Extraction of Petroleum Hydrocarbons from Soil by Mechanical Shaking

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A shaking extraction method for petroleum hydrocarbons in soil was developed and compared to Soxhlet extraction. Soxhlet extraction is an EPA-approved method for volatile and semivolatile organic contaminants from solid materials, but it has many disadvantages including long extraction periods and potential loss of volatile compounds. When field-moist soils are used, variability in subsamples is higher, and the extraction of hydrocarbons with a nonpolar solvent may be less efficient. A shaking method was designed to fill the need for simpler and more efficient extraction of petroleum hydrocarbons from soil. A systematic study of extraction conditions was performed for various soil types, soil weights, solvents, extraction times, and extraction cycles. The results were compared to those for Soxhlet extraction. Shaking 1 g of soil with a sequence of three 10-mL aliquots of dichloromethane or acetone was found to be equivalent to Soxhlet extraction for total petroleum hydrocarbons and polycyclic aromatic hydrocarbons. Shaking with acetone was more consistent than all other methods for the extraction of specific compounds from aged, contaminated soil. The shaking method appears to be applicable to a wide range of soil types and petroleum contaminants but should be compared to Soxhlet extraction for new conditions.

Introduction

Petroleum is a common soil contaminant from a variety of sources, including leaking fuel storage tanks, crude oil spills, and production waste products. Chemical analysis plays a crucial role in evaluating contaminated soils, and solvent extraction is a critical step. A rapid and reliable extraction method is needed to accurately analyze large numbers of soil samples, including moist soils.

Soxhlet extraction, an accepted protocol for extraction of semivolatile and nonvolatile organic compounds from soil matrices, has been outlined in detail by the United States Environmental Protection Agency (EPA) Method 3540A (*1*). However, Soxhlet extraction has several potential disadvantages: (a) the soil sample is static during the extraction process, which may limit contact between solvent and soil micropores; (b) Soxhlet extraction requires up to 24 h of extraction and specialized apparatus, which may be prohibitive for large numbers of samples; (c) large volumes of solvent are used; (d) high moisture content in soil samples may increase variability in the analysis because of the difficulty

in obtaining representative subsamples and the poor interaction between nonpolar solvents and hydrated soil surfaces.

Several alternatives to Soxhlet extraction of soils have been developed, and some have become accepted protocols. Sonication (EPA Method 3550/3550B) may be used interchangeably with Soxhlet and has been tested for soils (*2*−*5*). This method consumes large quantities of solvent (similar to Soxhlet), is labor intensive, and requires specialty equipment. Eckert-Tilotta et al. (*6*) used a supercritical fluid extraction (SFE) method to extract total petroleum hydrocarbons in soil. This method is more rapid than Soxhlet and eliminates the use of organic solvents. Unfortunately, SFE instrumentation is expensive and, when used to extract natural soil samples, may be subject to low accuracy and high variability (*7*). Accelerated solvent extraction, involving higher temperatures and pressures, was found to be generally equivalent to Soxhlet extraction (*8*) but also requires specialized, expensive equipment.

A batch (shaking) extraction method (*9*) was compared to Soxhlet and sonication. The method consisted of three sequential shaking extractions with 1:1 (v/v) methanol: dichloromethane; the first extraction was 3 days, and the final two extractions were 18 h. The extraction methods were found to be equivalent in the removal of PAHs and surrogate spikes. Shorter extraction times were not tested.

The overall objective of this study was to evaluate shaking methods for the extraction of volatile and semivolatile petroleum hydrocarbons from solids such as soils and sediments. If several shaking cycles are employed, fresh solvent contacts the sample for each iteration of the sequence. Shaking ensures more complete contact with the solid phase, thus increasing extraction efficiency. The potential advantages of this protocol are the use of simple and common equipment, reduced volumes of organic solvents, extracting many samples simultaneously, and cumulative extraction periods of less than 3 h. Subobjectives were to (a) test several organic solvents with a range of properties to evaluate their ability to extract petroleum contaminants from soil; (b) determine if shaking with several consecutive aliquots of fresh solvent would increase extraction efficiency; (c) examine the impact of aging and soil moisture on extraction of various petroleum contaminants for both field-aged soils and spiked uncontaminated soils; and (d) determine the best shaking protocol for total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), aliphatic hydrocarbons, branched alkanes, and other compounds of interest. Concentrations extracted by shaking were compared to those obtained by standard Soxhlet extraction.

Experimental Section

Procedures and materials used in each experiment are listed, followed by details specific to the given experiments.

