Analytical Methods for the Determination of Total Petroleum Hydrocarbons in Soil

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Analytical Methods for the Determination of Total Petroleum Hydrocarbons in Soil

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ABSTRACT

This paper describes methods for determination of hydrocarbons in soil. Hydrocarbons may enter the soil environment from a number of sources and thus widely different spectra of these molecules appear at contaminated sites. The relevant chemistry of hydrocarbons likely to be encountered at contaminated sites is briefly reviewed and the importance of hydrocarbon speciation noted in terms of a toxicological basis for risk assessment. Hydrocarbon interaction with soil contaminants is important both in terms of their toxicology and also their accessibility by analytical methods. There is no simple procedure that will give an overall picture of hydrocarbons present at contaminated sites. This is largely because the molecules are present in two separate categories - viz. volatile and semi or non-volatile. These two categories require significantly different sample collection, handling and management techniques. Volatile hydrocarbons may be collected by zero headspace procedures or by immediate immersion of the soil into methanol. Their analysis involves gas chromatographic methods such as purge and trap, vacuum distillation and headspace. On the other hand, samples for the determination of semi and non-volatile hydrocarbons need not be collected in such a rigorous manner. They require extraction by techniques such as solvent or supercritical fluid on arrival at the laboratory. Some cleanup of extracts is also necessary in most cases and the analytical finish is again by gas chromatography. Detectors used range from flame ionisation to Fourier transform infrared and mass spectrometric, the latter types being necessary to achieve speciation of the component hydrocarbons. The use of special components of crude oil (known as biomarkers) for estimation of weathering and determination of source is also discussed. Some consideration is also given to screening procedures, which may be used to roughly delineate the extent of hydrocarbon pollution at a site and their limitations are also discussed.

1   INTRODUCTION

The determination of hydrocarbon contaminants in soil is one of the most frequently performed analyses in the study of contaminated sites and is also one of the least standardized. Given the wide variety of hydrocarbon contaminants that can potentially enter and exist in the soil environment, a need exists for methods that satisfactorily quantitate these chemicals. Formerly, the idea of total hydrocarbon determination in soil was seen as providing a satisfactory tool for assessing contaminated sites. Modern assessment methodology for contaminated sites however dictates a risk-based approach and hence quantitation of particular hydrocarbon species is required.

2   ORIGINS OF HYDROCARBONS IN SOIL

Hydrocarbon species can enter the soil environment from a number of sources. The origin of the contaminants has a significant bearing upon the species present and hence the

analytical methodology to be used. Unlike other chemicals (notably pesticides) hydrocarbons were generally not applied to soils for a purpose and thus hydrocarbon contamination results almost entirely from misadventure. The source that is probably most familiar to persons involved in the study of contaminated sites is leakage from underground storage tanks. This is particularly important at the site of former petrol stations and the hydrocarbons involved are generally in the gasoline range. Other major sources include spillage during refueling and lubrication (notably in places such as railway yards), the hydrocarbons here being within the diesel and heavy oil range. Places in which transfer and handling of crude oils takes place (such as tanker terminals and oil refineries) are also potential places of contamination, the oil being largely of the heavier hydrocarbon type. Shale oil retorting plants provide another source of hydrocarbon contamination as do coal gasworks sites, particularly those at which "benzole recovery" was practiced (Barash and Gooderham, 1961).

Although the majority of hydrocarbons in the soil environment are anthropogenic in nature, there are some natural sources of these materials. Included in this category are seeps from oil deposits (such as shale oil mineralisations) and degradation of organic matter. There is also a body of evidence to show that certain organisms, notably higher plants are capable of synthesising hydrocarbons (De et. al, 1997) and these too could find their way into the soil environment. These latter sources are however fairly minor and are unlikely to result in significant soil contamination.

Scheme 1: Hydrocarbon Inputs to the Soil Environment

$C_6 - C_9$ $C_{12} - C_{14}$ $C_{10} - C_{50}$

$C_{12} - C_{22}$ $C_6 - C_{30}$ $> C_{20}$
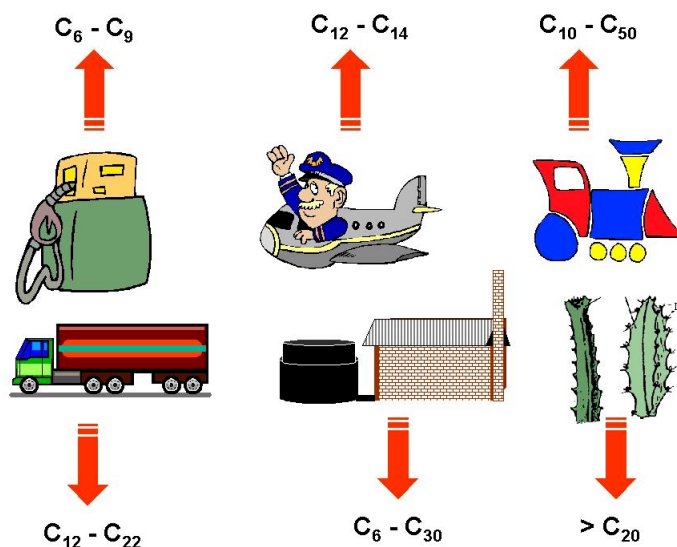
3   COMPONENTS OF HYDROCARBONS FOUND AT CONTAMINATED SITES

Before further considering the chemistry of hydrocarbons, it is necessary to establish definitions for two commonly-used acronyms. PHC (petroleum hydrocarbons) is widely used to refer to the hydrogen and carbon-containing compounds that originate from crude oil. TPH (total petroleum hydrocarbons) refers to the measurable amount of petroleum-based hydrocarbons in an environmental matrix. Thus, whilst PHC deals with an absolute and somewhat intangible quantity, TPH pertains to actual results obtained by sampling and analysis. As mentioned above, in its strictest sense, TPH pertains to a

mixture and hence the results of simple TPH analysis are not of great help in terms of risk assessment (ATSDR, 1998).

A full discussion of the elementary chemistry associated with hydrocarbons is beyond the scope of this paper and the reader is referred to standard organic chemistry texts (eg. Morrison and Boyd, 1973). Table 1 lists the properties of a range of simple paraffin alkanes, which could be found at contaminated sites.

