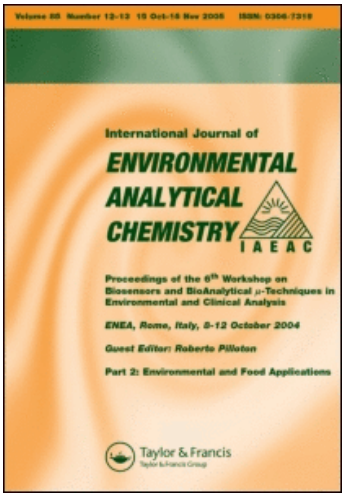

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DETERMINATION OF PETROLEUM HYDROCARBONS IN SOIL: SFE VERSUS SOXHLET AND WATER EFFECT ON RECOVERY

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In an interlaboratory study to determine the concentration of petroleum hydrocarbons (PHCs) in an above ground bioreactor at a refinery site in Montreal we found that the EPA Method # 418.1 for the analysis of semi-volatile hydrocarbons gave concentrations up two fold higher than expected. The silica mixing step used to clean-up the crude Soxhlet extract and the inclusion of chlorobenzene or benzene in the composition of the IR quantitative standard were later implicated as major sources of bias in the Method. In another comparative study we have determined water effect on the recovery of PHCs from wood preserving soil using the Soxhlet EPA Method # 3450 (with Freon-113) and the SFE Method # 3560 (with CO_2). In the Soxhlet method water did not seem to affect the recovery of PHCs since variations in PHC concentrations did not exceed RSD values, i. e., ± 2% to ± 8%. While in SFE, an optimal extraction efficiency occurred when the water content in the soil was around the 20% limit, similar to what has been described in the EPA Method # 3560. In the case of a bioslurry both SFE and Soxhlet showed that water removal enhanced the recovery of PHCs, i. e., a reduction in the water content by a factor of two resulted in an increase in the recovery of PHCs by roughly a factor of two.

KEY WORDS: Soxhlet, SFE, petroleum hydrocarbons, soil, bioslurry, EPA.

INTRODUCTION

The extensive use of petroleum products (over 2 billion metric tons produced per annum)[1] in the chemical, petrochemicals and transportation industries has resulted in severe accidental spills and contamination in the terrestrial and marine environments. Due to the toxicity and carcinogenicity of some of these products, particularly polynuclear aromatic hydrocarbons (PAHs),[2] considerable effort and capital are allocated to monitor their fate in the environment. Such monitoring processes are also required to assess the effectiveness of oil remediation whether in closed gas stations or in sites previously used for the treatment and disposal of oily wastes.

Current understanding of the fate of PHCs, whether in a controlled system such as *in-situ* or *ex situ* remediation of soil or in an open environment such as in the case of oil

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spill, is limited due to the lack of uniform methods for the identification and quantitation of PHCs in soil/water suspensions.[3] For example petroleum is composed of a complex mixture of hydrocarbon-based products ranging from straight chain and branched aliphatics (paraffins) to simple and complicated PAHs. This extreme complexity in the composition of PHCs require a compound class separation prior to analysis. Furthermore, sorption of PHCs on soil particles, water content, and the presence of other organic constituents in the soil constitute major extraction problems. Recently, it has been reported that the Environmental Protection Agency (EPA) Method 418.1 is not an appropriate technique for measuring PHCs in certain types of soil.[4] The complexity of PHC recovery becomes even greater when working with bioslurries where water and biomass make reproducibility and accuracy of measurements very difficult to attain.

All literature reports clearly reflect the lack of consistency among various methods used to analyze PHCs. For example, discrepancies as high as 300% are obtained when PHCs are analyzed in sediments.[5] Douglas *et al.*[3] have recently reviewed the limitations associated with some of the most prominent standard methods in this field. Furthermore, Voice *et al.*[6] have recently reported that the static head space technique for the analysis of volatile organic compounds (VOCs) in soil is superior over the dynamic purge and trap technique recommended by EPA. In general, the flow of literature reports on petroleum analysis clearly warns that analysts should be aware of all the limitations associated with each method. This is extremely important when the analytical data are used to evaluate the effectiveness of PHC remediation since decisions of far reaching consequences are made.

Recently, we have been involved in assessing the effectiveness of oil removal in an aboveground bioreactor at a refinery site in East Montreal.[7] Normally standard analytical methodologies that take into consideration all process components are followed. However, the standard American Public Health Association Method (APHA Method 5520)[8] and EPA Method 418.1,[9] originally developed to analyze total recoverable petroleum hydrocarbon in waste water and sludge and later developed for soil, were found to be inapplicable to the present study without modification. In an attempt to learn more about the standard oil test and to minimize the bias associated with the test a side-by-side comparison of SFE (with CO_2) and Soxhlet (with Freon-113) was undertaken to determine PHCs in real soil samples. Three soils were selected: a soil taken from an above ground bioreactor treating petroleum hydrocarbons at a refinery site, a soil taken from a site treating heavy oil using a joint soil washing/bioremediation process, and finally, a soil taken near a wood preserving facility.

EXPERIMENTAL

Material and reagents

Hexadecane, eicosane, tetracosane, octacosane, triacontane, iso-octane, benzene and p-terphenyl were from Aldrich, Millwaukee. Glass distilled Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) was obtained from Caledon. Silica gel (100–200 mesh) was obtained from Fisher (Fisher Davisil grade 644) and was activated at 150°C for 16 h before use. Whatman cellulose thimbles for the Soxhlet extractor were washed with pesticide grade hexane in a sonicator for 2.5 h prior to extraction. Otherwise adipate and other binding polymers in the thimble would be extracted and would contaminate the IR spectra of oil extracts.

