The use of Forensic Polycyclic Aromatic Hydrocarbon Signatures and Compound Ratio Analysis Techniques (CORAT) for the Source Characterisation of Petrogenic / Pyrogenic Environmental Releases

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Declaration

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Dedication

To Pauline and my Parents

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I would like to extend my gratitude to (aunty) Janet Jones who listened to me complain more than I should have.

Finally to my friends and family I have finally cleaned my room Judy… Again, I thank all of you for your contributions. I dedicate this thesis to my parents and Pauline.

Abbreviations

Abbreviation	Explanation
%	Percentage
<	Less than
>	Greater than
≈	Approximately
µl	Micro-litre
5973N	5973 Networked
Ace	Acenaphthene
Acl	Acenaphthalene
AEHS	Association of Environmental Health and Science
An	Anthracene
API	American Petroleum Institute
AQC	Analytical Quality Control
ASTM	American Society for Testing and Materials
BaA	Benz(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BkF	Benzo(k)fluoranthene
BOC	Brin's Oxygen Company
BP	Benzo(ghi)perylene
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
C	Carbon
C	Chrysene
C	C_0-chrysene
C1	C_1-methylchrysene
C2	C_2-dimethylchrysene
C3	C_3-trimethylchrysene
CORAT	Compound Ratio Analysis Technique
CRM	Certified Reference Material
D	C_0-dibenzothiophene
D1	C_1-methyldibenzothiophene
D2	C_2-dimethyldibenzothiophene
D3	C_3-trimethyldibenzothiophene
DA	Dibenzo(ah)anthracene
DBT	Dibenzothiophene
DRO	Diesel Range Organics
EH	Extractable Hydrocarbon
EPA	Environmental Protection Agency
EPH	Extractable Petroleum Hydrocarbon
F	Fluorene
F	C_0-fluorene
F1	C_1-methylfluorene
F2	C_2-dimethylfluorene
F3	C_3-trimethylfluorene
FID	Flame Ionisation Detection
Fl	Fluoranthene
Ft	Foot
G	Gram
GC	Gas Chromatograph
GC-FID	Gas Chromatograph Coupled to a Flame Ionisation Detector
GRO	Gasoline Range Organics
H	Hydrogen
IP	Indeno(123cd)pyrene

Abbreviation	**Explanation**
ISEF	International Society of Environmental Forensics
Jet A1	Jet Aviation
JP	Jet Propulsion
m/z	Mass to Charge Ratio
MADEP	Massachusetts Department of Environmental Protection
mg	Milligram
mg/l	Milligrams Per Litre
ml	Millilitre
MMT	Manganese Tricarbonyl
MS	Mass Spectrometer
MSD	Mass Selective Detector
MTBE	Methyl-teirtary butyl ether
n	Normal
N	Naphthalene
N	C_0-naphthalene
N1	C_1-methylnaphthalene
N2	C_2-dimethylnaphthalene
N3	C_3-trimethylnaphthalene
N4	C_4-tetramethylnaphthalene
NaCl	Sodium Chloride
NAPL	Non-Aqueous Phase Liquid
°C	Degree Centigrade
P	Phenanthrene
P	C_0-phenanthrene
P1	C_1-methylphenanthrene
P2	C_2-dimethylphenanthrene
P3	C_3-trimethylphenanthrene
P4	C_4-tetramethylphenanthrene
PAH	Polycyclic Aromatic Hydrocarbon
pH	Hydrogen Ion Content and Activity.
PHC	Petroleum Hydrocarbons
PI	Pyrogenic Index
PNAs	Polynuclear Aromatics
ppm	Parts per Million
Py	Pyrene
RFx	Response Factor
ROF	Reservoir Oil Fingerprint
rpm	Revolutions Per Minute
RSC	Royal Society of Chemistry
RTC	Resource Technology Corporation
S	Sulphur
S-1	Sample 1
S-1	Sample 1
SACB	South American Crude Bitumen
SCI	Society of Chemical Industry
SIM	Selective Ion Monitoring
SW	Solid Waste
T	Time
TEL	Tetraethyl Lead
TIC	Total Ion Count
TIC	Total Ion Chromatogram
TPH	Total Petroleum Hydrocarbon
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
TRPH	Total Recoverable Petroleum Hydrocarbon
UCM	Unresolved Complex Material
UCM	Unresolved Complex Mixture

Abbreviation	**Explanation**
USA	United States of America
USEPA	United States Environmental Protection Agency
VH	Volatile Hydrocarbon
VPH	Volatile Petroleum Hydrocarbon
Σ	Sum

Abstract

Abstract

This study utilised recent developments in forensic aromatic hydrocarbon fingerprint analysis to characterise and identify specific biogenic, pyrogenic and petrogenic contamination. The fingerprinting and data interpretation techniques discussed include the recognition of:

- The distribution patterns of hydrocarbons (alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene, chrysene and phenol isomers),
- Analysis of "source-specific marker" compounds (individual saturated hydrocarbons, including n-alkanes (n-C_5 through n-C_{40}),
- Selected benzene, toluene, ethylbenzene and xylene isomers (BTEX),
- The recalcitrant isoprenoids; pristane and phytane and
- The determination of diagnostic ratios of specific petroleum / non-petroleum constituents, and the application of various statistical and numerical analysis tools.

An unknown sample from the Irish Environmental Protection Agency (EPA) for origin characterisation was subjected to analysis by gas chromatography utilising both flame ionisation and mass spectral detection techniques in comparison to known reference materials. The percentage of the individual Polycyclic Aromatic Hydrocarbons (PAHs) and biomarker concentrations in the unknown sample were normalised to the sum of the analytes and the results were compared with the corresponding results with a range of reference materials. In addition, to the determination of conventional diagnostic PAH and biomarker ratios, a number of "source-specific markers" isomeric PAHs within the same alkylation levels were determined, and their relative abundance ratios were computed in order to definitively identify and differentiate the various sources. Statistical logarithmic star plots were generated from both sets of data to give a pictorial representation of the comparison between the unknown sample and reference products. The study successfully characterised the unknown sample as being contaminated with a "coal tar" and clearly demonstrates the future role of compound ratio analysis (CORAT) in the identification of possible source contaminants. The study was divided into chapters as follows;

Chapter 1	Introduction and Literature Review
Chapter 2	Methodology
Chapter 3	Discussion of Results

The findings of this study were presented at Loughborough University in the United Kingdom at a conference organised by the Environment Group of the Society of Chemical Industry (SCI) and the Water Science Forum of the Royal Society of Chemistry (RSC), with support from FirstFaraday (Scally *et al.*, 2004). The paper (Appendix 1) was published in the proceedings and was entitled;

Scally K., Farrell-Jones J., Keogh M., Keaveney G., (2004). *"Forensic Polycyclic Aromatic Hydrocarbon Fingerprint Interpretation and Source Characterisation Using Compound Ratio Analysis (CORAT)".* SCI / RSC Conference: Contaminated Land – Achievements and Aspirations 12 – 15 September 2004, Loughborough, UK. EPP Publications Ltd. ISBN: 1 900995 01 8

This paper was also presented at the 15th Annual meeting and West Coast conference on soil, sediment and water in March 2005 at the Mission Valley Marriott, San Diego, California CA 92108. This conference was organised by the Association for Environmental Health and Science (AEHS) and the International Society of Environmental Forensics (ISEF). The abstract was published in the proceedings.

A second paper from this work was published in the proceeding of the CABERNET 2005 conference, the international conference on managing urban land on the 13 – 15th April 2005, in Belfast. The paper was entitled:

Scally K., Nathanail P., Farrell-Jones J., Keogh M., Keaveney G., (2005). *"Is this Diesel mine...?": Advances in Forensic Identification of Petroleum Related Releases into the Environment Using Source Specific Markers.* CABERNET International Conference on Managing Urban Land, 13-15th April 2005, Belfast. University of Nottingham ISBN 0-9547474-1-0

A third paper was presented and published in the proceedings of the International Association of Hydrogeologists (IAH) conference which was held on the 19th and 20th of April 2005. The title of the paper was entitled;

Scally K., Nathanail P., Farrell-Jones J., Keogh M., Keaveney G., (2005). *Advances in Forensic Identification of Petroleum Related Releases into the Environment Using Source Specific Markers.* International Association of Hydrogeologists (Irish Group), Groundwater in Ireland, 25th Anniversary Conference, 19th and 20th of April. ISSN – 1393-1806

A fourth paper has been accepted for publication at the ConSoil 2005 the 9th International FZK / TNO Conference on Soil-Water Systems in Bordeaux Convention Center, Bordeaux, France, 3rd to the 7th October. The paper is entitled "Is this Diesel mine…?": Advances in Forensic Identification of Petroleum Related Releases into the Environment Using Source Specific Markers

A fifth paper will be presented at the "Southeast Asia Environmental Forensics Conference" in the National Chengchi University Taipei, Taiwan on the 19th to 21st of September 2005. The conference is sponsored by the International Society of Environmental Forensics (ISEF), Taiwan Industrial Technology Research Institute (ITRI) and Taiwan EPA.

A sixth paper will be presented at "The 21st Annual International Conference on Soil, Sediment & Water" in the University of Massachusetts at Amherst, USA on the 17th to the 20th of October 2005. This conference is jointly organised by the University and MaDEP.

A seventh paper is been presented at the ISSMGE's 5th International Congress on Environmental Geotechnics with Cardiff University on the 26th – 30th June 2006 entitled - The use of time of flight mass spectrometry in forensic polycyclic aromatic hydrocarbon fingerprinting interpretation and source characterisation using compound ratio analysis (CORAT).

Chapter 1

Introduction and Literature Review

Chapter 1 Introduction and Literature Review

1.0 Origins of Hydrocarbon Species 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 method 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 common is that of leaking underground storage tanks from former petrol stations, with the contaminants most likely to be found being petrol and diesel. Contaminants as a result of spillage at refuelling depots and railway storage yards may also include heavier refined oils such as lubricating and gearing oils. In addition, historical contamination can occur from shale oil retorting plants, coal carbonisation and gas works sites, particularly those at which "benzole recovery" was practiced (Sadler and Connell, 2003). 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 mineralisation) and degradation of organic matter. The latter can be prevalent in organic rich soils and are based upon teraphthalic, adipic acids and carboxylic acid. These compounds are referred to as "humic acids" (Chefetz *et al.*, 2002).

1.1 Components of Hydrocarbons Found at Contaminated Sites

Before considering the chemistry of hydrocarbons, it is necessary to establish definitions of the most commonly used acronyms.

- PHC (petroleum hydrocarbons) is widely used to refer to compounds originating from crude oil.
- TPH (total petroleum hydrocarbons) refers to a measurable amount of petroleum based hydrocarbons in an environmental matrix.
- VH (volatile hydrocarbons) in the range n-C_5 to n-C_9 and n-C_{10} *to* n-C_{12} including BTEX and naphthalene.
- EH (extractable hydrocarbons) in the range n-C_{10} to n-C_{40}.
- PAH (polycyclic aromatic hydrocarbons) in the range two to six ring compounds.

envelope referred to as a "UCM" or unresolved complex material. The shape and extension of this UCM is used to assess the product type and molecular weight as well as the degree of biodegradation.

There are two main classes of Aromatic species:-

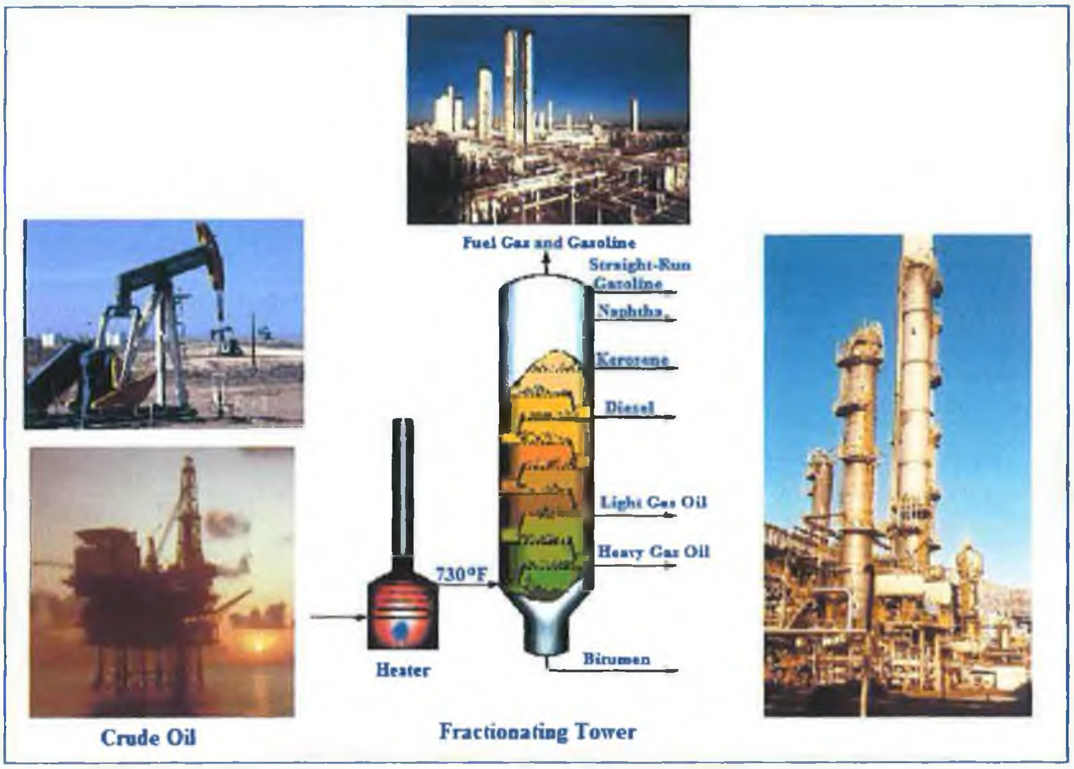
- **Monocyclic** - these compounds contain one aromatic carbon (benzene) ring which can be substituted with alkyl groups. These compounds, mainly found in gasoline and other lighter petroleum products, include compounds such as benzene, toluene, xylenes and other substituted compounds such as trimethyl benzenes. They are usually more soluble than their aliphatic counterparts and are considered to be carcinogenic.
- **Polycyclic Aromatics Hydrocarbons (PAH)** - these contain two or more fused aromatic rings and range from naphthalene (two ring) to coronene (six ring). These compounds also have alkylated derivatives such as methyl naphthalene and their derivatives can be used in assessing source differences. At least seven of the United States Environmental Protection Agency (USEPA) target compound lists are considered to be carcinogenic with benzo(a)pyrene being the most toxic.

Other minor constituents found in all crude's are:-

- **Porphyrin** formed from plant chlorophylls.
- **Sulphur** which may occur in the free form, as hydrogen sulphide or organic sulphur compound. The concentration depends on the source of its crude and can vary from 0.1% to 5%.
- **Metals** particularly those found in sea water, always occur. Of particular interest are vanadium and nickel. Vanadium porphyrin complexes and nickel-porphyrin complexes are associated with high sulphur and low sulphur crude's, respectively.

The primary separation technique used in the petroleum industry is fractional distillation which may be followed by other techniques such as solvent extraction. A typical process, showing the different fractions obtained is shown in Figure 1.1. Each fraction consists of a complex mixture of compounds. Typical fractions are with their boiling point ranges which are motor gasoline 25°C to 150°C, kerosene 150°C to 230°C, diesel 230°C to 340°C and bitumen fuel oil > 340°C.

Figure 1.1 Crude Oil Distillation Process



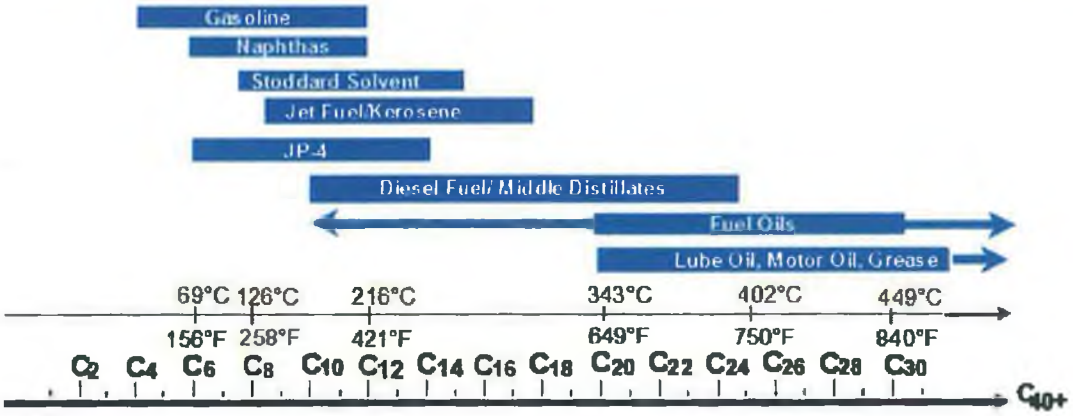
Source: Internet A, B and C

Fuel oils refined from crude petroleum can be classified either as distillate fuels, consisting predominantly of distilled process streams, or as residual fuel consisting of residues remaining after distillation, or blends of residues and distillates (IARC, 1989b). Distillate and residual fuel oils contain 80% to 90% aliphatic hydrocarbons and 10% to 20% aromatic hydrocarbons. Light distillate fuels consist primarily of hydrocarbons in the n-C_9 to n-C_{16} (kerosene), whereas hydrocarbons in the middle distillate fuels may range from n-C_{11} to n-C_{20} (gas oil, burner oil). Light and middle distillation residues generally contain less than 5% PAHs. The proportion of these fractions in a crude depends on its geographical origin and can range from Venezuelan Bachaquers heavy with >70% fuel oil to light Algerian with 25% fuel oil. At the extreme are the tar sands of the Orinoco Basin on the Athabasca oil sands of Canada from which most of the volatile material have been lost through evaporation.

1.3 Analytical Approach for Fingerprinting Petroleum

Several total petroleum hydrocarbon (TPH) fraction methods are either in development and/or are gaining regular usage. Two such methods include the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) method, developed with the assistance of Shell Development Company, and secondly the Massachusetts Department of Environmental protection (MADEP) extractable petroleum hydrocarbon / volatile petroleum hydrocarbon (EPH/VPH) method. The EPH/VPH is the promulgated TPH methodology for site cleanups in Massachusetts. The transition to this method has occurred over several years, and cleanup standards for both soil and groundwater have been developed for the measured EPH/VPH fractions. Petroleum fractions quantified in both of these methods have been paired with toxicity criteria so that human health risk associated with exposures to petroleum contaminated media can be assessed. TPHCWG analytical methodology is designed to characterise n-C_6 to n-C_{28+} petroleum hydrocarbons in soil as a series of aliphatic and aromatic carbon range fractions. The whole extract is separated into aliphatic and aromatic petroleum-derived fractions. This group-type separation is based on SW-846 EPA method 3611 (Alumina Column Cleanup and Separation of Petroleum Wastes) and SW-846 EPA method 3630 (Silica Gel Cleanup). The gas chromatograph is equipped with a boiling point column (non-polar capillary column). Gas Chromatography (GC) parameters allow the measurement of a hydrocarbon range of n-hexane (n-C_6) to noctacosane (n-C_{28+}), a boiling point range of approximately 65°C to 450°C (Figure 1.2).

Figure 1.2 Approximate Carbon and Boiling Ranges of Product Types from Petroleum



Source: Nathanail P., 2004

The TPHCWG analytical method exploits the relationship between petroleum hydrocarbon fate, transport properties and boiling point. The method has been specifically designed to resolve and quantify the thirteen aliphatic and aromatic, environmental fate and transport fractions, selected by the TPHCWG. The TPHCWG also assigned toxicity criteria to each fraction by selecting toxicity data most representative of the fraction from the toxicology literature on whole products, mixtures and individual petroleum constituents. When paired with the TPHCWG toxicity criteria, the fate and transport fraction data can be used to assess human health risk associated with exposures to petroleum-contaminated environmental media. The method not only separates and quantifies aliphatic and aromatic fractions, but it can also be used to obtain a TPH fingerprint for the sample. Experienced GC analysts can use the fingerprint to identify the type of petroleum release and the extent of weathering. The method is currently written as a tiered approach with fingerprint analysis preceding characterisation of aliphatic and aromatic fractions. In this way, the fingerprint can be used for a preliminary evaluation of the nature and extent of the release. The method is versatile and performance-based, therefore, it can be modified to accommodate data quality objectives. It has been successfully applied to the characterisation of neat crude oil and petroleum products as well as soils containing gasoline, JP-4, diesel and crude oil with different degrees of weathering.

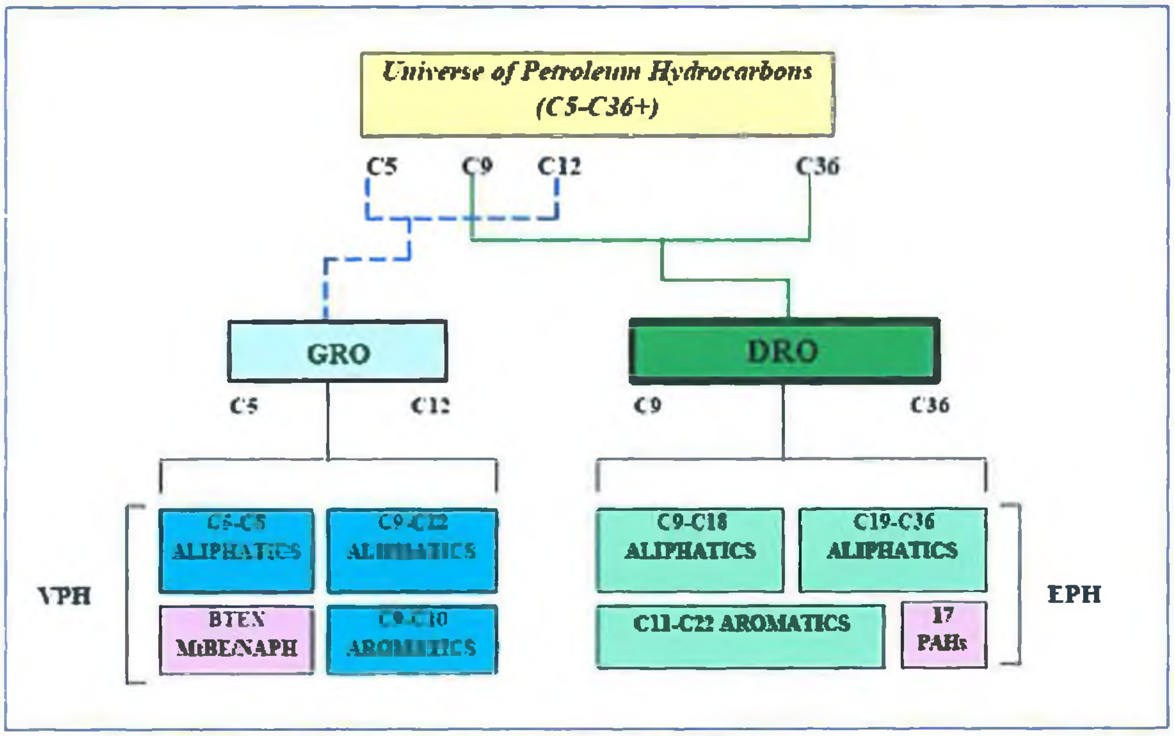
The MADEP published a regulatory framework for evaluating the TPH parameter in human health risk assessments (MADEP, 2002). This framework recommends using the EPH/VPH analytical procedure for petroleum hydrocarbon mixtures (Figure 1.3). This procedure consists of two steps;

1. Quantification of volatile petroleum hydrocarbons (VPH) previously termed gasoline range organics (GRO) and,
2. Quantification of extractable petroleum hydrocarbons (EPH), previously termed diesel range organics (DRO).

The VPH method includes the following analytes: benzene, toluene, ethylbenzene, and total xylenes (BTEX) as well as naphthalene and methyl-tertiary butyl ether (MTBE); alkanes/cycloalkanes in the n-C_5 to n-C_8 and n-C_9 to n-C_{12} carbon ranges; and aromatics/alkenes in the n-C_9 to n-C_{10} carbon range. The EPH method includes the following analytes: polycyclic aromatic hydrocarbons (PAHs); alkanes/cycloalkanes in the n-C_9 to n-C_{18} and n-C_{19} to n-C_{36} carbon range; and aromatics/alkenes in the n-C_{10} to n-C_{22} carbon range. MADEP developed the

EPH/VPH methodology for specific application in human health risk assessment. Similar to the TPHCWG fate and transport fractions, MADEP's fractions have been assigned toxicity criteria based on reference compounds selected to represent each fraction. Cleanup standards have been promulgated for the EPH/VPH fractions based on the toxicity of the reference compounds, and the state has recommended the use of either or both EPH and VPH analysis for a variety of petroleum mixtures. A large number of different hydrocarbon-biomarker parameters have been developed by petroleum organic geochemists to correlate different oils, and determine their source, original depositional environment, maturation and amount of biodegradation (Peters and Moldowan, 1993). Various analytical tools are available to produce biomarker "fingerprints", which like human fingerprints, can be visually compared. The amount of TPH found in a sample is useful as a general indicator of the petroleum contamination (ATSDR, 1999a). Gustafson (1997) stated that TPH is defined as the measurable amount of petroleum based hydrocarbon in an environmental media.

Figure 1.3 Total Petroleum Hydrocarbons Division into VPH and EPH



Source: MADEP, 2002

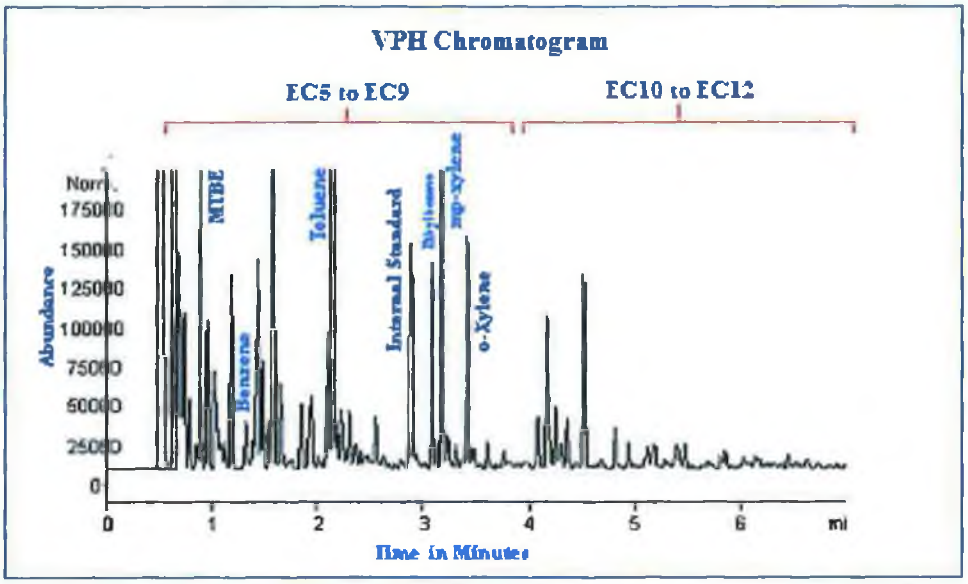
1.4 VPH - Gasoline

Automotive gasoline is a blended product. Refined to maximise cost-effectiveness, it is manufactured from the n-C_4 to n-C_{12} boiling range portions of distilled crude oil and a variety of processed refinery streams. Depending on the source, a barrel of crude oil can yield 10-40% gasoline from straight distillation. To increase yield and performance, refinery processes crack large molecules and alkylated or polymerise smaller molecules to produce molecules in the desired gasoline carbon range. Some molecules that are in the right range but burn unevenly will be reformed or isomerised to increase their octane value. Oxygenates that may be added to gasoline include MTBE, as well as alcohols. Gasoline contains additives which may be added in relatively small amounts to enhance certain performance characteristics. Its use demands that the end product meet specifications for volatility, octane, boiling range distribution, sulphur content, gum content, water tolerance, corrosion resistance, and additive-derived properties.

The composition of gasoline is well characterised. It is a blended product of many refinery streams. The potential number of isomers in this carbon range is relatively small so that detailed analysis is possible. There are more than 200 individual components in the n-C_4 to n-C_{12} boiling range. These hydrocarbons include 40% to 70% straight, branched and cyclic alkanes (normal paraffins, isoparaffins, and naphthenes); alkenes (olefins) in variable concentrations but usually less than 10% and 20% to 50% aromatics. The major components of gasoline that are targets in EPA methods are benzene, toluene, ethylbenzene, xylenes, and naphthalene. These compounds are sufficiently water soluble to leach to groundwater and are thus mobile in the environment. Gasoline can be produced to meet certain specifications.

Alkyl lead antiknock compounds, such as tetraethyl lead (TEL) and a manganese tricarbonyl compound (MMT), were used as octane improvers until the advent of unleaded gasolines in the mid 1970s when these additives were eventually phased out. Additives blended into gasolines affect their overall performance under many different conditions which exist during the operation of an automobile or other vehicle (Farrell-Jones, 2003). The proper octane levels are achieved in unleaded gasoline's today by the use of oxygenated additives, higher concentrations of aromatic hydrocarbons, and higher concentrations of branched chain hydrocarbons. These molecules have high research octane numbers and motor octane numbers. Figure 1.4 shows the volatile hydrocarbon gas chromatography utilising flame ionisation detection (GC-FID) chromatogram of an unleaded petrol standard.