Table 1: Simple Paraffin Alkanes

Molecular Formula	Name	Boiling Point (°C)	Melting Point (°C)	Density at 20°C
C_6H_{14}	*n*-Hexane	69	-94	0.658
C_8H_{18}	*n*-Octane	126	-98	0.702
$C_{10}H_{22}$	*n*-Decane	174	-32	0.747
$C_{12}H_{26}$	*n*-Dodecane	215	-12	0.768
$C_{16}H_{34}$	*n*-Hexadecane	287.5	18	0.775 (at mp)
$C_{20}H_{42}$	*n*-Eicosane	205	36.7	0.778 (at mp)
$C_{30}H_{62}$	*n*-Triacontane	449.7	66	0.775
$C_{35}H_{72}$	*n*-Pentatriacontane	490	74.6	0.781

Table 2 gives some corresponding physical properties for aromatic molecules that might occur at contaminated sites.

Table 2: Some Aromatic Compounds

Molecular Formula	Name	Boiling Point (°C)	Melting Point (°C)
C_6H_6	Benzene	80	5.5
$C_{10}H_8$	Naphthalene	218	80.3
$C_{14}H_{10}$	Phenanthrene	338	100.5
$C_{18}H_{12}$	Chrysene	448	253
$C_{20}H_{12}$	Benzo(a)pyrene	310-312	179
$C_{22}H_{12}$	Benzo(g,h,I)perylene	542	278

Tables 3 and 4 give some representative physical parameters for TPH analytical fractions based on correlations to relative boiling point indices for aliphatics.

Table 3: Physical Parameters for TPH Aliphatic Fractions

Carbon Equivalent Fraction	Log S_w (mg L^{-1})	Vapour Pressure (atm)	Henry's Law Constant (cm^3 cm^{-3})	Log K_{oc}
$C_5 – C_6$	1.56	3.5×10^{-1}	47	2.9
$C_{>6} – C_8$	0.73	6.3×10^{-2}	50	3.6
$C_{>8} – C_{10}$	-0.36	6.3×10^{-3}	55	4.5
$C_{>10} – C_{12}$	-1.46	6.3×10^{-4}	60	5.4
$C_{>12} – C_{16}$	-3.12	7.6×10^{-5}	69	6.7
$C_{>16} – C_{35}$	-5.60	1.1×10^{-6}	85	8.8

Ross Sadler[1] and Des Connell[2]

**Table 4: Physical Parameters for TPH Aromatic Fractions**

Carbon Equivalent Fraction	Log S_w (mg L^{-1})	Vapour Pressure (atm)	Henry's Law Constant (cm³ cm⁻³)	Log K_{oc}
$C_5 – C_7$	2.34	1.1×10^{-1}	1.5	3.0
$C_{>7} – C_8$	2.11	3.5×10^{-2}	8.6×10^{-1}	3.1
$C_{>8} – C_{10}$	1.81	6.3×10^{-3}	3.9×10^{-1}	3.2
$C_{>10} – C_{12}$	1.40	6.3×10^{-4}	1.3×10^{-1}	3.4
$C_{>12} – C_{16}$	0.76	4.8×10^{-5}	2.8×10^{-2}	3.7
$C_{>16} – C_{21}$	-0.19	1.1×10^{-6}	2.5×10^{-3}	4.2
$C_{>21} – C_{35}$	-2.18	4.4×10^{-10}	1.7×10^{-5}	5.1

From the above tables it is clear that the group of substances loosely referred to as TPH have widely differing properties and are likely to present a significant problem as regards analysis. If some generic type of analysis could be developed to represent TPH, it would be of little use in terms of a risk assessment strategy for contaminated sites. Figure 1 illustrates the manner in which the hydrocarbons will be sorbed in a soil. The hydrocarbons will be associated with sorbed organic matter in the soil and hence the strength of the hydrocarbon sorption will vary according to the nature of the hydrocarbon (as indexed by the K_{oc} values) and the organic matter content of the soil.

Figure 1: Hydrocarbon Interactions with Soil
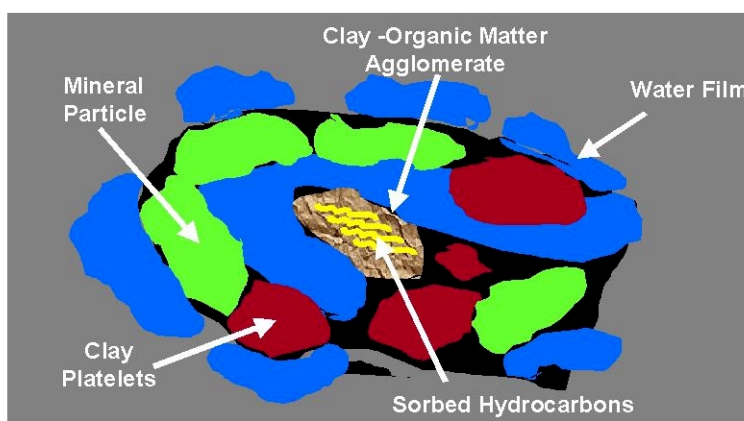
The situation is further complicated by the various ultimate fates that can befall hydrocarbon molecules in soil and thus modify the observed composition. Figure 2 illustrates some of these processes:

Ross Sadler[1] and Des Connell[2]

Figure 2
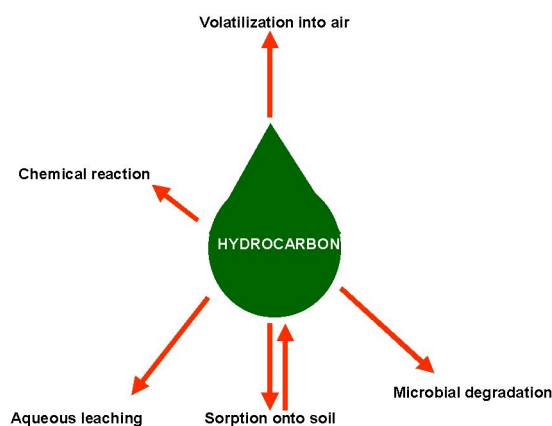
4   FATE OF HYDROCARBONS IN SOIL

The result of these processes is an alteration in the composition of the hydrocarbon discharged into the soil. Clearly, those hydrocarbons that are most strongly sorbed onto soil organic matter will be most resistant to loss or alteration by the other processes. Conversely, the more volatile/soluble hydrocarbons will be the most susceptible to change by volatilization/reaction/leaching/biodegradation. The ultimate result will be "weathering" of the hydrocarbon mixture discharged into the soil, with an accompanying change in its composition and a preferential transport of certain fractions to other environmental compartments.