Sampling sites

Case A. Site (A) is located at a refinery site in East Montreal, Canada. The treatment technology is basically an aboveground bioreactor with a capacity to biotreat 1,500 m^3 of contaminated soil using soil indigenous bacteria and a vacuum pump for aeration (pump and treat). Further details on the site and the technology used in remediating the site can be obtained by consulting Samson *et al.*[7] The soil, contaminated with roughly 6,700 mg/Kg of mainly C_{12} to C_{30} aliphatic hydrocarbon, was first cleaned of stones and enriched with nutrients, saw dust and gypsum in concentrations not exceeding 10% of the total volume. The soil pH was 7.6 and its water content was 20%. It was composed, on dry basis, of 33% clay, 31% silt and 36% sand. Control reactors (100 m^3 capacity) were also used to assess losses due to weathering and other abiotic changes such as evaporation, leaching and irreversible adsorption. Three samples were collected at 0.6 m depth and another three at 1.2 m depth. Extraction and analysis of the semi-volatile PHCs were carried out as described below.

Case B. Site (B) represents a wood preserving facility that uses petroleum derived products mixed with other chemicals such as pentachlorophenol (PCP) to preserve wood. The sampling area at the facility was from an area used to store the wood after treatment A comparative SFE (using CO2) and Soxhlet (using Freon-113) extraction was carried out to determine the most appropriate extraction technique for PHCs. More information on the site and soil characteristics can be obtained from Sylvestre *et al.*[10] The control was taken from a forest 1 Km away from the facility.

Case C. Site (C) represents a joint soil washing/biodegradation plant that was developed to remediate soil contaminated with heavy industrial oil (*ca* 100,000 mg/Kg). The treatment technology is composed of three major independent processes. The soil was first washed, the resulting slurry was oxidized and then bioremediated. The present work does not deal with the technology itself, rather it addresses the determination of the residual concentrations of semi-volatile PHCs in the soil bioslurry after treatment.

Sample pretreatment

In case of the refinery site or the wood preserving facility soil samples were first sieved, homogenized and then dried at 105°C for 16 h to determine water content. Further details on the two sites can be found in Samson *et al.*[7] and Sylvestre *et al.*[10], respectively. In case of the bioslurry, samples were first centrifuged: the remaining pellet was extracted by the Soxhlet method and the decanted aqueous phase was extracted by CH_2Cl_2. The biomass content of the bioslurry (4.1%) was determined by either measuring organic nitrogen in the washed and dried slurry using C,H,N-elemental analyzer (Control; Equipment Corporation, Model 240 XA, USA) or by measuring the protein content of the soil. The protein was extracted by trichloroacetic acid, treated with bicinchoninic acid and then determined at 562 nm. The biomass was calculated taking into account that 16% of nitrogen is protein and 50% of protein is biomass.[11]

Soxhlet extraction. The soil (20 g) was mixed with anhydrous magnesium sulfate, $MgSO_4$ (25 g) and grounded in a porcelain mortar. Hexadecane (100 µL) and p-terphenyl (100 µL) each from a stock solution of 2 g/L in methylene chloride were used as recovery standards and the soil samples were Soxhlet extracted with Freon-113 (200 ml) for a total of 80 cycles. To verify the presence of PAHs in the samples, the extraction

was carried out as described above but Freon was replaced by methylene chloride and $MgSO_4$ by Na_2SO_4. The final extracts were dried over sodium sulfate and then concentrated to 2 ml using a water pump or Kuderna Danish concentrator as required.

SFE extraction. Two commercial SFE extractors were used: a Dionex extractor (SFE-703) and an Hewlett Packard extractor (HP 7680 A SFE Model). In case of the Dionex instrument, the soil (3 g) was mixed with $MgSO_4$ (1/1 w/w) and extracted with CO_2 (340 atm and 400 ml gas/min). Oven temperature was maintained at 80°C while that of the restrictor was kept at 150°C. Analytes were collected in a vial that contained Freon-113 (10 ml). On the Hewlett Packard Model 7680, extractions were conducted using 7 ml extraction thimbles. Extractions were performed using 100 bar and 50°C with a CO_2 flow rate of 3 ml/min for 30 min with subsequent collection of the oil on a trap filled with stainless steel balls. The collection trap was then rinsed with hexane at 1 ml/min for 10 min, and the eluent was collected in vials for subsequent analysis.

Analysis

Class separation of PHCs: Portions of each of the above crude extracts (0.5–2 ml) from either the Soxhlet or SFE extraction were successively eluted on a silica gel column (id 10.5 mm) using 8 g silica for the Soxhlet extract and 8 g for the SFE extract. Each crude extract was then separated to its major components using solvents of different polarities: Freon 113 to elute the aliphatic fraction using hexadecane as an aliphatic marker, methylene chloride (20%) in hexane to elute the aromatic PHCs (PAHs) using *p*-terphenyl as an aromatic marker and finally methanol to elute the polar fraction.

IR analysis was carried out on a Philips Pye Unicam PU 9512 IR Spectrometer in 1 cm Infrasil quartz cells. Two standards for IR quantification were used: benzene/hexadecane/iso-octane, (25/37.5/37.5% v/v/v), when there is aromatic components in the oil extract, and hexadecane/iso-octane (1/1 w/w) when the oil does not contain aromatics (Figure 1) Freon was selected as the extracting solvent because it is less toxic than other organic solvents, insoluble in water, with a low boiling point (48°C), and above all is transparent in the range of 2700–3000 cm^{-1} where the IR measurements (υ_{C-H}, 2930 cm^{-1}) of hydrocarbons are made for quantification.