Soil Samples. Uncontaminated soils that were amended with petroleum compounds were obtained in the vicinity of Manhattan, KS. For the test of solvents on soils with different textures, soils were chosen based on sand and clay content. Sarpy soil (mixed, mesic, Typic Udipsamments) was very sandy; Eudora (coarse-silty, mixed mesic Fluventic Hapludolls) had intermediate texture; and Smolan (fine, montmorillonitic mesic Pachic Argiustolls) had a high clay content (Table 1). Water contents at saturation (*10*) were 16% for Sarpy, 37% for Eudora, and 48% for Smolan.

Contaminated soils were selected from two sites based on type of contaminant, aging, and soil texture. One soil was from the Craney Island Fuel Terminal, Portsmouth, VA. This soil was contaminated by diesel fuel approximately 30 years

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TABLE 1. Chemical and Physical Properties of the Soils Used in This Study

property	Virginia	refinery sludge	Sarpy	Eudora	Smolan
pH	7.4	7.5	8.1	8.0	6.7
elec cond (dS/m)	3.4	3.8	0.9	0.6	0.8
CEC (cmol$_c$/kg)	31	25	5.5	12	21
organic C (g/kg)	11	10	0.1	0.8	2.4
sand (%)	60	48	71	33	27
silt (%)	21	28	26	57	46
clay (%)	19	24	3	10	27

ago. Selected chemical and physical properties of this soil are given in Table 1. Although the electrical conductivity (EC) was elevated (4 dS/m) as compared to normal soils (<1 dS/m), none of the other properties was unusual. The second "soil" was an oxidation pond sludge from the Chevron Oil Refinery in Richmond, CA. It was a mixture of refinery sludge and sediment. As with the Virginia soil, the elevated EC (3.3 dS/m) was the only unusual soil test property (Table 1). The petroleum contaminants were a minimum of 25 years old and were found to span the diesel and motor oil ranges of hydrocarbons.

Moist, contaminated soil was homogenized and split into two subsamples. One subsample was dried at 30 °C and ground to pass a 0.25-mm sieve before extraction. The other subsample was passed through a 1-mm sieve, sealed in a glass bottle, and stored at 4 °C to maintain moisture and minimize degradation.

Soil Extraction. *Soxhlet Extraction.* Five grams of each soil was extracted using 100 mL of dichloromethane for 24 h. Replication ranged from $n = 3$ to $n = 5$. The extraction solutions were sealed in glass vials and stored at 4 °C until analysis. For moist soils, from 10 to 25 g of anhydrous sodium sulfate was mixed with the soil immediately prior to extraction to remove water.

Shaking Extraction. For all shaking extractions, 1−5 g of soil was weighed into 20-mL glass scintillation vials, and 10 mL of solvent was added to each vial. The vials were sealed with a foil-lined cap and shaken on a reciprocating, platform shaker (Eberbach 6010, Fisher Scientific, St. Louis, MO) at 120 cycles/min. Shaking periods ranged from 30 min to 1 h. The extracts were centrifuged for 10 min at 180g and removed carefully from the centrifuge, and the extraction solution was decanted and saved.

When more than one extraction cycle was used, 10 mL of clean solvent was added to the soil used previously to begin a new extraction cycle, and the process was repeated until the required number of cycles was completed. The extracts from all cycles for a given sample were combined and weighed. Thus, a sample extracted with only one cycle would have approximately 10 mL of extract, a sample with two cycles would have approximately 20 mL, and so on. Extracts were stored at 4 °C until analysis.

Analytical Methods. Analytical methods were chosen based upon the analyte. Total petroleum hydrocarbons were determined by infrared spectrometry or gas chromatography, and PAHs were determined only by gas chromatography/mass spectrometry.

TPH Analysis by Infrared Spectrometry. Extraction solvents were removed completely by evaporation to dryness under a nitrogen stream at room temperature. One gram of chromatographic silica gel (100−200 mesh chromatographic silica gel activated at 110 °C for 24 h) and 10 mL of Freon were added to analyze TPH. Absorption was measured at 2930 cm^{-1} (HC-404 Buck Scientific, Inc, East Norwalk, CT). The infrared (IR) spectrometer was calibrated using an EPA Reference Oil Standard (Buck Scientific) containing isooctane, chlorobenzene, and hexadecane. A five-point standard curve

was used to establish the relationship between absorbance and concentration. Absorbances of TPH in the Freon solutions were converted to concentrations of TPH in solution using a standard curve.

TPH Analysis by Gas Chromatography. Although IR analysis is relatively simple and an adequate survey method, it is not sensitive to all components of petroleum hydrocarbons. Therefore, TPH also was analyzed by GC. Extracts were injected into a Hewlett-Packard 5890A gas chromatograph equipped with a 7673A autosampler (Hewlett-Packard, Avondale, PA). A DB-TPH capillary column with dimensions of 30 m × 0.32-mm i.d. with a stationary phase thickness of 0.25 μm (J & W Scientific, Folsom, CA) was used for analytical separation, and a flame ionization detector was used for analyte detection. Hewlett-Packard DOS Chemstation software was used for integrating the total chromatogram area to encompass straight chain hydrocarbons from C_{10} to C_{28} (diesel range) for Virginia samples. For California samples, the chromatogram was integrated to include straight chain hydrocarbons from C_{16} to C_{34} (motor oil range).