Because of the overall complexity of the problem and of the spectrum of hydrocarbons likely to be encountered, it is impossible to view TPH as a single entity. There have been many approaches to the problem, but the simplest and one most frequently used is the one based on the vapour pressure ranges of the organics in question. This also relates to the sampling methodology employed.   The approach consists of sub-dividing the hydrocarbons into the most volatile fraction (referred to as gasoline range organics or GRO) and the less volatile fraction. In the case of monitoring of storage tanks, a sub-fraction (known as diesel range organics or DRO) is often distinguished amongst the semi-volatile fraction.   Figure 3 illustrates the differences in these fractions as demonstrated by gas chromatography.

Figure 3: Oil Fractions as determined by Gas Chromatography

Ross Sadler[1] and Des Connell[2]
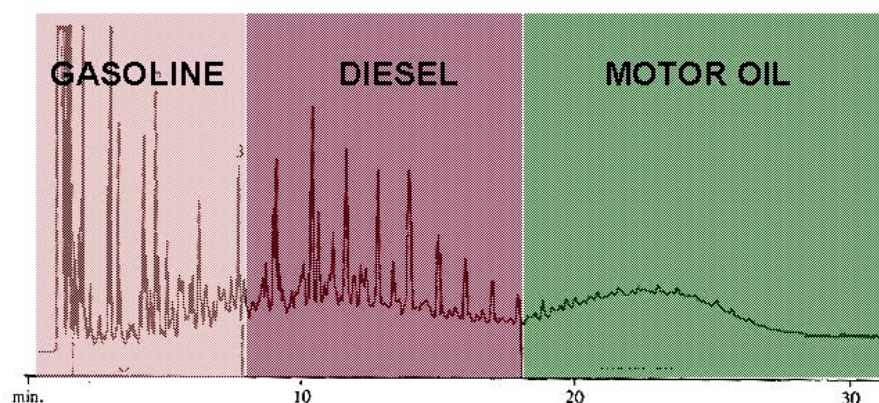
These are typical of results that would be obtained if water is spiked with a mixture of the various hydrocarbons. As regards a contaminated soil, this type of analysis is not possible for a number of reasons, most particularly because the various hydrocarbons cannot be extracted from the sample with equal efficiency. In particular, volatiles require special procedures to achieve satisfactory recovery from the matrix. It thus becomes important to distinguish between those compounds that are considered to be volatile and those that rank as semi- or non-volatiles.

5 VOLATILE HYDROCARBONS (INCLUDING GROS)

Very few authorities today employ a boiling-point based definition of volatiles, because some volatile substances (e.g. naphthalene) sublime rather than boil, whilst others emit significant quantities of vapour well below their boiling point. Standards Australia (1999) defines a volatile substance as one whose boiling point or sublimation temperature are such that it exists to a significant extent in the gaseous phase under ambient conditions. Table 5 (below) lists some common hydrocarbons that are generally considered as volatile. Most (but not all) of these would be considered as GROs.

Table 5: Some Commonly Encountered Volatile Hydrocarbons

Aliphatic	Aromatic
Pentanes	Benzene
Hexanes	Toluene
Heptanes	Ethylbenzene
Octanes	Xylenes
Nonanes	Naphthalene
Decanes	Phenanthrene
	Anthracene
	Acenaphthylene

As regards the sampling of volatile hydrocarbons in the field, two procedures are generally recommended, viz. zero headspace and solvent extraction (Minnich 1993). It should be noted that these two procedures do not necessarily give equivalent results.

Zero headspace procedures involve the collection of a soil sample with immediate transfer to a container into which the sample fits exactly. The only space for gases is that within the soil pores. The volume of sample collected depends upon the concentration of volatiles in the soil. It is imperative that the container employed can be interfaced directly with the gas chromatograph. Several commercial versions of zero headspace sampling devices are available. The sample is transported to the laboratory at 4°C, where it is analysed directly by purge and trap gas chromatography (US EPA 5035, 1996) or other appropriate techniques such as Vacuum Distillation (US EPA 5032, 1996) or Headspace (US EPA 5021, 1996).

Solvent extraction procedures involve collection of sample by an appropriate device and subsequent immediate placement into a borosilicate glass vessel, which contains a known quantity of ultrapure methanol. The bottle is then transported to the laboratory at 4°C, and the methanol fraction analysed by purge-and-trap gas chromatography (or similar procedure).

In general, the zero headspace procedures are employed when the concentrations of volatiles in the soil are relatively low and the solvent extraction methods are used for more polluted soils (Standards Australia, 1999). Irrespective of which procedure is used, quantitation of volatiles in soil is subject to serious errors if sufficient care is not taken with the sampling operation (Siegrist and Jenssen 1990). Although direct purge-and-trap methods are frequently advocated for determination of volatiles in samples collected by zero headspace procedures, there are certain problems associated with this technique. It has been hypothesised that the procedure really only collects that fraction of the volatile that exists in a free form within the soil pore spaces, or is at least in a facile equilibrium with this fraction. Askari *et. al*. (1996) compared three methods for extraction of volatiles from soil samples. In addition to the standard direct purge-and-trap and methanol extractions, they also employed a 40°C methanol procedure, in which the vial containing the sample was sonicated to improve efficiency. The results for benzene are shown in Figure 4.

Figure 4: Comparison of Extractions for Benzene from Florida Soil
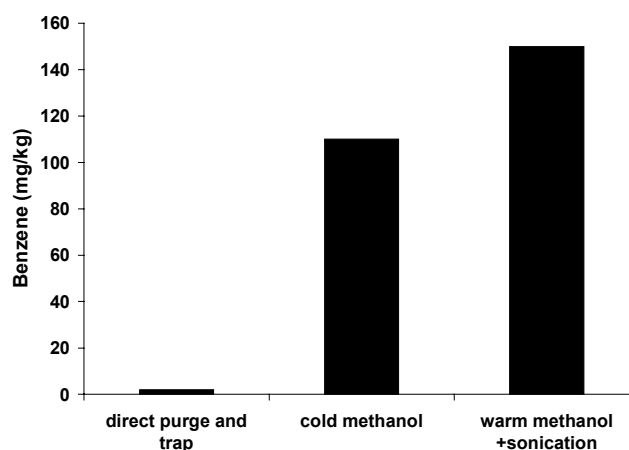
As can be seen, the direct purge and trap procedure was by far the least efficient of the three, and thus, serious doubts must be raised regarding its ability to give a representative picture of the true situation in a contaminated soil. Other studies with (non-hydrocarbon) volatiles have also pointed to the relative inefficiency of direct purge-and-trap procedures (West *et al* 1995).