GC-MS was performed with an HP 5890 GC connected to a PH-5790 MSD. Briefly, the sample in methylene chloride (1 µl) was injected (split ratio 1 : 10) into a DB-5 capillary column (30 m × 0.25 mm) using a HP 7673 A automatic sampler. The oven temperature was programmed from 55°C (held for 3 min) and raised at a rate of 4°C/min unit 275°C and held for 15 min. The temperature interface between the GC and the MSD (EI 70 eV) was held at 280°C and the injector temperature was held at 275°C. Helium was used as carrier gas. The PHCs were quantitated using 1 µl of a standard mixture composed of hexadecane (12 mg/L) eicosane (12 mg/L), tetracosane (12 mg/L), octacosane (12 mg/L) and triacontane (12 mg/L) in Freon 113. A typical GC-MS spectrum is show in Figure 2.

RESULTS AND DISCUSSION

PHCs at the refinery treatment site – IR study

Concentrations of PHCs were corrected reference to the recovery of the internal standards hexadecane and p-terphenyl, assuming that no discrimination between losses

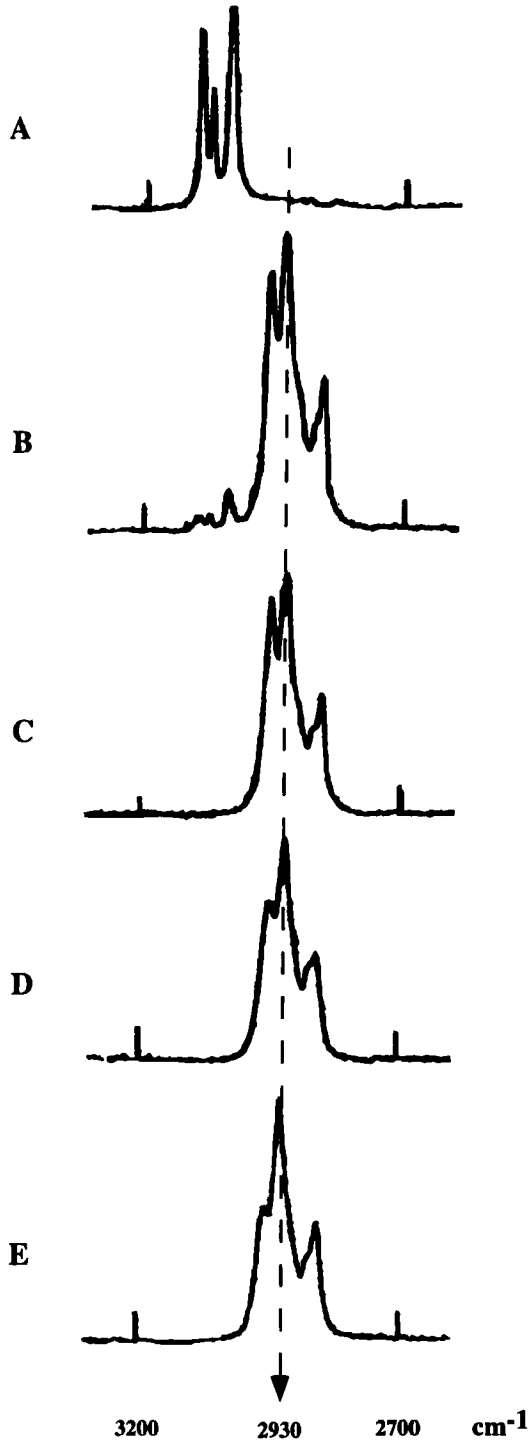

Figure 1 IR absorption spectra of : A: benzene B: benzene/hexadecane/iso-octane C: hexadecane/iso-octane, D: paraffin oil, E: mineral oil extracted from the refinery soil.