A 1.0-mL aliquot of each extract was transferred to a GC vial and spiked with 5α-androstane (Accustandard, Inc., New Haven, CT) as an internal standard. Analytical standards of diesel and motor oil were prepared over a range of 20−250 mg/L. A minimum of five nonzero standards was used in each analysis.

Gas Chromatography/Mass Spectrometry for PAHs. The PAHs extracted from the California oxidation pond sludge were analyzed by GC/MS after an initial cleanup procedure. A chromatographic column with a Teflon stopcock (250 × 15 mm i.d.) was plugged with Pyrex glass wool at the end. Ten grams of silica gel (100−200 mesh chromatographic silica gel activated at 110 °C for 24 h) was mixed with 20 mL of hexane and then transferred to the column. Another 20 mL of hexane was used to rinse the column. Twenty milliliters of dichloromethane extract (from soil) was evaporated to dryness under a nitrogen stream, redissolved in 20 mL of hexane, and loaded on the top of the column. The column was eluted with 120 mL of hexane and 120 mL of hexane and benzene (1:1 v:v). The eluent was evaporated to dryness under a nitrogen stream, redissolved in 1 mL of dichloromethane, and transferred to a GC vial. A mixed internal standard (acenaphthene-d_{12}, chrysene-d_{12}, naphthalene-d_8, phenanthrene-d_{10}; ULTRA Scientific, North Kingstown, RI) was added before GC/MS analysis. The PAHs were analyzed by an HP model 6890 gas chromatograph equipped with a 7673A autosampler (Hewlett-Packard, Avondale, PA). A HP-5MS fused silica column with dimensions of 30 m × 0.25-mm i.d. (0.25 μm film) was used for analytical separation, and a mass selective detector (MSD) was used for analyte detection. For target analytes, selected ion monitoring was used for identification and quantification.

Experiment 1: Extraction of PAHs from Spiked Soils as Affected by Solvent Choice and Soil Properties. The purpose of this experiment was to test the ability of several organic solvents to remove PAHs from soils of different textures. Air-dried samples of Sarpy, Eudora, and Smolan soil (Table 1) were spiked with anthracene, pyrene, and benzo[a]pyrene (BaP) to a concentration of approximately 30 mg/kg. A stock solution of the compounds was prepared by dissolving each in acetone to obtain a concentration of 500 mg/L. Each soil was spiked by spraying 30 mL of the PAH stock solution in three equal parts onto 500 g of soil. The soil was mixed thoroughly after each addition to ensure uniform distribution of contaminants. The contaminated soils then were allowed to stand for 24 h with intermittent stirring to allow complete evaporation of the acetone (verified by headspace analysis).

The moisture content of each soil was adjusted to 25%, 50%, and 100% of saturation by adding the appropriate amount of distilled water (*10*). The "air-dried" soils were

obtained by wetting 500 g of each of the soils to 50% saturation and drying under ambient conditions in a greenhouse for 72 h. Air-dry moisture contents were 0.9% (mass basis) for Sarpy, 1.6% for Eudora, and 3.1% for Smolan.

The soil samples in this experiment were extracted using the shaking procedure described previously with 2.5 g of moist soil. Five extraction solvents were chosen to represent a range of properties: hexane, dichloromethane, acetone, methanol, and methanol with 10% (v:v) water. One extraction cycle was used, and the extracts were analyzed by gas chromatography.

Experiment 2: Shaking versus Soxhlet Extraction for Aged Petroleum Hydrocarbons. This study evaluated Soxhlet versus shaking extraction of total petroleum hydrocarbons using different solvents, shaking times, and soil mass. Differences between the extraction of air-dried and field-moist soils also were quantified. The test soils were the Virginia and refinery sludge (Table 1), both of which had been contaminated with petroleum hydrocarbons for at least 25 years. Soil mass ranged from 1 to 5 g, the extraction period was 0.5−4.0 h, and the number of cycles ranged from 1 to 4. For Soxhlet extraction of moist soil, the previously described procedure was followed using 5 g of soil and 10 g of anhydrous Na_2SO_4. The TPH concentrations in extracts from both shaking and Soxhlet were determined by IR and GC.

