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The bituminous material in Arctic peat: implications for analyses of petroleum contamination

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Abstract

The concentration of a contaminant in soil may be quantified by one of many laboratory procedures. In the organic soils of Arctic Alaska, however, procedures intended to quantify a contaminant cannot always differentiate between organic molecules derived from the contamination and molecules derived from the natural organic material (NOM). Research was conducted to assess the impact of NOM on standard methods for quantifying the concentration of crude oil in organic soil. The fraction of organic material extractable in various solvents used for petroleum extraction was quantified, and ranged between 0.5 and 10% of soil NOM. Gravimetric, infrared spectroscopic and GC/MS methods were considered in terms of their ability to differentiate and separate petroleum compounds from NOM. Gravimetric and spectroscopic methods were neither able to separate nor differentiate between compounds from petroleum and NOM. Using GC/MS, compounds from NOM could be differentiated, but not separated from compounds derived from crude oil. Extractable compounds from NOM were identified as n-alkanes (C_{19}-C_{31}), alcohols, aldehydes and ketones.

Keywords: Bioremediation; Peat; Lipid; Extraction; Petroleum; Organic soil

1. Introduction

In order to evaluate any soil remediation program, the concentration of the soil contaminant must be quantified to the maximum extent possible. To quantify a soil contaminant, the compounds must be extracted from the soil with a solvent. The solvent

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and soil must then be separated and the contaminant quantified based on its concentration in the solvent. In organic soils, natural organic material (NOM) complicates crude oil quantification by partitioning into the extraction solvent. Experiments were conducted to quantify the extractable organic material in uncontaminated tundra soils from Umiat, Alaska. The relative mass of NOM extracted by various solvents was compared to values in the literature. Extractable materials in Umiat soil were quantified gravimetrically and by infrared spectroscopy. Problems associated with each method are discussed as they relate to quantifying extractable material from NOM and crude oil. Compounds extracted from NOM were identified with gas chromatography/mass spectrometry (GC/MS).

2. Theory

2.1. Solvent extraction of petroleum compounds

Common solvents used for petroleum extraction are n-hexane, benzene, methylene chloride, carbon disulfide, and 1,1,2-trichloro-1,2,2-trifluoroethane (freon-113). Since crude oil is principally composed of non-polar compounds, the solvents used to extract oil from soil are equally non-polar. Since crude oil includes some polar compounds, the highly non-polar solvents (e.g., n-hexane) are not frequently used. In Fig. 1, the relative polarity of various solvents is illustrated by comparing their respective water solubilities. Since water is a polar solvent, an infinite water solubility indicates the greatest degree of polarity.

Since NOM contains some of the same compounds as crude oil (see Table 1), the solvent used to extract crude oil from soil will also extract a fraction of NOM. The

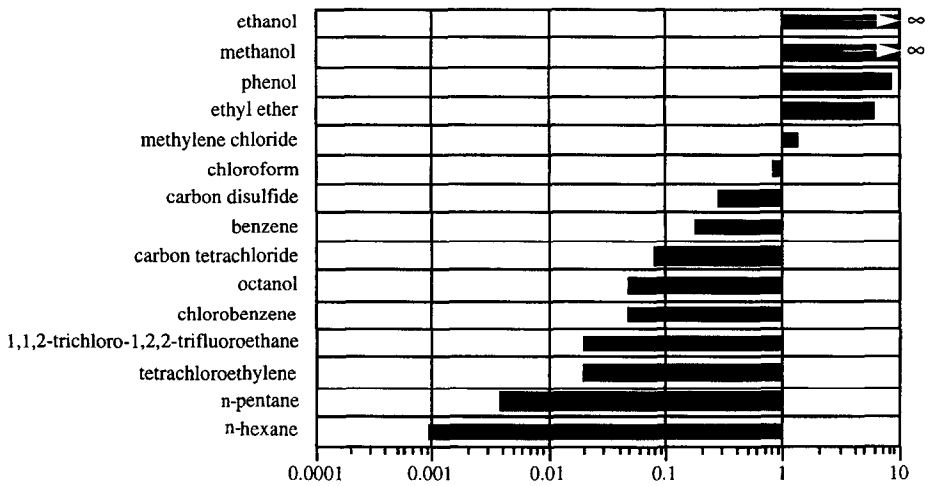

Fig. 1. Solubility of various solvents in water (from Riddick [1]).

Table 1
Compounds present in crude oil and NOM (modified from Jorgenson [2])

acetic acid	heptacosane	n-hentriacontane	octanoic acid
alkanes	heptacosanoic acid	n-heptadecane	o-xylene
benzene	hexacosane	n-hexadecane	pentacosane
1,2-benzofluorene	hexadecanoic acid	n-nonacosane	pentanoic acid
benzoic acid	methane	n-nonadecane	perylene
butanoic acid	methanethiol	nonanoic acid	phenanthrene
carbazole	methanol	n-octacosane	propanoic acid
decanoic acid	m-xylene	n-octadecane	p-xylene
2,6-dimethylundecane	napthalene	n-pentadecane	tetradecanoic acid
eicosanoic acid	n-dotriacontane	n-tetracosane	toluene
ethanol	n-docosane	n-tetradecane	
ethylbenzene	n-eicosane	n-triacosane	
formic acid	n-heneicosane	n-triacontane	

extraction solvent not only extracts those compounds from NOM with the same molecular conformation as compounds in crude oil, but all compounds with similar degrees of polarity. The compounds in NOM which partition into non-polar solvents (i.e., fat solvents) are called 'soil bitumens', or natural fats, waxes, and resins.

2.2. *The origin and composition of soil bitumens*

Soil bitumens compose between 1 and 5% or 10 and 20% of the NOM in mineral and organic soils, respectively [3]. Soil bitumens are composed of numerous types of compounds including aliphatic hydrocarbons, fatty acids, alcohols, polynuclear aromatic hydrocarbons, and other complex hydrophobic molecules.