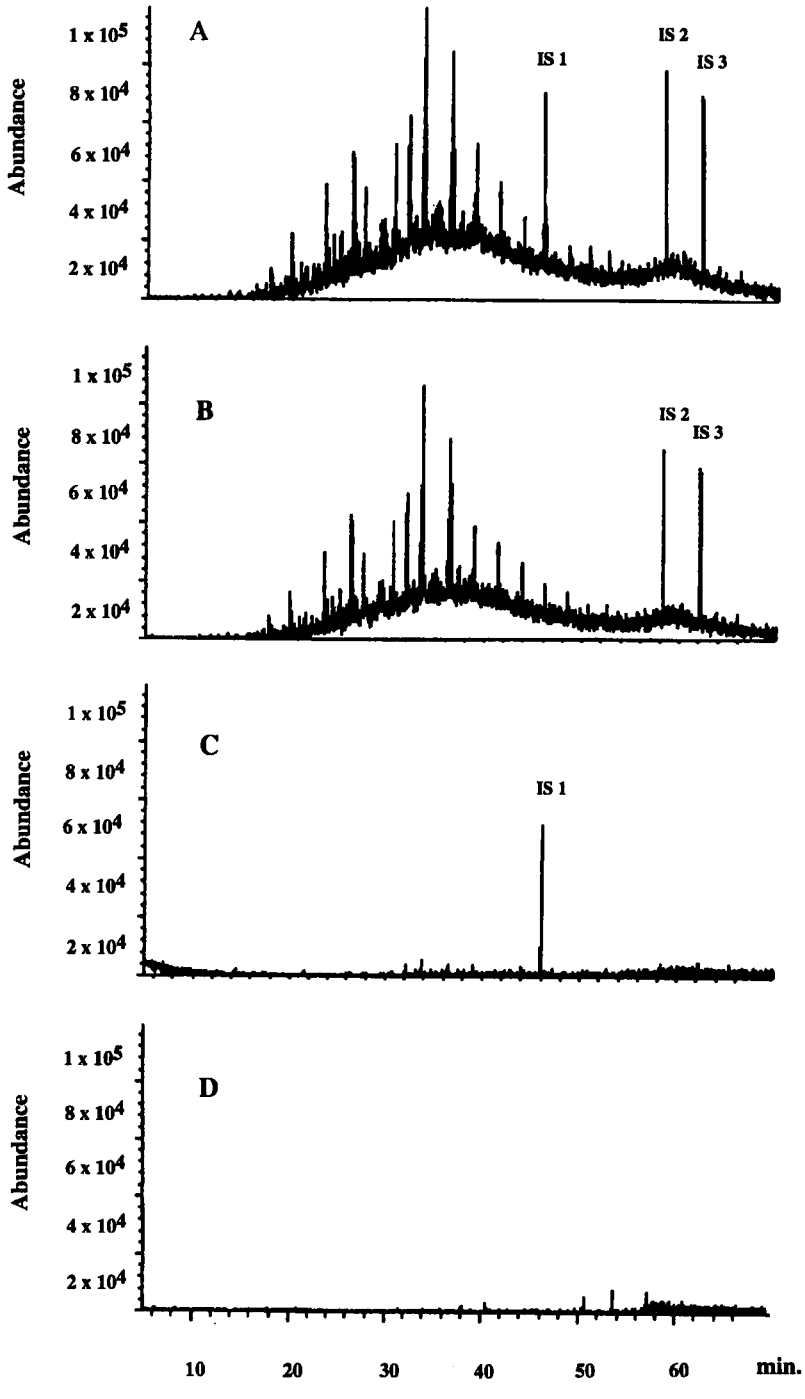

Figure 2 GC-MS total ion chromatogram of various silica fractions obtained from the extraction of soil samples obtained from the refinery site in Montreal: A: Crude extract B: Freon fraction, C: Hexane/CH_2Cl_2 (20% v/v) fraction and D: MeOH fraction. IS 1: p-terphenyl, IS2: octacosane and IS3: triacontane.

of the original pollutants and the internal standards took place throughout the analytical procedure. Reference extraction recoveries, using the Soxhlet, ranged from 90–107%. Furthermore when a clean soil was spiked with paraffin oil and subjected to the same analytical protocol (from extraction to IR analysis) > 90% recovery was obtained. Recovery of pristane and hexadecane was also found to be 88% and 91% respectively.

The first major problem encountered in applying the standard oil and grease test (EPA Method 418.1/APHA # 5520) for the analysis of PHCs by IR was the standard used to quantify the oil. A severe analytical bias was observed due to a marked difference in the molar absorptivity between the calibration standard (benzene, hexadecane, iso-octane, 25%, 37.5%, 37.5%, v/v/v, respectively) and PHCs analytes. For example, Method 418.1 measures the IR absorbance (2930 cm^{-1}, -C-H stretch, Figure 1) of Freon-extracted PHCs relative to the mixed calibration standard: benzene, hexadecane, iso-octane. Whereas, the IR absorption of the refinery extracts after the silica clean-up did not show any aromatics (Figure 1). Benzene does not absorb in the IR region where measurements for the paraffinic hydrocarbons are taken and consequently the use of benzene or chlorobenzene in the standard is bound to make measurements positively biased (Figure 1). Further evidence on the predominance of aliphatic hydrocarbon in these samples came from GC-MS analysis. Only traces (*ca* 1 mg/Kg) of alkylated polynuclear aromatics, R-PAHs, were observed (Figure 2). This observation prompted us to eliminate chlorobenzene (or benzene) from the EPA compositional standard and to use instead the closely representative standard (hexadecane/iso-octane, 1 : 1, w/w).

When Freon was replaced with methylene chloride as Soxhlet extracting solvent only traces of PAHs (< 10 mg/Kg) were obtained. Apparently, any aromatic compounds, if any, that were in the site before treatment might have been degraded preferentially over the aliphatic fraction.

Naturally, the private laboratory, which used the EPA compositional standard (benzene/iso-octane/hexadecane), reported oil concentrations up to two fold higher than the ones obtained by our laboratory (Figure 3). When we used the EPA standard instead of the aliphatic composition hexadecane/iso-octane there was an apparent increase of 20% to 30% in the concentrations of PHCs (Figure 4).

In one experiment both labs analyzed PHCs in six soil samples drawn from the treatment site under exactly similar conditions. Each sample was devided into two halves and each lab received a set of six identical samples for subsequent analysis. Interestingly the oil concentrations reported by the private lab before and after silica cleaning were almost identical (Table 1). Indicating the inefficiency of silica mixing in cleaning the soil extract. Whereas when the crude extracts were subjected to a compound class separation using a silica column less than 50% of total crude oil extract was collected as PHCs as shown in (Table 1). This clearly shows that compound class separation on a silica column is superior to that of simple silica mixing in cleaning hydrocarbons of petroleum origin from those of biomass and other soil organic matter (Namely, paraffinic (Freon fraction), aromatic (CH_2Cl_2/hexane 20% fraction) PHCs and polar organics including biomass (MeOH fraction)).