Figure 1.4 GC-FID Analysis of Unleaded Petrol

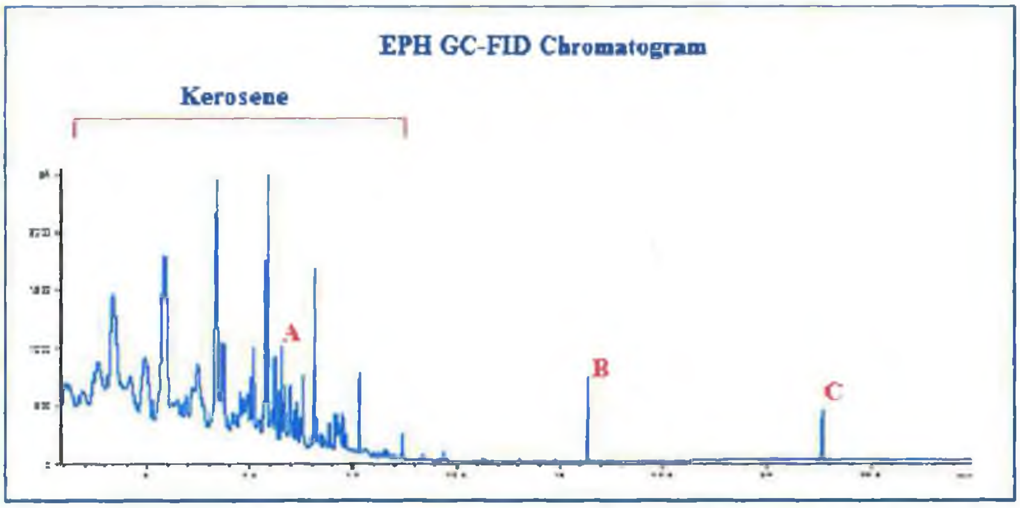


Source: Alcontrol Laboratories Dublin 2003

1.5 EPH – Kerosene and Jet A-1

Kerosene has essentially the same boiling range distillation as Jet Aviation 1 (Jet A1) and is thus of similar composition. Jet A or A-1 or JP8 (US Air Force) – is a kerosene used by the world's airlines. These fuels are essentially a fraction distilled from crude oil mixed with some cracked material. Jet A fuels consist of 70% to 90% saturated hydrocarbons, 10% to 20% aromatics. Sulphur compounds and some alkenes are removed by hydro-treating. Jet fuels, like kerosene comprise hydrocarbons in the n-C_8 to n-C_{17} range but the majority are found in the n-C_{10} to n-C_{14} range. Kerosene consists of 70% to 90% aliphatic hydrocarbons, 10% to 30% aromatics. The main difference between Jet A1 and kerosene is the presence of sulphur species. A low sulphur grade kerosene is produced as well as a regular high sulphur grade. The carbon range is typically n-C_8 to n-C_{16} (Figure 1.5).

Figure 1.5 GC/FID Analysis of Kerosene



Note: Internal standard A heptamethylnonane and surrogate standard B 1-chlorooctadecane and C squalane were added as retention time markers and for quantification purposes.

Source: Alcontrol Laboratories Dublin 2003

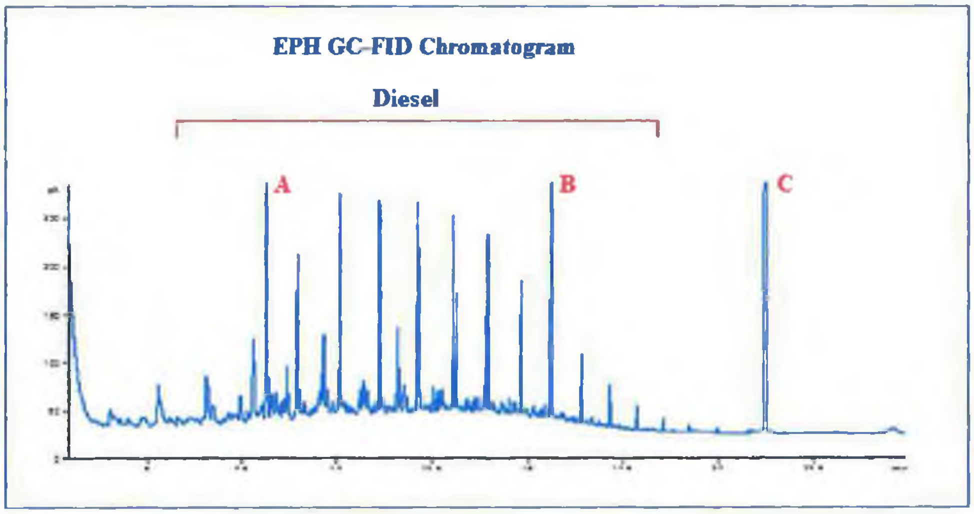
1.6 EPH - Diesel

Heavier fuel oils (marine diesel) may contain up to 15% distillation residues and more than 5% PAHs (ATSDR, 1995c). Residual fuel oils are more complex in composition than distillate fuels and contain significant portions of compounds with sulphur and nitrogen. Diesel fuels are similar to fuel oil but contain additives. They are classed as middle distillates and are denser than gasoline, thus providing more energy per unit volume than gasoline. The major components of diesel are similar to crude oils, but include a higher aromatic fraction (10% to 40%). The typical carbon range for transportation diesel is n-C_8 to n-C_{28}, however the vast majority of constituents are found in the n-C_{12} to n-C_{20} range. Saturated hydrocarbons account for 60% to 90% of diesel. The majority are naphthenes which appear as an unresolved envelope when analysed by gas chromatography. The recalcitrant isoprenoids pristane and phytane (Figure 1.6) are also dominant and are used for forensic purposes (Farrell-Jones, 2003). These compounds which are resistant to abiotic and biotic attack are commonly called biomarkers. Figure 1.7 shows a typical chromatographic trace of diesel analysed on a gas chromatograph utilising flame ionization detection.

Figure 1.6 Pristane and Phytane Chemical Structures

Source: Thompson and Nathanail, 2003

Figure 1.7 Diesel Chromatogram



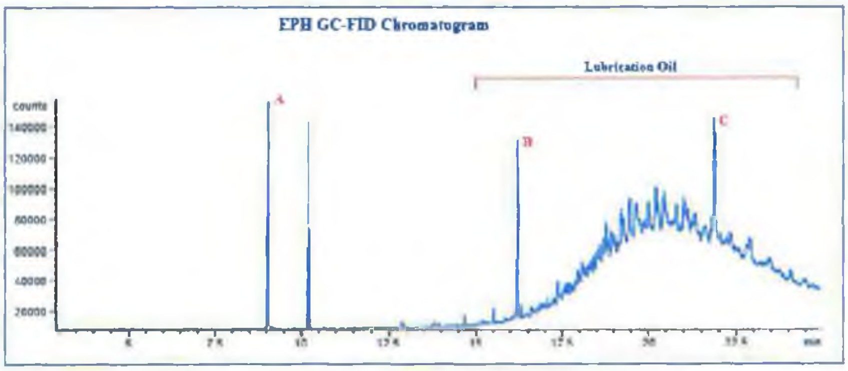
Source: Alcontrol Laboratories Dublin 2003

Fractions from crude oil distillation that are heavier than diesel/middle distillates are often called residual fuel oils. Other commonly used names are No. 4, 5, and 6 fuel oils and bunker C. These oils can be used as fuel or as feed to refinery conversion units to produce lighter, more valuable fuel fractions. The sources of fuel oils may be directly from the distillation process and/or a complex process of selection and blending of various petroleum fractions to meet definite specifications. In principle, these materials start in the n-C_{20} to n-C_{25} range and can go higher than n-C_{40}. Blending with lower molecular weight fractions to decrease viscosity of heavier fractions may widen the carbon range to as low as n-C_6. The composition of these oils is quite variable but they all contain saturated and aromatic hydrocarbons (including PAHs) as well as nonhydrocarbons (heteroatom containing molecules). There are seven different grades of fuel oil which are primarily used in different types of fuel burning equipment under different conditions of operation. They are grades 1 & 2, grades 4 (light) and 4 (heavy), grades 5 (light) and 5 (heavy), and 6. The specifications governing fuel oils are similar to those of diesel fuels with some variations. Maximum and minimum specifications for flash point, viscosity, American Petroleum Institute (API) gravity, ash content, water and sediment contents, distillation end point and amount recovered, sulphur content, octane number, copper strip corrosion rating, aromaticity, cloud point, and carbon residue are outlined in the standard American Society for Testing and Materials (ASTM) D 396 specification for fuel oils.

1.7 Lubricating Oil

Lubricating oils have a high molecular weight, high boiling point fractions covering the range n-C_{26} to n-C_{40+} but in extreme cases the range is wider n-C_{20} to n-C_{50}. Detailed compositions of lubricating oil fractions are difficult to obtain but it is known that these oils which are usually enriched in cyloparaffins (naphthenes), aromatics and nitrogen, sulphur and oxygen compounds (NSOs). The naphthenic envelope forms a characteristic profile by gas chromatography, Figure 1.8 which changes as viscosity changes. The aromatic fractions consist of predominantly the fused ring type with phenanthrene derivatives more common among three-ring aromatics. NSOs tend to be concentrated in the high boiling fractions. These oils have extensive application in the automotive, aviation, marine and rail industries. Greases are lubricating oils to which a thickening agent such as graphite has been added. Detergents are also common additives.

Figure 1.8 Chromatogram of Lubricating (Lube) Oil



Source: Alcontrol Laboratories Dublin, 2003

1.8 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a group of chemicals that are typically formed during the incomplete combustion of organic substances but also occur naturally in coal and oil. Sometimes referred to as PNAs (polynuclear aromatics) these are ubiquitous compounds found in many sites contaminated with petroleum or coal residues. They consist of two or more fused benzene rings. The PAHs of most interest in environmental chemistry are the 16 USEPA PAHs as listed in Table 1.1 as these compounds were considered to pose a significant environmental risk. Some PAHs in diesel oils are suspected carcinogens and some can persist for considerable periods of time in bottom sediments (Irwin *et al*., 1997). Specific PAHs are known to be mutagenic hence, measuring the concentration levels of these compounds is important in assessing risk from these combustion sources. There are more than 100 different PAHs and these generally occur as complex mixtures. PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes. PAHs are contained in asphalt used in road construction (ATSDR, 1995b), and can also be found in substances such as crude oil, creosote, and roofing tar. They are found throughout the environment in water and soil, and can occur in the air attached to dust particles or as solids in soil or sediment.

Table 1.1 Sixteen USEPA Priority PAHs

Naphthalene (2 ring)
Acenaphthylene (2 ring)
Phenanthrene (3 ring)
Fluorene (2 ring)
Chrysene (4 ring)
Acenaphthene (2 ring)
Anthracene (3 ring)
Fluoranthene (3 ring)
Pyrene (3 ring)
Benz(a)anthracene (4 ring)
Indeno(1,2,3-cd)pyrene (5 ring)
Benz(b)fluoranthene (4 ring)
Benz(k)fluoranthene (4 ring)
Benz(a)pyrene (5 ring)
Dibenz(a,h)anthracene (5 ring)
Benzo(ghi)perylene (6 ring)

Source: Thompson and Nathanail, 2003

These sixteen PAH compounds were selected as representative of the most hazardous, after the analysis of numerous contaminated samples found at sites around the USA. It was found over 80% of the total PAH contribution could be attributed to these sixteen PAHs. One of the most significant and harmful effects of PAHs is due to their carcinogenic nature, although this is not consistent across the whole range of compounds. Eight of the four, five and six member ringed PAHs are considered to be carcinogens (Table 1.2). With benzo(a)pyrene and benzo(a,h)anthracene being the most potent carcinogens.

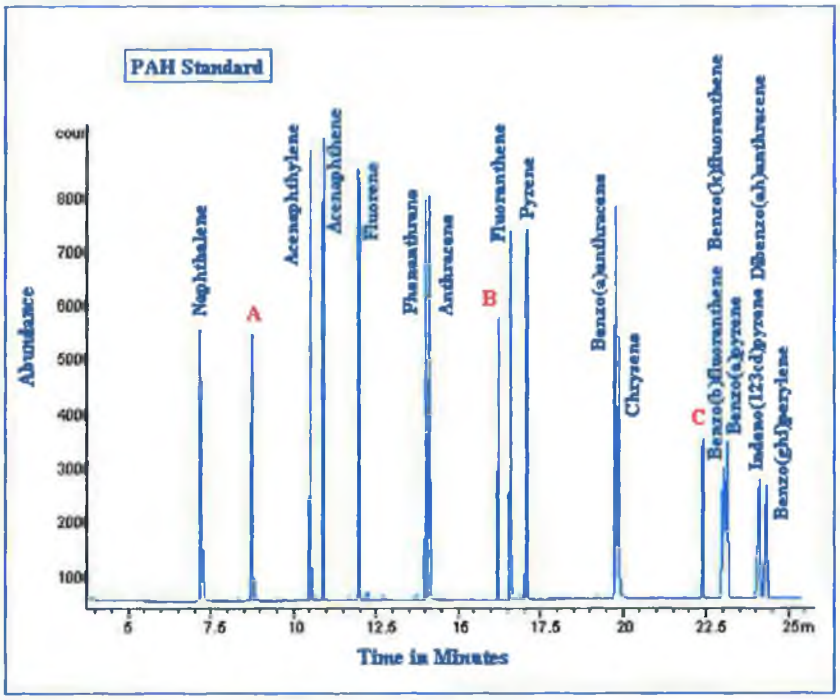
Table 1.2 Carcinogenic PAHs

PAH	Number of Rings	PAH	Number of Rings
Benzo(a)pyrene	5	Benzo(k)fluoranthene	4
Dibenzo(a,h)anthracene	5	Benzo(a)anthracene	4
Indeno(1,2,3-cd)pyrene	5	Chrysene	4
Benzo(b)fluoranthene	4	Benzo(ghi)perylene	6

Source: Thompson and Nathanail, 2003

Figure 1.9 illustrates the EPH analysis of the recommended USEPA sixteen priority PAH compounds.

Figure 1.9 EPH Chromatogram of PAH Standard



Source: Alcontrol Laboratories Dublin, 2003

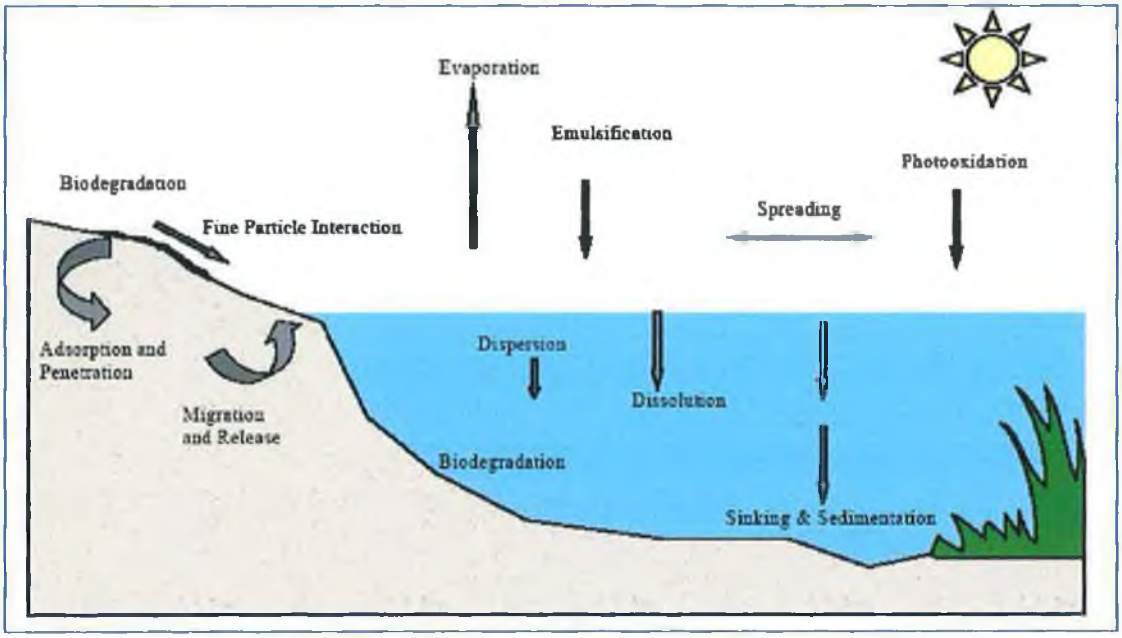
1.9 Coal Tar Chemistry

Coal tar, as the name suggests, is a by-product from the process of heating coal to produce gas and coke. Historically the main use of coal was for coal-gas lighting and, as a result, carbonising coal became commonplace in many large towns. The by-products, coal tar and pitch, were distilled to produce refined products which, until the advent of petroleum, were the feedstock for most chemical industry. Motor benzole, a refined by-product of coal carbonisation, was used as a fuel similar to modern day motor spirits. By the 1950s there were a large number of benzole producing plants associated with gas works or the steel industry. With the decline of the coking coal as a fuel, benzole production decreased. Its chemical composition was similar to leaded gasoline's, but it had a significantly higher concentration of naphthalene's, and because its source was coal/coal tar, there was an absence of n-alkanes. The chemical fingerprint for the BTEX compounds is similar for both benzole and petroleum sourced gasoline. Another main industrial use for one of refined tar products was as an antifungal agent. This was adopted throughout the wood preserving industry as creosote, not to be confused with the medicinal form of creosote, which was used in the pharmaceutical industry and was derived from beech wood tar. These creosotes constitute a significant source of polycyclic aromatic hydrocarbons (PAHs). The complete range of mono and polynuclear aromatics are also found in petroleum, but their content and distribution profiles are usually significantly different from those found in creosote. These differences in composition and distribution can be used to determine the source of the PAHs, and determine whether the source is of a petroleum or coal tar origin (Jones, 2004).

1.10 Behaviour of Oil in the Environment

Zhu *et al.,* (2001) associated with the USEPA discussed at length the behaviour of oil in the environment and made the following observations. When oil is introduced into the environment, it immediately goes through a variety of physical, chemical and biological changes (Figure 1.10). These weathering processes will alter oil composition and properties in ways that may affect spill response strategies. Bioremediation is a relatively slow process that is often used as a polishing step after conventional cleanup options have been applied. Weathering processes, include biodegradation, which have been reviewed and described extensively in the literature.

Figure 1.10 Major Weathering Processes



Source: Zhu *et al.*, 2001

1.10.1 Spreading of Oil Following Release

The spreading of oil on water is one of the first processes which will occur within the first few hours after a spill, provided that the oil pour point is lower than the ambient temperature. Gravity, inertia, friction, viscosity and surface tension are the principal forces which influence the oil spread. This process increases the overall surface area of the spill, thus enhancing mass transfer via evaporation, dissolution, and later biodegradation.

1.10.2 Weathering Process - Evaporation

Evaporation is the most important weathering process in terms of environmental impact. This process during the early stages of an oil spill can be responsible for the removal of a large fraction of the oil including the more toxic, lower molecular weight components. Evaporation removes virtually all the normal alkanes smaller than n-C_{15} within the first few days following the spill. Volatile aromatic compounds, such as benzene and toluene, can also be rapidly removed from an oil slick through evaporation. However, these volatile oil components may be more persistent when oil is stranded in sediments. The volatile components make up 20% to

50% of most crude oils, about 75% of No. 2 fuel oil, and about 100% of gasoline and kerosene. As a result of the compositional differences, the physical properties of the remaining slick can change significantly. Major factors influencing the rate of evaporation which include composition and physical properties of the oil are wave action, wind velocity, and water temperature (Jordan and Payne, 1980; Zhu *et al.*, 2001).

1.10.3 Dissolution

Dissolution is a less important factor for mass loss during an oil spill. Dissolved hydrocarbon concentrations in water are particularly important due to their potential influence on the success of bioremediation and the effect of toxicity on biological systems. The solubility of the spilled oil, weather conditions, and the characteristics of the spill site are the factors which will depend on the extent of the dissolution. The low molecular weight toxic aromatic components in crude and refined oils are the most soluble oil components. Many of these components may be removed through evaporation, however their impact on the environment is much greater (National Academy of Science, 1985). Photochemical and biological processes also influence the rates of dissolution (Zhu *et al.*, 2001).

1.10.4 Photo-oxidation a Weathering Process

An additional weathering process which has a biological consequence is photo-oxidation. Natural sunlight in the presence of oxygen has sufficient energy to transform many complex petroleum compounds into simpler compounds through a series of free-radical chain reactions. Through this process the formation of hydro peroxides, aldehydes, ketones, phenols, and carboxylic acids may increase the solubility of oil in water. An increase bioavailability may be associated with this increase in the solubility of oil in water. Photo-oxidation may increase the formation of toxic compounds which will have detrimental environmental and biological impacts. However, the formation of polar compounds may increase the rate of biodegradation of petroleum, particularly at lower concentrations where acute toxicity effects are limited (Nicodem *et al.*, 1997). Photo-oxidation leads to the formation of more soluble compounds, which are often more biodegradable.

1.10.5 Dispersion

Dispersion, or formation of oil-in-water emulsions, involves incorporating small droplets of oil into the water column, resulting in an increase in surface area of the oil. In general, oil-in-water emulsions are not stable. However, they can be maintained by continuous agitation, interaction with suspended particulates, and the addition of chemical dispersants. Dispersion may influence oil biodegradation rates by increasing the contact between oil and micro-organisms and/or by increasing the dissolution rates of the more soluble oil components (Zhu *et al.*, 2001).

1.10.6 Emulsification

The process of emulsification of oils involves a change of state from an oil-on-water slick or an oil-in-water dispersion to a water-in-oil emulsion, with the eventual possible formation of a thick, sticky mixture that may contain up to 80% water, commonly called "chocolate mousse" (Zhu *et al.*, 2001). Surface-active materials generated through photochemical and biological processes, wax, asphaltic material and the chemical composition of the oil enhance the formation and stability of emulsions. An emulsion decreases the effectiveness of the clean-up process of oil spills and suppresses the natural rates of oil biodegradation. Adsorption onto suspended particulate materials, sinking and sedimentation, and tar ball formation are some other important physical and chemical weathering processes that influence the rates of oil degradation (Zhu *et al.*, 2001).

1.11 Environmental Factors Affecting Oil Biodegradation

When oil spills occur in the environment, the rate of oil biodegradation is also greatly influenced by the characteristics of the contaminated environment. Major environmental factors affecting oil biodegradation include weathering processes, temperature, pH, availability and concentration of nutrients, and oxygen.

1.11.1 Weathering Processes

The weathering processes have profound effects on oil biodegradation. Evaporation of volatile oil components may benefit micro-organisms by removing more toxic low-molecular-weight components such as benzene and smaller *n*-alkanes. The oil surface area is important because growth of oil degraders occurs almost exclusively at the oil-water interface (Atlas and Bartha, 1992). The reduction of the surface area is caused by the formation of water-in-oil emulsions, therefore decreasing biodegradation. Tarballs, which are large aggregates of weathered and undegraded oil, also restrict access to micro-organisms because of their limited surface area (Leahy and Colwell, 1990). Dispersion of hydrocarbons in the water column in the form of oil-in-water emulsions increases the surface area of the oil and thus its availability for microbial attack (Zhu *et al.*, 2001). The applications of chemical dispersants have produced mixed results and has not been shown to be an effective way to enhance oil biodegradation. The concentration of individual oil constituents influence the biodegradation rates, which may be affected by various weathering processes. For example, microbes may attack very low concentrations of pollutants in the environment inefficiently (Foght and Westlake, 1987). However, high concentrations of hydrocarbons may cause inhibition of biodegradation by nutrient or oxygen limitations or toxic effects. Weathering processes will affect the ultimate concentrations of petroleum hydrocarbons in the environment in different ways. Evaporation may reduce the concentrations of volatile compounds but concentrate some other constituents. Sorption and emulsification may concentrate the pollutants, while dispersion and dissolution tend to dilute them (Zhu *et al.*, 2001).

1.11.2 Temperature

The ambient temperature of an environment affects both the properties of spilled oil and the activity or population of micro-organisms. The viscosity of the oil increases at low temperatures, while the volatility of toxic low-molecular-weight hydrocarbons is reduced. This process delays the onset of biodegradation (Atlas, 1981). Short-chain alkanes are more soluble at lower temperatures, and some low-molecular-weight aromatics are more soluble at the higher temperature (Foght and Westlake, 1987). Hydrocarbon biodegradation can occur over a wide range of temperatures, and the rate of biodegradation generally decreases with decreasing temperature. In soils at 30°C to 40°C the highest degradation rates generally occur, which also occurs in some freshwater environments at 20°C to 30°C, and at 15°C to 20°C in marine environments. Other factors such as the composition of the microbial population can be complicated by the effects of temperature. Hydrocarbon biodegradation has been observed at temperatures as low as 0°C to 2°C in seawater and -1.1°C in a soil (Zhu *et al.*, 2001).

1.11.3 Oxygen

Aerobic conditions are necessary for extensive degradation of oil hydrocarbons in the environment since major degradative pathways for both aliphatics and aromatics involve oxygenases (Atlas, 1981). Many studies have shown that oxygen depletion leads to sharply reduced biodegradation activities in marine sediments and in soils (Bossert and Bartha, 1984).

Anaerobic oil degradation has been shown in some studies to occur only at negligible rates, as reviewed by Atlas (1981), leading to the conclusion that the environmental importance of anaerobic hydrocarbon degradation can be discounted. However, anaerobic hydrocarbon metabolism may be an important process in under other conditions (Head and Swannell, 1999). The biodegradation of some aromatic hydrocarbons, has been clearly demonstrated to occur under a variety of anaerobic conditions (Krumholz *et al.*, 1996). PAHs and alkanes can be degraded under sulphate-reducing conditions at similar rates to those under aerobic conditions in some marine sediment (Zhu *et al.*, 2001).

1.11.4 Nutrients

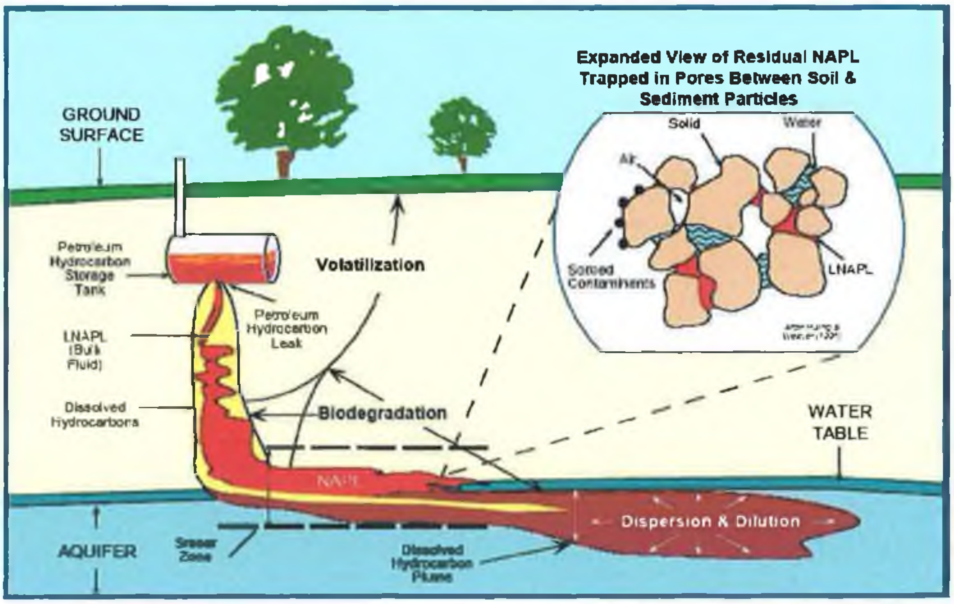
Approximately 150mg of nitrogen and 30mg of phosphorus are utilised in the conversion of 1g of hydrocarbon to cell materials (Rosenberg and Ron, 1996; Zhu *et al.*, 2001). When a major oil spill occurs in marine and freshwater environments the supply of carbon is dramatically increased and the availability of nitrogen and phosphorus generally becomes the limiting factor for oil degradation (Leahy and Colwell, 1990). Freshwater wetlands are typically considered to be nutrient limited due to heavy demand for nutrients by the plants. They are also viewed as being nutrient traps as a substantial amount of nutrients may be bound in biomass (Mitsch and Gosselink, 1993). Seasonal variations in nutrient levels in both freshwater lakes and wetlands will affect the performance of oil biodegradation.

1.11.5 Other Factors

Factors affecting biodegradation of petroleum hydrocarbons can include pH and salinity. The pH of seawater is generally stable and slightly alkaline (Bossert and Bartha, 1984). In contrast, the pH of freshwater and soil environments can vary widely. Organic soils in wetlands are often acidic, while mineral soils have more neutral and alkaline conditions. Most heterotrophic bacteria and fungi favour a neutral pH, with fungi being more tolerant of acidic conditions. The degradation of oil increases with increasing pH, and optimum degradation occurs under slightly alkaline conditions (Zhu *et al.*, 2001). Changes in salinity may affect oil biodegradation through alteration of the microbial population.