2.2.1. *Aliphatic hydrocarbons*

Most hydrocarbons in NOM are in the form of straight-chain alkanes and are primarily derived from plants and microorganisms [4]. Some plant waxes, such as that of the *Solandra grandiflora* contain up to 92% alkanes. The alkanes in plant waxes are primarily odd chain alkanes (n-C_{21} to n-C_{37}) [3,5,6], and, depending on the plant, n-C_{27}, n-C_{29}, n-C_{31} or n-C_{33} may be the n-alkane component with the highest relative concentration. Alkanes in plant waxes are most likely produced through the elongation–decarboxylation mechanism in which elongation occurs in 2-carbon units (i.e., lipid synthesis) followed by decarboxylation of the terminal carboxyl group [7]. Although branched chain alkanes are present in plants, they typically represent only a small fraction of the hydrocarbons. Alkenes are also present in some plants, but are generally minor components.

Hydrocarbons in microorganisms are difficult to quantify and characterize since the hydrocarbon composition changes with culture age and growth substrate. In most photosynthetic bacteria, the composition of hydrocarbons ranges from n-C_{14} to n-C_{20}, and in non-photosynthetic organisms from n-C_{26} to n-C_{30}. In one strain of *Micrococcaceae*, 20% of the lipid material consists of monounsaturated hydrocarbons [8].

2.2.2. Other bituminous material

Fatty acids are primarily present in soil as the straight chains between n-C_7 and n-C_{29}, but also as branched fatty acids (C_{12} to C_{19}), unsaturated fatty acids (n-C_{16}, n-C_{18}, n-C_{20}), hydroxy fatty acids (C_{12} to C_{16}), and α, ω-diacids (C_{15} to C_{25}). In soils, the fatty acids n-C_{26} to n-C_{38} typically are derived from plants and insects. The fatty acids n-C_4 to n-C_{26}, on the other hand, are thought to be derived primarily from microorganisms [4]. Consistent with lipid synthesis (2 carbon additions), the predominant fatty acids have an even carbon number, are unbranched and saturated.

Waxes in soil are primarily esters of a higher aliphatic acid to a higher aliphatic or cyclic alcohol [9]. Consistently, the fatty acids and alcohols are principally composed of even carbon number subunits [4]. Polynuclear aromatic hydrocarbons (e.g., pyrene, chrysene, phenanthrene), alcohols (e.g., ceryl alcohol, n-alkanol C_{16} to C_{30}), sterols (e.g., β-sitosterol) and terpenes (e.g., friedelin), pigments (e.g., β-carotene, a-chlorophyll), and heterocyclic compounds (e.g., carbazole) are also present in soil bitumens [3].

2.3. Soil collection

All soils reported on herein were collected from Umiat, Alaska (69° 21′ 00″ N, 152° 10′ 00″ W). A location was selected for soil sampling from the trough and center of a weakly defined, low-centered polygon. The specific location was selected since the surface vegetation, microtopographical classification, and vertical organic profile were characteristic of North Slope tundra. The soils were also selected to be consistent with the type of soil studied in the International Biological Program, Tundra Biome Project [10]. Prior to soil collection, the surface vegetation and rhizosphere were removed from a 30×200 cm section of tundra. Soil was then collected to the depth of permafrost, approximately 36 cm in the polygon trough, and 23 cm at the polygon center. In total, 136 kg of uncontaminated soil were sealed in coolers and returned to Notre Dame where they were stored at 4°C. A second trip was made to Umiat, September 1994, to refresh the original soil stock. Soil was collected from the polygon center at approximately the same location but from a slightly shallower depth due to the location of the permafrost table (i.e., 20 cm in 1994 versus 23 cm in 1992). Because of the slightly different depth and omission of trough material, the new soil contained a greater percentage of organic material (i.e., 60–65% versus 20–25% organic material). All Umiat soil from the first or second sampling dates (i.e., Umiat soil (#1) and Umiat soil (#2), respectively) was uncontaminated.

2.3.1. Physical description

The soils collected from the trough and basin were classified as *Histic Pergelic Cryaquepts* (organic mineral soil with organic material in the top 25 cm) and *Pergelic Cryohemists* (organic soil with organic material in the top 40 cm), respectively. The particle size distribution of Umiat soil (#1), as determined by sieve analysis [11], is illustrated in Fig. 2. Based on a textural diagram (Fig. 3), Umiat soil (#1) is similar to the *Histic Pergelic Cryaquepts* or *Pergelic Cryohemists* of Barrow, Alaska [10].

The soil samples collected in 1992 were from the 15–36 cm depth and contained the

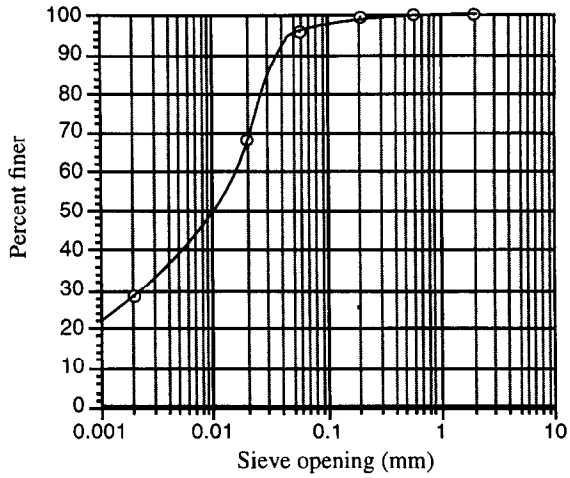

Fig. 2. Particle size distribution for Umiat soil (#1).

fibrous and partly decomposed plant material of the 15–30 cm depth, and the highly decomposed organic material of the 30–36 cm depth. The soil collected during the second sampling (10–20 cm) consisted of fibrous and partly decomposed plant material with small inclusions of highly decomposed organics. The C:N ratio of a representative sample of Umiat soil (#1) was 18.45 (9.6–10.5% C). Umiat soil (#2) had a representative C:N ratio of 24.2 (29.0–32% C), as determined by carbon, hydrogen, nitrogen (CHN) analysis (Carlo Erba CHNS-O EA1108 Elemental Analyzer).