Gas chromatography detectors employed for the determination of volatile organics in soil are generally FID, PID or mass spectrometry. FID detectors will respond to all carbon compounds in the sample, whereas the PID is capable of some sensitivity by virtue of the energy of the lamp employed. A 10.2 or 10.0 eV lamp yields more specific response to unsaturated (including aromatic) hydrocarbons and may also be employed to give a complete BTEX (benzene, toluene, ethyl benzene and xylene) characterisation at sites where this is likely to be an issue. As regards the columns used for the analysis of volatile hydrocarbons, a wide variety can be used. Wide bore capillary columns of length typically about 105 metres are generally employed and they must be capable of resolving 3-methyl pentane from methanol as well as ethyl benzene from the xylenes. There may be some variation in choice of column, however, according to the resolution required by the authority. There is some debate concerning appropriate limits for the gasoline range and this is reflected in disparate legislation amongst various countries. For instance, the upper range of the gasoline organics may be defined by naphthalene or dodecane.

Typical gas chromatography conditions involve an oven temperature ramped between 40°C and 240°C, with a detector maintained at 250°C and an injector at 200°C. There are two methods of calibration for the gas chromatograph. One method consists of analysing a mixture of individual hydrocarbons that bracket the gasoline range and calculating an average response factor from the response for each individual component. The other method involves analyzing a standard that contains one or more gasolines. Figure 5 gives typical FID/PID traces for analysis of a gasoline sample.

Figure 5: Analysis of a Gasoline Sample by Gas Chromatography
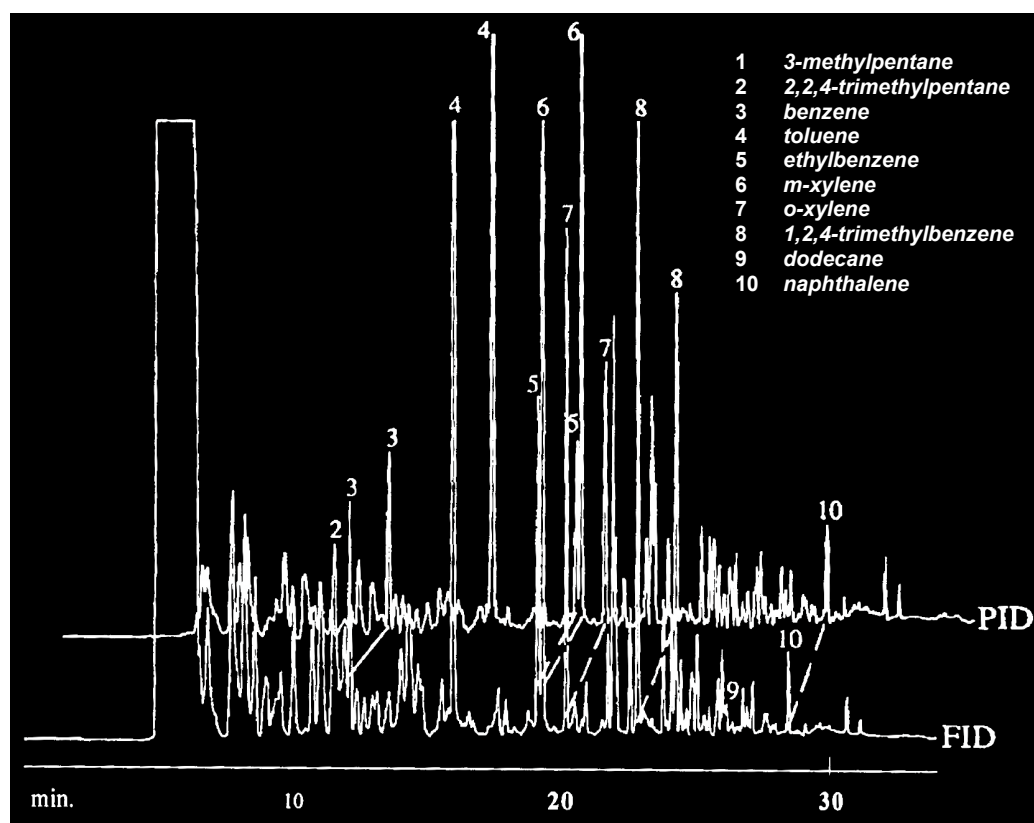
6   SEMI- AND NON-VOLATILE HYDROCARBONS (INCLUDING DROS)

In almost all cases of hydrocarbon contamination, some attention will have to be paid to the presence of semi- and non-volatile hydrocarbons. Even at service station sites, the leakage of diesel and kerosene storage tanks is a possibility and requires checking. A gas chromatography-based finish is generally employed in the analysis of semi- or non-volatile hydrocarbons. However the collection, handling of samples and their ultimate preparation for analysis is entirely different from that used for volatile hydrocarbons. In general, it is not necessary to take such rigorous procedures to prevent loss of analyte following collection, although the procedures should still be verified using appropriate quality control measures (Standards Australia, 1997)

Before analysis of semi- or non-volatile components can proceed, it is necessary that the hydrocarbon components be brought into solution. In a sample from a contaminated site, semi- and non-volatile molecules may exist in the soil pores in the free form within the pore spaces, but are far more likely to be adsorbed by organic matter attached to the soil

(see Figure 1). Indeed the probability of such adsorption increases with increasing hydrophobicity of the molecules (Connell and Miller, 1984).