In the soil above the water table, gravity causes liquid to migrate downward from the release source. The infiltrating liquid loses its most volatile components into the soil air and its fumes) soluble constituents to the water surrounding the particles. Fuel components are also lost because of sorption and capillary retention in the vadose zone. When a quantity of the released fuel is larger than the losses to volatilisation, dissolution and capillary retention, the liquid fuel reaches the water table and begins to accumulate as a free phase floating product often referred to as a non aqueous phase liquid (NAPL). Hydrocarbons released into the environment are also subject to biotic and abiotic weathering reactions in the soil/groundwater media. These processes act in concert, with the rate of transformation being related to the chemical composition of the fuel and local environmental factors, including nutrient, oxygen content and temperature. Grain size and clay content are also important parameters for controlling weathering process in soil. Underground storage tanks are an example of such an environment where evaporation and leaching is low or non-existent and the proportion of water, oxygen, and nutrients is such that microbial action is inhibited (Zhu *et al.,* 2001). In contrast, soils favour rapid degradation and can completely remove oil within months. All of the above process can be illustrated in the figure below (Figure 1.11).

Figure 1.11 Major Fuel Alterations in the Environment



Source: USEPA, 1999

1.12 Biodegradation of Oil

Biodegradation of oil is one of the most important processes involved in weathering and the eventual removal of petroleum from the environment, particularly for the non-volatile components of petroleum. Numerous scientific review articles have covered various aspects of this process and the environmental factors that influence the rate of biodegradation (Zhu *et al.*, 2001).

1.12.1 Mechanism of Oil Biodegradation, Hydrocarbon-Degrading Micro-organisms

Micro-organisms capable of degrading petroleum hydrocarbons and related compounds are ubiquitous in marine, freshwater, and soil habitats. Over 200 species of bacteria, yeasts and fungi have been shown to degrade hydrocarbons ranging from methane to compounds of over 40 carbon atoms (Zobell, 1973). The distribution of hydrocarbon-utilising micro-organisms is also related to the historical exposure of the environment to hydrocarbons. In “pristine” ecosystems, hydrocarbon degraders may make up less than 0.1% of the microbial community and in oil-polluted environments, they can constitute up to 100% of the viable micro-organisms (Atlas, 1981). There is no single strain of bacteria with the metabolic capacity to degrade all the components found within crude oil. Micro-organisms classified as non-hydrocarbon utilisers may also assist in the removal of petroleum from the environment. Progressive or sequential reactions are the main process in the degradation of petroleum.

Certain organisms may carry out the initial breakdown on the petroleum constituent. This produces intermediate compounds that are subsequently utilised by a different group of organisms in the process that results in further degradation (Karrick, 1977). Major metabolic pathways for many of these compounds have been well studied and documented to explain these compounds differences in susceptibility to biodegradation (Atlas, 1984; Cerniglia, 1992 and Zhu *et al.,* 2001).

1.12.2 Biodegradation of Aliphatics

In petroleum mixtures, the *n*-alkanes are the most readily degraded (Atlas, 1981). Biodegradation of *n*-alkanes with molecular weights up to n-C_{44} have been demonstrated (Haines and Alexander, 1974) while those alkanes in the n-C_{10} to n-C_{26} range are considered the most readily and frequently utilized hydrocarbons (Atlas, 1995). The predominant mechanism of n-alkane degradation involves terminal oxidation to the corresponding alcohol, aldehydes, or fatty acid. Branched alkanes are less readily degraded in comparison to *n*-alkanes. Methyl branching increases the resistance to microbial attack because fewer alkane degraders can overcome the blockage of beta-oxidation (National Academy of Science, 1985) therefore, compounds like pristane and phytane which are in diesel are typically used as source markers. Cycloalkanes, however, are particularly resistant to biodegradation. The complex polycyclic compounds such as the hopanes and steranes are extremely resistant to biodegradation and persist in the environment for a considerable time after a petroleum spill (Zhu *et al.*, 2001).

1.12.3 Biodegradation of Aromatics

Although the aromatics are generally more resistant to biodegradation, some low molecular weight aromatics such as naphthalene may actually be oxidized before many aliphatics (Foght and Westlake, 1987). Monocyclic aromatics are toxic to some micro-organisms due to their solvent action on cell membranes, however, in low concentrations they are easily biodegradable under aerobic conditions. The two to four ring PAHs are less toxic and are more available for biodegradation. They are biodegradable at rates that decrease with the level of complexity. Alkylated aromatics are degraded less rapidly than their parent compounds. The more highly alkylated groups are degraded less rapidly than less alkylated ones. The formation of a diol followed by ring cleavage and formation of a di-carboxylic acid is the expected mechanism following bacterial degradation of aromatics. Fungi and other eukaryotes normally oxidize aromatics using mono-oxygenases, forming a trans-diol (Zhu *et al.*, 2001).

1.12.4 Biodegradation of Resins and Asphaltenes

Due to the complex structure of resins, which are difficult to analyse, very little is known about their biodegradation process. Resins and asphaltenes have previously been considered to be refractory to degradation. However, there is recent evidence of asphaltene degradation through co-metabolism (Leahy and Colwell, 1990). Further research is still needed to understand the biodegradation of these compounds.

In summary, the susceptibility of petroleum hydrocarbons to microbial degradation is generally in the following order: n-alkanes > branched alkanes > low-molecular-weight aromatics > cyclic alkanes (Zhu *et al.*, 2001). The rate of biodegradation of different oil is affected by the compositional heterogeneity. The degradation rate for the same oil constituents may vary significantly for different oils. Co-metabolism also plays an important role in oil biodegradation. Many complex branched, cyclic, and aromatic hydrocarbons, which otherwise would not be biodegraded individually, can be oxidised through co-metabolism in an oil mixture due to the abundance of other substrates that can be metabolized easily within the oil (Atlas, 1981). The biological fate of oil components in an oil mixture still requires further research. Particularly, efforts should be made to establish a database regarding the biodegradability of different types of oils and petroleum products (Zhu *et al.*, 2001).

1.13 Weathering Check and Biodegradation Check

Hydrocarbons are classified as petrogenic are derived directly from crude oil and pyrogenic are obtained by the pyrolysis of organic matter. When a pyrogenic or petrogenic product is introduced into the environment the chemical composition immediately begins to change, but the rate of change will vary with the environmental conditions. The processes by which the product changes in composition after it is spilled are referred to collectively as "weathering". Initial changes in spilt product occur fairly quickly, and the rate of change then slows down over time. Hydrocarbon in the carbon range up to n-C_{20} and a boiling range of 400°C are affected by this process. The major compositional changes of alkylated PAH compounds due to evaporative weathering is usually indicated by a pronounced depletion of naphthalene and its alkylated homologues relative to other PAHs homologous series. Most homologous groups show the same evaporative loss trend $C_0>C_1>C_2>C_3>C_4$ (Wang *et al.*, 1998). Beyond the alkyl chrysenes (four rings) no loss of evaporation is generally observed. By comparing ratios of these substances the degree of weathering can be estimated by a comparison to a reference product.

Chapter 2 Methodology

Chapter 2 Methodology

2.0 Instrumentation

Forensic fingerprinting analysis of the soil sample S-1 was undertaken for Volatile Hydrocarbon (VH), Extractable Hydrocarbon (EH) and Polycyclic Aromatic Hydrocarbon (PAH). This was carried out using both liquid and headspace sample introduction techniques, followed by gas chromatographic (GC) separation coupled with both flame ionisation (FID) and mass spectral (MS) detection techniques. The sample were analysed as follows;

- Headspace VH analysis utilising a CTC Analytics Combi*PAL* system combined with an Agilent Technologies 6890N GC-FID equipped with a column suitable for VH analysis,
- EH analysis using an Agilent Technologies 7683 series liquid injector/auto-sampler. GC separation was followed by FID detection using an Agilent Technologies 6890N GC-FID, equipped with a column suitable for EH analysis,
- PAH analysis utilised an Agilent Technologies 7683 series liquid injector/auto-sampler, a 6890N GC coupled with a 5973N mass selective detector (MSD) in both selective ion monitoring (SIM) and total ion count (TIC) scan modes. The GC was equipped with a column which was selectivity suitable for PAH analysis.

The instrumental operating conditions are detailed in Table 2.1, Table 2.2 and Table 2.3.

Table 2.1 GC Operating Conditions for VH, EH and PAH Analysis

Column VH	Fused silica capillary column 15m x 0.25mm x 1.0µm film RTX-MS
Column EH, PAH	Fused silica capillary column 30m x 0.25mm x 0.25µm film RTX-MS
Detector VH, EH	FID (Agilent 6890N)
Detector PAH	Agilent 5973N mass selective detector (MSD), solvent delay 3min
Temperature VH	50°C Isothermal for 0.5 minutes, 50°C to 140 °C programmed at 15.0°C/minute, 140°C isothermal for 0.5 minutes. Injection port - 200°C. Detector – 200°C
Temperature EH	75°C Isothermal for 1.5 minutes, 75°C to 290°C programmed at 12.4°C/minute, 290°C isothermal for 7.0 minutes. Injection port - 280°C. Detector – 320°C
Temperature PAH	40°C Isothermal for 1.0 minutes, 40°C to 160°C programmed at 10°C/minute, 160°C to 290°C programmed at 15°C/minute isothermal for 8.0 minutes. Injection port - 280°C. Detector - MS Quad 150°C, MS source 230°C and transfer line 275°C
Gases VH	Helium carrier – constant flow of 4.4 mls/min. Nitrogen makeup – 30 mls/min. Hydrogen FID – 30 mls/min. Air FID – 300 mls/min
Gases EH	Helium carrier – constant flow of 1.4mls/min. Nitrogen makeup – 30 mls/min. Hydrogen FID – 30 mls/min. Air FID – 300 mls/min
Gases PAH	Helium carrier – constant flow of 1.4 mls/min.
Injection VH	Split (ratio 21:1), volume 250µl
Injection EH	Splitless, volume 1.0µl
Injection PAH	Pulse splitless, volume 1.0µl

Source: Alcontrol Laboratories Dublin, 2003

Table 2.2 Headspace Sampler Operating Conditions for VH Analysis

Incubation temperature / time	80°C / 10 minutes
Agitation cycle / speed	5 sec run 3 sec stop / 1600 rpm
Run time	12 minutes
Syringe heater temperature	85°C
Volume of sample injected	250µl
Syringe bake out	Increase 10°C for 10 seconds
Syringe flushing time	10 minutes at an air pressure of 5psi

Source: Alcontrol Laboratories Dublin, 2003

Table 2.3 SIM Ions for PAH

Compound	**Target Ion (SIM Mass)**	**Compound**	**Target Ion (SIM Mass)**
Naphthalene (C_0)	128 m/z	Anthracene	178 m/z
C_1 Methyl Naphthalene	142 m/z	Fluoranthene	202 m/z
C_2 Dimethyl Naphthalene	156 m/z	Pyrene	202 m/z
C_3 Trimethyl Naphthalene	170 m/z	Benz(a)anthracene	228 m/z
C_4 Tetramethyl Naphthalene	184 m/z	**Chrysene (C_0)**	228 m/z
Acenaphthylene	152 m/z	C_1 Methyl Chrysene	241 m/z
Acenaphthene	154 m/z	C_2 Dimethyl Chrysene	256 m/z
Fluorene (C_0)	166 m/z	C_3 Trimethyl Chrysene	270 m/z
C_1 Methyl Fluorene	180 m/z	Benzo(b)fluoranthene	252 m/z
C_2 Dimethyl Fluorene	194 m/z	Benzo(k)fluoranthene	252 m/z
C_3 Trimethyl Fluorene	208 m/z	Benzo(a)pyrene	252 m/z
Phenanthrene (C_0)	178 m/z	Indeno(123,cd)pyrene	276 m/z
C_1 Methyl Phenantrene	192 m/z	Dibenzo(ah)anthracene	278 m/z
C_2 Dimethyl Phenantrene	206 m/z	Benzo(ghi)perylene	276 m/z
C_3 Trimethyl Phenantrene	220 m/z	Naphthalene-d8 (Surr)	136 m/z
C_4 Tetramethyl Phenantrene	234 m/z	Acenaphthene-d8 (Surr)	164 m/z
Dibenzothiophene (C_0)	184 m/z	Phenanthrene-d10 (Surr)	188 m/z
C_1 Methyl Dibenzothiophene	198 m/z	Chrysene-d12 (Surr)	240 m/z
C_2 Dimethyl Dibenzothiophene	212 m/z	Perylene-d12 (Surr)	264 m/z
C_3 Trimethyl Dibenzothiophene	226 m/z	Biphenyl-d10 (IS)	164 m/z

Source: Alcontrol Laboratories Dublin, 2003

2.1 Solvents and Reagents

The GC gases used for the VH, EH and PAH analysis were all of high quality supplied by British Oxygen Company (BOC) gasses Ireland Ltd. They consisted of helium (carrier) 99.99% min, hydrogen (flame) 99.99% min and air/service air, compressed gas, -40°C dew point. Super purified water or deionised water, methanol purge and trap grade, n-hexane (95% min), dichloromethane (Distol grade), acetone (Distol grade) and sodium chloride, general purpose grade were used at different stages during the study.

2.2 Sample and Reference Material Extraction

For most analyses, it is necessary to isolate the analytes of interest from the matrix (e.g. the soil, water). Extraction processes are quite complex and there is no universal procedure that caters for all analytes with the same degree of efficiency. Before considering the extraction technique, the choice of solvent was assessed. The extraction of hydrocarbons from soils is largely influenced by the polarity of the solvent used. A change in polarity of a solvent will change the type and yield of the extract obtained. The solubility of organic compounds in selected solvents may be estimated from the "like dissolves like" rule of thumb. Whilst this approach is adequate, it is at best only qualitative and does not take into account the matrix and other effects present. Cocktails of solvents of different polarity can be prepared to give the same polarity as solvents which have or maybe withdrawn from use for health and safety reasons. However, the presence of water in the sample can affect the polarity of the solvent and ultimately the extract. The choice of solvents is determined by cost, spectral qualities (for HPLC use), extraction efficiency, toxicity and commercial availability. Methylene chloride (dichloromethane) has been the preferred solvent for many semi-volatile compounds due to its high extraction efficiency and low relative cost. However, for most petroleum species a non-polar solvent such as hexane is more than effective for relatively fresh or recent spills. In aged polluted sites where absorption may have taken place, the addition of a polar solvent such as acetone to the hexane is common. The hexane/acetone cocktail usually meets all requirements but may not always be compatible with the extraction technique.

2.3 Manual Shake Extraction for Coal, Road Tar, South American Crude Bitumen and Sample S-1

The coal, road tar, South American crude bitumen and sample S-1 was solvent extracted for the analysis of EH using acetone and hexane. The sample was coned and quartered to ensure a heterogeneous aliquot was taken; 15g of the wet sample was weighed and placed into a 100ml clear glass bottle. 20mls of acetone was added to the sample bottle and placed on a shaker for 15 minutes at 250 motion/minute. A further 20mls of n-hexane was added and the bottle was placed on the shaker for a further 15 minutes. Approximately 50mls of deionised water was then added to the bottle and left to stand for 5 minutes. The top layer ≈20mls was removed and placed in a 40ml vial and centrifuged for 3 minutes at 1500 rpm. 1ml was removed from the extract and analysed. A portion of the sample was weighed and dried in an oven for 12 hours at 30°C to determine the moisture content. This simple effective procedure involved shaking the soil matrix with a suitable solvent for a period of time. It is suitable for most highly polluted soils (TPH of >1000 mg/kg). The lack of mechanical forces inhibits extraction when using non-polar solvents with moist soils. For this reason, acetone was added to the non-polar solvent. The procedure was modified to include ultrasonic agitation, which utilises high frequency sound waves to disaggregate the soil, thereby increasing the surface area of sample in contact with the extracting solvent.

2.4 Extraction Reference Materials - Kerosene, Diesel, Jeyes Fluid and Lubrication Oil

5g's of each reference material was weighed and made up to the 100ml mark with dichloromethane in a volumetric. The approximated concentration was calculated to be 50,000mg/l. 2ml's of this stock was diluted with dichloromethane to 100mls to give a working concentration of 1,000mg/l.

2.5 Volatile Hydrocarbon Analysis (VH)

5.0 ± 0.2g of sample S-1, made up to the 5ml mark with reagent water, 100μl of reference material (chlorobenzene), 1.5 ± 0.2g of sodium chloride were sealed in a headspace glass vial. The glass vial was subjected to agitation and heat outlined in the operating conditions above. The sample was also extracted using 5mls of methanol instead of reagent water. 1ml of this liquid extract was taken and made to the 5ml mark with reagent water and 100μl of reference material was added.

2.6 Volatile Hydrocarbons (VH) Analytical Procedure

The time ranges for integration purposes of the total Volatile Hydrocarbons (VH) and the bands n-C_4 to n-C_9 (i.e. up to but not including n-C_{10}) and n-C_{10} to n-C_{12} were assessed using the Washington VPH spiking matrix. Although the exact integration times are GC dependent, the start time, n-C_4, (end of the methanol solvent front) was found to be approximately 0.4 minutes, n-C_{10} (up to but not including n-C_{10}) was found to be approximately 4.0 minutes and the end time was up to but not including n-C_{12} at approximately 6.2 minutes.

2.7 Polycyclic Aromatic Hydrocarbons (PAH) Analytical Procedure

2.7.1 Compound Identification

The qualitative identification of compounds determined by this method was based on retention time and on comparison of the sample analyte selected ion ratios with the same ions in the standards run with the samples. The characteristic ions were chosen as the ions of greatest relative intensity that occur in the reference mass spectrum, or more particularly have characteristic structural significance. Ions present in the reference spectrum were only accepted if the sample spectrum was at the same ratio, this ratio was within 20%.

Chapter 3

Discussion of Results

Chapter 3 Discussion of Results

3.0 Introduction

Following routine monitoring of groundwater and river sediments, elevated levels of hydrocarbons were reported. On further investigation an area of suspected fly tipping was encountered on a local farm land which had no previous history of chemical activity. A representative sample taken at two meters from this waste material, and was assigned the identification S-1. The sample was submitted by the Environmental Protection Agency (EPA) for analysis to determine the nature of the contaminants present. The identity and location of the soil sample S-1 is not disclosed in this study due to legal constraints. It was suspected that the landowner had been involved in illegally accepting waste material from third party sources. The objective of the study was to determine the nature of contaminants present in the sample and demonstrate by means of various analytical and mathematical subroutines the source of the contaminant.

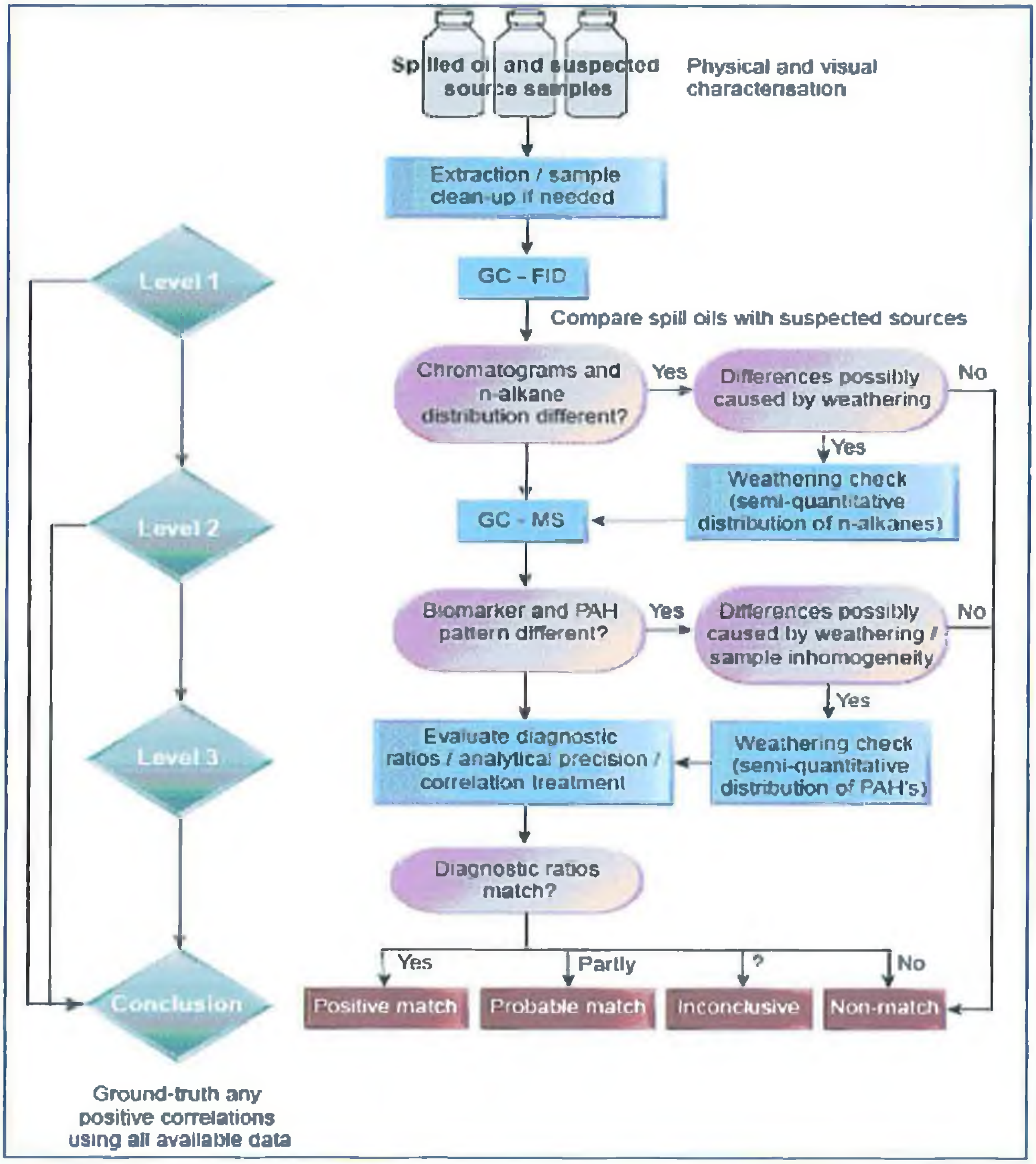
3.1 Gas Chromatography Analysis of Petroleum Products

Hydrocarbon fuels and derivatives found in the environment are often characterised by gas chromatography/flame ionisation detection (GC/FID). The identification and interpretation of GC fingerprints is largely qualitative and subjective, as it is dependant upon the skill and expertise of the interpreter. It is for this reason that a tiered approach is adopted to give a quantitative and objective interpretation of the data which came from the extract of sample S-1:-

Level 1 – Chemical Fingerprinting by GC-FID
Level 2 – Detailed Analysis by GC-MS
Level 3 – Statistical Analysis of the Data

This extract for the reference materials and the sample S-1, was analysed using a tiered approach Daling *et al.*, 2002 (Figure 3.1). The interpretation of the data obtained at each level allowed for the determination and possible identification of the source of the contaminant found in the sample S-1. The movement from Level 1 to level 3 focused the investigation and confirmed the findings at each level.

Figure 3.1 Tiered Three Level Approach



Source: Daling *et al.*, 2002

3.2 Level 1 Chemical Fingerprinting by GC-FID

Identification of the product type in contaminated samples is the single most important stage in any environmental forensic investigation as it frequently forms the foundation on which many of the relevant conclusions are derived. Among the analytical methods used to identify a wide range of contaminants are those that focus on specific hydrocarbon classes, such as alkanes and PAHs. This screening Level 1, allows for the general characterisation of the sample S-1 and reference materials for the volatile hydrocarbons (VH) components by headspace GC/FID in the carbon ranges n-C_5 to n-C_9, n-C_{10} *to* n-C_{12} and analysis of the extractable hydrocarbons (EH) in the carbon range n-C_{10} to n-C_{40}. Chemical fingerprinting of these can form the basis for:-

- Characterising the sample by obtaining the overall boiling (carbon) range of the contaminants.
- Comparing distribution patterns/profiles.
- Establishing selected acyclic isoprenoid indices/ratios.
- Establishing a weathering/biodegradation check.

If the data obtained from Level 1 is insufficient to identify the oil products (due to biodegradation or weathering), a Level 2 investigation may be included to evaluate additional compounds which are masked by GC/FID.

3.3 Level 2 Detailed Analysis by GC-MS

These additional analyses involve the GC/MS targeting of selected compounds which are less resistant to biodegradation. Examples of such compounds are terpenoid biomarkers (steranes and hopanes), and the USEPA sixteen polycyclic target compounds. Additional information on source can also be obtained by analysing the alkyl isomers of PAH compounds. Selected ratios can be plotted, or algorithms determined to obtain the degree of weathering, or to correlate to a suspected source. This analysis is useful for determining the content and profile/distribution of a suite of petroleum or PAH targets analytes. The results of this data can be used in: -

- Generating a suite of diagnostic ratios based upon selected PAHs which can be used to estimate the degree of weathering and source identifications.
- Generating a suite of calculated diagnostic ratios for selected biomarkers for source identification.
- Establishing a weathering check from a suite of selected PAH groups.

As the main classes of compounds usually identified as contaminants can be derived from both petrogenic and pyrogenic sources, the distribution and abundances of compounds can differ and these differences can be used to identify the source (Dahle *et al.*, 2003).

3.4 Level 3 Statistical Analysis of the Data

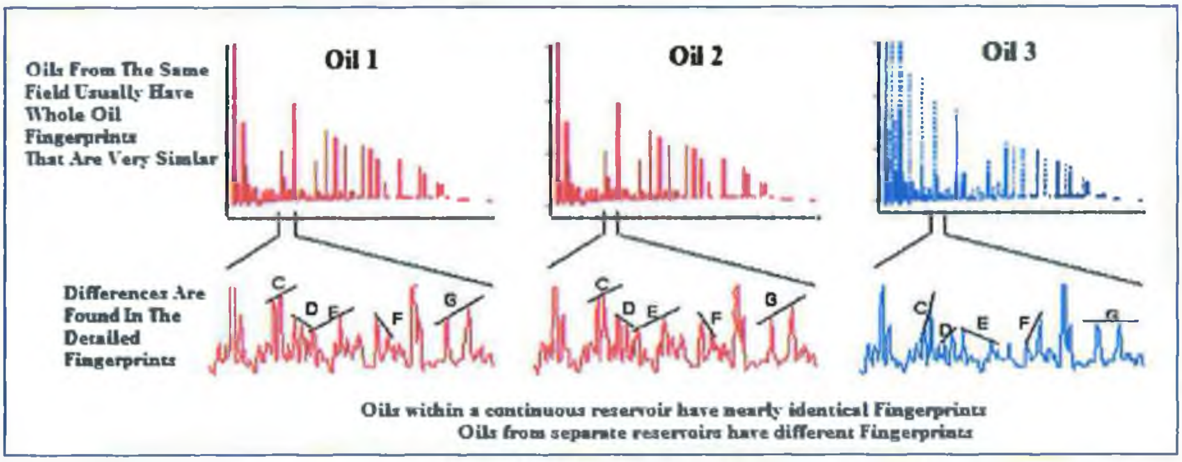
Having conducted Level 1 and 2 investigations, data obtained from both these procedures can be utilised in various mathematical routines to determine the degree of similarity to reference materials, degrees of weathering and / or biodegradation. Evaluation of those diagnostic ratios exhibiting considerable variability due to analytical variance and sample heterogeneity is determined using Compound Ratio Analysis Technique (CORAT). Further weathering check and biodegradation check are conducted in this level. The following categories are used to represent degrees of differences between sample S-1 and the reference oils;

- **Positive match** the chromatographic patterns of the sample S-1 are virtually identical with those of the source and the only observed differences are attributable to acceptable analytical variance and/or weathering.
- **Probable match** the chromatographic patterns of the sample S-1 is similar to that of the reference samples submitted for comparison, except obvious changes which could be attributed to weathering (e.g. loss of lower-molecular-weight peaks), or differences attributable to specific contamination.
- **Inconclusive** the chromatographic patterns of the sample S-1 is somewhat similar to that of the sample submitted for comparison, except for certain differences that are of such magnitude that it is impossible to ascertain whether the unknown is the same oil, heavily weathered or a totally different oil. These differences may be due to heterogeneities of the oil quality either within the spill or within the suspected source that is not reflected in the available samples analysed.
- **Non-match** unlike the sample S-1 submitted for comparison.