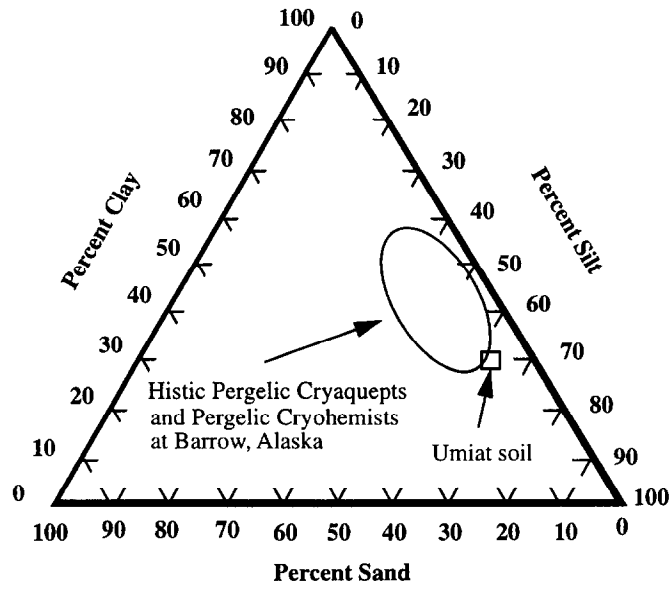

Fig. 3. Textural diagram (modified from Gersper [10]).

3. Experimental

3.1. Gravimetric analyses

Gravimetric analyses were used to quantify the mass of solvent extractable NOM from Umiat soil (#2). Solvent extraction of soil bitumens was based on procedures used by Yocum [12]. Instead of 1.5–3 ml solvent per gram dry soil, however, 10 ml of solvent per gram were used to obtain better contact between the solvent and soil (based on visual observation). The solvents used for extracting soil bitumens were benzene:ethanol (2:1), methylene chloride, ethyl ether, carbon disulfide, benzene, 1,1,2-trichloro-1,2,2-trifluoroethane (freon-113), and n-hexane.

Extractions were prepared by combining 2.0 g of moist Umiat soil (#2) (i.e., 0.578 g dry wt.) and 4.36 ml double distilled water (i.e., to achieve a solids concentration of 10%, w/w) in 20 ml screw-cap test tubes. A solvent volume of 5.78 ml was then added to each sample (i.e., 10 ml g^{-1} dry soil) along with 5 drops of 1:1 HCl and distilled water to achieve a pH less than 2. All extractions were prepared in duplicate. All test tubes were sealed with a teflon lined screw cap and vigorously shaken on a Burrell Wrist Action Shaker, Model 75 for 30 min. All tubes were then centrifuged in a Fischer Centrific on a setting of 8 for 20 min. From all tubes, 2 ml of the solvent phase were withdrawn, 1 ml at a time, with a Hamilton 1 ml gastight syringe. In the case of the benzene:ethanol mixture, 2 ml of benzene only were recovered. All solvent extracts were filtered through a 0.45 μm CR Acrodisc PTFE (teflon) filter (Fischer) directly into pre-weighed tins. Prior to each sample filtration, the filter was washed with the respective clean solvent to eliminate any leachable materials. Blanks were included with samples to ensure that the mass of any leachable materials was negligible. The solvent was allowed to evaporate from the weigh tins which were covered by overturned, 500 ml beakers for 20 h. The mass of extracted material was determined gravimetrically on a Mettler AT261 DeltaRange scale.

The evaporation rate of soil bitumens and crude oil were separately determined by adding 2 mg of soil bitumens in a freon solution, or 2 g of crude oil (ARCO, Alaska) to weigh tins (with a surface area of approximately 6.5 cm^2). The tins were incubated at 4 or 20 °C and weighed periodically.

3.2. Gas chromatography / mass spectrometry

Extraction procedures were used according to Yocum [12]. Samples of Umiat soil (#1) ranging in weight between 3 and 6 g of moist soil (40% moisture w/w) were mixed with 4 ml of CS_2 and 6 ml of water in 15 ml screw cap vials. The vials were then shaken on a Burrell Wrist Action Shaker Model 75 for 1 h and centrifuged at 10 000 rpm for 40 min on a Hettich Model EB8 35 centrifuge. The CS_2 was recovered with a Hamilton 1 ml gas-tight syringe and sealed in 1.5 ml GC auto-sampler vials. Standards, prepared by dissolving crude oil in CS_2, were sealed in GC auto-sampler vials and analyzed by GC/MS in sequence with the samples.

The GC was an HP Series II with an Ultra 2 column (5% Ph Me Silicon) 50 m × 0.2 m × 0.1 μm film thickness fitted with an HP model 7673 autosampler and plumed

directly to an HP 5971 Series Mass Selective Detector on EI mode. The MS scanned mass units 46 to 650. The computer hardware was an HP Apollo Series 400 with HP *Chemsystem 400* software. All mass spectra were compared to the Wiley 138.1 mass spectral library. Chromatographic conditions were 50 °C for 8 min then 10 °C min^{-1} to 300 °C and hold for 15 min. The column pressure was held at 137 kPa using helium as a carrier gas at 0.5 cc min^{-1}. The sample was injected with a split ratio of 1:100.

A standard curve of crude oil concentration vs. total area was prepared by integrating the total chromatographic area for crude oil standards. The standard curve was fitted with a straight line having an 'R^2' of 0.997.