Our results were validated by drawing a mass balance between the crude oil extracts and various organic fractions obtained from the silica column. A convenient mass balance (97%–107%) was obtained between crude oil extracts and those of the silica fractions. Also, we found an excellent agreement between the concentrations of mineral oil obtained by IR on one hand and GC-MS on the other (Figure 5). Due to the time length required to complete each analysis the concentrations of PHCs were determined using single extractions and duplicate analysis. In a few cases triplicate extractions were carried out to determine the precision of measurements. Relative standard deviations

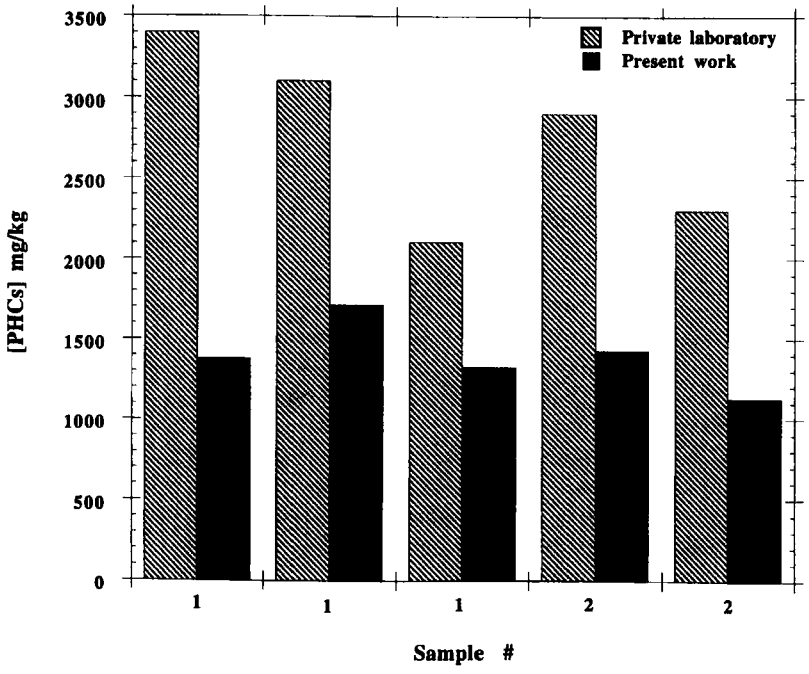

Figure 3 IR determination of PHCs in soil samples collected from the above ground refinery treatment site. 1: sampled at 0.6 m depth and 2: sampled at 1.2 m depth: interlaboratory study.

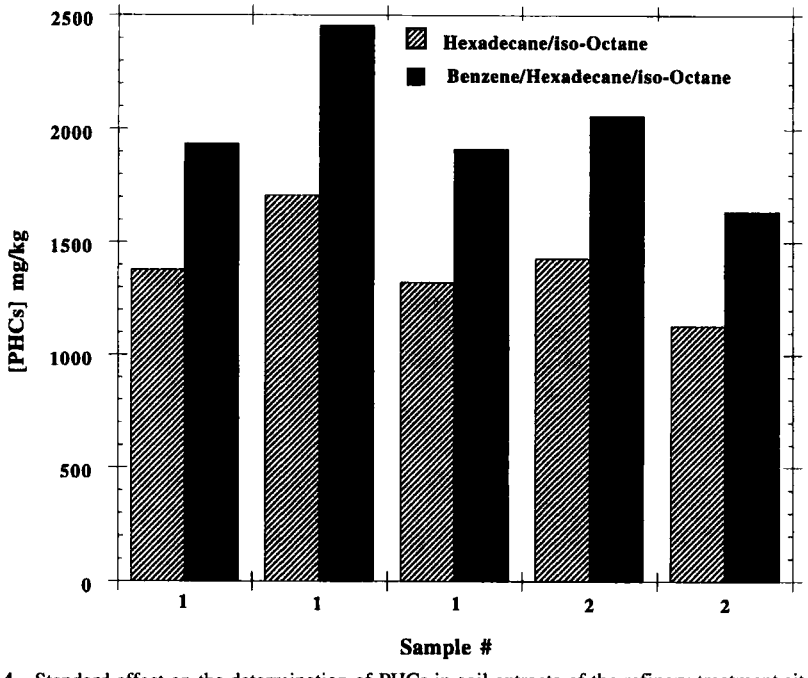

Figure 4 Standard effect on the determination of PHCs in soil extracts of the refinery treatment site: sample 1 collected at 0.6 m depth and sample 2 collected at 1.2 m depth.

Table 1 Soxhlet extraction of PHCs (with Freon-113) from soil at an above ground bioreactor at a refinery site: interlaboratory study.

Sample #[a]	*Present work*		*Private laboratory*[b]	
	Total oil extract (mg/Kg)	*Mineral oil*[c] *(mg/Kg)*	*Total oil extract (mg/Kg)*	*Mineral oil*[d] *(mg/Kg)*
1	2362	1377	3400	3400
2	2774	1708	3100	3100
3	2055	1323[e]	2100	2100
4	2139	1428	3000	2900
5	3382	2331	1400	1400
6	1640	1130[e]	2400	2300

[a] each soil sample was divided into two halves for subsequent analysis by the two labs, samples 1,2 and 3 were collected at 0.6 m depth while samples 4,5 and 6 were collected at 1.2 m depth.
[b] single extraction, single analysis.
[c] after clean-up on a silica column using Freon-113, hexadecane/isooctane ws used as quantitative standard.
[d] extracts were treated by mixing with silica, benzene/hexadecane/isooctane composition as quantitative standards as in EPA Method # 418.1
[e] due to the length of time required for analysis triplicates were carried out in few cases with RSD not exceeding ±10%.