3.5 Compound Ratio Analysis Technique (CORAT)

In modern forensic investigations, various analysis techniques have been developed and applied to data interpretation. The application of sophisticated statistical analysis techniques for analysis is a relatively new phenomenon of which compound ratio plotting is one such approach. This is a dynamic area of research which enhances the interpretive power of hydrocarbon fingerprinting and promises to greatly improve the identification of spill sources. Compound Ratio Analysis Technique (CORAT) is a combination of analytical and interpretive techniques that utilises "fingerprint" chromatograms of crude oil samples used in the petroleum geochemistry industry. This technique is also called "Reservoir Oil Fingerprinting" (ROF) and was originally developed by scientists at Chevron in the USA for crude oil comparisons. This technique has been adapted in this study to compare the compositional variations of source specific PAH markers in a number of reference products with those of the contaminated soil sample in an effort to determine whether the contaminant is of petrogenic or pyrogenic origin. Since a GC fingerprint is a representation of the relative concentrations of compounds present in a sample it can be used to measure the relative abundances of each compound. The results can then be plotted on a star plot diagram. In the example (Figure 3.2) oils 1-3 all have a very similar chemical fingerprints and are known to come from the same source rock. However, it can be observed that oils 1 and 2 have nearly identical distributions of the minor hydrocarbons which elute between the major *n*-alkane peaks in the example, whereas oil 3 has quite a different distribution. This can be observed by referring to ratio "F" which is reversed in oil 3 compared to oils 1 and 2. This technique assesses whether or not two or more products correlate by comparing the relative abundance of selected compounds obtained from the chemical fingerprint and rationing them to each other. Values for these ratios for each sample product are plotted on a polar CORAT star plot. On such diagrams the composition of each product is represented by a star in which each point on the star corresponds to the value for a given peak ratio (Kaufman *et al.*, 1990).

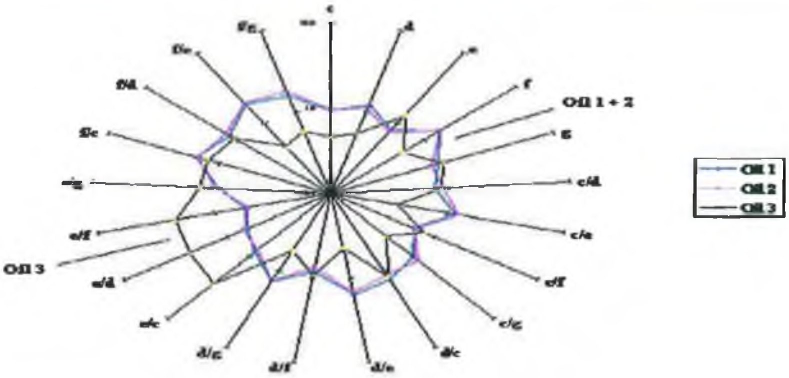
Figure 3.2 Example of Oil 1 to 3



Source: Kaufman *et al.,* 1990

A CORAT star plot of various peak ratios illustrates that oils 1 and 2 are nearly identical, whereas that of oil 3 is quite different (Figure 3.3). The formula used to determine the ratio for the pair (naphthalene/methyl naphthalene) used in the CORAT star plots is presented in Figure 3.4. The differences observed in CORAT fingerprints are usually related to source differences rather than differences due to weathering or biodegradation. This results in variations in the star diagrams. CORAT "Star" diagrams are a simple way to illustrate differences in GC fingerprints, particularly selected peak ratios used to distinguish possible sources. CORAT star plots maximise the apparent differences between samples by stripping away what samples have in common and focusing on how they differ. These plots allow discrete groups of samples to be readily visually identified. Logarithmic star plots are generated for ease of interpretation.

Figure 3.3 CORAT Star Plot of the Ratios of the Three Oils



Note: CORAT star plot of selected peak ratios from GC analysis of oil samples. Oils 1 and 2 are similar and likely in the same reservoir compartment, whereas oil 3 is in a different compartment.

Source: Kaufman *et al.*, 1990

Figure 3.4 Naphthalene (C0-N) Ratios to Methylnaphthalene (C1-N)

$$\text{Ratio } (C_0\text{-N}/C_1\text{-N}) = \frac{\text{Normalised Percentage of } C_0\text{-Naphthalene in S-1}}{\text{Normalised Percentage of } C_1\text{-Naphthalene in S-1}}$$

Naphthalene to Methylnaphthalene Ratio = 40.0 / 25 = 1.6

3.6 Level 1 - Investigation Chemical Fingerprinting by GC-FID Characterising the Sample by Obtaining the Overall Boiling (Carbon) Range of the Contaminants

Analysis of the headspace gas of the sample S-1 by GC/FID indicated the presence of BTEX complex. In addition other alkylated benzene isomers along with naphthalene were prevalent (Figure 3.5 and Table 3.1). The presence of BTEX compounds can be indicative of either a petroleum or coal tar source. However, the presence of high concentrations of indene and naphthalene suggest the latter. Although naphthalene is present in gasoline its abundance is very low (<0.1%). The naphthalene content in sample S-1 was >30%. This high level of naphthalene is more indicative of a coal tar source. In addition, other substituted benzenes usually associated with gasoline were found to be absent (Lundstedt, 2003). Furthermore MTBE, an oxygenate additive in gasoline was not present suggesting if the product was gasoline it was not of recent origin (Gallagher *et al.*, 2001).

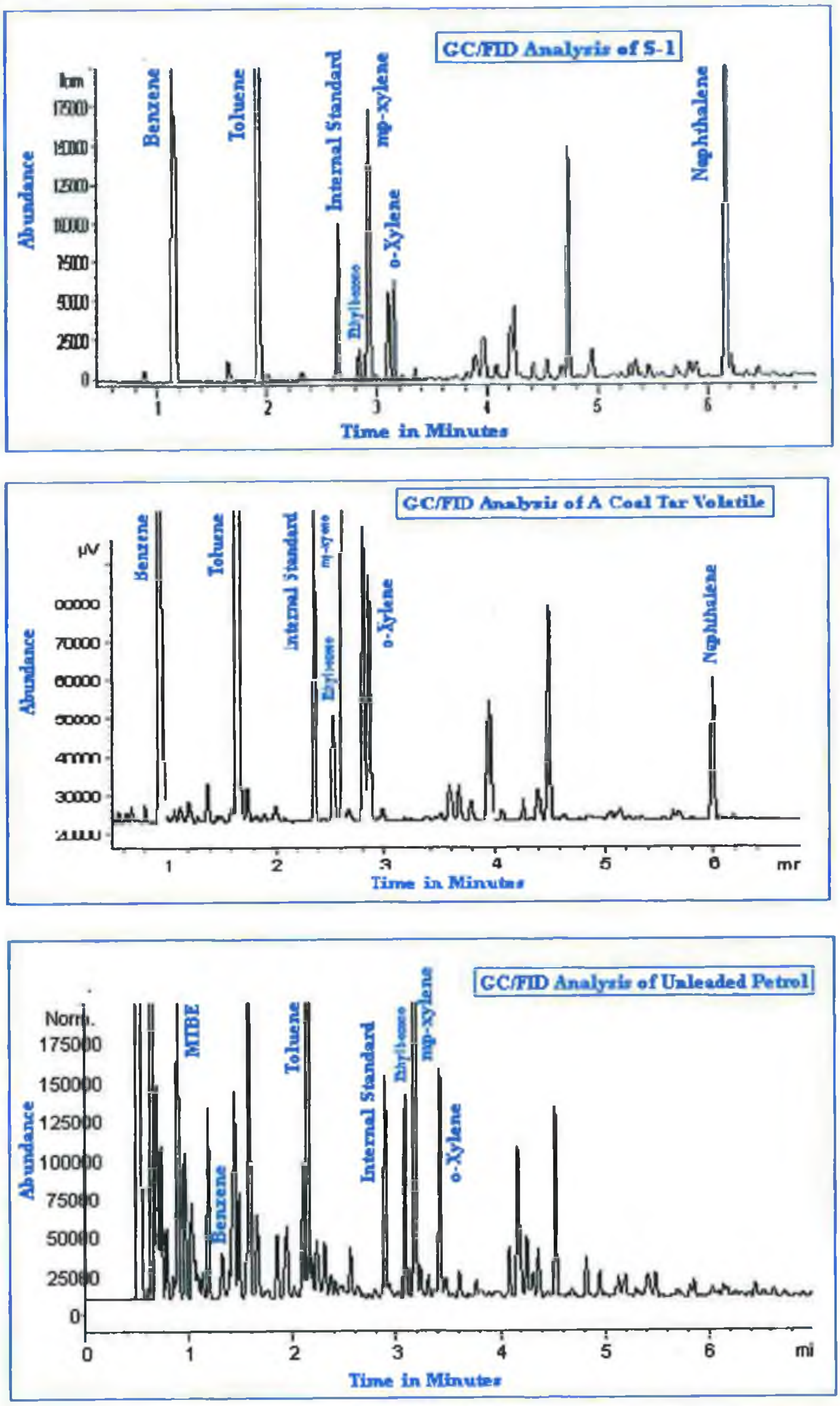
3.6.1 Comparing Distribution Patterns/Profiles

In order to confirm the product type, reference samples of unleaded gasoline and a gas works coal tar volatile (Benzole) were analysed in a similar manner to S-1. The chemical fingerprint produced from the unleaded gasoline was dominated by toluene, the presence of naphthalene was minimal at <0.1% of the total as expected while the coal tar volatile showed high levels of benzene, toluene and xylene with a significant amount of naphthalene. A comparison of these two products with sample S-1 indicated that the latter gave a more probable match with the coal tar volatile, (Table 3.1). This was emphasised by the presence of significant amounts of naphthalene.

Table 3.1 VH Including BTEX by GC-FID

Determinant	Sample S-1	Gasoline	Coal Tar
Benzene	51,056 µg/kg	6,543 µg/kg	155,626 µg/kg
Toluene	31,505 µg/kg	74,602 µg/kg	135,931 µg/kg
Ethylbenzene	2,043 µg/kg	16,942 µg/kg	6,533 µg/kg
m/p-Xylene	23,129 µg/kg	52,297 µg/kg	47,162 µg/kg
o-Xylene	6,129 µg/kg	22,591 µg/kg	17,378 µg/kg
Naphthalene	51,865 µg/kg	<10 µg/kg	8,710 µg/kg
n-C_{10} to n-C_{12}	98,006 µg/kg	46,141 µg/kg	83,405 µg/kg

Figure 3.5 VH and BTEX Analysis of S-1



The presence of a complete suite of the volatile BTEX compounds and naphthalene indicates that weathering has been minimal. The low level of naphthalene in S-1 could be ascribed to weathering. However, for such low levels of naphthalene to occur the degree of weathering would have to be at least 90%; the presence of BTEX at the levels found discounts this view (Jones, 2004). Provisional indications are that the most probable source of this hydrocarbon is coal tar volatiles such as creosote from the distillates having boiling points in excess of 200°C, fractions distilling below 200°C contain BTEX compounds together with phenol. Creosotes can also be made from wood tar but this type of creosote has a low boiling point and consists of phenol and cresols.

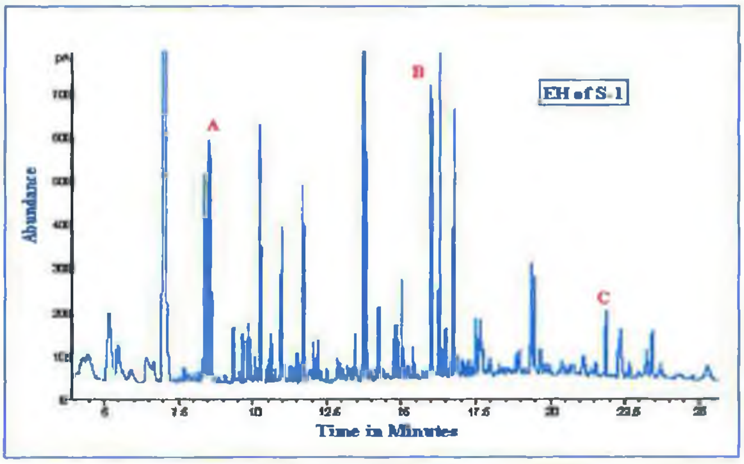
3.6.2 Analysis of Extractable Hydrocarbons (EH)

A known weight of soil sample S-1 was extracted with hexane / acetone. During this process two surrogate compounds namely 1-chlorooctadecane (B) and squalane (C) were added to monitor extraction efficiency. An internal standard heptamethylnonane (A) was added prior to injection to quantify the hydrocarbons detected.

3.6.2.1 Characterising Overall Boiling (Carbon) Range of the Contaminants

The extract was analysed by GC using a suitable non-polar column (Fused silica capillary column 30m x 0.25mm x 0.25μm film RTX-MS), which elutes compounds in order of boiling point. The subsequent chemical fingerprint indicated the presence of possible PAHs, (Figure 3.6).

Figure 3.6 EH n-C_{10} to n-C_{40} by GC-FID Chromatogram



3.6.2.2 Comparing Distribution Patterns/Profiles

The peaks between 5 minutes and the internal standard A were broad and were likely to be phenolic. The major constituent was identified as naphthalene together with other PAHs such as phenanthrene, anthracene, fluoroanthene and pyrene. These were identified by a comparison of retention times obtained from the analysis of a standard made up of the 16 USEPA target compounds (Table 3.2 and Figure 3.7). The identification of these PAHs was later confirmed by GC-MS. The profile was consistent with that of a coal tar contaminant.

Figure 3.7 PAH n-C_{10} to n-C_{40} by GC-FID Chromatogram

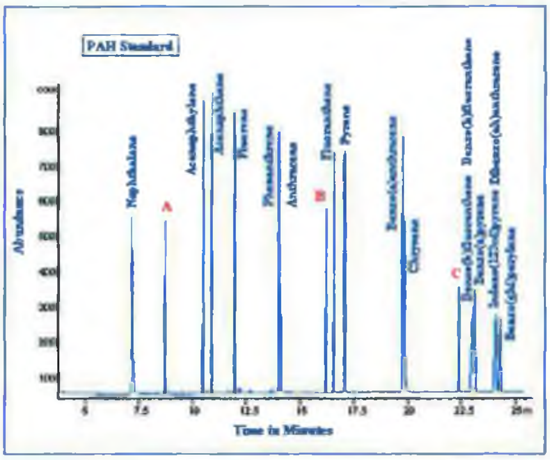


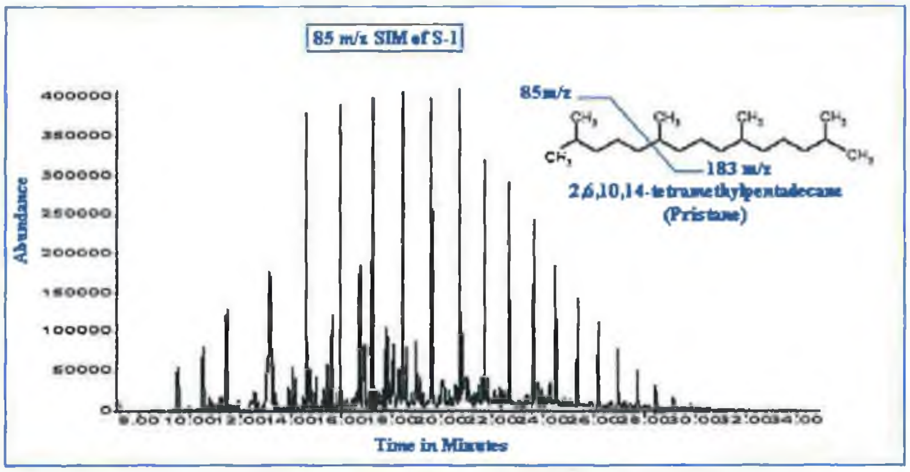
Table 3.2 PAH Retention Time Comparison for Standard and S-1

Compound	PAH Standard RT	S-1 RT
Naphthalene (N)	7.0 min	7.0 min
Internal A	**9.0 min**	**8.5 min**
Acenaphthalene (Acl)	10.5 min	10.5 min
Acenaphthene (Ace)	11.0 min	11.0 min
Fluorene (F)	12.0 min	12.0 min
Phenanthrene (P)	14.0 min	14.0 min
Anthracene (An)	14.0 min	14.0 min
Internal B	**16.0** min	**16.0 min**
Fluoranthene (Fl)	16.5 min	16.5 min
Pyrene (Py)	17.0 min	17.0 min
Benz(a)anthracene (BaA)	19.5 min	19.5 min
Chrysene (C)	20.0 min	19.5 min
Internal C	**22.5** min	**22.0 min**
Benzo(B)fluoranthene (BbF)	23.0 min	23.0 min
Benzo(k)fluoranthene (BkF)	23.0 min	23.0 min
Benzo(a)pyrene (BaP)	23.5 min	23.5 min
Indeno(123cd)pyrene (IP)	24.0 min	-
Dibenzo(ah)anthracene (DA)	24.0 min	-
Benzo(ghi)perylene (BP)	24.5 min	-

3.6.2.3 Establishing Selected Acyclic Isoprenoid Indices / Ratios

The fingerprint indicated that there was little evidence of refined petroleum products due to the lack of an unresolved complex mixture (UCM) and an even distribution of n-alkanes. In order to confirm this, the GC-MS extract previously used for confirmation of PAHs was scanned using ion 85 m/z which are the most abundant target ion for *n*-alkanes. The resulting fragment ion chromatogram (Figure 3.8) indicated the presence of an underlying homologous series of *n*-alkanes in the range *n*-C_{10} to *n*-C_{30}. This is possibly indicative of a diesel type fuel oil, and is further confirmed by the presence of the pristane and phytane branched n-alkanes which are source specific biomarkers present in diesel fuel oils.

Figure 3.8 Fragmentagram Using 85 *m/z* SIM of S-1

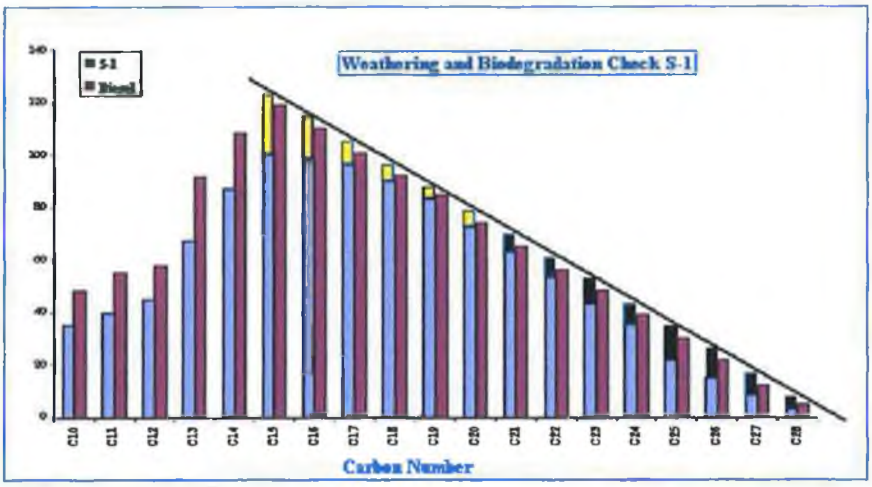


3.6.2.4 Establishing a Weathering/Biodegradation Check

3.6.2.4.1 Weathering Check

The data obtained from the fragment ion chromatogram associated with ion 85 *m/z* was used to estimate the degree of weathering of the sample S-1. This was determined by comparing the reference product sample diesel to the soil sample S-1 (Figure 3.9). All peak areas were normalised to *n*-C_{15}. The data was plotted on a histogram which showed a classic distribution pattern associated with the diesel, which manifests as a 90° triangle. In contrast the histogram associated with the soil sample indicates only minor losses due to weathering. The degree of weathering can be estimated as being less than 12%. This is estimated on the basis of the expected profile for a non-weathered or biodegraded reference diesel product. This is depicted by the extrapolation area Figure 3.9 coloured in yellow.

Figure 3.9 "Weathering Check" of S-1 versus a Suspected Non-Weathered Source Diesel by Comparing Peak Areas Normalised Relative to n-C_{15}



In the case of sample S-1, there is only minor evidence of depletion of the lighter carbon ranges. The profile associated with the histogram (Figure 3.9) indicates minor losses of the n-alkanes (n-C_{20+}), as indicating by the extrapolated area Figure 3.9 coloured in black. This indicates that the weathering process in S-1 was subjected to be both evaporation and biodegradation but overall, the weathering was minimal.

The source specific markers typically used in age analysis are the recalcitrant isoprenoid compounds, of which the two most abundant are pristane and phytane. These almost bioresistant compounds are present in diesels and can be used to tentatively age the product. The degree of change in diesel oil within the subsurface environment may be measured by comparing ratios of compounds with different physical, chemical or biological properties. It has been indicted above that the n-alkanes are readily biodegraded and the pristane and phytane are recalcitrant, and therefore ratios of these compounds can be used. The most common ratios are n-C_{17}/pristane, n-C_{18}/phytane and pristane/phytane. Comparison of n-C_{17}/pristane ratios from known oil spills produced a formula indicating a good correlation between the ratio and age of spill (Christensen and Larsen, 1993) (Figure 3.10). This is achieved by measuring the peak height of pristane peak on the chromatogram and the n-C_{17} n-alkane in cm and entering each measurement into the formula.

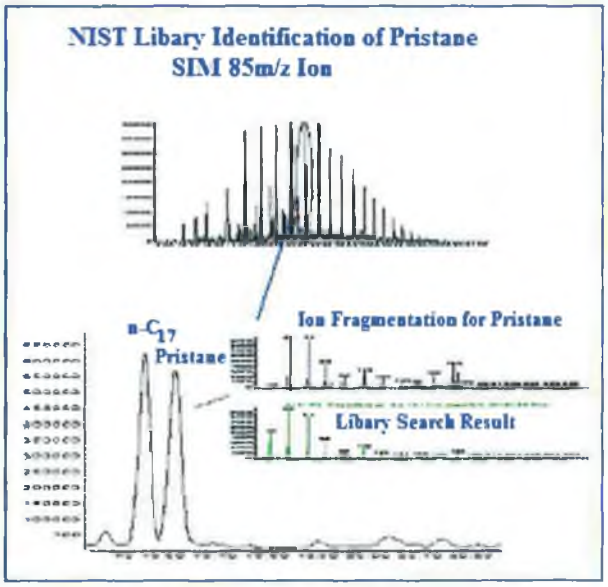
Figure 3.10 *n*-C_{17}/Pristane Ratio Age Formula

$$T\ (\text{Time}) = -8.4\ \frac{n\text{-}C_{17}}{\text{Pristane}} + 19.8$$

Source: Christensen and Larsen, 1993

Using the data obtained from the GC-MS analysis the extracted ions for *n*-C_{17} and pristane were processed, (Figure 3.11) and the ratio of these compounds was determined as being 1.56. The calculation presented indicates a release into the environment which occurred approximately 10 years ago. Applying the same ratios to the diesel standard the *n*-C_{17}/pristane was calculated to be 2.12. This indicated a fresh product. The presence of pristane in both the sample S-1 and the reference diesel sample was confirmed from the mass spectral library search (Figure 3.11).

Figure 3.11 Identification of Pristane



Source: Alcontrol Laboratories Dublin, 2003; NIST Library

The pattern and profile obtained indicates that the main source is pyrogenic and likely to be from a coal tar or creosote source. However, further analysis by GC-MS targeting ions 85*m/z* also indicated the presence of a petrogenic source which is likely to be diesel.

3.7 Level 2 Detailed Analysis by GC-MS

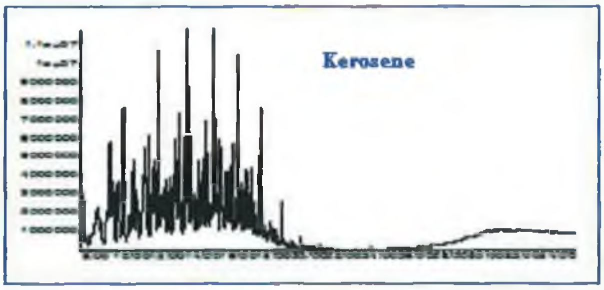
A Level 2 investigation involved the GC-MS targeting of selected compounds which are more resistant to biodegradation; examples of such compounds are terpenoid biomarkers (steranes and hopanes), as in this study, and the USEPA sixteen polycyclic aromatic hydrocarbon target compounds. Additional information on the source can also be obtained by analysing the alkyl isomers. The Level 1 investigation indicated the presence of a petrogenic and pyrogenic contamination. In order to investigate the primary source of these hydrocarbons, a series of reference materials were analysed. The pyrogenic and petrogenic reference products (Table 3.3) were chosen on the basis that they cover a similar carbon number and boiling range and all contain PAHs. The reference was analysed according to methods detailed in Chapter 2. The GC-MS total ion chromatograms (TIC) for each of the reference products are presented in Figure 3.12.

Table 3.3 Petrogenic and Pyrogenic Reference Product Descriptions

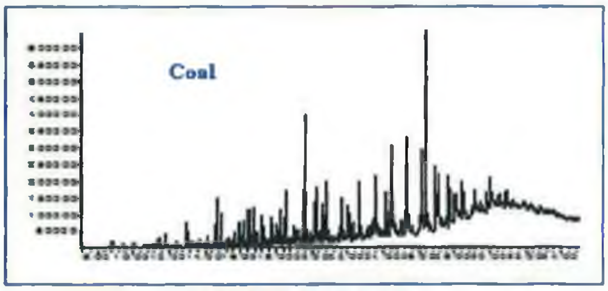
Petrogenic Products	**Description**
Kerosene	Light distillate fuel consisting primarily of *n*-alkanes (n-C$_9$ to n-C$_{16}$). 70% saturated hydrocarbons and 30% aromatics (Exxon Mobil Corp, 2003). Purchased from Esso 2003.
Diesel	Manufactured from residual fractions of crude oil blends with cracked gas oil. Typical carbon range for transportation diesel is n-C$_{10}$ to n-C$_{28}$, saturated hydrocarbons 60 – 90%, aromatics 10 – 40% (Exxon Mobil Corp, 2003). Purchased from Esso 2003.
Lubrication Oil	High molecular weight, high boiling point fractions covering range n-C$_{26}$ to n-C$_{40}$ (Castrol GTX 10W-40). Purchased from Esso 2003.
South American Crude Bitumen (SACB)	Used to identify the presence of sterane and terpane biomarkers (n-C$_{28}$ to n-C$_{40}$). Supplied by Irish Asphalt 2003.
Pyrogenic Products	**Description**
Jayes Fluid	Light creosote containing high naphthalene and phenol isomers (n-C$_9$ to n-C$_{18}$). Purchased from Esso 2003.
Coal	Domestic home heating coal (*Bord na Mona* Coal) (n-C$_{10}$ to n-C$_{40}$). Purchased from Esso 2003.
Road Tar	Fingal County Council on-site road tar (n-C$_{10}$ to n-C$_{40}$) 2003.

Figure 3.12 GC-MS TIC for the Reference Products and Sample S-1

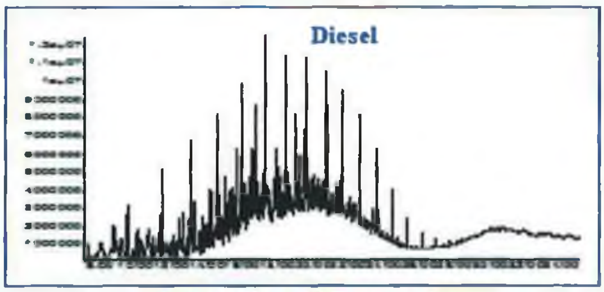
Kerosene Petrogenic



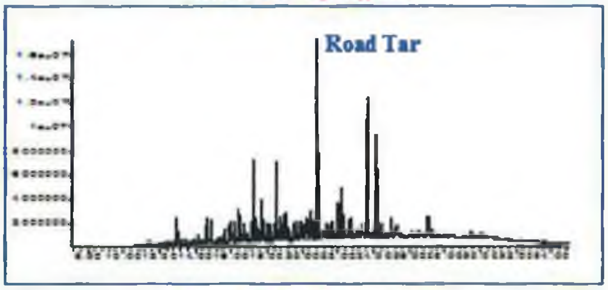
Coal Pyrogenic



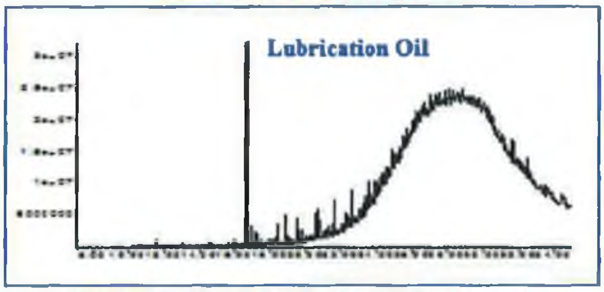
Diesel Petrogenic



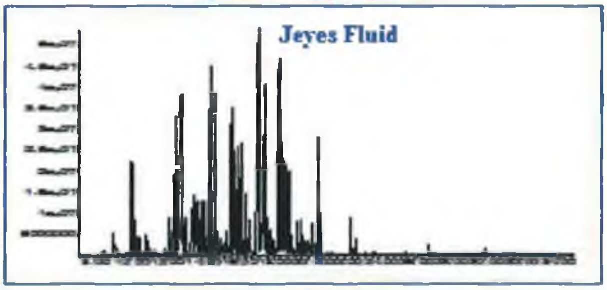
Road Tar Pyrogenic



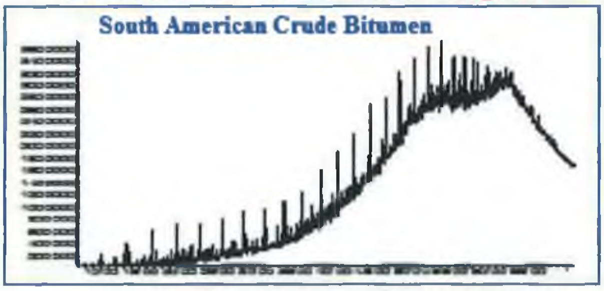
Lubrication Oil Petrogenic



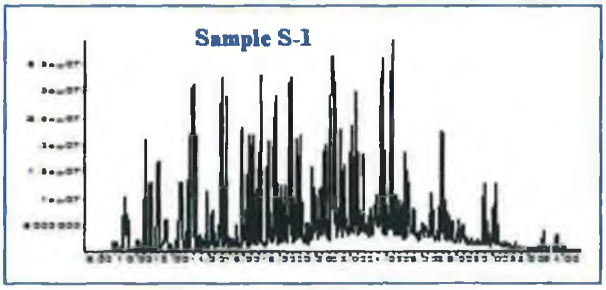
Jeyes Fluid Pyrogenic



South American Crude Bitumen Petrogenic



Sample S-1



3.7.1 Degree of Weathering Estimates and Source Identifications of Selected PAH Compounds

The reference products (kerosene, diesel, lubrication oil, South American crude bitumen, coal, road tar and Jeyes fluid) were dissolved in acetone / hexane and these together with the extract obtained from sample S-1 were analysed by GC-MS in the selective ion monitoring mode. The analysis targeted the USEPA 16 PAHs compounds which are an internationally recognised standard, (Table 3.4). Because of the differences of abundances within the reference materials the data was normalised against the total of the sum of the sixteen targeted compounds.