3.3. Infrared spectroscopy

Infrared spectroscopy (as for EPA methods 413.2 and 418.1 [13]) was used to quantify soil bitumens and crude oil in freon extracts. Analytes were recovered with extraction procedures previously described (Section 3.1). The effect of silica gel clean-up on recoverable soil bitumens (i.e., EPA Method 418.1) was demonstrated by rinsing 3 ml of the solvent extract through a Bond Elute (Varian), solid phase extraction column (500 mg of silica gel), attached directly to the end of the CR Acrodisc PTFE filter using a syringe adapter (Varian).

Standards were prepared according to EPA Methods 413.2 and 418.1. In addition, alternative standards were prepared by adding a known mass of crude oil to freon to achieve a concentration of 500 mg l^{-1} crude oil. Sub-samples of the standard were then diluted to 200 mg l^{-1} and 100 mg^{-1}. Prior to analysis, all samples and standards were filtered through a 0.45 μm CR Acrodisc PTFE filter which had been thoroughly rinsed with freon-113 to prevent leaching of filter material (confirmed by measuring the absorbance of freon-113 filtrate).

The absorbance of each solvent extract was measured on a Galaxy FTIR 5000. Testing conditions were 16 scans s^{-1} with a resolution of 4 wavenumbers. Wavenumbers 2800–3200 were scanned with mirror velocities of 0.6 cm s^{-1} forward and 1.3 cm s^{-1} reverse and a 25% iris opening. A cell with a 10 mm path length was used to contain samples.

4. Results and discussion

4.1. Gravimetric analyses

The mass percent of NOM extracted by each solvent tested is represented in Fig. 4. The largest percentage of NOM was extracted by the benzene:ethanol mixture. Ethanol acts to break lipoprotein or glycoprotein complexes, liberating 'bound' soil bitumens. Whereas 15.5% of the soil's NOM was extracted by benzene:ethanol (2:1), only 2.2% was extracted by benzene alone, illustrating the elevated extraction efficiency of benzene when coupled with ethanol. The soil bitumen fraction of NOM typically composes between 10 to 20% of the NOM in organic soils, and is divided into ether soluble (fats and waxes), and alcohol soluble (resins) materials. Ether soluble material from peat

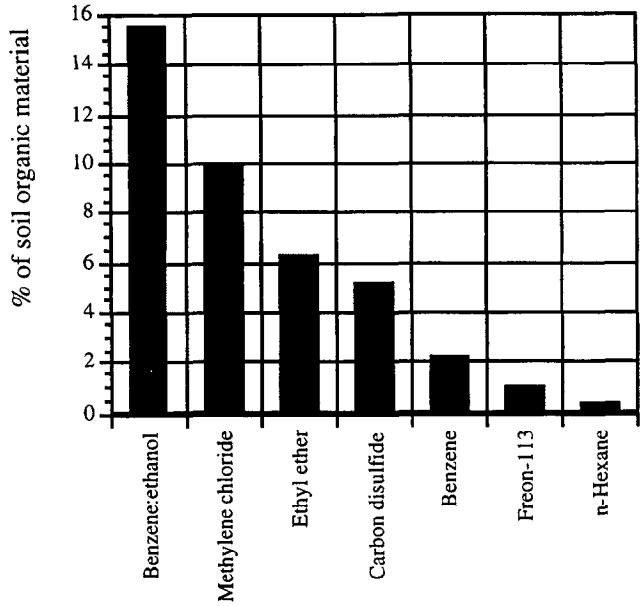

Fig. 4. Mass percent of soil bitumens extracted by various solvents.

typically ranges between 0.42–9.36% of the NOM [3]. From Fig. 4, the 'ether soluble' fraction of Umiat soil (#2) accounted for 6.2% of the total NOM, well within the reported range.

For solvents other than ethyl ether, the relative mass of NOM extracted by each solvent decreased with the degree of solvent polarity (see Fig. 5). Freon extracted approximately 1% of Umiat NOM (#2), corresponding to roughly 6000 mg organic material per kg dry soil. Carbon disulfide and methylene chloride, also used to extract petroleum from soil, extracted far more of the NOM (approximately 5–10 times that amount). All solvents extracted a sufficient mass of NOM to interfere with gravimetric quantification of crude oil (had the soil been contaminated).

4.1.1. The volatile fractions of crude oil and NOM

The inability to preserve volatile compounds during gravimetric measurement reduces recovery and introduces errors. As illustrated in Fig. 6, roughly 17 and 18% of a static crude oil sample evaporated in only 3 days at 4 and 20 °C, respectively. Since the volatile fraction of crude oil can be appreciable, the time during which the oil is exposed to the atmosphere is critical and must be considered in analyses. Unlike crude oil, the volatility of the soil bitumens was negligible during the same time period (see 'soil bitumens', Fig. 6). If the relative masses of crude oil and soil bitumens in a contaminated sample were not known, it would be difficult to compensate for evaporative losses during gravimetric analyses.

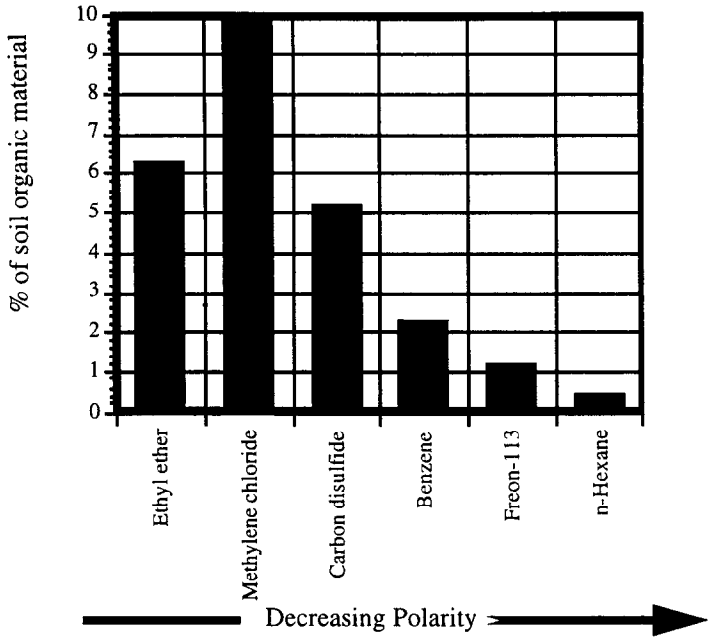

Fig. 5. Mass of soil bitumens extracted by various solvents.

