not extract at 20 ng/mL, the PAHs had the lowest CVs with this method, between 2.3 and 12.0%.

The CW/DVB fiber had lower CVs on average than the PDMS/DVB fiber as well as lower MDLs and longer linear ranges. The CW/DVB fiber also had a lower pooled coefficient of variance, 35.4%, than the PDMS/DVB fiber, 67.5%. This was probably because the Carbowax phase of the CW/DVB fiber was more polar than the PDMS phase of the PDMS/DVB fiber and thus better suited for extraction of polar analytes. The results demonstrated that the CW/DVB fiber was more sensitive and more reproducible for the USGS analytes and thus was selected for the field test.

Groundwater Samples. Fifty-eight groundwater and treated water samples were collected from the Highlands and Piedmont regions of northern New Jersey. The samples were analyzed by both direct and headspace SPME-GC/ITMS, using the CW/DVB fiber. Table 4 lists the USGS analytes detected by each method and the number of samples they were measured in.

Since the majority of these analytes are ubiquitous and can appear in blanks, 10% of water samples were water blanks. These values were then blank subtracted from the treated and raw water samples collected. Analytical artifacts associated with this method have been discussed in much greater detail in Stiles et al. (*10*).

The most prevalent analyte measured by SPME was bis(2-ethylhexyl) phthalate. It was detected, after blank subtraction, in 39 out of 58 samples by direct SPME and 28 samples by

TABLE 4. Analytes Detected in New Jersey Groundwater and Treated Water Samples[a]

		direct SPME		HS SPME		EPA 525.2	
analyte	use	raw	treated	raw	treated	raw	treated
butylated hydroxyanisole	antioxidant	19	12	9	4	8	1
butylated hydroxytoluene	antioxidant	10	6	9	9	14	1
bis(2-ethylhexyl) phthalate	plasticizer	22	17	15	13	2	1
diethyl phthalate	plasticizer	9	8	2	2	3	1
bisphenol A	plasticizer	8	4	3	4	2	0
di-(2-ethylhexyl) adipate	plasticizer	2	4	0	0	0	0
diethyltoulamide	insect repellant	0	0	0	0	1	1
1,4-dichlorobenzene	deodorizer	0	1	0	0	0	0
triphenyl phosphate	plasticizer	0	1	0	0	0	0

[a] A total of 58 well water samples were collected. The numbers in the entries represent the number of samples that contained each analyte. SPME stands for solid phase microextraction, HS stands for head space, and EPA stands for Environmental Protection Agency.

HS-SPME. The results showed that bis(2-ethylhexyl) phthalate was less likely to partition into the headspace than the aqueous phase. Bis(2-ethylhexyl) phthalate is a plasticizer and a ubiquitous environmental contaminant, so it was not surprising that it was detected in so many samples (*5*). The next most prominent analytes detected were BHT and BHA. BHA was one of the USGS analytes amenable to gas chromatography without derivatization but was not quantified because a standard could not be found. The other widely detected analytes—diethyl phthalate, bisphenol A, and bis(2-ethylhexyl) adipate—are all plasticizers. Of the analytes examined in this study, the results demonstrated that the most prominent analytes to contaminate both surface and groundwaters are plasticizers. This is not surprising considering the large production levels these compounds see and their chemical nature as additives and not reagents. Triphenyl phosphate and 1,4-dichlorbenzene were each found in one sample. It is possible that other USGS analytes are amenable to the SPME method but not measured in this study. In addition there were no breakdown products observed for analytes not targeted by the method.

Three analytes—triphenyl phosphate, 1,4-dichlorobenzene, and bis(2-ethylhexyl) adipate—were detected by SPME but not by SPE. More analytes were extracted using the SPME method than the SPE method, demonstrating that these analytes were more amenable to SPME. The exception to this was BHT. BHT was detected in 37 samples using SPE, while direct and HS-SPME detected the analyte in 16 and 18 samples, respectively.

The one analyte exclusively extracted using SPE but not by SPME was diethyltoulamide (DEET). DEET was not recovered by the SPME method because of the small linear response range (1–10 ng/mL) the CW/DVB fiber had for the analyte. DEET was recovered in one raw and one treated water sample but also in the blank. The samples were blank subtracted. It is unknown why DEET, an insect repellant, would appear in a blank.

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