A number of procedures are available to effect this dissolution. These include Soxhlet extraction (US EPA-3540C, 1996 and related methods; most applicable to "heavy hydrocarbons" and PAHs), ultrasonic extraction (US EPA-3550B, 1996), thermal extraction (US EPA-8275A, 1996) and supercritical fluid extraction (US EPA-3560, 1996 and US EPA-3561, 1996). Although these procedures are well documented in these and a number of other references, some of their important details are frequently overlooked, with the result that the extraction is unsatisfactory. In the case of ultrasonic extraction, the method (US EPA-3550B, 1996) clearly stipulates the use of an ultrasonic disrupter of the horn type, with a minimum power of 300 watts. Many laboratories however wrongly interpret this to mean an ultrasonic bath, used for cleaning glassware. Such baths are of far lower energy and are not capable of separating the hydrocarbons from their association with humic material. As regards the use of supercritical fluid extraction, a methanol modifier is required to achieve complete extraction of PAHs, whereas supercritical CO_2 is sufficient to elute normal hydrocarbons (cf. US EPA-3560, 1996 and US EPA-3561, 1996).

Whilst all of the above methods have been accepted by the US EPA, problems have been shown to exist under some circumstances. Although widely used, solvent extraction procedures have been demonstrated as sensitive to such variables as content of humic matter and moisture within samples. Supercritical fluid extraction appears to be a more robust procedure. Banerjee and Gray (1997) compared the effectiveness of thermal extraction techniques with conventional solvent procedures, for a variety of contaminated soils. The efficiency of thermal extraction procedures was sensitive to the size of the soil sample and in some cases, the technique resulted in the cracking of higher hydrocarbons.

In the case of solvent extraction procedures, it is necessary to concentrate and also to clean up the samples. A number of methods of cleanup are available and are further described in US EPA-3600c. With complex mixtures of semi-volatile hydrocarbons, it is generally advisable to separate the aliphatic and aromatic fractions.

As mentioned above, the most usual analytical finish for hydrocarbon determination is gas chromatography. Depending upon the degree of resolution and level of information required, a number of instrument configurations may be employed. The most common requirement is determination of TPHs and this will often largely consist of DROs. For this purpose, the most normal procedure is GC/FID, according to US EPA method 8015B. Because of the nature of the analytes (boiling point 170°C to 430°C), higher oven temperatures are required for chromatography of this fraction, compared to GROs. Commonly, fused silica capillary columns of 30 metres length with a 0.53 mm internal bore are used, the column being bonded with DB wax at a 1μm film thickness.

The sample is generally introduced by direct injection as the technique is less discriminatory than splitless injection. Temperatures of the injector and detector are maintained at 200°C and 340°C respectively throughout the run and the column temperature ramped from 45°C to 275°C. GC/FID may be used to simply fingerprint the components of a hydrocarbon pollution episode (Bruce and Schmidt, 1994), this strategy being most successful if the pollutant has only recently entered the soil environment. Most frequently however, some attempt is made to quantitate the hydrocarbon fractions represented. (Whittaker *et al*, 1995). It is possible to employ both external and internal

Ross Sadler[1] and Des Connell[2]

standards in these determinations. When internal standards are used, they are generally compounds such as hexafluoro-2-propanol, hexafluoro-2-methyl-2-propanol or 2-chloroacrylonitrile. As regards determination of DROs, regulatory authorities vary in terms of the prescribed range. Typically, the DRO range is considered to begin at C_{10} to C_{12} and end at C_{24} to C_{28}. Whatever the range, TPH is taken as the sum of the area within that region of the chromatogram.

More sophisticated detection methods for gas chromatography are also employed in the analysis of hydrocarbons, viz. GC/MS (cf. US EPA-8270C, 1996) and GC/FTIR (cf. US EPA-8410, 1994). These procedures have a significant advantage in providing a better characterization of the determinands and are thus of particular use where some environmental modification of the hydrocarbons has taken place subsequent to soil deposition. Quantification by GC/MS, based upon internal standards has been reported as being superior to that based upon external standards (Xie *et al*, 1999). In addition, they provide the only satisfactory means of resolving PAHs within complex mixtures. Figure 6 shows resolution of DROs by GC/MS.

Figure 6: Resolution of DROs by GC/MS.
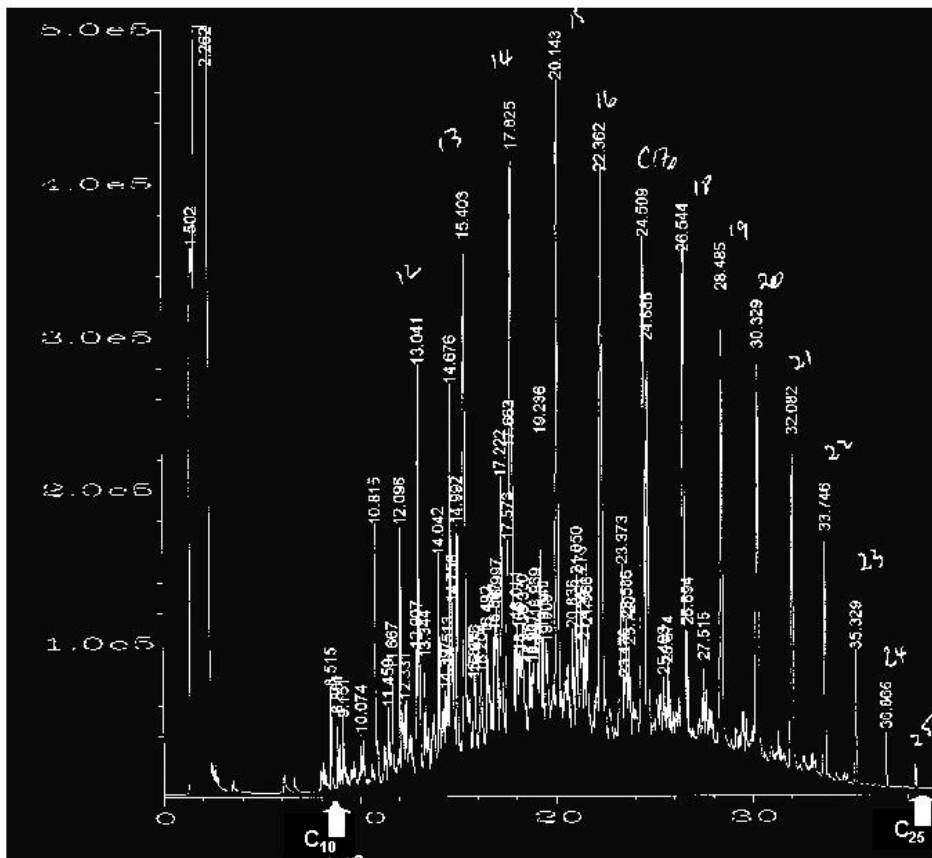
In terms of higher hydrocarbons, the resolution is generally less clear. Figure 7 shows a chromatogram of hydrocarbons extracted from sump oil contamination, as resolved by GC/MS.