Experiment 3: Effect of Aging on Extractability. This experiment determined the effects of aging on the extraction of specific organic compounds from soil by standard Soxhlet or by shaking with acetone or dichloromethane. Eudora soil (Table 1) was selected for this study because of its intermediate texture. The soil was spiked with a synthetic diesel fuel containing 17 compounds (Scott Cunningham, DuPont Central Research and Development, personal communication) in a manner similar to the spiking of the soils in experiment 1. The spiked soils were thoroughly homogenized, brought to 50% saturation, and allowed to age. A portion of the contaminated soil was weathered outdoors for 180 days in large containers to allow exposure to sunlight and rainfall. Another portion was aged only for 48 h at 28 °C. After their respective aging periods, the contaminated soils were stored at 4 °C for 180 days. Uncontaminated, moist soil was spiked with the synthetic diesel fuel immediately prior to extraction to test recovery from a nonaged sample. The water content of the moist soils averaged 18% on a weight basis.

Soil samples from each of the three aging periods were extracted in triplicate by shaking with dichloromethane and by Soxhlet. For Soxhlet extraction, the soils that had been aged and stored at 4 °C were extracted after grinding with 25 g of anhydrous sodium sulfate until the mixture flowed easily with no signs of clumping of moist soil. For nonaged treatments, uncontaminated soil was ground with 25 g of Na_2SO_4, transferred to a Soxhlet thimble, and spiked with the contaminant mixture; the extraction began immediately. For shaking extraction, 2.5 g of soil was shaken with dichloromethane or acetone for 30 min, using three sequential extractions. Extracts from both Soxhlet and shaking were analyzed by GC.

Experiment 4: Extraction of PAHs from Soil Contaminated by Diesel Fuel. In this experiment, PAHs were extracted from Virginia soil contaminated by diesel fuel using Soxhlet and shaking extraction with quantification by GC/MS. For shaking, 1 g of air-dried soil was extracted with dichloromethane using three 30-min cycles. For Soxhlet, 5 g of moist soil was mixed with 10 g of Na_2SO_4 immediately prior to extraction. The GC/MS analysis was performed as described in a previous section.

Statistical Analysis. All statistical analyses were executed with the aid of Cohort Software (Berkeley, CA) at $P < 0.05$. For multiple comparisons, a least significant difference (LSD) was calculated for a completely randomized design.

Results and Discussion

Experiment 1: Extraction of PAHs from Spiked Soils as Affected by Solvent Choice and Soil Properties. The purpose of this experiment was to assess the ability of several solvents to extract PAHs from soil as a function of soil texture and soil moisture. For the coarse-textured Sarpy soil, the extraction of anthracene and pyrene was not impacted by soil moisture content except for the most nonpolar solvents (hexane and dichloromethane) at 100% saturation (Figure 1). At this high moisture content, the soil visibly repelled nonpolar solvents and formed clumps rather than dispersing as observed with the other three solvents. For BaP, only acetone and methanol were able to extract more than 60% of the original 29 mg/kg.

Extraction of PAHs was less efficient from medium-textured Eudora soil than from Sarpy. Extraction of anthracene and pyrene from Eudora soil was impacted very little by moisture content, except for hexane and dichloromethane at saturation and 50% saturation. However, air-drying the soil significantly reduced extractability for both compounds by all solvents. Acetone removed nearly 100% of the BaP from moist soils (compared to a maximum of 80% for methanol), but even acetone extracted only 55% from the air-dried samples.

The trend toward decreased extractability with increasing clay content continued for Smolan soil. Although acetone generally was the best extractant, efficiencies for all three compounds were unacceptably low (<70%) for air-dried soil regardless of the solvent used. For BaP, acetone extracted more than 75% of the original concentration for all samples except air-dried soil; none of the other solvents extracted as much as 45% of the BaP at any moisture content.

The choice of solvent is critical in developing a shaking extraction protocol. Strongly adsorbed compounds will be affected by the soil texture and moisture content. The results for the air-dried soils also suggest potential problems with aging. For these soils, the moisture content was brought to 50% saturation after contamination and allowed to dry at ambient temperatures for a period of 72 h. For all soils except Sarpy, this process had a strong negative impact on extractability of all compounds. A more rigorous procedure (e.g., longer extraction time, more than one extraction cycle) would be needed to quantitatively remove these compounds.

Experiment 2: Shaking versus Soxhlet Extraction for Aged Petroleum Hydrocarbons. On the basis of the results from experiment 1, we tested acetone and dichloromethane (a typical solvent in EPA protocols) as extraction solvents using a more rigorous shaking procedure. In this experiment, extractability of total petroleum hydrocarbons by shaking was determined as affected by soil weight, solvent, shaking time, and soil moisture and compared to standard Soxhlet extraction. The test materials were diesel-contaminated soil from Virginia and petroleum-contaminated sediments from California.