4.2. Gas chromatography mass^{-1} spectrometry

Approximately 3800 mg kg^{-1} of soil bitumens were recovered from Umiat soil (#1) with carbon disulfide (CS_2). The compounds which extracted into the CS_2 from NOM

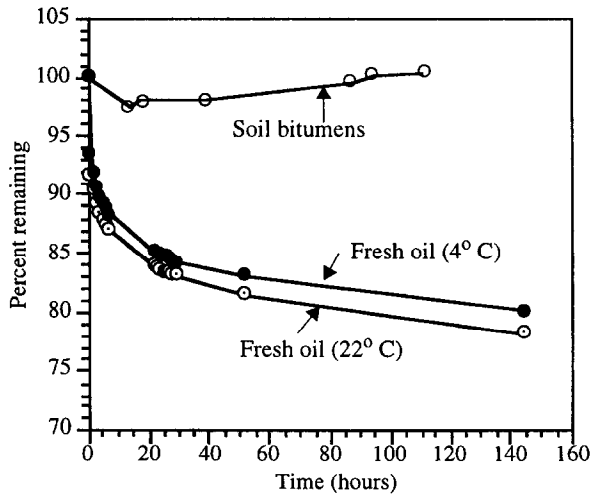

Fig. 6. Evaporative losses from crude oil.

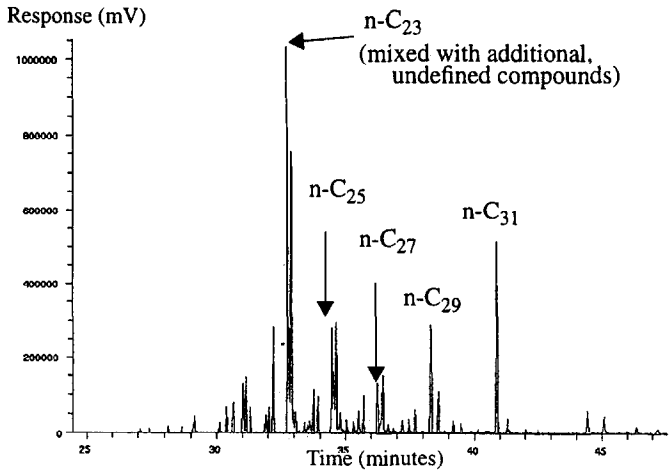

Fig. 7. Chromatogram of soil bitumens from Umiat soil (#1).

were identified by GC/MS as long chain n-alkanes, ketones, aldehydes and alcohols (Fig. 7).

To illustrate the impact of the soil bitumens on crude oil analyses, Umiat soil (#1) was artificially contaminated with 6400, 13 000, 51 000 and 103 000 mg kg^{-1} of crude oil. These values represent the actual crude oil added on a weight basis. The soil was then extracted and analyzed by GC/MS. The 4 chromatograms are illustrated in Fig. 8 and Fig. 9. From Fig. 8a (i.e., 6400 mg kg^{-1} of crude oil), it was observed that soil bitumens constituted a major fraction of the total organic material extracted. Despite the fact that the soil bitumens were easily identified, selectively separating them from compounds in crude oil was impossible since many compounds from each source were identical. In Fig. 9b (i.e., 103 000 mg kg^{-1} crude oil), the extractable NOM was not identified easily, even though 3800 mg kg^{-1} of soil bitumens were present.

4.3. Infrared spectroscopy

'Total petroleum hydrocarbons' (TPH) or 'oil and grease' (O + G) are standard ways to express petroleum contamination by EPA Methods 418.1 and 413.2, respectively. Both methods use infrared spectroscopy (IR SPEC) to quantify the mass of petroleum (e.g., crude oil) in a freon extract. The measurement is based solely on the relative absorbance of a CH bond between samples and standards. As a result, soil bitumens cannot be distinguished from petroleum compounds if the 2 mixtures are present in the freon extract. Since crude oil and NOM are indistinguishable in the IR SPEC signal, the 2 are discussed together in the following section.

4.3.1. Quantification of crude oil and NOM by infrared spectroscopy

The difference between EPA Methods 418.1 and 413.2 is that the solvent extract is pretreated with silica gel in Method 418.1. TPH or O + G are quantified by measuring

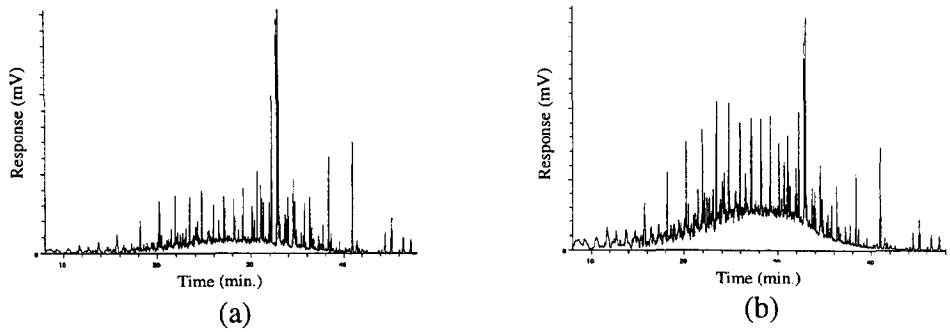

Fig. 8. Chromatograms of Umiat soil (#1) contaminated with (a) 6400 mg kg^{-1}, and (b) 13000 mg kg^{-1} of crude oil.

the height of the CH bond stretch (i.e., of a CH_2 sub-unit with in phase H) at wavenumber 2930 cm^{-1}. Infrared spectra are obtained for samples and standards, where each standard represents a known TPH, or O + G concentration. The CH bond stretch for samples and standards are then compared to quantify the 'petroleum' concentration of each sample. In the following discussion, the solvents were not pretreated with silica gel prior to IR SPEC (i.e., EPA Method 413.2), except where noted.