Ross Sadler[1] and Des Connell[2]

Figure 7: Resolution of Sump Oil Contamination by GC/MS.
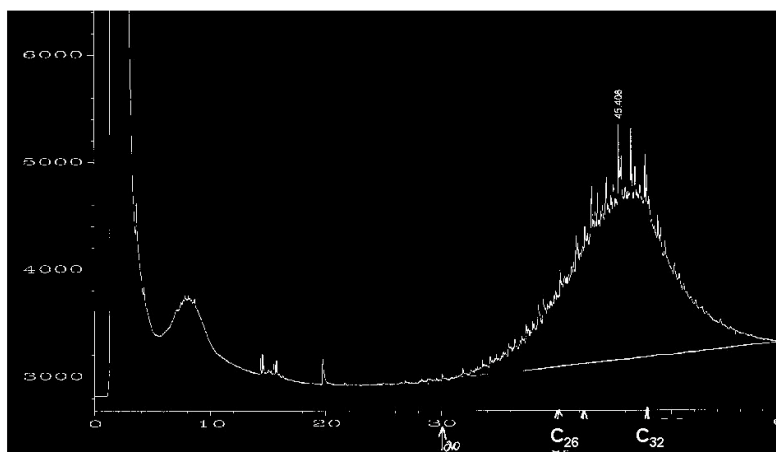
A superior approach to determination of TPHs in soil is the summation of areas under the curve for specific ranges of hydrocarbons. This allows a better profiling of the contaminants and also confers the ability to trace the source of the pollutant. Typical ranges for the determinands are n-C_{10} - n-C_{14}, n-C_{15} - n-C_{20}, n-C_{21} - n-C_{26} and n-C_{27} - n-C_{36}.

The following case study illustrates the use of this type of approach. An airport fire training ground was accused of causing hydrocarbon pollution in the soil and groundwater. The fire training involved spraying Avgas onto a series of objects (whose size and shape approximated an aircraft) and extinguishing a purposely-lit fire. TPH analysis (by infrared procedures) had demonstrated hydrocarbon pollution in the soil and it was assumed that this represented unburned Avgas. The fire ground is illustrated schematically in Figure 8.

Figure 8: Schematic Diagram of Airport Fire Training Area
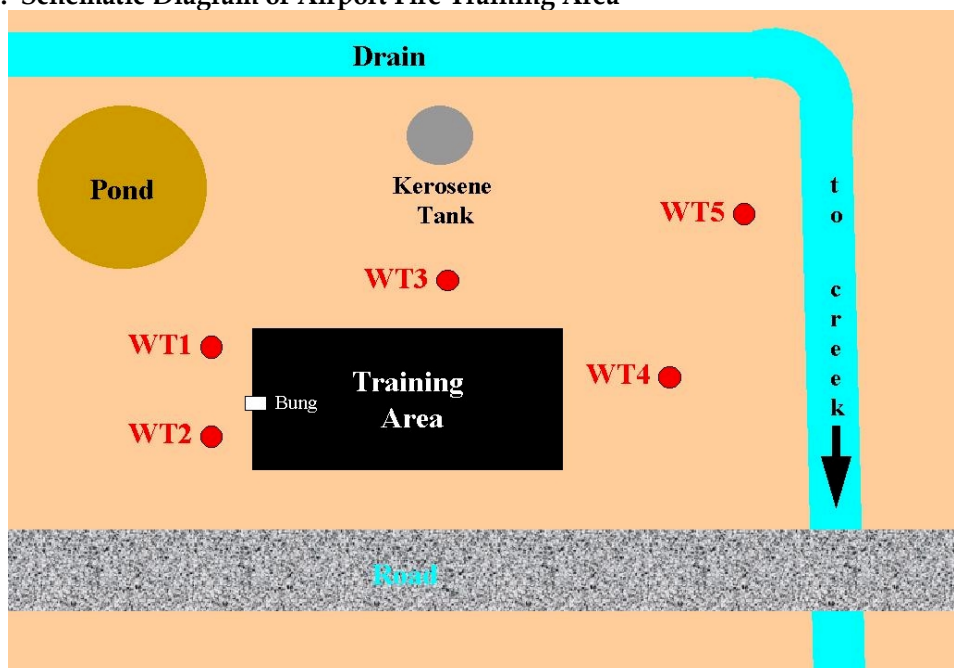
The results of hydrocarbon profiling are shown in Table 6 below:

Table 6: Profiling of Hydrocarbons around Airport Fire Training Ground

Hydrocarbon Chain Length	Hydrocarbon Concentration at Site				
	WT 1	WT 2	WT 3	WT 4	WT 5
n-C_{10} - n-C_{14}	960µg kg^{-1}	1 200µg kg^{-1}	1 510µg kg^{-1}	17 100µg kg^{-1}	700µg kg^{-1}
n-C_{15} - n-C_{20}	1 810µg kg^{-1}	1 240µg kg^{-1}	1 850µg kg^{-1}	37 000µg kg^{-1}	4 520µg kg^{-1}
n-C_{21} - n-C_{26}	3 120µg kg^{-1}	340µg kg^{-1}	940µg kg^{-1}	11 500µg kg^{-1}	1 510µg kg^{-1}
n-C_{27} - n-C_{36}	1 020µg kg^{-1}	<200µg kg^{-1}	<200µg kg^{-1}	<200µg kg^{-1}	<200µg kg^{-1}
Total Hydrocarbons	**6 940µg kg^{-1}**	**2 980µg kg^{-1}**	**4 300µg kg^{-1}**	**65 600µg kg^{-1}**	**6 730µg kg^{-1}**

It is clear that whilst significant hydrocarbon contamination in the kerosene range (n-C_{10} - n-C_{14}) can be demonstrated, the majority of the contamination lies in higher fractions. Thus, there are other inputs to the overall hydrocarbon contamination situation at the site and these need to be taken into account in any management scheme.