Virginia Soil. Table 2 summarizes TPH concentrations extracted from dry and moist samples of Virginia soil with shaking and Soxhlet extraction and quantified by IR Spectrometry. For Soxhlet extraction, five duplicate soil samples were analyzed with 2097 ± 50 mg of TPH/kg for dry soil and 2172 ± 110 mg/kg for wet soil (mean ± confidence interval, $P < 0.05$). The mean soil concentrations for wet and dry soil were not significantly different, but the 95% confidence interval was greater for wet soil. Subsampling variability is higher in wet soil than dry soil, because the dry soil that was ground and passed through a 0.25-mm sieve has greater homogeneity. However, the fact that the mean TPH concentrations were the same for dry and wet soil indicates that moderate amounts of soil moisture did not interfere with Soxhlet extraction of TPH with dichloromethane.
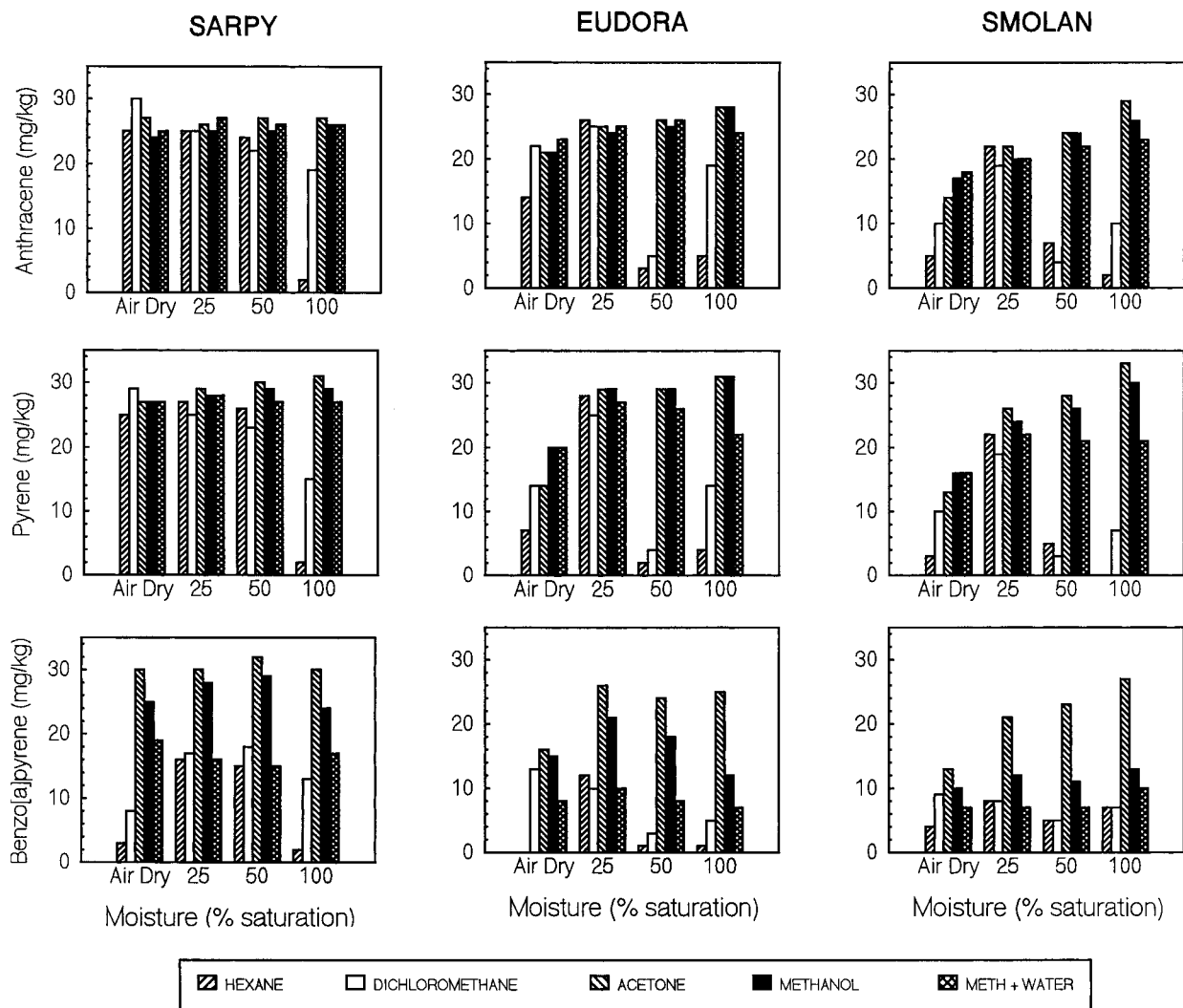
SARPY   EUDORA   SMOLAN

HEXANE   DICHLOROMETHANE   ACETONE   METHANOL   METH + WATER

FIGURE 1. Extraction of pyrene as impacted by solvent, soil moisture, and soil texture. Least significant difference ($P < 0.05$) was 2.8 mg/kg for all compounds. All extractions used a single 30-min cycle. Initial spiked concentrations were approximately 30 mg/kg.