The standard calibration mixture for the IR SPEC methods is prepared by combining chlorobenzene, iso-octane, and n-hexadecane at 25%, 37.5%, 37.5%, V:V respectively. Since samples do not typically contain the same compounds as the calibration mixture, the relationship used to quantify the sample is somewhat skewed. To illustrate the differences between the standard calibration mixture and samples of crude oil and soil bitumens, the relative magnitudes of CH bond stretches (besides the CH_2 – in phase H) are included in the following discussion. The IR spectrum of the calibration mixture (Fig. 10) shows CH absorbances of the asymmetric CH_3, symmetric CH_3, CH_2 (in phase H), CH_2 (out of phase H), and a minor aromatic CH bond stretch. The spectra of crude oil and soil bitumens (Fig. 11), compared to the calibration mixture, contain lower

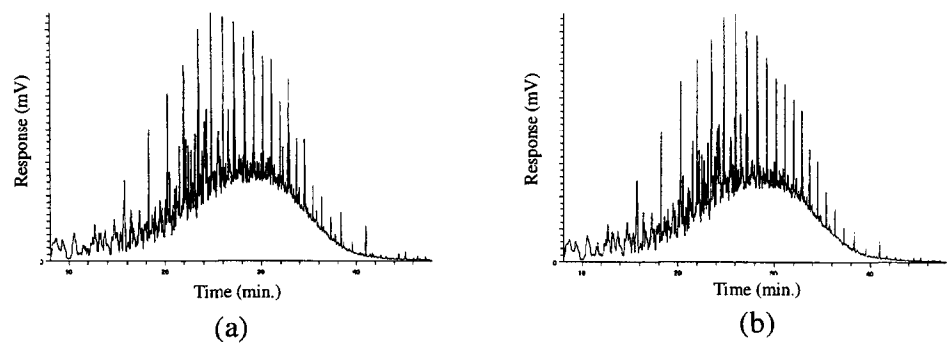

Fig. 9. Chromatograms of Umiat soil (#1) contaminated with (a) 51000 mg kg^{-1} and (b) 103000 mg kg^{-1} of crude oil.

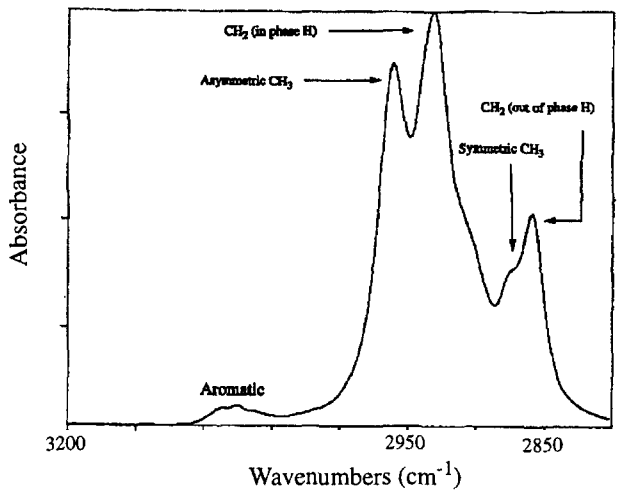

Fig. 10. IR spectrum for the standard calibration mixture.

ratios of CH_3/CH_2 bond stretches. The difference results from the fact that crude oil and soil bitumens consist of longer chain aliphatics than the calibration mixture. The alkanes represented in the calibration mixture are iso-octane (branched-C_5) and n-hexadecane (n-C_{16}). The n-alkanes represented in crude oil and soil bitumens, however, can extend up to n-triacontane (C_{33}) and n-heptacontane (C_{37}), respectively. Longer n-alkanes have a much higher molar absorptivity than shorter n-alkanes, and, therefore, are poorly represented by the calibration mixture. To illustrate this effect, IR spectra for HPLC grade n-hexane and n-hexadecane are illustrated in Fig. 12. The high molar absorptivity of n-hexadecane relative to n-hexane shows how the fraction of all CH stretches (i.e., symmetric and asymmetric CH_3, and CH_2 in and out of phase H) represented by the CH_2 (in phase H) is much greater for the longer n-alkanes.

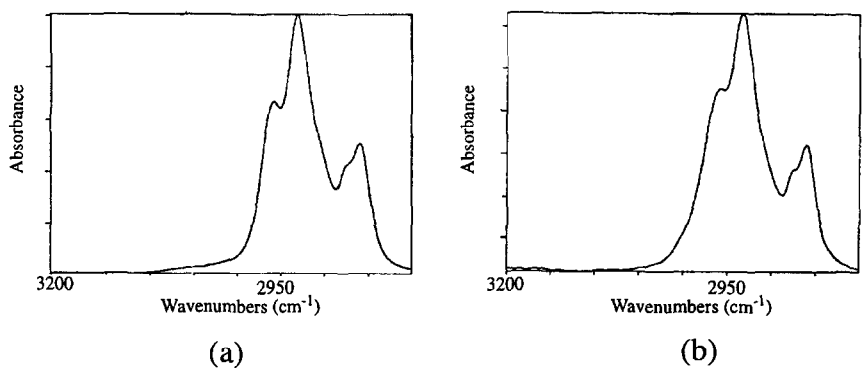

Fig. 11. IR spectra for (a) crude oil, and (b) NOM.