Table 3.4 Normalised Percentages of PAHs for S-1 and Reference Products

Compound	S-1	Kerosene	Diesel	Lube Oil	Coal	Road Tar	SACB	Jeyes Fluid
Naphthalene (N)	27.09	92.82	28.60	7.94	7.94	4.26	2.42	13.97
Acenaphthalene (Acl)	7.96	1.02	1.14	1.21	0.13	0.11	0.24	0.76
Acenaphthene (Ace)	1.32	3.75	11.20	0.83	0.25	8.51	0.86	48.79
Fluorene (F)	5.51	1.99	18.31	2.09	0.87	7.89	1.95	27.44
Phenanthrene (P)	11.42	0.25	25.03	8.92	11.15	17.65	8.83	5.81
Anthracene (An)	4.74	0.02	3.36	1.00	2.13	11.49	1.04	3.07
Fluoranthene (Fl)	8.57	0.01	1.46	3.22	2.72	13.99	0.86	0.06
Pyrene (Py)	7.04	0.06	10.26	4.56	8.62	11.38	5.04	0.05
Benz(a)anthracene (BaA)	4.15	0.05	0.40	7.91	10.65	6.58	6.58	0.02
Chrysene (C)	3.29	0.01	0.15	5.64	15.67	6.55	35.09	0.01
Benzo(B)fluoranthene (BbF)	5.46	0.00	0.04	12.42	5.68	2.23	7.50	0.01
Benzo(k)fluoranthene (BkF)	2.03	0.00	0.02	14.54	3.74	2.95	4.03	0.00
Benzo(a)pyrene (BaP)	4.60	0.00	0.01	8.87	9.72	3.05	5.71	0.00
Indeno(123cd)pyrene (IP)	3.07	0.01	0.00	8.30	2.94	1.70	3.36	0.00
Dibenzo(ah)anthracene (DA)	0.96	0.00	0.00	4.87	6.08	0.38	5.02	0.00
Benzo(ghi)perylene (BP)	2.80	0.00	0.01	7.68	11.70	1.29	11.47	0.00
Total PAH %	100%	100%	100%	100%	100%	100%	100%	100%

Table 3.4 shows that there is considerable variation in the individual abundance of each compound. These variations will be considered in Level 3. These variations are not restricted to the 16 USEPA PAH compounds. Diagnostic information was obtained by examining the alkyl homologues of the primary PAHs, in addition, sulphur containing compounds such as dibenzothiophene and its alkyl derivatives were used to determine the possible source. All reference products and the sample S-1 were analysed for the compounds detailed in Table 3.5 and are referred to in Level 3.

Table 3.5 Alkylated Homologues PAH Series

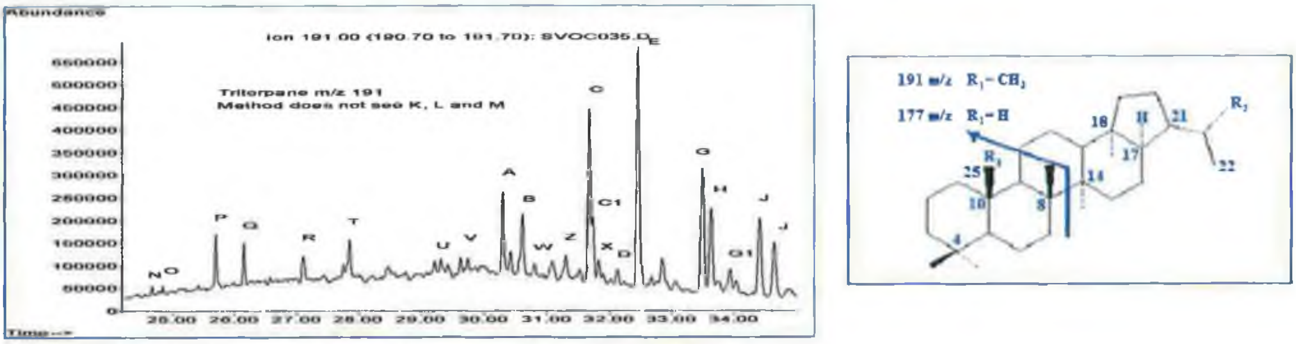
Compound	Code	Ring No	m/z
Naphthalene			
C_0-naphthalene	N	2	128 *m/z*
C_1-methylnaphthalene	N1	2	142 *m/z*
C_2-dimethylnaphthalene	N2	2	156 *m/z*
C_3-trimethylnaphthalene	N3	2	170 *m/z*
C_4-tetramethylnaphthalene	N4	2	184 *m/z*
Phenanthrene			
C_0-phenanthrene	P	3	178 *m/z*
C_1-methylphenanthrene	P1	3	192 *m/z*
C_2-dimethylphenanthrene	P2	3	206 *m/z*
C_3-trimethylphenanthrene	P3	3	220 *m/z*
C_4-tetramethylphenanthrene	P4	3	234 *m/z*
Dibenzothiophene			
C_0-dibenzothiophene	D	3	184 *m/z*
C_1-methyldibenzothiophene	D1	3	198 *m/z*
C_2-dimethyldibenzothiophene	D2	3	212 *m/z*
C_3-trimethyldibenzothiophene	D3	3	226 *m/z*
Fluorene			
C_0-fluorene	F	3	166 *m/z*
C_1-methylfluorene	F1	3	180 *m/z*
C_2-dimethylfluorene	F2	3	194 *m/z*
C_3-trimethylfluorene	F3	3	208 *m/z*
Chrysene			
C_0-chrysene	C	4	228 *m/z*
C_1-methylchrysene	C1	4	242 *m/z*
C_2-dimethylchrysene	C2	4	256 *m/z*
C_3-trimethylchrysene	C3	4	270 *m/z*
Acenaphthylene	Acl	3	152 *m/z*
Acenaphthene	Ace	3	154 *m/z*
Fluoranthene	Fl	4	202 *m/z*
Pyrene	Py	4	202 *m/z*
Benzo(a)anthracene	BaA	4	228 *m/z*
Benzo(b)fluoranthene	BbF	5	252 *m/z*
Benzo(k)fluoranthene	BkF	5	252 *m/z*
Benzo(a)pyrene	BaP	5	252 *m/z*
Indeno(1,2,3-cd)pyrene	IP	6	276 *m/z*
Dibenz(a,h)anthracene	DA	5	278 *m/z*
Benzo(g,h,i)perylene	BP	6	276 *m/z*
Anthracene	An	3	178 *m/z*

Source: Wang *et al.*, (1994)

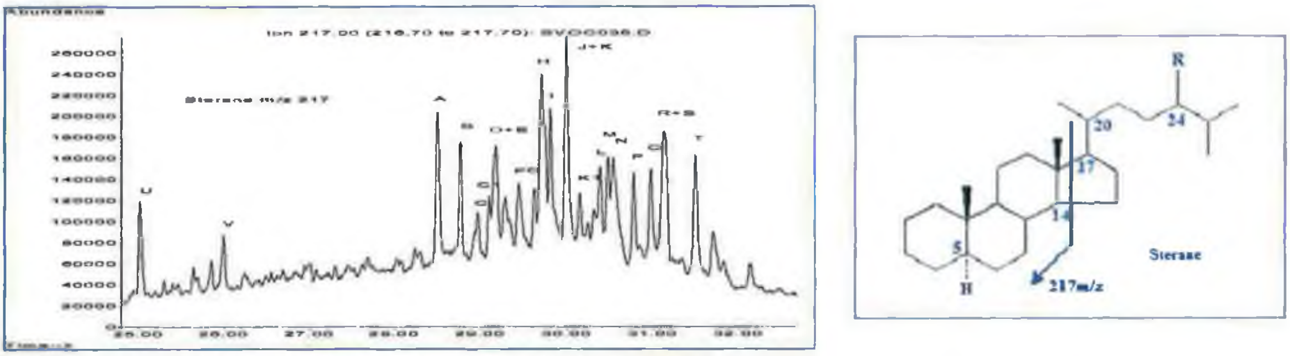
Historically biomarker fingerprinting has been used by petroleum geochemists in the characterisation of marine oils in terms of source rock, genetic family, migration and maturation properties, and in identification of petroleum deposits and more recently to indicate the likely origin of petroleum spills. Chemical analysis of source-characteristic and environmentally persistent biomarkers generates information to determine the source of spilled products, differentiating products, monitoring degradation and weathering under a variety of conditions and of particular interest are the biomarker compounds terpanes and hopanes. The samples were analysed using GC-MS in the selective ion mode monitoring 191m/z and 217m/z which are characteristic ions of terpanes and steranes respectively as shown in Figure 3.13. The data acquired in Figure 3.13 will be used in Level 3.

Figure 3.13 SIM Chromatograms of Terpanes (191m/z) and Sterane (217m/z)

Terpane (Hopane 191m/z)



Sterane (217m/z)



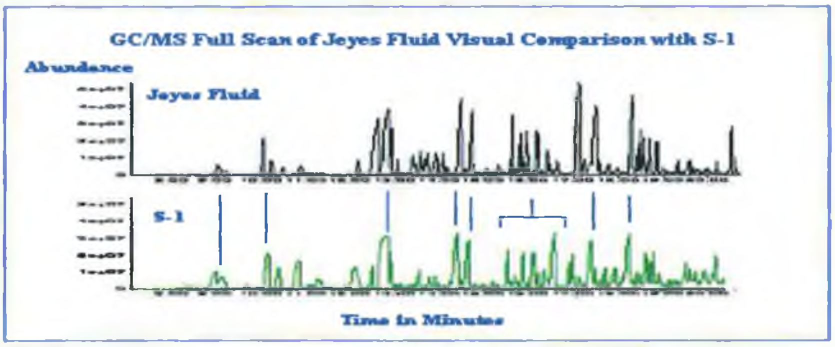
As has already been discussed, weathering is characterised by a decrease in the homologues series of PAH compounds. An examination of naphthalene series showed that S-1 has undergone minimal weathering. This confirms the finding from Level 1 that only minimal weathering has occurred. This will be further examined in Level 3.

3.8 Investigation of Possible Creosote Source

To confirm the presence of a creosote source present in sample S-1, the reference material Jeyes fluid which contains source specific phenol compounds was compared to sample S-1 by GC/MS using targeted m/z ions. The two chromatograms were overlaid and a visual comparison was made.

The chromatogram findings indicated a similar pattern with broad peaks at the start and similar clusters of peaks at a number of retention times in the two chromatograms. Using the SIM mode for naphthalene 128 *m/z*, phenol 94 *m/z*, methylphenol 108 *m/z* and dimethylphenol 122 *m/z* these ions were selected and compared in both the soil sample S-1 and Jeyes fluid chromatogram. The characteristic broad peaks at the start of each chromatogram are typical of phenol and its isomers, see Figure 3.14. The SIM mode showed the presence of all of these components in both the soil sample S-1 and Jeyes fluid. It was concluded that this creosote product contributed to the contamination of the soil sample S-1.

Figure 3.14 GC/MS Full Scan of Jeyes Fluid Visual Comparison with S-1



3.9 Level 3 Investigation Analysis of the Data

Having conducted a Level 1 and Level 2 investigation on the sample S-1, the CORAT routine was applied to the data from Level 2, (Table 3.4). The area responses of the individual PAHs were plotted as a logarithmic star plot, (Figure 3.15). The CORAT star plot was inconclusive in determining a likely source of the PAHs. The individual star plots are shown in Figure 3.16.

Figure 3.15 PAHs Star Plot (Logarithmic)

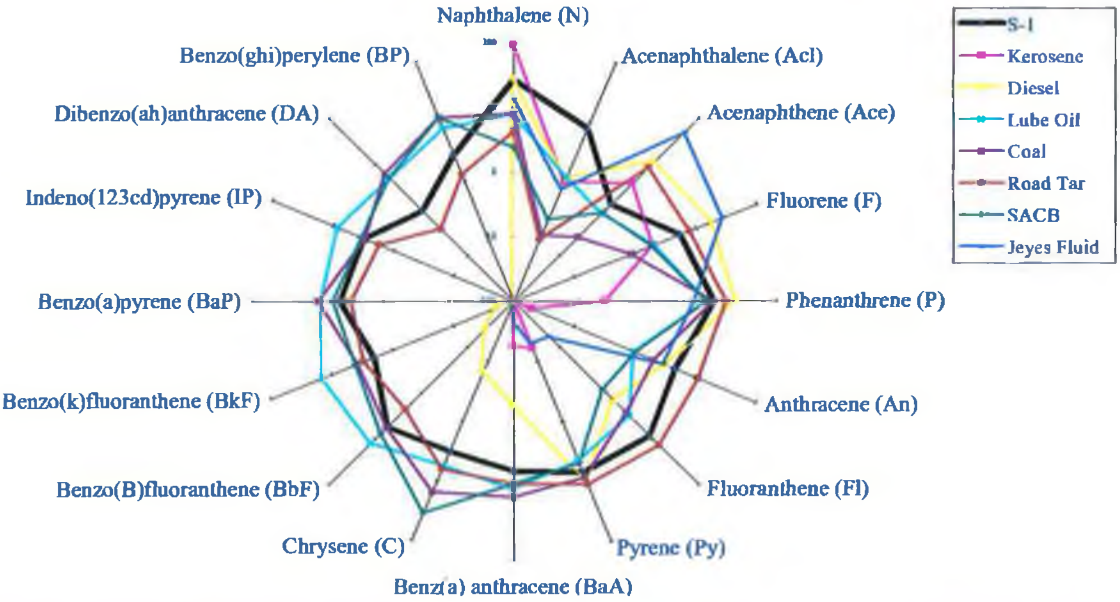
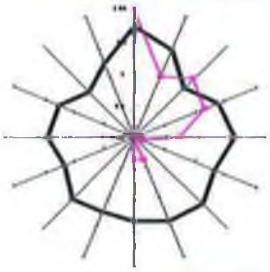
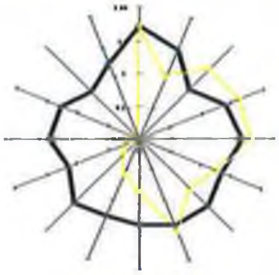


Figure 3.16 Star Plot PAH Distribution Compared to the Sample S-1

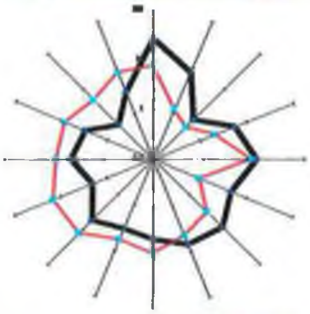
S-1 and Kerosene - Non Match



S-1 and Diesel - Non Match

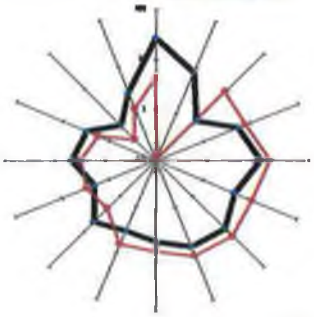


S-1 and Lubricant oil - Probable Match

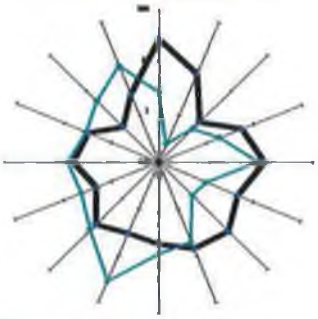


S-1 and Coal - Non Match

S-1 and Road Tar – Probable Match



S-1 and SACB - Non Match



S-1 and Jeyes Fluid - Non Match

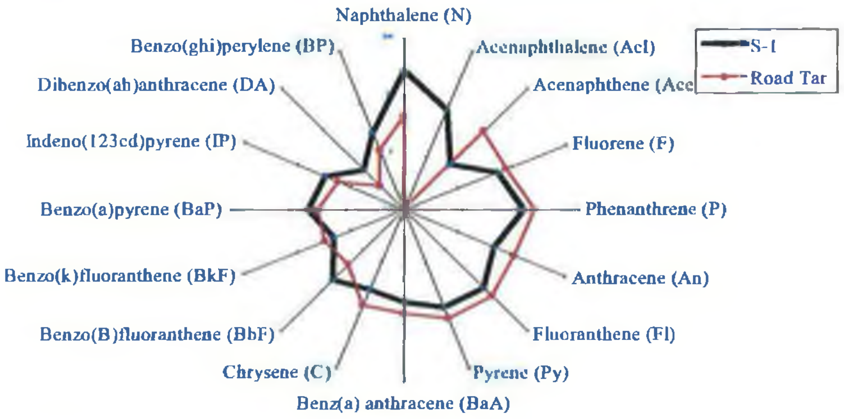
3.9.1 Summary Findings for PAH Analysis

The concentration of the individual PAHs and a number of diagnostic ratios have been successfully used in this study as indicators for spill identification. A benefit of comparing diagnostic ratios of spilled products and suspected source products is that concentration effects are minimised. In addition, the use of diagnostic ratios to correlate and differentiate products tends to induce a self-normalising effect on data since variations due to instrument operating conditions, operators, or matrix effects are minimised. This gives greater validity to the results in this study. Table 3.4, shows the PAH results of a range of reference products normalised (Level 2) to the total PAH value, showing the percentage distribution of individual PAHs. Following a review of the star plots using the categories indicated in the introduction, these conclusions were made.

3.9.2 Conclusion of PAH Comparison of S-1 with Petrogenic / Pyrogenic Sources

The conclusion following the comparison of the distribution of the sixteen priority pollutant PAHs found in the petrogenic reference sources with those found in the sample S-1 using CORAT indicated lubrication oil as a probable match with kerosene, diesel and SACB as non-matches. The findings when compared to the pyrogenic sources indicated Road Tar as a probable match with coal and Jeyes Fluid as non-matches. This level would appear to eliminate Jeyes fluid (suggested in Level 1) and the use of the USEPA 16 PAH results in all reference materials demonstrating a non-match with the exception of road tar, (Figure 3.17).

Figure 3.17 PAHs Star Plot S-1 and Road Tar (Logarithmic)



4.0 PAH Ratios

As previously discussed, the major environmental parameters involved in weathering are evaporation, dissolution, and biodegradation. In general, the order and rate of weathering of the PAHs appears to generally decrease in accordance with the increase of the number of the rings and alkyl groups. PAH compounds with two and three ring compositions are readily degraded, while the four-ring chrysenes are more resistant. Three ring alkylated PAH compounds are used for source identification because their concentrations vary among products, making them source specific (Page *et al.*, 1995). However, it has been shown that the resistance to biodegradation of each individual alkyl PAH is different (Wang and Fingas, 1995). In this study, PAH ratios are made of reference source products and compared to the test sample S-1. Numerous quantitative diagnostic ratios have been defined (Table 3.6). The Mobile Burn study found that the pyrogenic index (Equation 1) can be positively used to differentiate the pyrogenic and petrogenic PAHs (Wang *et al.*, 1999).

Equation 1 Pyrogenic Index (PI)

$$PI = \frac{\Sigma(\text{3 to 6 ring PAHs})}{\Sigma(\text{5 alkylated PAHs})}$$

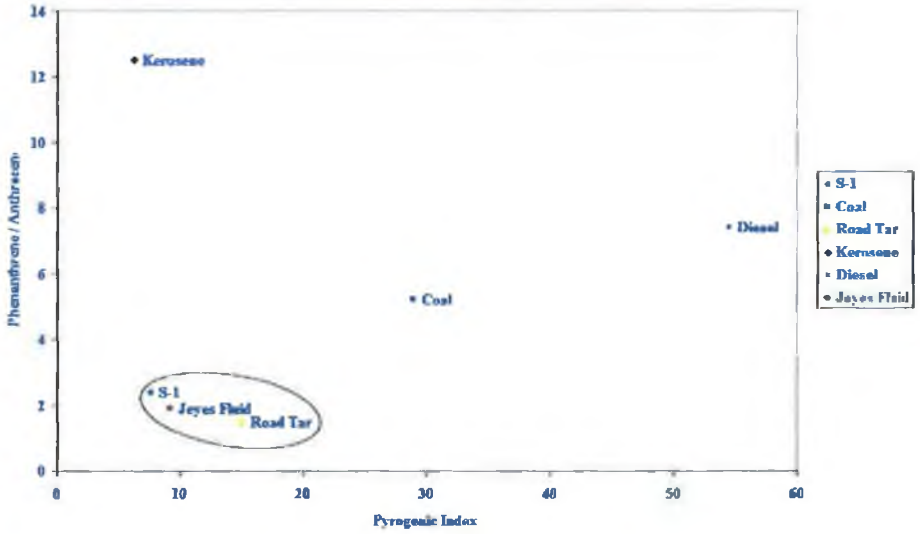
Note: Concentration or peak area can be used in this equation. Three to six ring PAHs include; phenanthrene, chrysene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and dibenzo(a,h)anthracene. The five alkylated PAHs include the homologues series of naphthalene, phenanthrene, dibenzothiophene, chrysene and fluorene.

Table 3.6 shows the PAH ratios applied to the reference products in this study and to the field sample S-1. Figure 3.18 demonstrates the signature of the different reference products compared to the sample S-1.

Table 3.6 Forensic PAH Ratios

Ratio	S-1	Kerosene	Diesel	Lube Oil	Coal	Road Tar	SACB	Jeyes Fluid
Phenanthrene / Anthracene	2.4	12.5	7.4	8.9	5.2	1.5	8.5	1.9
Phenanthrene / Methylphenanthrene	13.6	-	78.2	-	53.1	27.6	441.5	363.6
Fluoranthene / Pyrene	1.2	0.2	0.1	0.7	0.3	1.2	0.2	573.2
Benz(a)anthracene / Chrysene	1.3	5.0	2.7	1.4	0.7	1.0	0.2	1.5
Phenanthrene / (Phenanthrene + Anthracene)	0.7	0.9	0.9	0.9	0.8	0.6	0.9	0.7
Indeno(123cd)pyrene/(Indeno(123cd)pyrene+Benzo(ghi)perylene)	0.5	-	-	0.5	0.2	0.6	0.2	0.4
∑(other 3-6 ring PAH) / ∑(5 alkylated PAH)	7.6	6.2	54.5	9206	29	15.0	143.5	9.2
Naphthalene / Chrysene	8.2	-	191	1.4	0.5	0.6	0.1	-
Phenanthrene / Chrysene	3.5	-	167	1.6	0.7	2.7	0.3	-
Dibenzothiophene / Chrysene	0.1	-	-	-	0.004	0.03	-	-
Fluorene / Chrysene	1.7	-	122	0.4	0.06	1.2	0.1	-
4-:2-methyldibenzothiophene / 3-:1 m-Dibenzothiophene	1.0	-	-	-	1.3	1.3	-	-
(3-+2-methylphenanthrene) / (9-+1-methylphenanthrene)	1.7	-	15.0	-	2.0	1.4	-	1.8
C_2 – Dibenthiophene / C_2-Phenanthrene	0.4	-	-	-	0.3	0.3	-	-
C_3 - Dibenzothiophene / C_3-Phenanthrene	0.7	-	-	-	0.2	0.4	-	-
C_3 - Dibenzothiophene / C_3–Chrysene	3.7	-	-	-	0.2	5.0	-	-

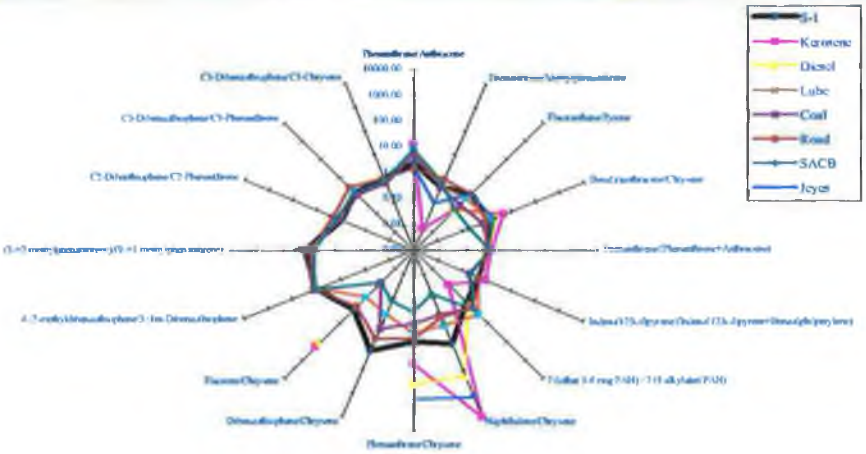
Figure 3.18 PAHs Double Ratio Pyrogenic Index Plot



Source: Wang *et al*, 1999

Some PAH compounds used in the CORAT ratio plots (Figure 3.19) may not be present in the product, therefore they were omitted from the calculations. Their absence suggest that the reference product kerosene and SACB may not be contributors to the contamination of the soil sample S-1.

Figure 3.19 PAH CORAT Ratio Plots (Logarithmic)

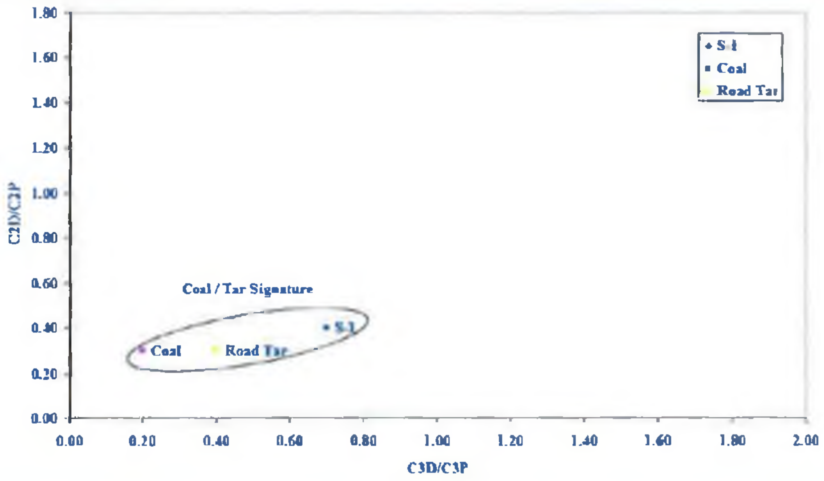


A range of diagnostic ratios used in the literature was applied to the reference products and the sample S-1 to determine the possible matches.

4.1 Dibenzothiophene, Chrysene and Phenanthrene Ratios

The ratio plots of C_2-Dibenzothiophenes / C_2-Phenanthrenes and C_3-Dibenzothiophenes / C_3-Phenanthrenes, can be used for identification and differentiation of sources. This has been developed and extensively used in the studies of the 1989 Exxon Valdez Oil Spill (Brown and Boehm, 1993). Furthermore, Douglas *et al.*, 1996, have defined the C_3D/C_3P and C_3D/C_3C as "source ratios (the ratios that are almost constant because the compounds degraded at the same rate)" and "weathering ratios (the ratios that change substantially with weathering and biodegradation)" respectively. Figure 3.20 illustrates a coal tar signature.

Figure 3.20 PAH Double Ratio Plots C_2D/C_2P and C_3D/C_3P



Source: Wang *et al.*, 1999

4.2 Ratio Plots for Methylphenanthrenes

The relative distribution of the phenanthrene isomers are subject to little interference from weathering in short-term or lightly weathered products. Hence this approach can be positively used for spill identification. On the other hand, it has been demonstrated that the position of the alkylation on the PAHs can influence the biodegradation rate of the isomers within an isomer group (Wang *et al.*, 1995). This information can be used to identify environmental factors, such as, the impact of biodegradation on PAH distribution and to differentiate product compositional changes due to physical weathering from those due to biodegradation. The use of the sum of the alkylated PAHs as multi-component analytes in deriving diagnostic ratios for oil characterisation and spill assessment have made considerable advances. Research can use individual source-specific isomers within the same alkylation level to determine the relative isomer-to-isomer distribution for source identification of spilled product.