One of the major problems associated with profiling of hydrocarbons at contaminated sites is the phenomenon known as "weathering". This term refers to change in composition of hydrocarbons with time, through the action of volatilisation, leaching, chemical reaction and biotransformation. As regards volatile organics, the most significant process is through volatilisation, resulting in a decrease of overall concentration with time. The longer chain hydrocarbons are however more prone to modification through other processes and it becomes necessary to identify the products of the various transformations. In addition, it is useful to obtain some index of overall weathering.

Such information cannot readily be obtained from simple GC/FID profiles and hence more sophisticated techniques must be used (Whittaker *et al* 1995). The majority of characterisations have made use of GC/MS. As is well-known, both "hard" (electron impact) ionisation (EI) and "soft" (chemical) ionisation (CI) procedures are available. Thus, the former procedure produces predominantly fragment ions, whereas the latter produces predominantly parent ions. With complex refractory hydrocarbon samples, chemical ionisation can produce ambiguous results, since many of the analytes have identical parent ion peaks. Thus, GC/EI/MS becomes the method of choice for analysis of most hydrocarbon studies (Altgelt and Boduszynski, 1994). The availability of GC/MS/MS has further enhanced the ability to examine environmental hydrocarbon samples for particular components.

Of particular significance in the study of petroleum weathering are the so-called 'biomarker' molecules. These substances, which include the components of crude oils known as pristane, phytane, the hopanes and steranes. The biomarkers have historically been employed as crude oil signatures in prospecting and characterisation. More recently, they have also been employed in the environmental field, both for the determination of pollutant source and estimation of the degree of weathering.
The structures of these biomarker molecules are shown below.

Pristane	Phytane
Hopane	Sterane
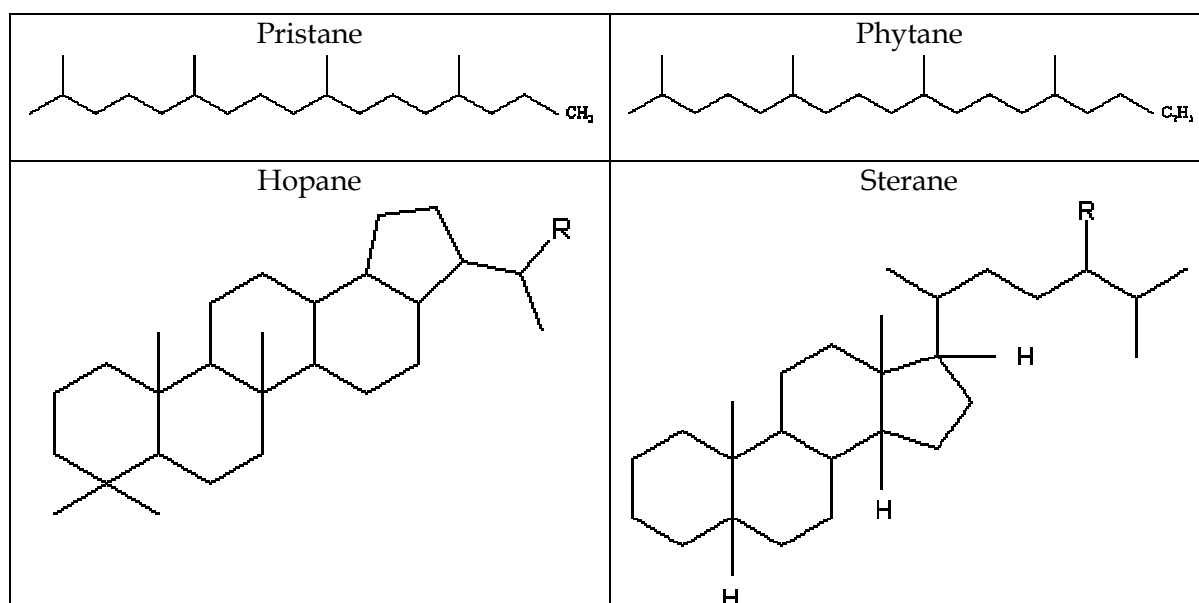
The biomarker molecules are particularly resistant to microbial attack and thus the ratio of other hydrocarbon components to the biomarker will decrease as the crude oil is biodegraded (Wang *et al.*, 1994). In the case of an ongoing oil discharge into the soil, this ratio will be highest nearest the source and will decrease with increasing distance from the source. Thus, the ratio may be used to locate the source of the contaminant (Whittaker *et al.* 1995). In a similar manner, expression of biodegradable hydrocarbons as a ratio to high molecular weight PAHs should have potential for fingerprinting purposes. The failure of some attempts to use PAHs for this purpose probably stems from an inappropriate choice of molecules for comparison. Low molecular weight PAHs such as naphthalene or phenanthrene are often selected because of their abundance and relative ease of measurement. Unfortunately, these molecules are also the most prone to biodegradation as well as other forms of attenuation (Sadler and Connell, 2002).

7   SCREENING PROCEDURES FOR TPH

Given the relative complexity (and expense) of the analytical methods described above, it is not surprising that there has been a considerable effort towards devising simplified procedures for determination of TPH. Particular efforts have been expended in terms of finding a satisfactory method for use in the field. Although some promising advances have been made in recent years, laboratory analysis remains the method of choice.

As with laboratory analysis, the major problem lies in the range of compounds covered by the term "hydrocarbons". Again, the most notable variation is in the relative volatility of the substances in question. As regards volatile organics (e.g. GROs), a number of portable devices are used to detect vapours in soil (cf. Standards Australia, 1999). Table 7 summarises some of these instruments.

Table 7: Some Examples of Equipment used for Field Screening of Volatile Substances

Instrument	Principle	Capabilities/Limitations
Portable gas chromatograph	Carrier gas used to move analyte through separation column at elevated temperatures. Detector is usually flame ionisation or photoionisation.	Affords some resolution of mixtures and permits some quantification. The sophistication of these instruments has increased markedly over the past five years.
Photoionisation detector (PID)	Ionization of analyte by ultraviolet radiation.	Detection is generally non-specific and response varies from compound to compound. By using lamps of different energy output, it is possible to limit the range of compounds detected. Presence of moisture may cause artificially high results.
Flame ionisation detector (FID)	Presence of analyte produces ions in an air-hydrogen flame.	Provides non-specific detection, incapable of resolving mixtures and response varies from compound to compound.
Photoacoustic Fourier transform infrared spectrometer	Determination of infrared absorbance.	Analyte must exhibit infrared absorption. Capable of some resolution of mixtures and of partially quantifying components.
Ultraviolet derivative specrometry	Determination of ultraviolet spectra.	Analyte must exhibit ultraviolet absorption. Capable of some resolution of mixtures and of partially quantifying components.