TABLE 2. Concentrations of TPH in Diesel-Contaminated Soil from Virginia as Affected by Moisture, Solvent, Shaking Period, and Number of Sequential Cycles of Extraction[a]

			TPH (mg/kg of soil)											
			dichloromethane cycles[d]				acetone cycles[d]				dichloromethane + acetone cycles[d]			
moisture content	soil mass (g)	extraction period (h)	1	2	3	4	1	2	3	4	1	2	3	4
air dry[b]	1	0.5	1701	1955	2035	2057	1828	2033	2066	2076	1771	2020	2054	2041
	3	0.5	1536	1856	1825	1909	1512	1747	1849	1855	1331	1600	1726	1912
	5	0.5	1427	1729	1879	1923	733	836	1088	1786	754	1583	1606	1828
moist[c]	1	0.5	1494	1588	2113	2223	1583	2030	2187	2201	1961	2166	2246	2259
	3	0.5	819	870	1100	1384	1328	1908	1882	2005	1579	1941	1838	1903
	5	0.5	713	927	978	1246	1230	1581	1635	1882	1247	1847	1826	1870

[a] All values are means of four replicates. For Soxhlet extraction, TPH concentrations were 2097 ± 50 mg/kg for dry soil and 2172 ± 110 for wet soil (mean of five replicates $\pm$ 95% confidence interval). [b] Least significant difference (LSD) = 133 mg/kg for dry soil. [c] Least significant difference (LSD) = 174 mg/kg for wet soil. [d] Cycles refer to the number of sequential extractions with clean solvent.

For shaking, all factors were important, and only a few combinations resulted in TPH concentrations equivalent to those from Soxhlet. For dichloromethane, only 1 g of soil in combination with three or four shaking cycles yielded TPH concentrations equivalent to those from Soxhlet (Table 2), and this was true for both wet and dry soils. When 3 or 5 g of soil or fewer than three cycles were used, concentrations from shaking were significantly less than those from Soxhlet. When acetone was part of the solvent (either as 100% or 50% acetone), 1 g of soil in combination with two or more shaking

cycles yielded TPH concentrations equivalent to those from Soxhlet (Table 2). Greater amounts of soil or only one shaking cycle yielded significantly lower concentrations.

The trends in TPH concentration extracted by acetone-containing solvents provided an interesting contrast to dichloromethane alone for both wet and dry samples. For a given number of cycles with 3 or 5 g of wet soil, acetone and 1:1 acetone:dichloromethane extracted more TPH from soil than dichloromethane alone. For dry soil, the three solvents extracted equivalent concentrations for all cycles with 1 or

TABLE 3. Mean TPH Concentrations ($n = 4$) for Extraction of Petroleum-Contaminated Soils[c] from California[a]

extraction period (h)	TPH (mg/kg of soil)					
	dichloromethane cycles[d]		acetone cycles[d]		dichloromethane + acetone cycles[d]	
	3	4	3	4	3	4
0.5	7993[b]	8231	8792	8348	7853	8620
1.5	7853	8058	7826	8349	7959	7660
4.0	7359	8637	9012	8329	8705	8180

[a] For Soxhlet extraction using dichloromethane ($n = 5$), the 95% confidence interval was 7984 ± 90 mg/kg. [b] Least significant difference (LSD, $P < 0.05$) for this analysis is 705 mg/kg. [c] All soils were air-dried and ground to pass a 0.25-mm sieve. [d] Cycles refer to the number of sequential extractions with clean solvent.

3 g of soil, but with 5 g of soil, dichloromethane removed more TPH than the other two solvents for all numbers of cycles. The amount of water in 3 and 5 g of moist soil apparently was more than the dichloromethane could dissolve or displace, and the nonpolar solvent was unable to fully interact with the soil and remove the entrained hydrocarbons. Because acetone has both nonpolar and polar properties (it is fully miscible with water), its presence in the extraction solvent overcame the hydrophobicity that dichloromethane alone could not.

Increasing the extraction time per cycle had no impact on the TPH concentrations removed from Virginia soil (data not shown). When 1 and 1.5 h/ cycle for three and four cycles were used, the concentrations did not significantly increase from the 2097 mg/kg removed by Soxhlet.