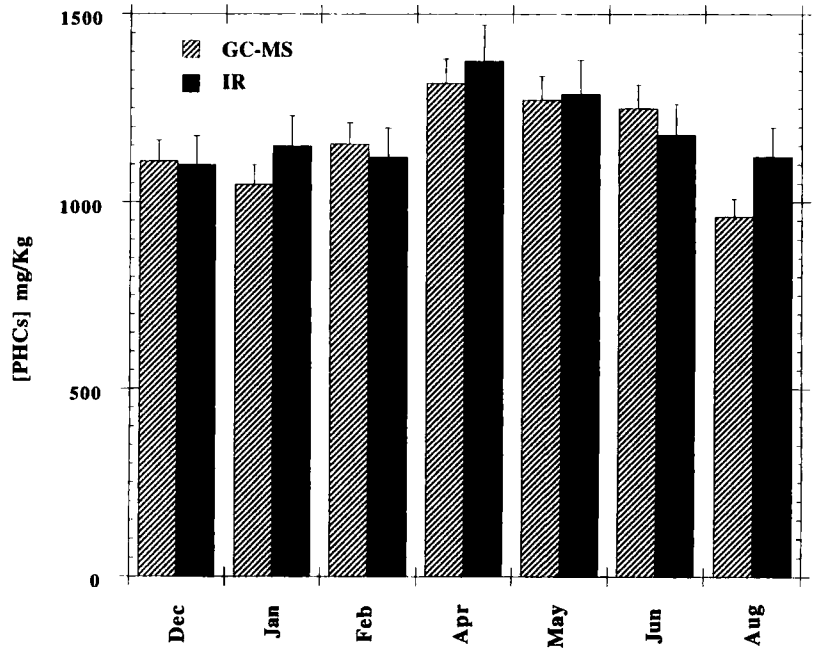

Figure 5 Determination of PHCs at an above ground bioreactor at different time intervals: GC-MS vs IR analysis.

(RSD) not exceeding ±10% were frequently obtained. Concentrations of PHCs were corrected for recovery using internal standards hexadecane and p-terphenyl (reference extraction recoveries ranged from 95%–110%) assuming that no discrimination between losses of the original pollutants and the internal standards took place throughout the analytical procedure.

PHCs determination in soil from a wood preserving facility

Both Soxhlet (with Freon-113) and SFE (with CO_2) were used to extract PHCs from soil samples collected from a site adjacent to a wood preserving facility. Concentrations of PHCs, as determined by Soxhlet, were corrected for recovery using internal standards hexadecane (100 µl from a stock solution of 2 g/L methylene chloride) and p-terphenyl (100 µl from a stock solution of 2 g/L methylene chloride), assuming that no discrimination between losses of the original pollutants and the internal standards took place throughout the analytical procedure. Reference extraction recoveries, using Soxhlet, ranged from 85–103%. As we mentioned earlier when a clean soil was spiked with paraffin oil and subjected to the same analytical protocol (from extraction to IR analysis) > 90% recovery was obtained. In comparison, SFE values were found to be comparable with those of the Soxhlet, i.e., 80% to 100% as shown in Table 2. In general changing the water content of the soil did not drastically affect the recovery of PHCs. As shown in Table 2 the variations in the PHC recovery did not exceed those of the RSD values, i.e., ±2% to ±8% in case of SFE and ±4% to ±13% in case of Soxhlet. However, extensive removal of water from the soil (water % 1.6) resulted in lower SFE recoveries (50% of Soxhlet) but as Figure 6 indicates maximum PHC recovery occurred when the water content stayed between 20% to 30%. Interestingly, in the most recent EPA Method # 3560 for the analysis of total recoverable PHCs in soil using supercritical fluid extraction (SFE), it is recommended that the presence of *ca* 20% water is essential for the enhancement of PHC recovery.[12]

Table 2 Effect of water on the recovery of PHCs from soil samples at a wood preserving facility using both SFE (with CO_2) and soxhelt (with Freon-113).

Water[a] *(%)*	*Soxhlet*		*SFE*	
	Recovery[b] *(mg/Kg)*	*RSD*[c] *(%)*	*Recovery*[b] *(mg/Kg)*	*RSD*[c] *(%)*
1.6	16 230	6.4	8 490	11.5
10	16 040	4.8	12 670	4.8
20	15 690	2.5	13 150	7.7
30	14 740	4.3	13 930	5.4
45	15 100	4.9	14 750	3.9
60	14 560	7.8	11 060	12.9

[a] water was either removed by drying the soil in the open air (fume hood) or by adding water to reach the desired water %.

[b] analysis by IR 2930 cm^{-1} using hexadecane/iso-octane (1/1 w:w) as quantitative standard.

[c] all analysis were done in triplicate.