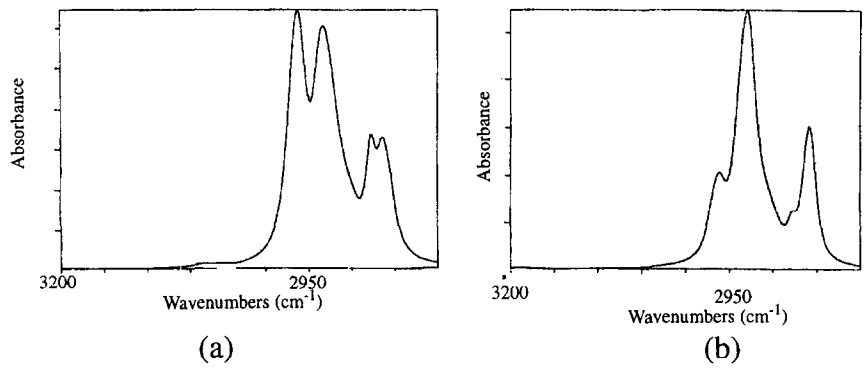

Fig. 12. Comparison of CH_2 (in phase H) stretch for (a) n-hexane, and (b) n-hexadecane.

Higher molar absorptivity in samples compared to standards is manifested in test results by an over-estimation of analyte concentration. When quantified by a standard curve of the calibration mixture, the concentration of crude oil in a prepared sample appeared 20% greater than when determined gravimetrically. For soil bitumens, the actual sample concentration was over-estimated by roughly 40%. To eliminate the errors introduced by using the standard calibration mixture, alternative standards were prepared with crude oil. The curve of absorbance versus concentration of a crude oil standard is illustrated in Fig. 13, accompanied by that of the standard calibration mixture. The percent IR/gravimetric was reduced to 100% for crude oil when using the crude oil standard. The IR/gravimetric ratio for soil bitumens was correspondingly reduced to roughly 115% (from 140%) with the crude oil standards. The remaining over-estimation of soil bitumens resulted from the higher molar absorptivity of the average NOM n-alkane (C_{19}-C_{37}) compared to the average crude oil n-alkane (C_{10}-C_{33}).

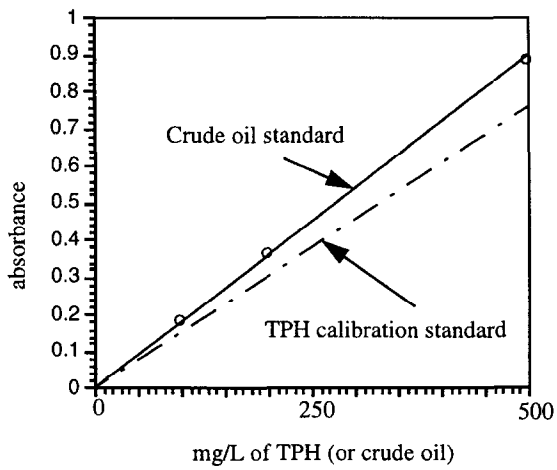

Fig. 13. Comparison of TPH calibration standard and modified crude oil standard.

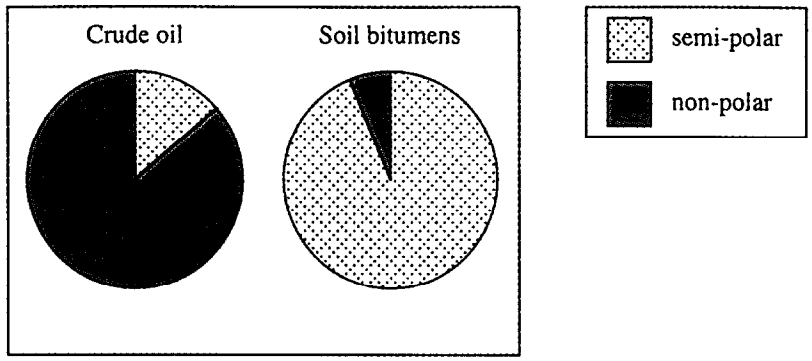

Fig. 14. The effect of silica gel rinse on crude oil and NOM extracts.

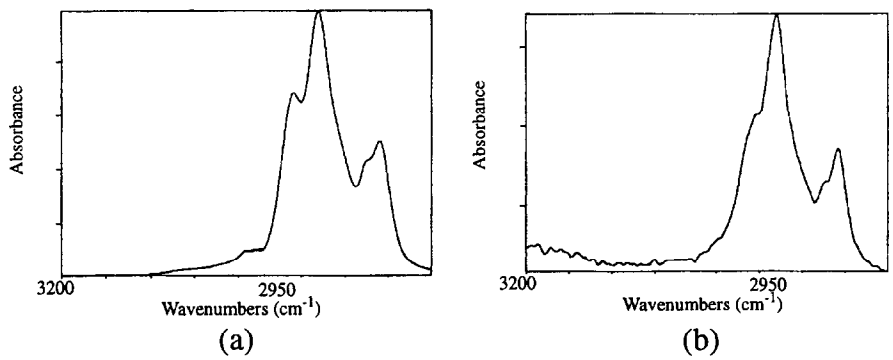

Fig. 15. IR spectra following a silica gel rinse of (a) crude oil, and (b) NOM.

4.3.2. Polar materials

Since EPA Method 418.1 is intended for hydrocarbons (as opposed to 'oil and grease'), a silica gel clean-up is included to remove semi-polar materials from the solvent phase. The effects of a silica gel wash on crude oil and on soil bitumens were compared. As illustrated in Fig. 14, the concentration of the crude oil standard was

Table 2
Mass of soil bitumens based on IR quantification

Sample	Soil bitumens (based on a crude oil standard) ($mg\,kg^{-1}$)		Soil bitumens (based on the standard calibration mixture) ($mg\,kg^{-1}$)	
	Before gel wash	After gel wash	Before gel wash	After gel wash
1	4025	278	4797	331
2	4082	278	4865	331
3	4348	323	5182	385

lower by approximately 13.5% after silica gel wash while that of the soil bitumens was lower by 94%. The high percent reduction of soil bitumens confirms their semi-polar character. The concentration of polar material in crude oil is reported to range between 2.9 and 17% w/w [14]. Actual values for 'TPH' of the soil bitumens illustrated in Fig. 14 are listed in Table 2.