4.3 Ratio Plots Methyldibenzothiophenes (m-DBT)

The chromatographically well-separated four isomers of methyldibenzothiophene (4-m-DBT, 2-m-DBT, 3-m-DBT and 1-m-DBT) are present in most products at a relatively high concentrations but their relative abundance to each other can vary significantly in different sources (Wang and Fingas, 1995). The differences between the isomers reflect the physical environmental conditions during formation of different crude oils. Wang *et al.*,(1995), developed a GC-MS method to evaluate the differentiation and source identification characteristics of different crude oils, which may have undergone some degree of weathered and biodegraded, using the relative abundances of the four isomers C_1-DBT (Equation 2).

Equation 2 C_1-Dibenzothiophene Source Ratio

$$C_1\text{-DBT} \quad \frac{4\text{-m-DBT} + 2\text{-m-DBT}}{3\text{-m-DBT} + 1\text{-m-DBT}}$$

The relative distribution of these isomers have been reviewed in this study and compared to the reference products and it was found to indicate coal and road tar as probable matches to the sample S-1.

4.4 Chrysene Ratios

Enhancement of the chrysenes relative to other PAH series along with significant decrease in the relative ratios of the sum of naphthalenes, phenanthrenes, dibenzothiophenes, and fluorene to chrysene can be indicative of a pyrogenic source (Wang *et al.*, 1997). The distribution observed in the soil sample S-1 was very similar to that of road tar with the exception of the naphthalene / chrysene ratio.

4.5 Ratio Plots Phenanthrene / Anthracene and Fluoranthene / Pryene

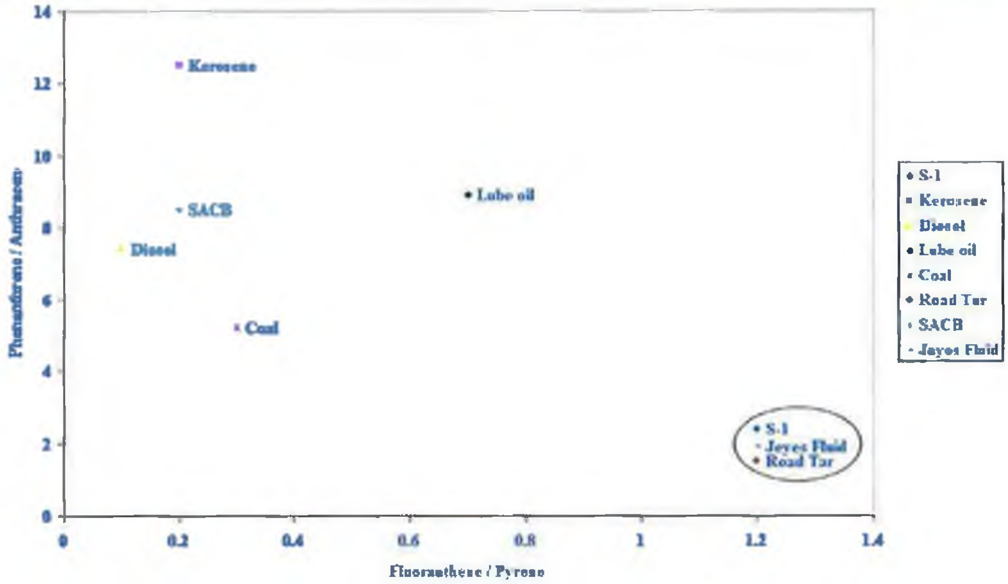
In the soil sample S-1, the PAH distribution tends to lean towards the four to six ring PAHs. The signature ratios of phenanthrene / anthracene and fluoranthene / pyrene were found to be similar to both road tar and Jeyes Fluid (Figure 3.21). To identify a combustion process the ratio of phenanthrene / anthracene and fluoranthene / pyrene can be used where the ratios fall between <10 and >1 has successfully been used to indicate combustion (Benlahcen *et al.*, 1997). The results presented in Table 3.7 also demonstrated that the sample S-1 has undergone combustion similar to road tar and Jeyes fluid.

Table 3.7 Combustion Ratio

Ratio	S-1	Kerosene	Diesel	Lube oil	Coal	Road Tar	SACB	Jeyes Fluid
Phenanthrene / Anthracene	**2.4**	12.5	7.4	8.9	5.2	**1.5**	8.5	**1.9**
Fluoranthene / Pyrene	**1.2**	0.2	0.1	0.7	0.3	**1.2**	0.2	**1.2**

Source: Benlahcen *et al.*, 1997

Figure 3.21 Double Ratio Plots Fluoranthene / Pyrene vs Phenanthrene / Anthracene

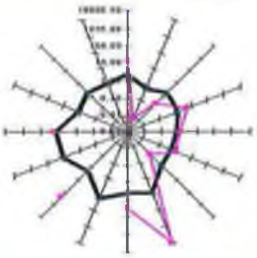


Source: Wang *et al.*, 1999

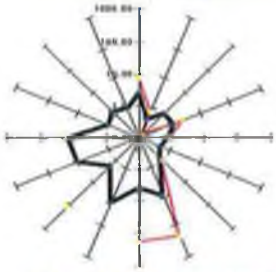
All of the ratios discussed were presented in CORAT plots (Figure 3.22).

Figure 3.22 PAH CORAT Ratio Plots

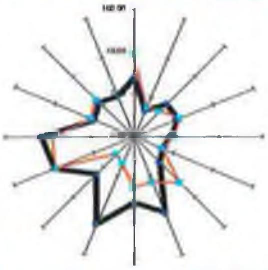
S-1 and Kerosene - Non Match



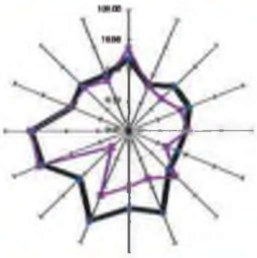
S-1 and Diesel - Non Match



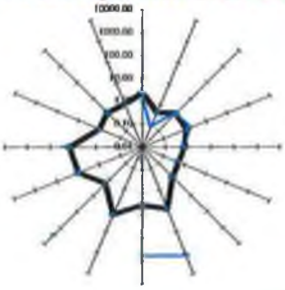
S-1 and Lubricant Oil - Non Match



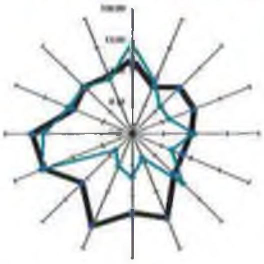
S-1 and Coal - Non Match



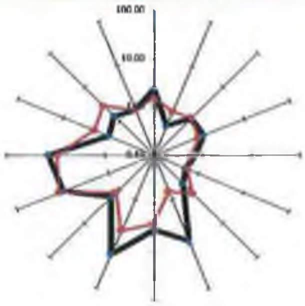
S-1 and Jeyes Fluid – Non Match



S-1 and SACB - Non Match



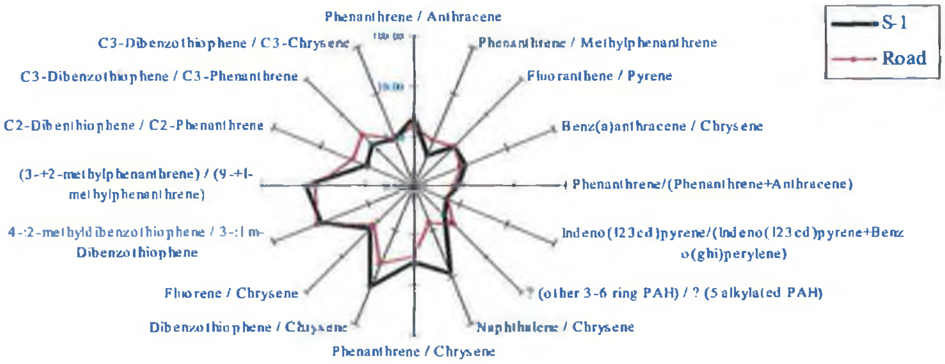
S-1 and Road Tar Probable - Probable Match



4.6 Summary Findings for PAH Ratio Analysis

The dominance of the unsubstituted naphthalene, phenanthrene, and dibenzothiophene over their alkylated homologues was observed and is characteristic of a pyrogenic source signature (Costa and Sauer, 2005). It can be concluded from the individual product comparisons with the soil sample S-1 that similarities are apparent between the pyrogenic sources and the best fit CORAT star plot (Figure 3.23) would indicate road tar. All the double ratio plots further indicated a pyrogenic signature similar to the findings of CORAT.

Figure 3.23 PAH Ratios CORAT S-1 and Road Tar (Logarithmic)



4.7 Comparison of Ratios for Naphthalene, Phenanthrene, Dibenzothiophene, Fluorene and Chrysene in S-1 to the Reference Products

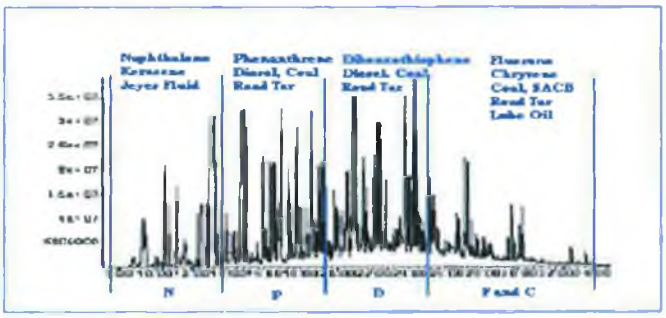
In general qualitative chemical analysis and visual comparison of chromatograms of a contaminated soil sample by GC/FID or GC/MS determined in Levels 1 and Level 2 with suspected candidate source may sufficiently meet the needs of most forensic investigation. However, when the chemical similarity/difference between a spilled product and the suspected source is not obvious, due to;

- large number of sources involved,
- the spilled product has undergone a degree of weathering,
- significant alteration in its chemical composition,

A quantitative approach can be difficult, and therefore the qualitative analysis of the recalcitrant degradation-resistant PAH compounds should then be performed.

In addition to the determination of conventional diagnostic PAH ratios, a number of "source-specific" isomeric PAHs within the same alkylation levels were quantified, and their relative abundance ratios were computed in order to identify and differentiate the sources. The CORAT star plot data interpretation technique discussed in this study includes the recognition of distribution patterns of the five target polycyclic aromatic hydrocarbons (alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene). The soil sample S-1 GC/MS chromatogram (Figure 3.24) was divided into sections (N, P, D, F and C) where source specific marker components of the reference products were reviewed using the CORAT star plot diagrams. Using selected ion monitoring (SIM) each alkylated homologous series C_0 - parent compound, C_1 - methyl isomers, C_2 - dimethyl isomers, C_3 - trimethyl isomers and C_4 - tetramethyl isomers, were determined from the chromatograms of the soil sample S-1 and the reference products.

Figure 3.24 Division of Sample S-1



4.7.1 Section N of the GC/MS Chromatogram - Naphthalene Homologues Analysis

Using SIM analysis the selected ion for each naphthalene ($C_{10}H_8$) isomer was selected in the chromatograms of S-1 and reference products. The peak area of each alkylated isomer was determined and the relative percentage calculated. Figure 3.25, Appendix 2, shows the selected ion chromatograms for the different homologues of naphthalene. It was observed that the retention time and the number of naphthalene alkylated homologues increased from C_0 to C_4. Since both C_0-dibenzothiophene and C_4-tetramethylnaphthalene contain the 184 m/z ion, caution must be taken not to include the dibenzothiophene peak in the calculations for tetramethylnaphthalene isomers. Table 3.8 shows the normalised results for naphthalene and the alkylated naphthalene isomers in the sample S-1 and the seven reference products used in the study.

Table 3.8 Normalised Percentage Distributions of Naphthalene Homologues

Alkylated Isomer	S-1	Kerosene	Diesel	Lube Oil	Coal	Road Tar	SACB	Jeyes Fluid
C_0-Naphthalene	40	18	5	4	9	13	4	31
C_1-Naphthalene	25	35	12	14	17	13	13	31
2-methylnaphthalene	15	20	7	8	10	7	7	19
1-methylnaphthalene	10	14	4	6	7	6	6	13
C_2-Naphthalene	20	32	29	29	24	26	27	27
C_3-Naphthalene	11	12	32	30	33	31	32	8
C_4-Naphthalene	4	2	22	23	17	18	25	2

A number of ratios of the alkylated naphthalene series are used so that differences can be observed between the soil sample S-1 and the reference products. These ratios are presented in Table 3.9. A CORAT star plot diagram (Figure 3.26) was constructed from these ratios, for the identification of the best fit ratios between the soil sample S-1 and the reference products. This star plot allows comparisons to be made between the reference products and the soil sample S-1. Each product was individually compared to the soil sample S-1 (Figure 3.27), to determine the best fit plot.

Table 3.9 Naphthalene Homologous Series Ratios

Ratios Naphthalene	S-1 %	Kerosene %	Diesel %	Lube Oil %	Coal %	Road Tar %	SACB%	Jayes Fluid %
C0-N / C1-N	1.6	0.5	0.5	0.3	0.5	1.0	0.3	1.0
C0-N / C2-N	2.0	0.6	0.2	0.1	0.4	0.5	0.1	1.1
C0-N / C3-N	3.8	1.5	0.2	0.1	0.3	0.4	0.1	3.7
C0-N / C4-N	9.9	8.5	0.2	0.2	0.5	0.8	0.2	16.2
C1-N / C0-N	0.6	1.9	2.2	3.3	1.9	1.0	3.4	1.0
C1-N / C2-N	1.3	1.1	0.4	0.5	0.7	0.5	0.5	1.1
C1-N / C3-N	2.4	2.8	0.4	0.4	0.5	0.4	0.4	3.7
C1-N / C4-N	6.2	15.9	0.5	0.6	1.0	0.7	0.5	16.4
C2-N / C0-N	0.5	1.8	5.5	7.1	2.6	2.0	7.3	0.9
C2-N / C1-N	0.8	0.9	2.5	2.2	1.4	2.0	2.1	0.9
C2-N / C3-N	1.8	2.6	0.9	1.0	0.7	0.8	0.9	3.3
C2-N / C4-N	4.8	14.9	1.3	1.3	1.4	1.5	1.1	14.4
C3-N / C0-N	0.3	0.7	6.1	7.4	3.6	2.3	8.5	0.3
C3-N / C1-N	0.4	0.4	2.8	2.2	1.9	2.4	2.5	0.3
C3-N / C2-N	0.5	0.4	1.1	1.0	1.4	1.2	1.2	0.3
C3-N / C4-N	2.6	5.7	1.4	1.3	1.9	1.7	1.3	4.4
C4-N / C0-N	0.1	0.1	4.3	5.5	1.9	1.3	6.6	0.1
C4-N / C1-N	0.2	0.1	1.9	1.7	1.0	1.4	1.9	0.1
C4-N / C2-N	0.2	0.1	0.8	0.8	0.7	0.7	0.9	0.1
C4-N / C3-N	0.4	0.2	0.7	0.7	0.5	0.6	0.8	0.2
2-mN / C1-N	0.6	0.6	0.6	0.6	0.6	0.5	0.6	0.6
1-mN / C1-N	0.4	0.4	0.4	0.4	0.4	0.5	0.4	0.4

Figure 3.26 Naphthalene CORAT Analysis (Logarithmic)

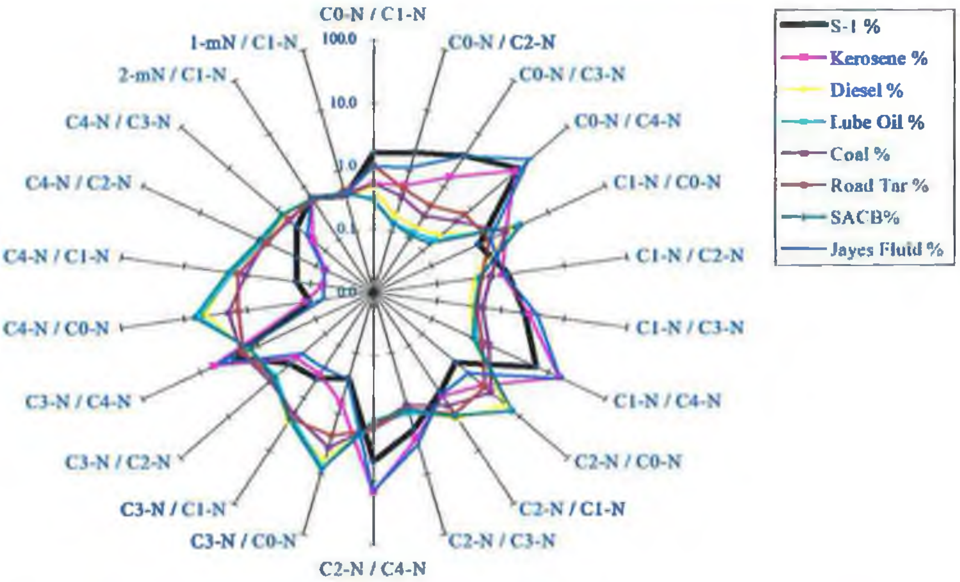


Figure 3.27 Naphthalene CORAT Analysis of S-1 Compared to Reference Products

S-1 and Kerosene – Probable Match

S-1 and Diesel – Non Match

S-1 and Coal – Non Match

S-1 and Road Tar – Non Match

S-1 and Jeyes Fluid – Probable Match

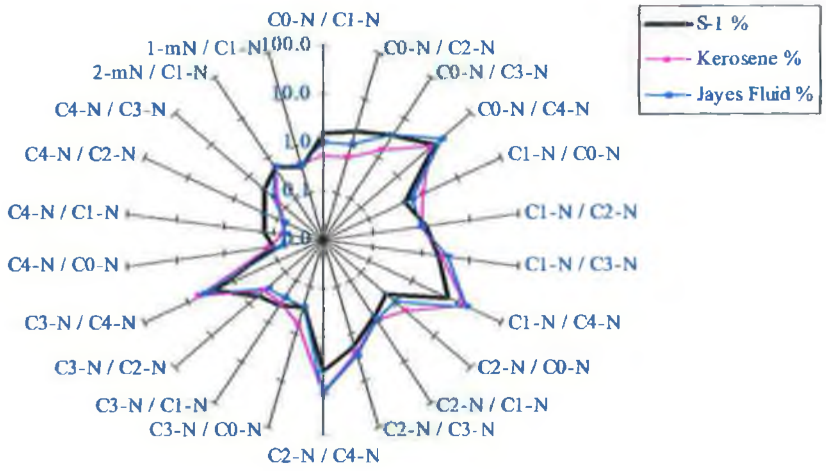
S-1 and Lubrication Oil – Non Match

S-1 and South American Crude Bitumen – Non Match

4.7.1.1 Summary of Naphthalene Series Analysis

It can be concluded from the CORAT star plot diagrams in Figure 5.27 that diesel, road tar, lubrication oil, coal and South American crude bitumen have different naphthalene alkylated series distribution patterns when compared to the soil sample S-1. Kerosene and Jeyes fluid showed the best fit when compared to the soil sample S-1. Figure 3.28, can be used to give an indication of the best fit for the possible naphthalene source in the sample. S-1 contains a relatively high abundance of the alkylated naphthalene isomers. This is common in a pyrogenic type complex matrix; however, in petrogenic matrices this can be different as the same bioavailable isomers are more susceptible to the weathering process. The identification of phenols in the sample S-1, Level 2, confirms the findings that Jeyes fluid, a pyrogenic source, is the most probable source of naphthalene contamination and suggests that kerosene is not contributing to this contamination. An important characteristic of naphthalene PAH is that its composition changes due to abiotic weathering, typically water washing or evaporation.

Figure 3.28 Naphthalene CORAT Star Plot S-1, Kerosene and Jeyes Fluid (Logarithmic)



4.7.2 Section P of the GC/MS Chromatogram - Phenanthrene Homologues Analysis

Another pronounced PAH compositional feature is that of the phenanthrene alkylated series. The methyl isomers are almost resistant to biodegradation and can used to determine a correlation between sources. The relative distribution of phenanthrene isomers is subjected to little interference from weathering in the short term (Scally *et al.*, 2004). Using SIM analysis the selected ions for each phenanthrene ($C_{14}H_{10}$) was selected in the chromatograms of the sample S-1 and the reference products. Phenanthrene a three member ring PAH, and its alkylated homologies were reviewed using SIM ions (Figure 3.29, Appendix 2). The normalised percentage distribution of the alkylated phenanthrene series for soil sample S-1 and the reference products are shown in Table 3.10. Kerosene does not contain phenanthrene and was excluded.

Table 3.10 Normalised Distribution of Phenanthrene Homologues

Alkylated Isomer Phenanthrene (P)	S-1 %	Diesel %	Lube Oil %	Coal %	Road Tar %	SACB%	Jeyes Fluid %
C_0-Phenanthrene	49	13	5	21	58	4	8
C_1-Phenanthrene	25	32	16	26	18	13	61
3-methylphenanthrene	7	9	3	7	5	2	21
2-methylphenanthrene	9	12	4	10	6	4	18
9-methylphenanthrene	5	6	5	4	4	4	15
1-methylphenanthrene	5	6	4	5	3	3	7
C_2-Phenanthrene	17	32	28	25	13	23	14
C_3-Phenanthrene	6	17	30	17	7	33	12
C_4-Phenanthrene	3	5	21	11	3	27	5

The sample and reference products were reviewed similarly to naphthalene isomers using the range of ratios detailed in Table 3.11. A CORAT star plot diagram was constructed from the ratios detailed in Table 3.11 for the identification of the best fit plot between the soil sample S-1 and the reference products for the alkylated phenanthrene series (Figure 3.30). The CORAT star plot diagram demonstrated differences in the reference products to the soil sample S-1. Figure 3.31 shows the distribution of the alkylated phenanthrene isomers compared to the sample S-1 for all the individual reference products to determine the best fit ratios for this series.

Table 3.11 Phenanthrene Homologoues Series Ratios

Ratios Phenanthrene	S-1 %	Diesel %	Lube Oil %	Coal %	Road Tar %	SACB%	Jayes Fluid%
C0-P / C1-P	1.9	0.4	0.3	0.8	3.2	0.3	0.1
C0-P / C2-P	2.9	0.4	0.2	0.8	4.4	0.2	0.5
C0-P / C3-P	7.7	0.7	0.2	1.3	7.7	0.1	0.6
C0-P / C4-P	18.3	2.5	0.2	1.9	17.3	0.2	1.4
C1-P / C0-P	0.5	2.5	3.1	1.2	0.3	3.2	8.1
C1-P / C2-P	1.5	1.0	0.6	1.0	1.4	0.6	4.3
C1-P / C3-P	4.0	1.9	0.5	1.6	2.4	0.4	5.1
C1-P / C4-P	9.5	6.4	0.8	2.3	5.5	0.5	11.3
C2-P / C0-P	0.3	2.5	5.3	1.2	0.2	5.7	1.9
C2-P / C1-P	0.7	1.0	1.7	1.0	0.7	1.8	0.2
C2-P / C3-P	2.6	1.8	0.9	1.5	1.8	0.7	1.2
C2-P / C4-P	6.3	6.3	1.3	2.2	4.0	0.9	2.7
C3-P / C0-P	0.1	1.4	5.7	0.8	0.1	8.1	1.6
C3-P / C1-P	0.3	0.5	1.8	0.6	0.4	2.5	0.2
C3-P / C2-P	0.4	0.5	1.1	0.7	0.6	1.4	0.8
C3-P / C4-P	2.4	3.4	1.4	1.5	2.2	1.2	2.2
C4-P / C0-P	0.1	0.4	4.1	0.5	0.1	6.6	0.7
C4-P / C1-P	0.1	0.2	1.3	0.4	0.2	2.0	0.1
C4-P / C2-P	0.2	0.2	0.8	0.4	0.3	1.2	0.4
C4-P / C3-P	0.4	0.3	0.7	0.7	0.4	0.8	0.4
3-mP / C1-P	0.3	0.3	0.2	0.3	0.3	0.2	0.4
2-mP / C1-P	0.3	0.4	0.3	0.4	0.3	0.3	0.3
9-mP / C1-P	0.2	0.2	0.3	0.2	0.2	0.3	0.2
1-mP / C1-P	0.2	0.2	0.2	0.2	0.2	0.2	0.1

Figure 3.30 Phenanthrene CORAT Analysis (Logarithmic)

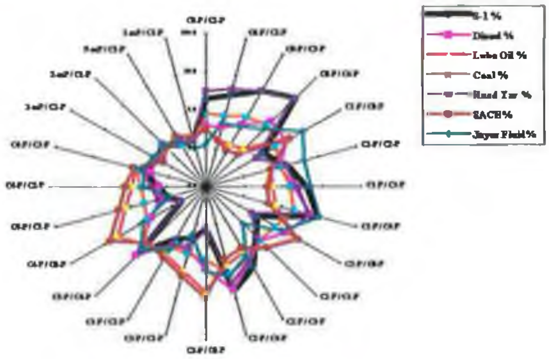
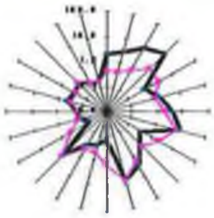
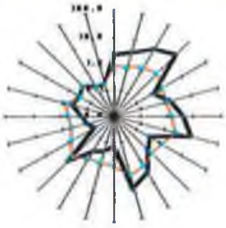


Figure 3.31 Phenanthrene CORAT Analysis of S-1 Compared to Reference Products

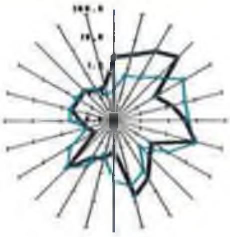
S-1 and Diesel – Non Match



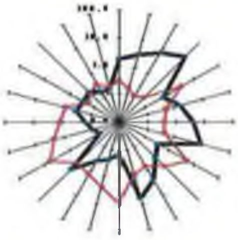
S-1 and Coal – Non Match



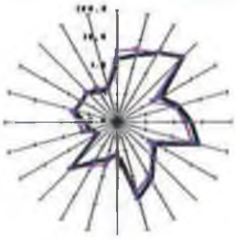
S-1 and Jeyes Fluid – Non Match



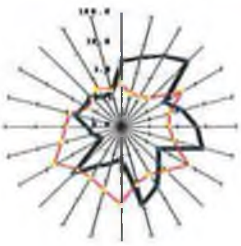
S-1 and SACB – Non Match



S-1 and Road Tar – Positive Match



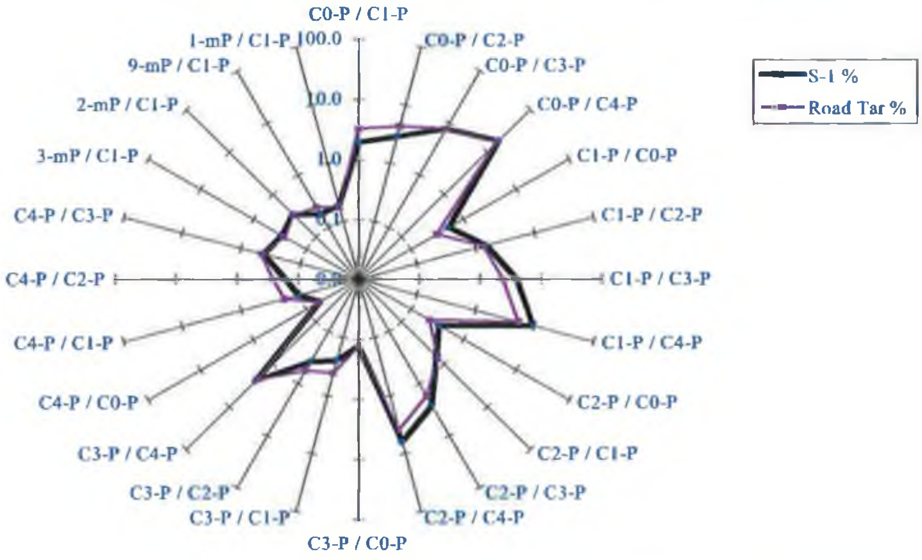
S-1 and Lube oil – Non Match



4.7.2.1 Summary of Phenanthrene Series Analysis

The alkylated phenanthrene in sample S-1 showed similar distribution found with naphthalene alkylated series. The bioavailability appears to be inhibited by possible matrix effects in the soil sample S-1. The sample showed a relatively high abundance of alkylated phenanthrenes with parent ion dominance. This CORAT distribution of phenanthrene series in the soil sample S-1 reflects a pyrogenic sources signature which had a positive match with road tar. Figure 3.32, illustrates the best fit CORAT star plot diagram for the alkylated phenanthrene series between the soil sample S-1 and the reference product road tar.