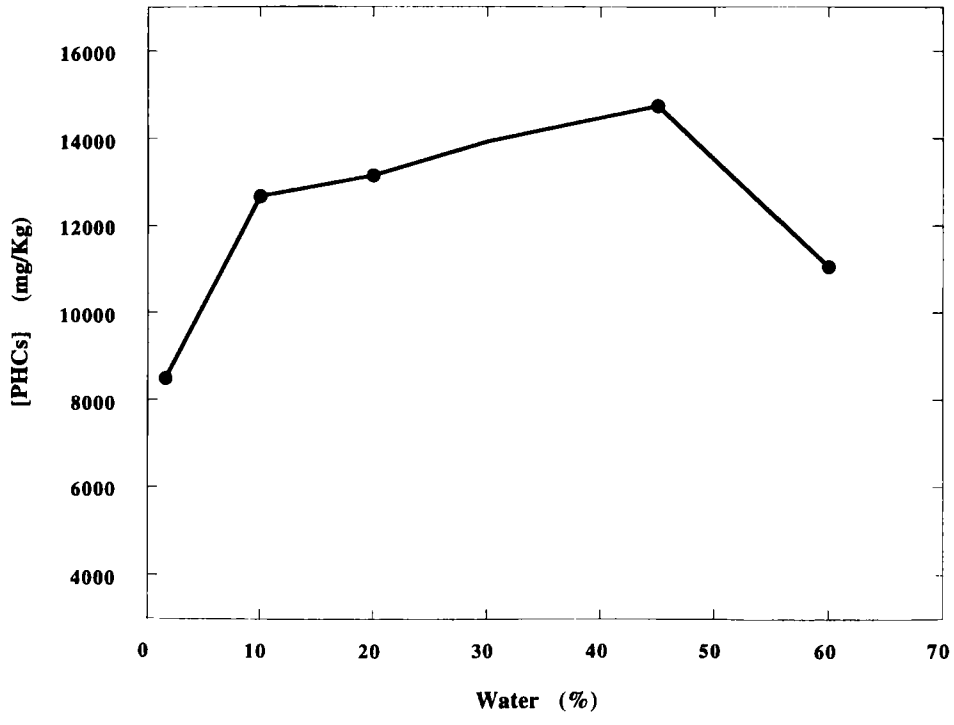

Figure 6 Recovery of PHCs from soil at a wood preserving facility by SFE (with CO_2): water effect.

PHCs in slurry samples from a soil washing/bioremediation process

In a separate study we have investigated the effect of water on the extraction efficiency of PHCs from slurry samples (< 50 μm) originally contaminated with close to 100,000 mg/Kg heavy oil. Water in a slurry was gradually reduced from an original content of 77% to *ca* 1% using centrifugation followed by dehydration using a Dean and Stark Separator. The Dean and Stark separation technique is based on distilling water as an azeotropic mixture with benzene at a relatively mild temperature (< 80°C) and with a short period of time (*ca* 1h). This method of dehydration was found more convenient than other processes such as freeze-drying where dramatic losses of PHCs (up to C_{20}) have been observed.[5] The slurry pellet was extracted using Soxhlet and the extract was purified on a silica column as described above. Once again an excellent mass balance (89% to 103%.) was observed between the crude oil extracts on one hand and various silica fractions on the other using hexadecane as an aliphatic marker and p-terphenyl as an aromatic marker.

Figure 7 clearly indicates a steady increase in the recovery of crude oil extracts and of purified aliphatic PHCs as the water content of the slurry decreased. This increase in the recovery did not level off even at slurry water concentrations approaching 1%. This is the first time that such an extensive study on the effect of water on the recovery of PHCs from slurries has been addressed. We should warn however, that our observation on the water effect on the recovery of PHCs from soil is not necessarily universal and each heterogeneous matrix should be treated independently.

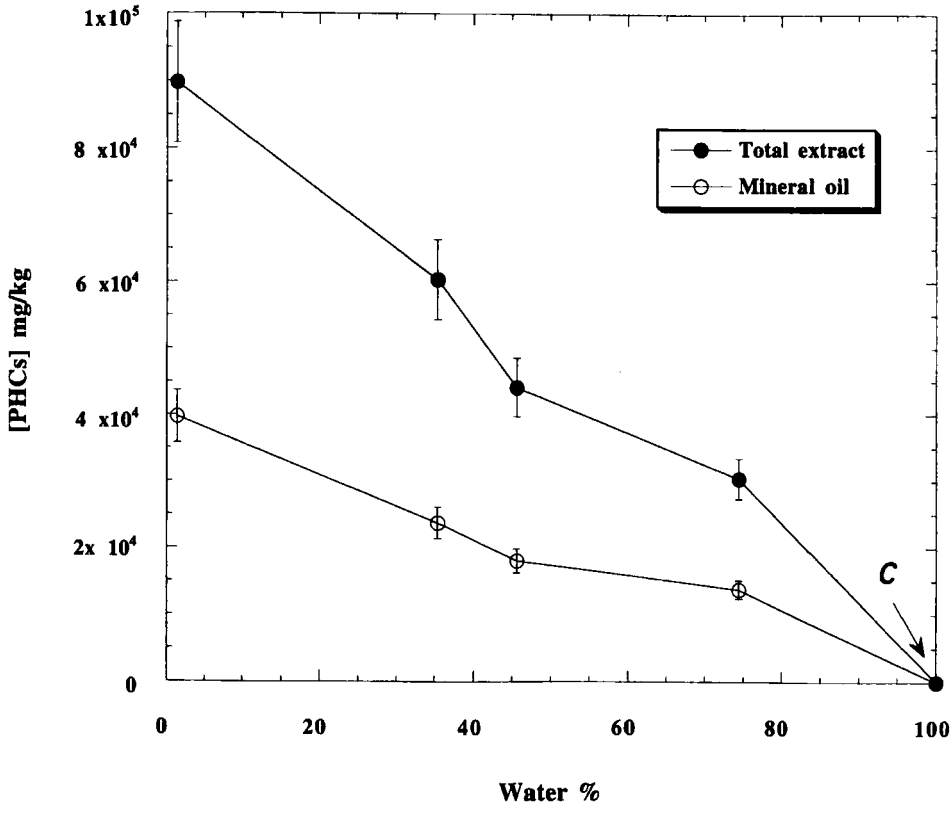

Figure 7 Effect of water on the recovery of PHCs from slurry. Errors were calculated at RSD ±10%. Point C indicates PHCs (10 mg/L) recovered from the water phase alone.