California Soil. For the California material, only dry soil was used because of the ease of handling, lack of volatile compounds in the original samples, and the positive results with Virginia soil. Soxhlet extraction removed 7984 ± 90 mg of TPH/kg as determined by IR analysis (Table 3). Gas chromatographic analysis of the Soxhlet extracts clearly demonstrated that the hydrocarbons in this contaminated soil were associated with much longer carbons chains (up to at least C_{36}). This information coupled with the age of the material and the results from Virginia soil led us to examine only three and four extraction cycles. Fewer cycles were likely to be less efficient than Soxhlet. The same solvents as used previously (dichloromethane, acetone, and 1:1 acetone: dichloromethane) and extraction periods of 0.5, 1.5, and 4.0 h were tested.

Shaking extracted TPH concentrations that were equal to or greater than those from Soxhlet for all conditions tested (Table 3). The variability was high for these samples, but the trends are readily apparent. Solvent, number of cycles, and extraction period did not have consistent effects on the TPH concentrations extracted.

Despite large differences between the contaminants in California and Virginia soils, shaking a 1-g soil sample for 30 min with three successive aliquots of 10 mL of dichloromethane or acetone extracted TPH concentrations equivalent to those from standard Soxhlet extraction.

Extended Comparison for Virginia Soils. As a comparison of Soxhlet versus shaking for a large number of samples, 96 samples were taken from the Virginia site and extracted with dichloromethane using 1 g of dry soil and three shaking cycles. The TPH concentrations (determined by IR) in samples extracted by shaking were highly correlated to TPH from Soxhlet with $R^2 = 0.82$. The slope of the regression line (with Soxhlet as the independent variable) was 0.91 ± 0.11 (not statistically different than 1.0, $P < 0.05$) with an intercept of -23 ± 41 (not significantly different from zero, $P < 0.05$).

An important aspect of this comparison is the reduction in labor required to obtain the extracts. Twenty-three h was

TABLE 4. Extraction of Compounds from a Simulated Diesel Fuel Mixture Added to Soil and Aged[a]

compound	acetone (mg/kg)	dichloromethane (mg/kg)	Soxhlet[b] (mg/kg)	LSD ($P < 0.05$) (mg/kg)
No Aging				
tetradecane	141	150	152	9
pristane	123	124	124	12
1-octadecene	145	147	148	9
phenanthrene	137	141	133	15
pyrene	139	141	134	14
tetracosane	140	138	136	14
2 Days Aging				
tetradecane	107	120	86	11
pristane	98	100	82	11
1-octadecene	114	116	93	12
phenanthrene	106	108	93	12
pyrene	107	108	96	13
tetracosane	112	105	92	14
180 Days Aging				
tetradecane	23	nd[b]	13	3
pristane	68	24	35	6
1-octadecene	55	15	28	6
phenanthrene	11	5	nd	6
pyrene	9	12	13	11
tetracosane	81	21	41	7

[a] Soil samples were shaken for three 30-min cycles either with acetone or dichloromethane or by Soxhlet after mixing with Na_2SO_4 and extraction with dichloromethane ($n = 3$ for all determinations). [b] Not detectable.

required for the entire process of extracting 96 soils by shaking in contrast to 72 h required by Soxhlet. This is a very significant savings in time without any loss in extraction efficiency.

To evaluate TPH concentrations more accurately, GC also was used to analyze for TPH after shaking extraction. Concentrations of TPH from shaking extraction (1 g of dry soil, three extraction cycles, and each cycle using 0.5 h) and quantified by IR were highly correlated ($R^2 = 0.94$) with concentrations quantified by GC. The slope of the regression line (with concentrations from IR as the independent variable) was 1.04 ± 0.06 (not significantly different than 1.0) with an intercept of 16 ± 29 (not statistically different from 0.0, $P < 0.05$). Thus, IR provided TPH concentrations equivalent to those quantified by GC analysis, despite known shortcomings of the IR method (*9*).

Experiment 3: Effect of Aging on Extractability. The objective of this experiment was to compare extraction by shaking with acetone and dichloromethane with Soxhlet extraction for a suite of 17 compounds that had been added to soil and aged up to 1 year. Results for six representative compounds are discussed. All soil samples were extracted moist (approximately 10% H_2O). The initial concentrations were approximately 150 mg/kg of soil for all compounds except pristane, which had an initial concentration of approximately 125 mg/kg.

A set of soils was amended with the contaminants immediately prior to extraction to serve as a measure of recovery by all methods. Recoveries of all compounds by all solvents and methods were essentially 100% (Table 4, No Aging), and concentrations were not statistically different than the known, initial concentrations.