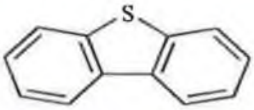
Figure 3.32 Phenanthrene S-1 and Road Tar (Logarithmic)



4.7.3 Section D of the GC/MS Chromatogram - Dibenzothiophene Homologues Analysis

Dibenzothiophene (DBT) is ubiquitous in almost all crude oils. Hence it has been considered as a model sulphur compound for compounds such as thiophenes and benzothiophenes. Dibenzothiophenes are more resistant to degradation in fuel oils due to the stereochemistry of their hindered sulphur atoms, which are not easily accessible to abiotic and/or biotic attack. The selected ion 184m/z for the parent C_0 DBT is the same ion for the C_4 tetramethylnaphthalene isomers. Care was taken to identify the correct peak. Using SIM analysis the selected ions for dibenzothiophene, Figure 3.33 ($C_{12}H_8S$), a three member ring PAH containing sulphur and its alkylated homologies were reviewed. Figure 3.34, Appendix 1, shows the SIM ions chromatograms for the different homologues of dibenzothiophene. Using similar distribution approaches for naphthalene and phenanthrene the relative percentage distributions of the alkylated isomers were determined from the soil sample S-1 and the reference products, see Table 3.12. The reference product diesel in this study was purchased from an Esso in 2003. Prior to the year 2000, diesel contained a range of sulphur compounds (Jones, 2003). Dibenzothiophene was not detected in the diesel reference product. The history of the sample indicates that the contamination was between the 1950's and 1960's when dibenzothiophene was present in diesel.

Figure 3.33 Structure of Dibenzothiophene



Dibenzothiophene $C_{12}H_8S$

Table 3.12 Normalised Distribution of Dibenzothiophene Homologues

Alkylated Isomer Dibenzothiophene (D)	S-1 %	Kerosene %	Diesel %	Lube Oil %	Coal %	Road Tar %	SACB%	Jeyes Fluid %
C_0-Dibenzothiophene	56	-	-	3	32	33	5	-
C_1-Dibenzothiophene	18	-	-	12	24	19	16	-
4-methyl-Dibenzothiophene	5	-	-	6	9	7	6	-
3+2-methyl-Dibenzothiophene	10	-	-	4	13	8	5	-
1-methyl-Dibenzothiophene	4	-	-	2	3	4	4	-
C_2-Dibenzothiophene	17	-	-	33	26	27	34	-
C_3-Dibenzothiophene	9	-	-	52	17	21	46	-

Table 3.12 shows the soil sample S-1 having similar properties already observed with the alkylated naphthalene and phenanthrene series. Kerosene and Jeyes fluid do not contain dibenzothiophene so they were excluded. Similar interpretation using CORAT star plot diagrams was conducted using the ratios presented in Table 3.13. The CORAT star plot diagram (Figure 3.35) for the dibenzothiophene series shows differences and similarities between the

reference products and the soil sample S-1. Each reference product was individually compared to the soil sample S-1 in Figure 3.36, to determine the best fit plot.

Table 3.13 Dibenzothiophene Homologoues Series Ratios

Ratios Dibenzothiophene	S-1 %	Lube Oil %	Coal %	Road Tar %	SACB%
C0-D / C1-D	3.0	0.2	1.3	1.7	0.3
C0-D / C2-D	3.3	0.1	1.2	1.3	0.1
C0-D / C3-D	6.3	0.1	1.9	1.6	0.1
C1-D / C0-D	0.3	4.5	0.8	0.6	3.4
C1-D / C2-D	1.1	0.4	0.9	0.7	0.5
C1-P / C3-D	2.1	0.2	1.4	0.9	0.3
C2-D / C0-D	0.3	12.3	0.8	0.8	7.4
C2-D / C1-D	0.9	2.7	1.1	1.4	2.2
C2-D / C3-D	1.9	0.6	1.5	1.3	0.7
C3-D / C0-D	0.2	19.0	0.5	0.6	9.9
C3-D / C1-D	0.5	4.2	0.7	1.1	2.9
C3-D / C2-D	0.5	1.5	0.6	0.8	1.3
4-mD / C1-D	0.2	0.5	0.4	0.4	0.4
3+2-mD / C1-D	0.5	0.4	0.5	0.4	0.3
1-mD / C1-D	0.2	0.2	0.1	0.2	0.3

Figure 3.35 Dibenzothiophene CORAT (Logarithmic)

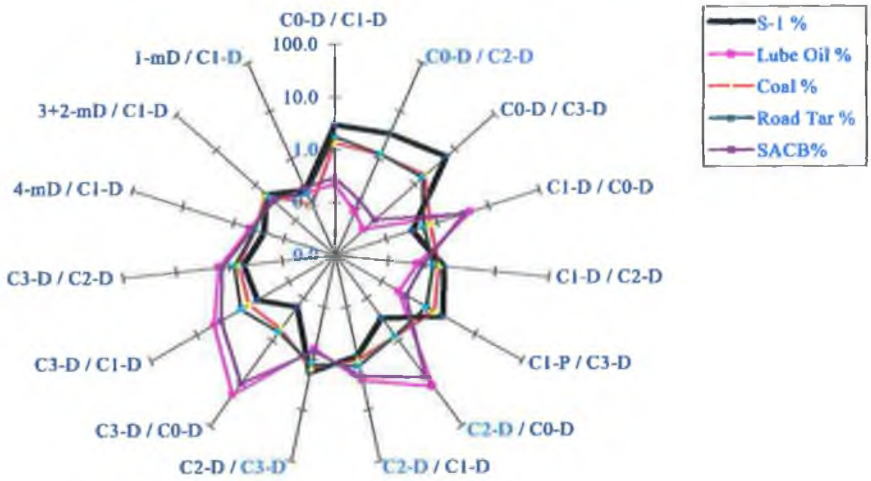


Figure 3.36 Dibenzothiophene CORAT Analysis of S-1 Compared to Reference Products


S-1 and Coal – Probable Match

S-1 and Road Tar – Probable Match

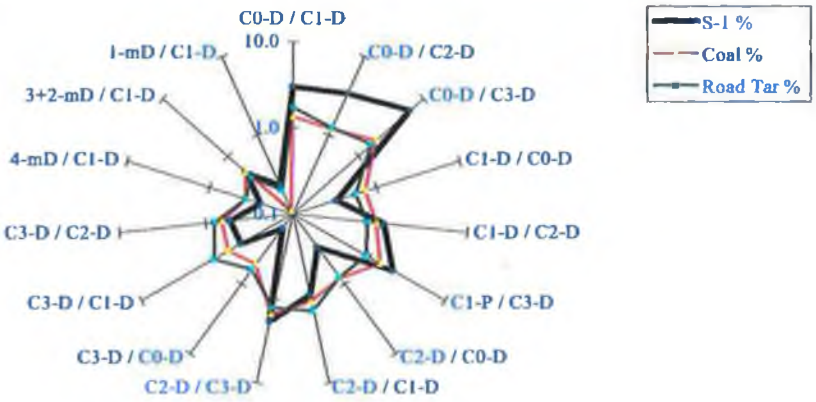

S-1 and Lubrication Oil – Non Match

S-1 and SACB – Non Match

4.7.3.1 Summary of Dibenzothiophene Findings

The best fit CORAT plots (Figure 3.36) with the soil sample S-1 were with the coal and road tar reference products (Figure 3.37) while those of SACB and lubrication oil were quite different.

Figure 3.37 Dibenzothiophene CORAT S-1 and Road Tar and Coal (Logarithmic)



4.7.4 Section F and C of the GC/MS Chromatogram - Fluorene and Chrysene Homologues Analysis

Using SIM analysis of the selected ions for each fluorene isomer ($C_{13}H_{10}$) and chrysene isomer ($C_{18}H_{12}$), a three and four member ring PAH respectively, and its alkylated homologies were reviewed (Figure 3.38, Appendix 1). Using the same approaches used for naphthalene, phenanthrene and dibenzothiophene the relative percentage distribution of the alkylated isomers were determined for fluorene and chrysene, see Table 3.14. The study found fluorene and chrysene were not present in the reference products kerosene and Jeyes fluid. Chrysene was not determined in diesel or lubrication oil. A CORAT star plot diagram was constructed for chrysene and fluorene using the ratios in Table 3.15 for the soil sample S-1 and the reference products (Figure 3.39). The CORAT plots for fluorene isomers compared to the soil sample S-1 was presented in Figure 3.40.

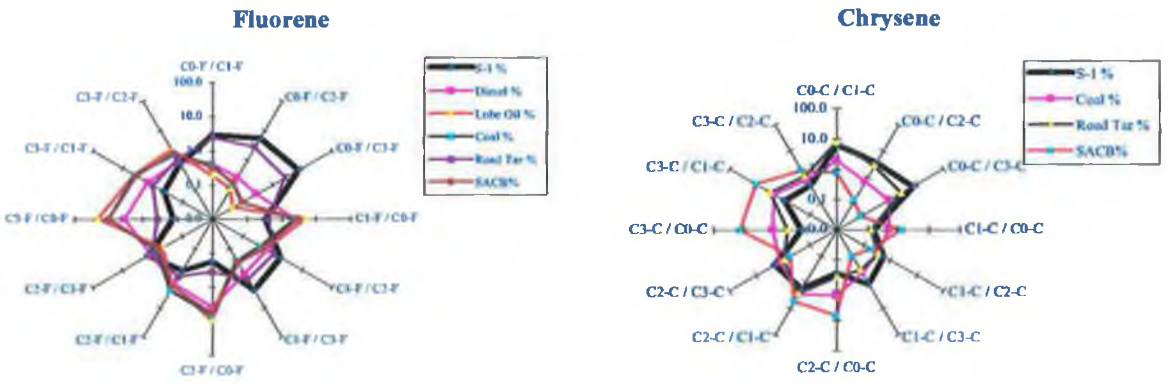
Table 3.14 Normalised Distribution of Fluorene/Chrysene S-1 to the Reference Samples

Alkylated Isomer	S-1 %	Kerosene %	Diesel %	Lube Oil %	Coal %	Road Tar %	SACB%	Jeyes Fluid %
Fluorene (F)								
C_0-F	61	-	9	3	5	47	5	-
C_1-F	20	-	23	15	13	19	15	-
C_2-F	11	-	36	25	33	17	29	-
C_3-F	8	-	32	57	50	17	50	-
Chrysene (C)								
C_0-C	64	-	-	-	24	54	4	-
C_1-C	10	-	-	-	13	7	6	-
C_2-C	18	-	-	-	36	19	32	-
C_3-C	9	-	-	-	28	20	58	-

Table 3.15 Fluorene and Chrysene Homologoues Series Ratios

	Ratios Fluorene	S-1 %	Diesel %	Lube Oil %	Coal %	Road Tar %	SACB%
Fluorene	C0-F / C1-F	3.0	0.4	0.2	0.4	2.5	0.3
	C0-F / C2-F	5.6	0.3	0.1	0.2	2.8	0.2
	C0-F / C3-F	7.4	0.3	0.0	0.1	2.7	0.1
	C1-F / C0-F	0.3	2.5	5.2	2.5	0.4	3.1
	C1-F / C2-F	1.9	0.6	0.6	0.4	1.1	0.5
	C1-F / C3-F	2.5	0.7	0.3	0.3	1.1	0.3
	C2-F / C0-F	0.2	3.8	9.1	6.6	0.4	5.8
	C2-F / C1-F	0.5	1.5	1.7	2.6	0.9	1.9
	C2-F / C3-F	1.3	1.1	0.4	0.7	1.0	0.6
	C3-F / C0-F	0.1	3.4	20.6	10.0	0.4	10.0
	C3-F / C1-F	0.4	1.4	3.9	4.0	0.9	3.3
	C3-F / C2-F	0.8	0.9	2.3	1.5	1.0	1.7
Chrysene	C0-F / C1-C	6.4	-	-	1.9	7.7	0.8
	C0-C / C2-C	3.6	-	-	0.7	2.8	0.1
	C0-C / C3-C	7.4	-	-	0.9	2.6	0.1
	C1-C / C0-C	0.2	-	-	0.5	0.1	1.3
	C1-C / C2-C	0.6	-	-	0.4	0.4	0.2
	C1-C / C3-C	1.2	-	-	0.5	0.3	0.1
	C2-C / C0-C	0.3	-	-	1.5	0.4	7.1
	C2-C / C1-C	1.8	-	-	2.9	2.8	5.4
	C2-C / C3-C	2.0	-	-	1.3	0.9	0.6
	C3-C / C0-C	0.1	-	-	1.1	0.4	12.9
	C3-C / C1-C	0.9	-	-	2.2	2.9	9.7
	C3-C / C2-C	0.5	-	-	0.8	1.1	1.8

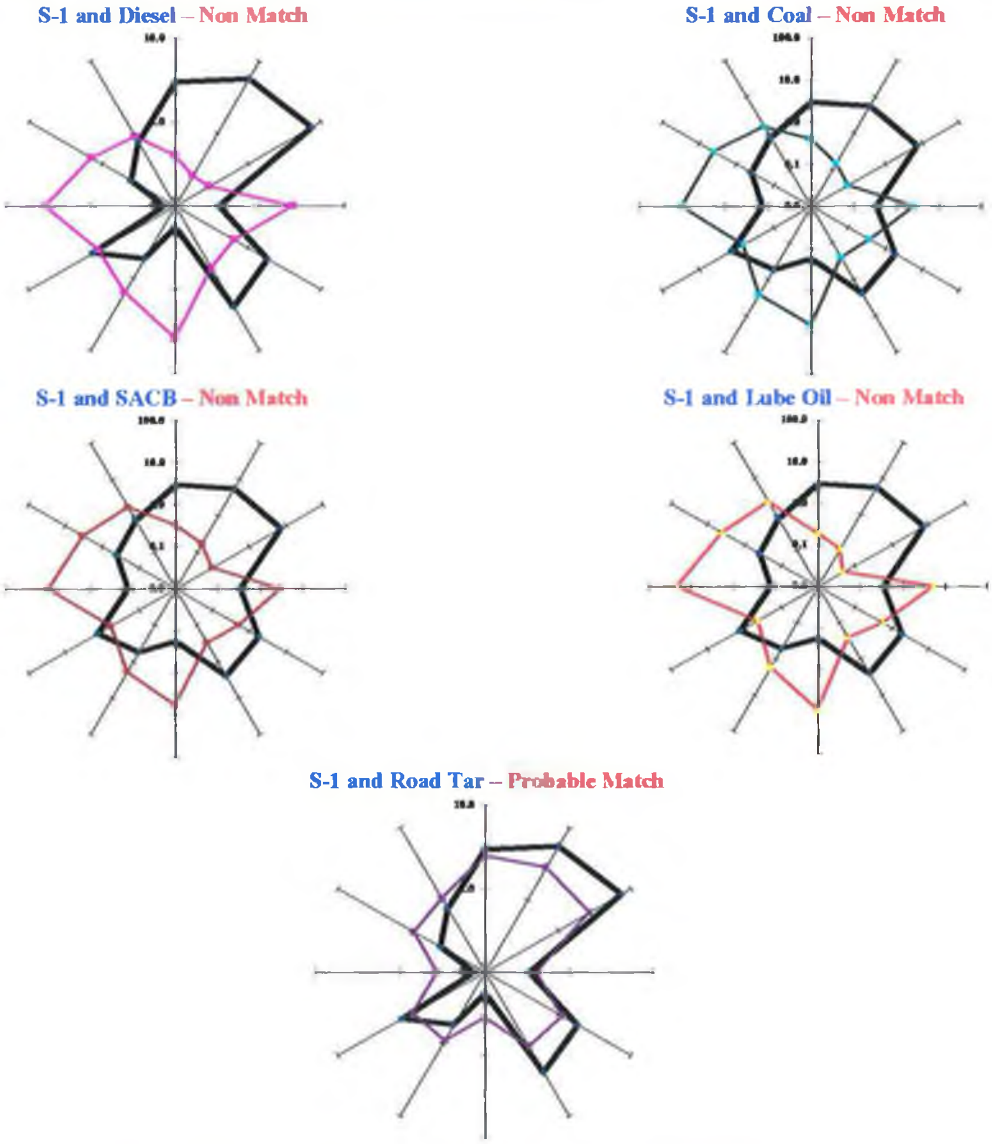
Figure 3.39 Fluorene and Chrysene CORAT (Logarithmic)



Fluorene

Chrysene

Figure 3.40 Fluorene CORAT of S-1 Compared to Reference Products



S-1 and Diesel – Non Match

S-1 and Coal – Non Match

S-1 and SACB – Non Match

S-1 and Lube Oil – Non Match

S-1 and Road Tar – Probable Match

4.7.4.1 Summary Findings for Fluorene Analysis

It was concluded from the above results that diesel, coal, SACB, and lubrication oil all have different fluorene distribution patterns compared to sample S-1. The best fit CORAT star plot diagram compared to the soil sample S-1 was with the reference road tar product (Figure 3.41). The individual CORAT star plot diagrams for chrysene isomers compared to the soil sample S-1 was presented in Figure 3.42.

Figure 3.41 Fluorene CORAT Star Plot S-1, Road Tar (Logarithmic)

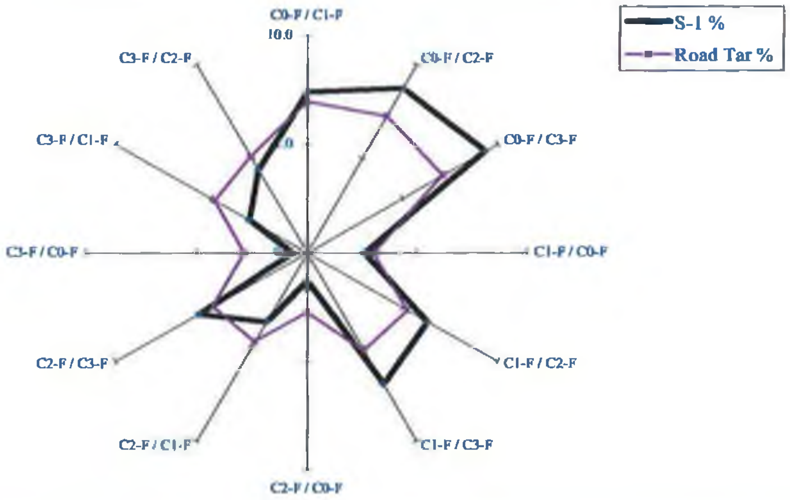
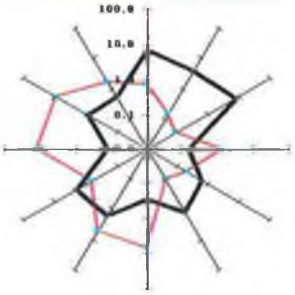


Figure 3.42 Chrysene CORAT of S-1 Compared to Reference Products

S-1 and Road Tar - Probable Match

S-1 and Coal – Non Match

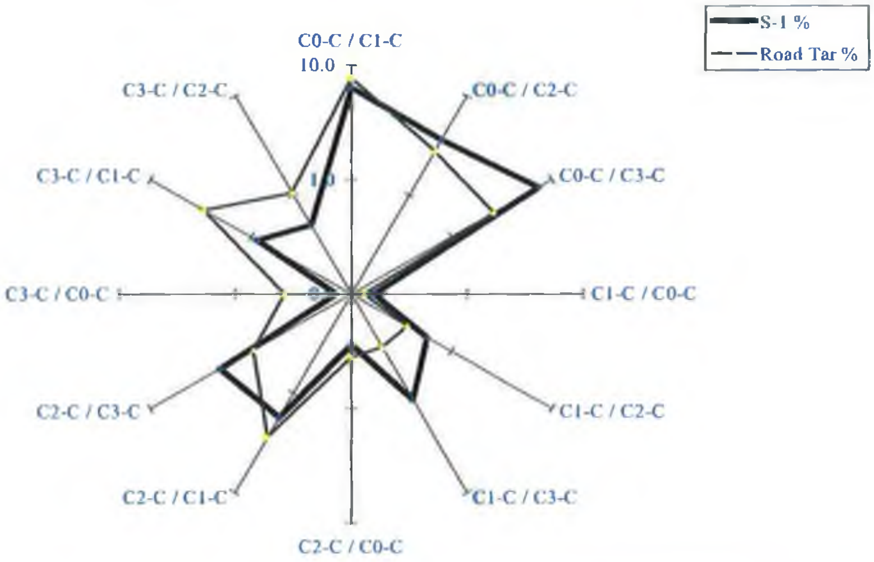
S-1 and SACB – Non Match



4.7.4.2 Summary Findings for Chrysene Analysis

It can be concluded from the CORAT star plot diagrams that the distribution pattern for the chrysene isomers for the soil sample S-1 compared to the reference samples coal and SACB are different. The best fit CORAT star plot diagram for the chrysene series is between the soil sample S-1 and the reference road tar product, see Figure 3.43.

Figure 3.43 Chrysene CORAT S-1 and Road Tar (Logarithmic)



4.8 Conclusions of Summary Findings

The chemical fingerprint from the VH analysis during Level 1 analysis and the associated data indicated the contaminants were enriched in BTEX and naphthalene. Provisional indications were that the most probable source of this type of hydrocarbon contamination was from a coal tar volatile. The abundance of BTEX indicates that wood tar creosote is a possible source of contamination of sample S-1. The most likely conclusion is that the contaminants are sourced from a coal tar and are similar in composition to a benzole fuel refined from the coal carbonisation process. Further analytical investigation using EH analysis indicated the chemical fingerprint obtained from sample S-1 indicated a product consisting mainly of PAH. The pattern and profile obtained indicated that the main source is pyrogenic. The concentration of the individual PAHs and a number of diagnostic ratios were successfully used in this study as indicators for spill identification. A benefit of comparing diagnostic ratios of spilled products and suspected source products is that concentration effects are minimised. The elimination of Jeyes fluid (suggested in Level 1) and the use of the USEPA 16 PAH resulted in all reference materials demonstrating a non-match with the exception of road tar and lubrication oil.

The abundances of alkylated PAHs differ between pyrogenic and petrogenic products. It can be concluded from the individual product comparisons with the soil sample S-1 that the petrogenic sources had different percentage distribution of the PAH ratios. The best fit CORAT star plot diagram to the sample S-1 was with road tar, a pyrogenic source. Individual PAH alkylated series compounds were investigated to further confirm the finding of the study. Naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene isomers were used. For the Naphthalene series kerosene and Jeyes fluid showed the best fit CORAT star plot diagrams. The alkylated phenanthrene in the sample S-1 showed similar distributions with naphthalene where the bioavailability of the sample appears to be inhibited by possible matrix effects. The sample showed a relatively high abundance of alkylated phenanthrenes with parent ion dominance. This distribution of phenanthrene in the soil sample S-1 is found in pyrogenic sources which had a positive match with road tar. The best fit CORAT plots for the dibenzothiophene alkylated series were with the coal and road tar reference products. It was concluded from the fluorene and chrysene analysis that the best fit CORAT star plot diagram compared to the soil sample S-1 was with the reference road tar product.

4.9 Terpane and Sterane Biomarker Analysis

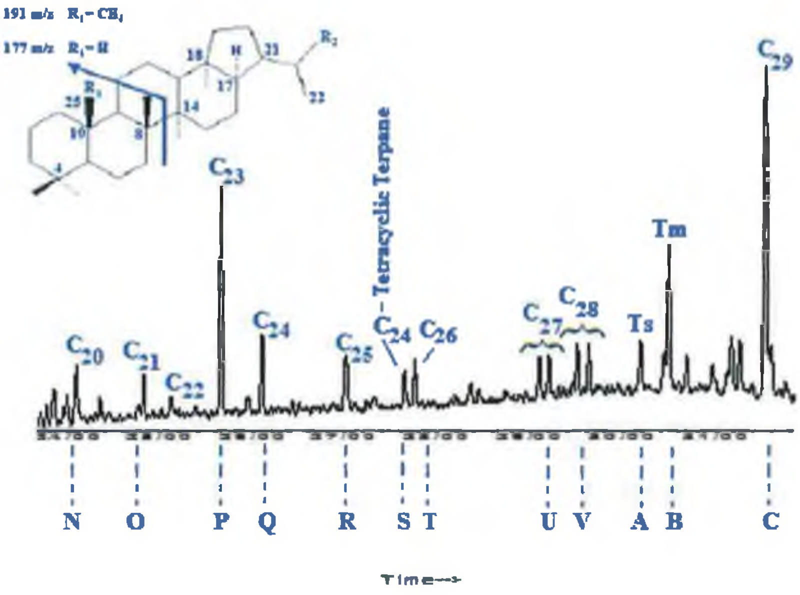
A wide variety of biomarkers have been identified as useful in the characterisation of crude oils and oil fractions, including tricyclic, tetracyclic, pentacyclic terpanes (m/z 191), methylhopanes (205 m/z), steranes (217/218 m/z), methylsteranes (217/231 m/z), and diasteranes (217/259 m/z). Hopanes are found in almost all ancient sediments and crude oils. They are derived from oxygenated analogues such as the bacteriohopanetetrols found in most bacteria and cyanobacteria (Volkman *et al.*, (1997). Tricyclic terpanes recently have assumed an important role in geochemical and petroleum studies. It has been shown that many crude oils and source rock extracts contain a homologous series of tricyclic terpanes in the range $C_{19}H_{34}$ to $C_{45}H_{86}$ and possibly higher (Philp, 1985). Pentacyclic triterpanes are based on the hopane structure and are ubiquitous biomarkers. The general structure for this member of the series is shown in Figure 3.44 along with the characteristic fragmentation ion 191m/z. Variation in the relative distributions of individual components within the series as determined by GC/MS ensures that these compounds are useful for correlation purposes. The distribution patterns are, in general, different from oil to oil. Saturated biomarker n-C_{19} to n-C_{35} terpanes m/z 191 and n-C_{21} to n-C_{29} regular steranes m/z 217 are the most common biomarkers in crude oils. Their middle and heavy refined products are most useful biomarkers for environmental investigations because they are relatively resistant to the weathering processes. South American crude bitumen (SACB) is used as a reference product source as it is known to contain these biomarkers in abundance. Table 3.16 list the peak identification, Carbon number and compound name for the hopanes and steranes. Steranes are also widely used to fingerprint petroleum. These compounds are produced by a sequence of oxidation-reduction reactions in sediment from sterol derived from living organisms. These processes tend to leave the sterol-derived side-chain intact, and so different proportions of nC_{27}, nC_{28} and nC_{29} constituents can be used to characterise different oils. Sterane typical mass fragmentograms ions are at 217 m/z and 218 m/z (Figure 3.45).