In an earlier study,[13] three slurry samples with various water contents have been extracted using the HP 7680 A SFE (with CO_2) and Soxhlet apparatus using Freon-113 (Table 3). In general, the SFE results indicate that water removal prior to extraction enhances the recovery of PHCs from bioslurries where most of the soil clay fraction is concentrated (average particle size 50 μm). Table 3 also shows that the concentrations of PHCs obtained by SFE are roughly in agreement with those of the Soxhlet, i. e., 70% to 106%. As we mentioned earlier the present analysis by SFE was carried out using commercial units. The validity of SFE as a routine technique is still under question and many researchers have developed their methods using noncommercial apparatus.[14,15] However, Lopez-Avila and coworkers results for the SFE of soil samples were identical on four different commercial SFE systems.[16]

Although several studies have described the effect of humidity on the extraction of hydrocarbons from soil little is known about the detailed effect of water on the recovery of PHCs from flooded soil. For example, English *et al.*[17] Thibaud *et al.*[18] and Rutherford *et al.*[19] have shown that the adsorption of volatile organic compounds (VOCs) by soil minerals decreases with moisture content and becomes minimal when the soil is fully saturated with water. The weak interactions between VOCs and clay has been attributed as due to stronger dipole/dipole interactions between water molecules and the clay part of the soil. These findings are considered extremely important when soil ventilation or

Table 3 Determination of semi-volatile PHCs in a soil bioslurry using EPA method 418.1 and hexadecane/iso-octane as the IR quantitative standard: SFE vs soxhlet.

Matrix	*H_2O %*	*Soxhlet[a] (mg/Kg)*	*SFE[b] (mg/Kg)*	*SFE/Soxhlet (%)*
Soil slurry[c]	23.3	77,822	64,502	83
Soil bioslurry[d]	70.0	30,848	32,628	106
Soil bioslurry[e]	38.0	60,708	42,105	70

[a] Freon-113 as solvent for 80 cycles (replacing Freon with CH_2Cl_2 we were able to extract PAHs including all 16 EPA priority pollutants).
[b] HP 7680 A system, extraction with CO_2 at 50°C using 3 g slurry in 7 mL thimble.
[c] the soil after washing but before biotreatment.
[d] represents the soil slurry after biotreatment then mixed with $MgSO_4$ and extracted.
[e] represents the soil slurry after biotreatment then centrifuged and the pellet was mixed with $MgSO_4$ then extracted.

stripping is used as a remediation technology to clean-up the soil from VOCs such as BTEX: wet air reduces the sorption of VOCs on soil and enhances their desorption (extraction).[18]

In the case of flooded soil, Morel *et al.*[20] has suggested that sediments must be centrifuged before extraction and proposed a Freundlich adsorption/desorption model to evaluate the extraction efficiency of PHCs from sediments. The flow of literature reports clearly warns that the extraction efficiency of PHCs from soil will eventually depend on the extent of soil/contaminant interactions. The low organic content (< 5%) and biomass (< 3.8%) of the present soil, might have resulted in leaving some of the PHCs suspended in water. When the drying agent, $MgSO_4$, was added to the soil/water suspension the suspended PHC fraction might have been irreversibly entrapped within the resulting matrix rendering its extraction virtually impossible. However, when water was centrifuged off and analyzed separately for PHCs we were unable to detect more than 20 mg/L. Still one may argue that the water phase of the bioslurry is expected to contain several soluble humic materials, extra cellular polymers and several other unidentified water soluble molecules. These water soluble organic materials might also irreversibly bind some of the PHCs rendering their extraction very difficult. Interestingly, when we removed water using the Dean and Stark technique we magnified the recovery of the PHCs as shown in Figure 7. In some cases when the slurry sample was digested with HCl (6 M) before extraction up to 10% increase in the recovery of PHCs was observed. Whatever the reasons behind the enhanced recovery of PHCs with the decrease in the water content of the slurry (or bioslurry) the present result clearly demonstrates that each soil or slurry sample, whether taken from an oil spill site or from an *in-situ* or *ex-situ* remediation process must be analyzed carefully for water. The recovery of PHCs should be optimized with reference to the water content of the matrix and reported as such. This would help establish a badly needed mass balance to account for the fate of PHCs in a remediation process. Otherwise a false assessment on the extent of remediation might be obtained.

Commenting on remediation assessment

It is estimated that bioremediation could be a half billion dollar business by the turn of the century. However, this will not happen without controversy because of the rapidly

increasing number of vendors of bioremediation services that has resulted from the availability of site clean-up funding.[21] One major problem in providing a reasonable assessment on the extent of oil remediation is the compositional difference among the samples obtained at different stages of remediation. It is thus strongly recommended that the nature of the matrix, water effect, the clean-up process and the analytical technique must be carefully worked out to minimize the above difference and its effect on oil determination. This is critical to the oil industry (e.g., ocean-tanker spills, closed gas stations and refineries) where environmental decisions with far reaching economic and social consequences are made. The results of this study should serve as a warning against overinterpretation of hydrocarbon measurements even when well established standard methods are followed. Our results on petroleum hydrocarbon analysis in heterogeneous matrices should not be used as an argument against currently available methods, but should be used as encouragement for the continued development of state-of-the-art analytical methods for the determination of PHCs in real matrices such as soil and bioslurries. Therefore, to develop adequate analytical methodology to assess the effectiveness of oil remediation in soil, it is necessary to understand the fundamental processes and interactive mechanisms that occur between these compounds and the soil.

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