The IR spectra of crude oil, before and after silica gel wash, indicate that the character of oil did not change appreciably as a result of treatment with silica gel (Fig. 15a vs. Fig. 11a). The IR spectra of soil bitumens exhibited a slight increase in the relative absorptivity at the CH_2 (in phase H) stretch after silica gel wash (Fig. 15b vs. Fig. 11b).

5. Conclusions

5.1. Solvent extraction

5.1.1. Solvent selection

Naturally occurring soil bitumens complicate methods for quantifying crude oil in organic soils. These bitumens should be excluded from the solvent phase if the integrity of the target analyte (i.e., crude oil) can be maintained. Many of the same compounds are present in crude oil and soil bitumens, however, and exclusion of the soil bitumens is only done at the expense of some fraction of crude oil (i.e., presumably desired for quantification). The use of a specific solvent or extraction method may result in different interpretations of contaminant concentration in soil.

5.1.2. Solvent clean-up

Clean-up procedures can be used to remove much of the NOM from a solvent extract. If the semi-polar compounds from NOM are eliminated from the extract, however, the same compounds are eliminated from the dissolved crude oil. If the mass of extractable NOM in a sample is sufficiently high to prevent accurate assessment of the mass of crude oil, a clean-up procedure must be used.

5.2. Analytical techniques

5.2.1. Potential for gravimetric analyses

The advantages of gravimetric analyses over all other quantification methods are its simplicity and cost-effectiveness. The disadvantages are that it cannot be used to differentiate individual compounds and the results are subject to analyte volatility (an effect which changes with the length of the solvent evaporation period). In addition, the difference in evaporation rates of crude oil and soil bitumens may further complicate analyses.

5.2.2. Potential for gas chromatography / mass spectrometry

Gas chromatography/mass spectrometry is a common method for quantifying the mass of a contaminant in an extraction solvent. Although GC/MS can be used to

distinguish soil bitumens from a simple petroleum product, such as gasoline, soil bitumens cannot be separated from a complex mixture such as crude oil. As was illustrated in Fig. 8 and Fig. 9, at a high level of contamination (i.e., 102 000 mg kg^{-1}), 3800 mg kg^{-1} of soil bitumens were not easily isolated; at a low level of contamination (e.g., 6400 mg kg^{-1}), however, the soil bitumens dominated the chromatographic signal.

5.2.3. Potential for IR spectroscopy

The advantage of IR spectroscopy over gravimetric techniques is that contaminants are analyzed in a liquid solvent, and evaporation does not become an issue inasmuch as the analytical measurement is concerned. It is also a fast method (i.e., 30 sec), and an IR spectrophotometer is a common piece of laboratory equipment. The use of IR spectroscopy, however, mandates the use of specific extraction solvents. Any solvent with a C-H bond cannot be used, eliminating n-hexane, benzene, and ethyl ether. In addition, the IR measurement can be biased by the molar absorptivity of the sample relative to the standard calibration mixture.

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References

[1] J.A. Riddick and W.B. Bunger, Organic Solvents, Wiley-Interscience, New York, NY, 1970, pp. 61–551.
[2] M.T. Jorgenson, T.C. Cater and K.Kielland, Bioremediation and Tundra Restoration After a Crude Oil Spill Near Drill Site 2U, Kuparuk Oilfield, Alaska, personal communication, 1990.
[3] O.C. Braids and R.H. Miller, in J.E. Gieseking (Ed.), Soil components: Vol. 1, Organic Components, Springer-Verlag, New York, NY, 1975, pp. 343–368.
[4] F.J. Stevenson, Humus Chemistry, John Wiley and Sons, New York, NY, 1994, pp. 1–211; 259–302.
[5] A.P. Tulloch, in P.E. Kolattukudy (Ed.), Chemistry and Biochemistry of Natural Waxes, Elsevier, New York, NY, 1976. pp. 236–290.
[6] F.J. Stevenson, J. Am. Oil Chem. Soc., 43 (1966) 203.
[7] P.E. Kolattukudy, R. Croteau and J.S. Buckner, in P.E. Kolattukudy (Ed.), Chemistry and Biochemistry of Natural Waxes, Elsevier, New York, NY, 1976, pp. 289–350.
[8] P.W. Albro, in P.E. Kolattukudy (Ed.), Chemistry and Biochemistry of Natural Waxes, Elsevier, New York, NY, 1976, pp. 419–445.
[9] W. Bergmann, in I.A. Berger (Ed.), Organic Geochemistry, Pergamon Press, London, 1963, pp. 504–542.
[10] P.L. Gersper, V. Alexander, S.A. Barkley, R.J. Barsdate and P.S. Flint, in J. Brown, P.C. Miller, L.L. Tieszen and F.L. Bunnell (Eds.), An Arctic Ecosystem, Dowden, Hutchinson and Ross, Stroudsburg, 1980, pp. 219–254.
[11] G.W. Gee and J.W. Bauder, in A. Klute (Ed.), Methods of Soil Analysis, Pt. 1, ASA-SSSA, Madison, 1986, pp. 383–408.
[12] P.S. Yocum, Bioremediation of Leachate and Soil Contaminated with Petroleum Products, Ph.D. Dissertation, University of Notre Dame, IN, 1993, p. 173.
[13] J.F. Kopp and G.D. McKee, Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Cincinnati, 1983, pp. 415.1–3.
[14] R.A. Gill and P.W.J. Robotham, in J. Green and M.W. Trett (Eds.), The Fate and Effects of Oil in Freshwater, Elsevier Applied Science, New York, NY, 1989, pp. 11–40.