All of the procedures are of use only in the case of volatile analytes and in circumstances where the opportunity exists for sufficient soil gas to accumulate. A more sophisticated approach to the problem involves collection of the contaminated soil and sealing it in a container, where the soil gas can accumulate. This gas is then analysed by one of the above procedures. More often, however, (particularly in the case of PID and FID), the soil is often analysed *in situ*, by direct insertion of the probe into the vadose zone.

At best, this can only give a rough qualitative idea of the presence of volatile components. In the case of a recent gasoline spill into sandy soil with low organic matter content, such an approximation may be a useful guide. The instrument however gives no information on the presence of non-volatile components and because of differential responses to various compounds, may give misleading information in the case of mixtures. In terms of toxicological assessment of contaminated sites, results of such field monitoring are

useless. Naphthalene is by far the most prevalent PAH in coal tar (Johnston *et al.*, 1993) and will evoke a response from a PID or FID device. It is however the least significant PAH in terms of human health, whereas carcinogenic PAHs such as benzo(*a*)pyrene will not be detected by the techniques used to sense volatiles.

As a partial compromise between the use of instruments described above and laboratory analysis, a number of investigators have made use of passive sampling procedures, notably the Petrex technique. The underlying principle of these methods is immersion of a passive sampler into the soil and collection of evolved gases, which are adsorbed onto a solid phase support. The sampler is then removed to the laboratory, where the gases are transferred by Curie point desorption, directly into the ion source of an interfaced quadrupole mass spectrometer. The procedures have their origin in the petroleum exploration industry and the samplers can be used at a considerable range of depths (Einhorn *et al*, 1992). The most normal procedure for the use of these sampling devices consists of augering a hole to a depth of 45 cm, into which the sampler is placed (cf. Figure 9). Once the holes have been sealed, the soil vapours are allowed to equilibrate with the sampler for a time period between several hours to several days, depending upon the nature of the contamination and soil. At the end of this period, the samplers are removed to the laboratory for analysis. Generally, Petrex samplers are placed in a grid pattern over the contaminated site. They have the advantage of may other methods of allowing some collection of semi-volatile hydrocarbons and can achieve detection limits as low as parts per trillion.

Figure 9: Petrex Sampler in Soil
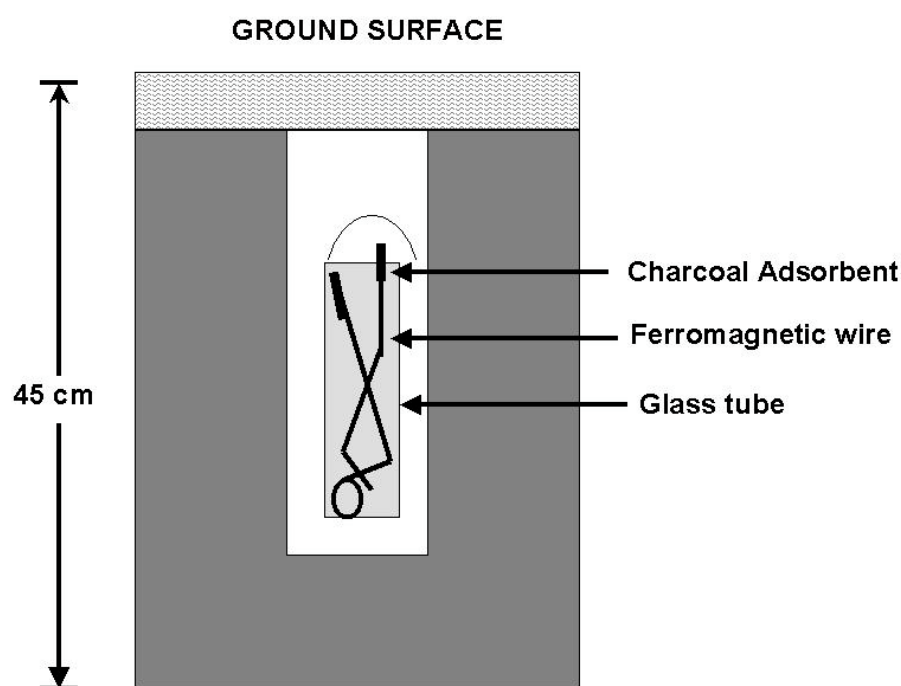
A number of procedures, based on microanalysis of samples for known physical properties have also been employed. For example, field screening, which uses infrared spectroscopy has been practised, employing a portable version of the well-known laboratory procedure (Kasper *et al.*, 1991). Unlike other procedures, field turbidometric methods (such as the commercially-available Petro-FLAG®) favour the determination of heavy hydrocarbons and are of some use in delineating such pollution within soil (Kahrs *et al*, 1999). The fluorescence spectra exhibited by the aromatic components provide the

basis for laser-induced fluorescence spectroscopy. This has been used by a number of authors for field screening and *in situ* techniques have been devised (Apitz *et al.*, 1992; Löhmannsröben *et al.*, 1999). They allow detection of polycyclic aromatic compounds and thus are able to take account of a fraction not measured by other field screening techniques. All these procedures have potential application at contaminated sites and yet none is free from interference.

A somewhat more specific approach is offered by chemical-based procedures. Immunoassay methods are available for both petroleum hydrocarbons (cf. US EPA-4030) and PAHs (cf. US EPA-4035) and a number of commercial kits are on the market. In the case of petroleum hydrocarbons, the kits are available in a number of ranges, bracketing hydrocarbon concentrations between 5 mg kg^{-1} and 500 mg kg^{-1}. The PAH kits are generally most sensitive to three and four ring PAHs, although they show some recognition of most larger members of the series. In both cases, the procedure consists of making an extract of the soil and performing the immunoassay test on the extract.

Another chemical procedure is the Hanby method, which is based on the production of coloured Friedel-Crafts reaction products by aromatic compounds present in the sample. The colour of the reaction product is compared with a standard chart to tentatively identify the contaminant. Commercial test kits, based on this reaction are available (see Driscoll *et al*, 1992).

In summary, although these procedures are of use in locating possible hydrocarbon contamination, their results are only indicative of the presence of these substances and ultimate confirmation can only come from laboratory analysis.

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