Aging had a strong effect on extractable concentrations by all methods. Concentrations of the target compounds often were observed to decline with time, probably because of volatilization, degradation, and/or incorporation into the soil matrix during aging. Thus, this experiment essentially compared the ability of different methods and solvents to extract the residual contaminants that have been largely sequestered into the soil matrix. For samples aged at 28 °C
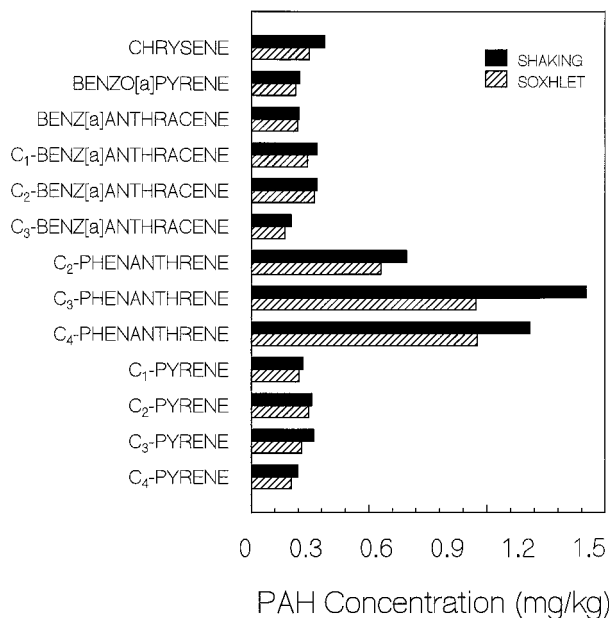
FIGURE 2. Concentrations of a suite of PAHs extracted from Virginia soil by shaking and Soxhlet quantified by mass spectrometry. Least significant difference (P < 0.05) was 0.06 mg/kg for all compounds. All shaking extractions used three, 30-min cycles of dichloromethane.

for 48 h followed by 180 days at 4 °C, shaking with acetone or dichloromethane for three cycles extracted the greatest concentrations, approximately 75% of the original levels for the compounds in Table 4. Soxhlet extraction following grinding with Na_2SO_4 to eliminate moisture removed significantly lower concentrations of all analytes except pyrene when compared to shaking.

Aging for 180 days outdoors followed by 180 days at 4 °C further decreased extractable concentrations. Shaking with acetone was the most effective method, and shaking with dichloromethane was generally the least effective. Recovery by Soxhlet often was approximately 50% of that by shaking with acetone.

Experiment 4: Extraction of PAHs from Soil Contaminated by Diesel Fuel. Individual PAHs extracted by shaking and Soxhlet extractions were quantified by GC/MS. Both extraction methods were performed in quadruplicate on a single sample of diesel-contaminated Virginia soil. Shaking and Soxhlet extracted the same pattern of PAHs (Figure 2), and the mean concentration of each PAH extracted by shaking was equal to or greater than the concentration obtained by Soxhlet (P < 0.05).

Shaking and Soxhlet extraction methods were compared for a wide range of contaminated soils. A single cycle of shaking was adequate for complete recovery of anthracene and pyrene from a moist, sandy soil with water content ranging from air-dry to 100% saturation. The low polarity solvents, hexane and dichloromethane, had very poor recoveries of benzo[a]pyrene at all moisture contents, but

acetone maintained complete recovery. Extraction efficiencies for all solvents declined with increasing clay content, increasing molecular weight of PAHs, and particularly air-drying of contaminated soil initially at 50% moisture saturation. Low recoveries probably were because the solvents were unable to remove PAHs that were strongly sorbed or entrained in the soil micropores during a single, short-duration shaking extraction. Under all circumstances, acetone consistently was the best extracting solvent.

In an effort to improve shaking-extraction efficiency, we tested the effects of drying, grinding, and multiple sequential extractions. For aged, contaminated soils from sites in Virginia and California, three sequential extractions by shaking with acetone or dichloromethane for 30 min recovered TPH concentrations that were equivalent to those from Soxhlet extraction. This same shaking procedure extracted 13 PAHs from the Virginia, diesel-contaminated soil at concentrations that were equal to or greater than those from Soxhlet extraction. Drying and grinding had no impact on TPH concentrations recovered by shaking when 1 g of contaminated soil was extracted; however, when 3 g or more of soil was used, extraction efficiencies generally were <100% regardless of the solvent used or if the soil was extracted moist or dry. This protocol has not been tested on very low concentrations (<10 μg/kg), and the short extraction times may be an impediment to extraction efficiency for highly sorbed compounds at trace concentrations.

Shaking 1 g of field-moist soil three times sequentially with 10 mL of acetone should yield petroleum hydrocarbon concentrations equivalent to or greater than those from Soxhlet extraction. This method requires approximately one-third of the time needed for Soxhlet, while using 30% of the solvent and a much simpler apparatus. However, concentrations obtained by this method should be compared to Soxhlet results for each new matrix (e.g., soil, sludge) because of the strong dependence of extractability on soil texture, contaminant, and aging.

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