Table 3.16 Hopane and Sterane Identification

Peak Identification	Carbon Number	Hopanes Steranes
	Hopane	
N	n-C_{20}	Tricyclic Terpane
O	n-C_{21}	Tricyclic Terpane
P	n-C_{23}	Tricyclic Terpane
Q	n-C_{24}	Tricyclic Terpane
R	n-C_{25}	Tricyclic Terpane
S	n-C_{24}	Tetracyclic Terpane
T	n-C_{26}	Tricyclic Terpane
U	n-C_{27}	Tricyclic Terpane
V	n-C_{28}	Tricyclic Terpane
	Tetracyclic Terpane	
A	n-C_{27}	18α(H)-22,29,30-trisnorneohopane (Ts)
B	n-C_{27}	17α(H)-22,29,30-trisnorhopane (Tm)
C	n-C_{29}	17α(H),21β(H)-30-norhopane
C1	n-C_{29}	18α(H),21β(H)-29-norneohopane (C_{29} Ts)
D	n-C_{29}	17β(H),21α(H)-30-normoretane
E	n-C_{30}	17α(H),21β(H)-hopane
F	n-C_{30}	17β(H),21α(H)-moretane
G	n-C_{31}	(22S)-17α(H),21β(H)-homohopane
H	n-C_{31}	(22R)-17α(H),21β(H)-homohopane
I	n-C_{31}	(22S + R)-17β(H),21α(H)-homomoretane
J	n-C_{32}	(22S)-17α(H),21β(H)-bishomohopane
J	n-C_{32}	(22R)-17α(H),21β(H)-bishomohopane
	Steranes	
G	n-C_{27}	(20R)-5α(H), 14α(H), 17α(H),-cholestane
H	n-C_{27}	(20R)-5α(H), 14β(H), 17β(H),-cholestane
I	n-C_{27}	(20S)-5α(H), 14β(H), 17β(H),-cholestane
J	n-C_{27}	(20R)-5α(H), 14 α(H), 17α(H),-cholestane
L	n-C_{28}	(20S)-5α(H), 14α(H), 17α(H)-ergostane
M	n-C_{28}	(20R)-5α(H), 14β(H), 17β(H)-ergostane
N	n-C_{28}	(20S)-5α(H), 14β(H), 17β(H)-ergostane
P	n-C_{28}	(20R)-5α(H), 14α(H), 17α(H)-ergostane
Q	n-C_{29}	(20S)-5α(H), 14α(H), 17α(H)-stigmastane
R	n-C_{29}	(20R)-5α(H), 14β(H), 17β(H)-stigmastane
S	n-C_{29}	(20S)-5α(H), 14β(H), 17β(H)-stigmastane
T	n-C_{29}	(20R)-5α(H), 14α(H), 17α(H)-stigmastane

Figure 3.44 Hopanes (191 m/z)

Tricyclic and Tetracyclic Terpanes GC/MS 191 m/z



Tetracyclic and Pentacyclic Triterpanes GC/MS 191m/z

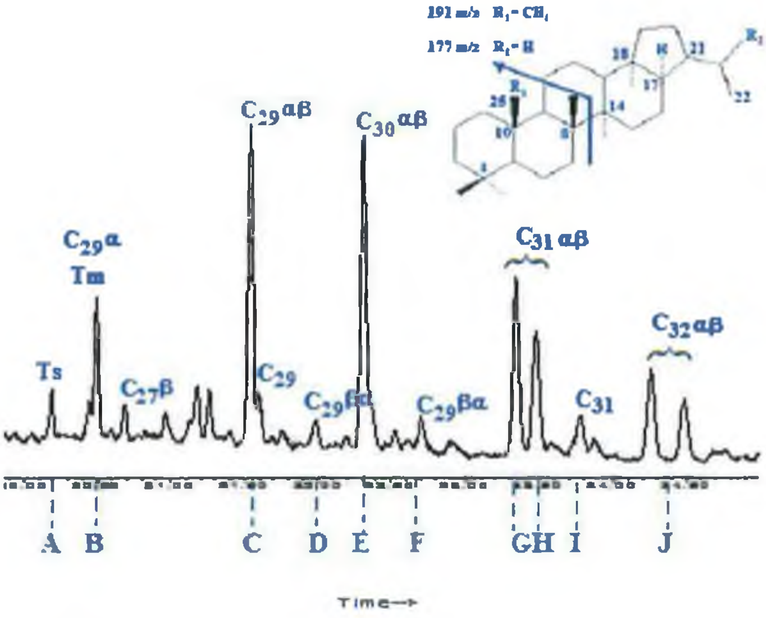
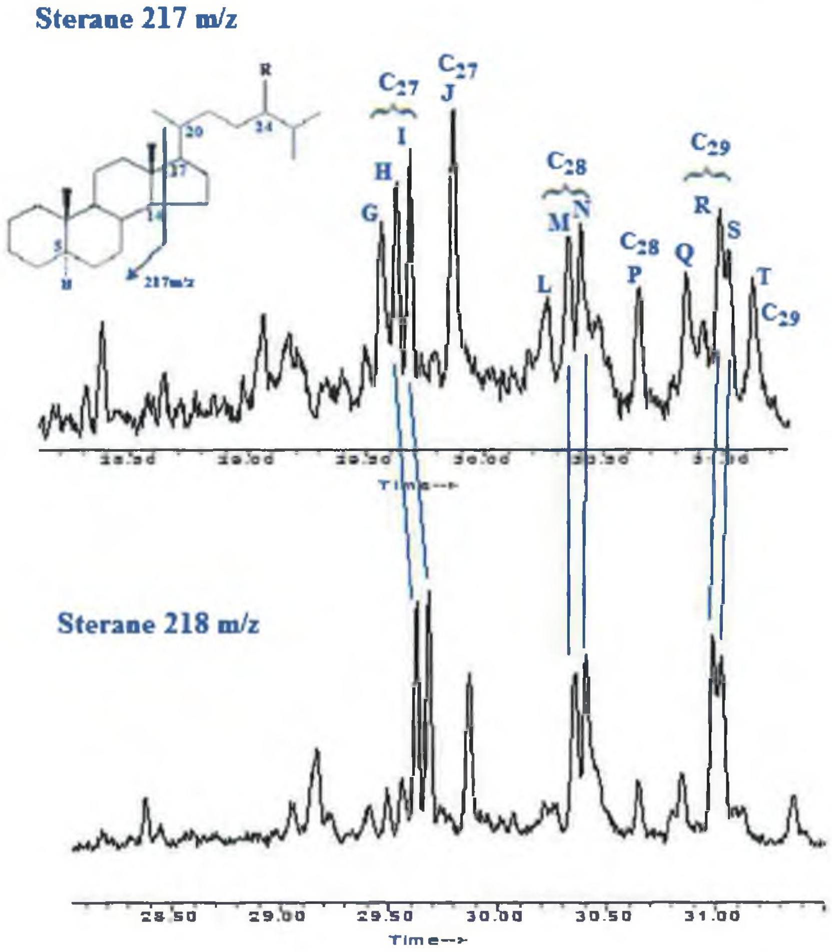


Figure 3.45 Sterane 217 m/z and 218 m/z


Sterane 217 m/z

Sterane 218 m/z

Figure 3.46 shows the SIM for tricyclic, tetracyclic and pentacyclic terpanes (191m/z) for the petrogenic reference source product SACB and pyrogenic road tar and the sample S-1. Both the SACB and road tar contain these terpanes. Overlaying the chromatograms shows that S-1 also contains similar terpanes at a relatively low abundance. A review was conducted of the presence of the methylhopanes (205 m/z) and it was found that the sample S-1 contained low abundances of these biomarkers (Figure 3.47). The sample was again compared to the reference products SACB and road tar. The distribution of the biomarker isomers of sterane (217m/z) was reviewed in Figure 3.48 and the overlay chromatogram found that sample S-1 did not appear to contain this biomarker. However, both reference samples SACB and road tar do contained these compounds. From this it can be concluded that the reference sample road tar may not be the only contributor to the contamination of sample, S-1. To try and identify additional possible sources of contamination, an examination was conducted of all the reference samples to find a possible source sample which would reveal the presence of the terpane biomarkers and have a unique absence of the sterane biomarkers. The reference pyrogenic product, coal was found to contain the terpane biomarkers (Figure 3.49), and had an absence of the sterane biomarkers Figure 3.50.

Figure 3.46 Terpane for SACB, Road Tar and S-1

Tricyclic, Tetracyclic and Pentacyclic Terpanes (191m/z)

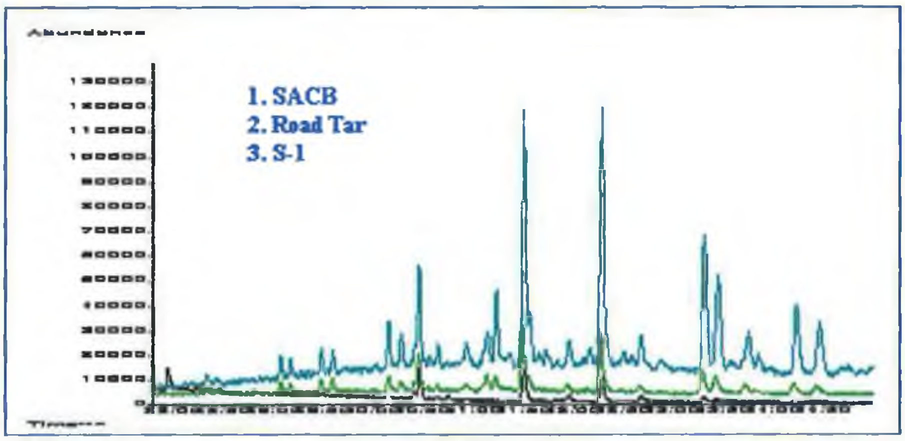


Figure 3.47 Methylhopanes for SACB, Road Tar and S-1

Methylhopanes (205m/z)

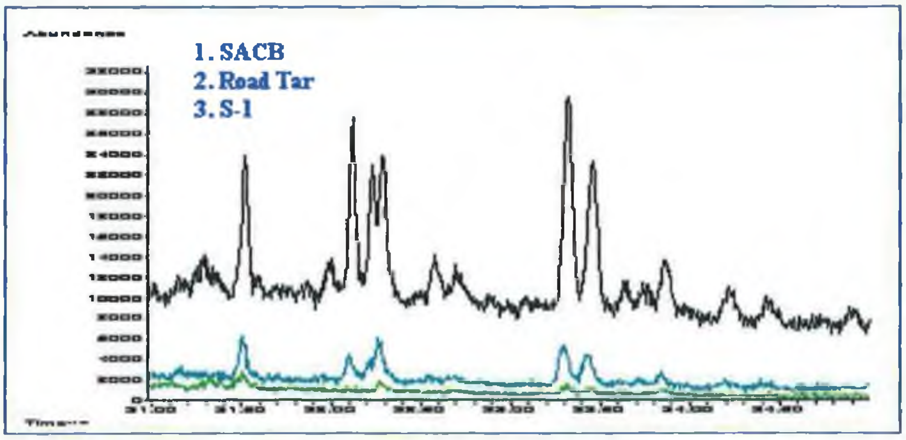


Figure 3.48 Sterane Biomarkers in SACB, Road Tar and S-1

Sterane (217m/z)

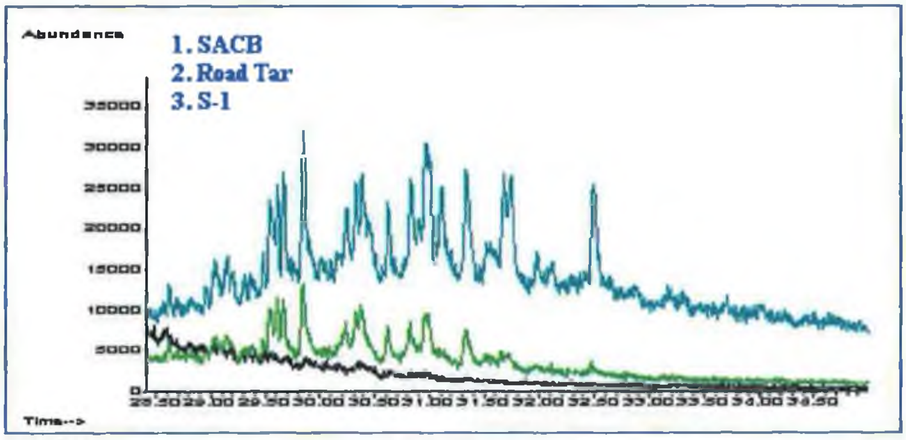
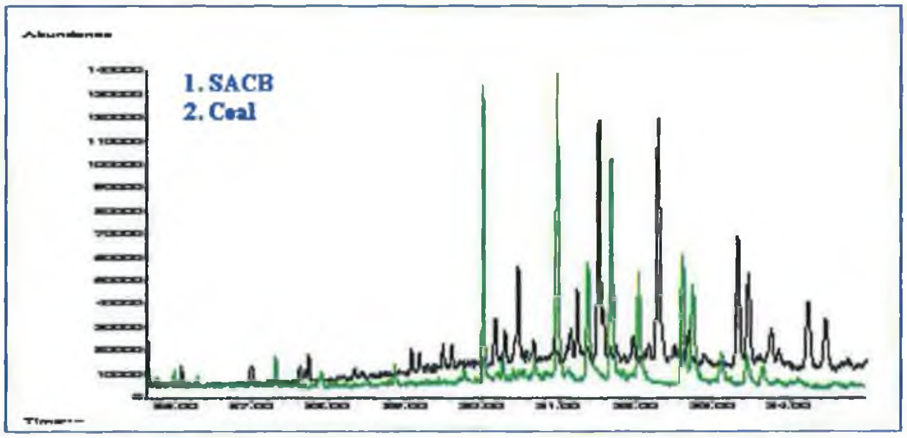


Figure 3.49 Terpane Biomarkers in Coal

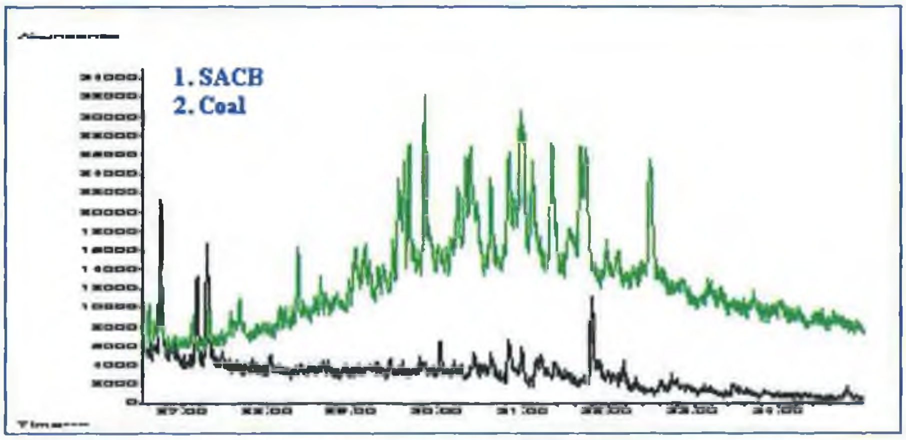
Terpane (191m/z)



Note: The retention time has shifted between the analysis of SACB and Coal. This is due to column maintance on the instrument.

Figure 3.50 Sterane Biomarker for the Comparison of SACB and Coal

Sterane (217m/z)



4.9.1 Summary Findings for Sterane and Hopane Analysis

It can be concluded that the sterane and hopane analysis indicate a pyrogenic (coal and by-products) source of contamination of the sample S-1.

4.10 Conclusion of Chapter 3

The successful use of environmental forensics encompasses an understanding of a variety of disciplines and the wisdom to understand which forensic tool(s) are best suited for a particular set of facts. It involves the systematic examination of environmental information that is used in litigation to allocate responsibility for contamination. This study demonstrated the advantages in recent developments and advances in methodologies that are most frequently used in the characterisation and identification of aliphatic and aromatic hydrocarbons at petroleum spill sites. The study found compound ratio analysis technique (CORAT) to be a suitable tool in the identification of source contamination. The contaminants found during the level 1, were polycyclic aromatic hydrocarbons (PAH). These contaminants, including the four-, five- and six-ring PAHs such as chrysene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene which are considered to be probable or possible human carcinogens, benzo(a)pyrene being the most potent carcinogen among the PAHs (Armstrong *et al.*, 2004; CARB, 1994; DEC, 2003). Level 1 concluded that the road tar contained levels of BTEX and naphthalene which can only be associated with coal tar. Therefore, it was considered that the contamination was from a pyrogenic source. Coal and road tar together with the petrogenic source SACB were analysed for biomarkers. The resulting data indicated that SACB contained both steranes and terpanes whereas the coal contained predominantly only terpanes. The analysis of soil sample S-1 also showed the presence of terpanes and the absence or very low abundance of steranes and was therefore considered to be a pyrogenic source.

The overall conclusion was that the soil sample S-1 was contaminated with a pyrogenic source which was based upon a coal tar feedstock used during from the 1950's to 1970's at gas work sites, in the manufacture of pyrogenic products (Table 3.17).

Table 3.17 Conclusion of Forensic Analysis

Analysis	**Gasoline**
Level 1	
Volatile Hydrocarbon n-C_5 to n-C_9 and n-C_{10} *to* n-C_{12}	x
Extractable Hydrocarbons n-C_{10} to n-C_{40}	x
Level 2	x
Level 3	
PAHs	x
PAH Ratios	x
Alkylated Naphthalene Homologues Series	x
Alkylated Phenanthrene Homologues Series	x
Alkylated Dibenzothiophene Homologues Series	x
Alkylated Fluorene Homologues Series	x
Alkylated Chrysene Homologues Series	x
Biomarkers Sterane and Terpane	x

Petrogenic Source				Pyrogenic Source			
Kerosene	Diesel	Lube Oil	SACB	Coal Tar	Coal	Jeyes Fluid	Road Tar
x	x	x	x	✓	x	x	x
x	✓	x	x	x	x	x	x
x	x	x	x	x	x	✓	x
x	x	x	x	x	x	x	✓
x	x	x	x	x	x	x	✓
✓	x	x	x	x	x	✓	x
x	x	x	x	x	x	x	✓
x	x	x	x	x	✓	x	✓
x	x	x	x	x	x	x	✓
x	x	x	x	x	x	x	✓
x	x	x	x	x	✓	x	x

Appendix 1

Paper 1: **Contaminated Land – achievements and aspirations, 12th – 15th September 2004, Loughbourough University, UK. EPP Publications Ltd., ISBN 1-900995-01-8**

FORENSIC POLYCYCLIC AROMATIC HYDROCARBON FINGERPRINT INTERPRETATION AND SOURCE CHARACTERISATION USING COMPOUND RATIO ANALYSIS (CORAT)

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1 INTRODUCTION

This study utilised recent developments in forensic aromatic hydrocarbon fingerprint analysis to characterise and identify specific biogenic, pyrogenic and petrogenic contamination using compound ratio analysis technique (CORAT). This technique is used to map and identify petroleum and non-petroleum compositional variations within products to determine the degree of similarity, the method utilises the difference in composition by selecting source specific markers, which are primarily resistant to degradation. Statistical verification of compositional differences between products is best achieved using logarithmic plots. The fingerprinting and data interpretation techniques discussed include the recognition of distribution patterns of the five target polycyclic aromatic hydrocarbons (alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene), which have been analysed in several papers[1 - 5]. In general, the larger the number of rings, the more stable the compound, e.g. chrysene>phenanthrene>naphthalene. Furthermore an increase in alkylation level decreases the susceptibility to microbial attack, e.g. $C_4<C_3<C_2<C_1<C_0$[6].

Creosote, including phenol isomers, were reviewed along with source-specific marker compounds found in a range of products, individual saturated hydrocarbons, including *n*-alkanes (*n*-C_5 through *n*-C_{40}), selected benzene, toluene, ethylbenzene and xylene isomers (BTEX), and the isoprenoids; pristane and phytane. Diagnostic ratios of specific petroleum and non-petroleum constituents, and the application of various statistical and numerical analysis tools were reviewed.

In the present communication we describe a hyphenated method, consisting of chemical analysis by gas chromatography utilising detection by mass spectrometry (GC/MS) techniques and selective ion monitoring (SIM), followed by CORAT statistical data analysis. The method is applied to a soil sample S-1, submitted to ALcontrol Laboratories on behalf of the Irish Environmental Protection Agency (EPA). S-1 was from a site contaminated with soil supplied from a suspected gas works site, which was contaminated in between about 1950 to 1970 with feed stock coal tar[7].

The sample was received in the laboratory for analysis on the 14th August 2003. Comparison were made with the following reference products; light creosote (Jeyes Fluid), domestic coal, road tar, commercial bought kerosene and Esso diesel (Exxon Mobil Corp), lubricant oil; Castrol GTX 10W-40, and South American crude bitumen (Irish Asphalt) to distinguish between biogenic, pyrogenic and petrogenic source contaminant.

The purpose of this study was to evaluate CORAT as a powerful visual tool in origin characterisation. S-1 was subjected to analysis by GC/MS (SIM), followed by normalisation of the individual polycyclic aromatic hydrocarbons (PAHs) to the sum of the PAH analytes and the results were compared with the corresponding results with a range of reference materials using CORAT.

In addition, to the determination of conventional diagnostic PAH, phenanthrene/anthracene (Ph/An) phenanthrene/methylphenanthrene (Ph/m-Ph), fluoranthene/pyrene (Fl/Py), benzo(a)anthracene/chrysene (BaA/Ch), pyrogenic index (PI) was reviewed. PI was defined in the 1994, Mobile Burn study[7,8] as the ratios of the total of the other USEPA priority unsubstituted three to six ring PAHs to the total of the five targeted alkylated PAH homologues series, $\sum$(other 3-6 ring PAHs)/$\sum$(5 alkylated PAHs). The PI can be used to differentiate pyrogenic and petrogenic PAHs[7,8]. The application of this is reviewed in this study.

Statistical logarithmic star plots were generated from the data to give a pictorial representation of the comparison between S-1 and the reference products. The study successfully characterised S-1 as being contaminated with coal tar and clearly demonstrates the useful future role of CORAT in the identification of possible source contaminants.

2 METHOD

2.1 Chemical Analysis (GC/MS)

All samples were analysed on a HP-6890 (Agilent Technologies) equipment with a 30 m fused silica capillary column 95% dimethylpolysiloxane XTI-5 with 0.25 mm id and a film thickness of 0.25µm (Restec), interfaced to a HP 5973N low-resolution quadrupole Mass Selective Detector (MSD), (Agilent Technologies), operating in EI mode. Chromatographic conditions: 1-µL aliquots were injected in splitless mode. Carrier gas, helium (1.0 ml/min); injection and detector temperature, 250°C and 280°C, respectively; temperature program: 5.0 min isothermal at 50°C, then ramp (10°C/min) to 200°C and hold for 5.0 min isothermal. Mass spectrometric condition: Ion source monitoring (SIM) after sample were run in full scan mode. MSD: MS Quad. 150°C, MS Source 230°C, and Transfer Line 280°C.

3 RESULTS AND DISCUSSION

3.1 Data Analysis

GC/MS chromatogram of S-1 was extracted for 85 *m/z* ion one of the most abundant fragment ion common to *n*-alkanes[9]. A visual comparison of the SIM chromatograms was made with the reference product diesel. S-1 extracted ion chromatogram was overlaid with the reference product diesel, which indicated the presence of five isoprenoids including pristane and phytane with an even distribution of *n*-alkanes in the *n*-C_{10} to *n*-C_{28} range. The isoprenoids pristane and phytane can be observed in S-1, under these SIM conditions (Figure 1).

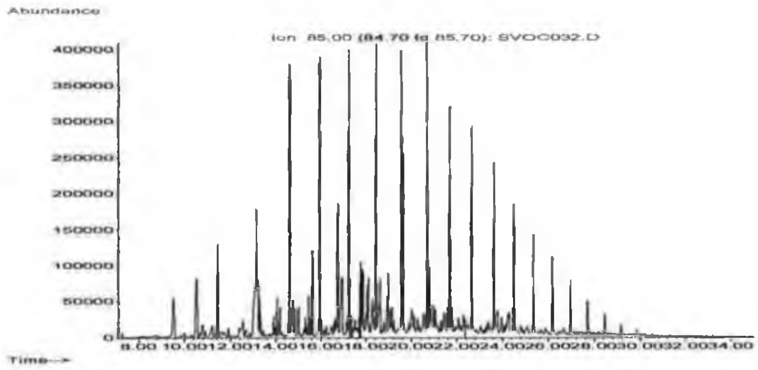


Figure 1 *85 m/z SIM analysis of S-1. Pristane and phytane were confirmed by comparison with reference diesel and with qualifier ions 57 m/z, 71 m/z, 97 m/z, 113 m/z, 127 m/z and 183 m/z. Abcissa is minutes.*

From the SIM chromatogram (Figure 1) the sample S-1, appears to have undergone some degree of weathering of the *n*-alkanes *n*-C_{10} forward, while the *n*-C_{14} to *n*-C_{30} alkanes have some degree of biodegradation, however, microbial degradation is possibly inhibited by lack of bioavailability of compounds due to the refractory coal matrix effects within the sample[10]. Perylene 252 *m/z* was tentatively identified in S-1, and this compound is known to be of biogenic origin[7]. Figure 2, depicts the volatile petroleum hydrocarbon (VPH) analysis chromatogram for BTEX and *n*-alkanes *n*-C_{10} to *n*-C_{12} in S-1.

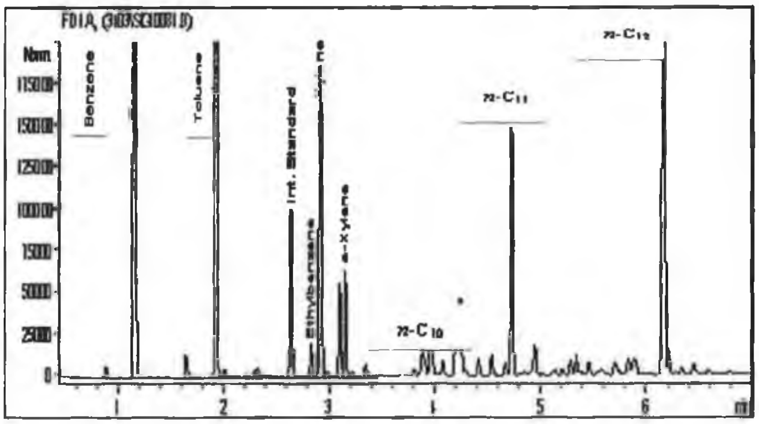


Figure 2 *VPH analysis of BTEX.*

The concentrations of benzene (51,056 µg/kg) and toluene (31,505 µg/kg) relative to the other constituents of ethylbenzene (2,043 µg/kg), total xylene (29,258 µg/kg), n-C_{10} to n-C_{12} (98,006 µg/kg) possibly indicate a contamination source of gasoline or a feed stock, coal tar, which was used in the 1950s in the gas works industry[11] with which S-1 is suspected of being contaminated[7].

A reference sample of Jeyes fluid, a light creosote[11], was compared to S-1, where the chromatograms were overlaid and the visually comparison (Figure 3) of the findings indicated a similar pattern. The characteristic broad peaks at the start of each chromatogram (Figure 3) are typical of phenol and its isomers.

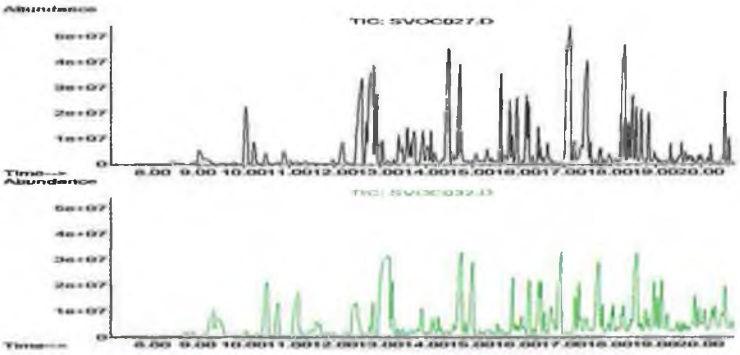


Figure 3 *GC/MS full scan. Top chromatogram; Jeyes Fluid, bottom chromatogram; S-1*

Creosote is known to contain phenol[7,11] 94 *m/z*, methylphenol 108 *m/z* and dimethylphenol 122 *m/z*, and these ions were extracted from S-1 by SIM and the ratios of each were compared to the reference creosote sample, Jeyes fluid. The phenol isomers present in S-1 showed a degree of degradation for dimethylphenol to methylphenol, but the normalised percentage contribution of this species was similar to that of Jeyes fluid.

3.2 Polycyclic Aromatic Hydrocarbon Data Analysis Using CORAT.

Qualitative chemical analysis and visual comparison of chromatograms of spilled sample by GC/FID or GC/MS, suspected candidate sources, and background materials may sufficiently meet the needs of most forensic investigation. However, when the chemical similarity/difference between spilled product and the suspected source is not obvious, or a large number of candidate sources are involved, or where the spilled product has undergone a degree of weathering, or significant alteration in its chemical composition, the qualitative approach can be difficult, and therefore the quantitative forensic fingerprinting analysis of degradation-resistant PAH compounds should be performed[8]. In this study a combination of both qualitative and quantitative analysis of the alkylated PAHs and USEPA priority pollutant PAHs was performed (Table 1).

Table 1 *Alkylated homologues PAH series and the USEPA Priority pollutant PAHs.*

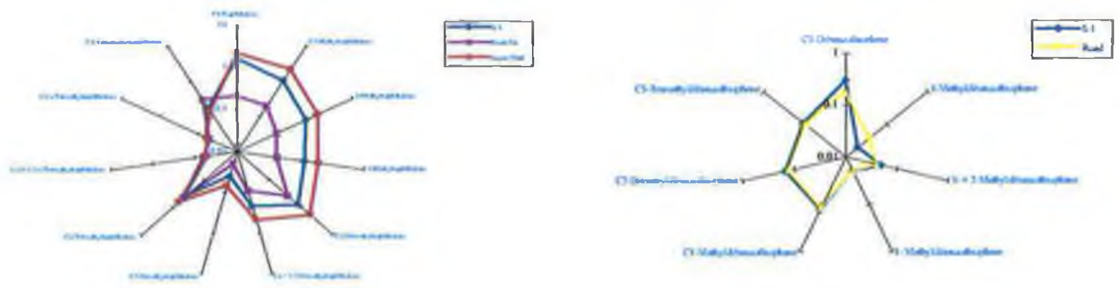
Compound	**Code**	**Ring No.**
Naphtalenes		
C_0-naphthalene	N	2
C_1-naphthalene	N1	2
C_2-naphthalene	N2	2
C_3-naphthalene	N3	2
C_4-naphthalene	N4	2
Phenanthrenes		
C_0-phenanthrene	P	3
C_1-phenanthrene	P1	3
C_2-phenanthrene	P2	3
C_3-phenanthrene	P3	3
C_4-phenanthrene	P4	3
Dibenzothiophene		
C_0-dibenzothiophene	D	3
C_1-dibenzothiophene	D1	3
C_2-dibenzothiophene	D2	3
C_3-dibenzothiophene	D3	3
Fluorene		
C_0-fluorene	F	3
C_1-fluorene	F1	3
C_2-fluorene	F2	3
C_3-fluorene	F3	3

Compound	**Code**	**Ring No.**
Chrysene		
C_0-chrysene	C	4
C_1-chrysene	C1	4
C_2-chrysene	C2	4
C_3-chrysene	C3	4
USEPA Priority PAH Pollutant		
Acenaphthylene	Acl	3
Acenaphthene	Ace	3
Fluoranthene	Fl	4
Pyrene	Py	4
Benzo(a)anthracene	BaA	4
Benzo(b)fluoranthene	BbF	5
Benzo(k)fluoranthene	BkF	5
Benzo(a)pyrene	BaP	5
Perylene	Pe	5
Indeno(1,2,3-cd)pyrene	IP	6
Dibenz(a,h)anthracene	DA	5
Benzo(ghi)perylene	BP	6
Anthracene	An	3

3.3 PAH Homologous Series Data Analysis

The fingerprinting and data analysis of the five homologous PAH series naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene were reviewed and a comparison between the reference products was made. The distribution patterns indicated for each series for S-1, to have a possible pyrogenic contaminant influence. Graphic display of selected peak ratios simplifies chromatographic interpretation. These ratios are best demonstrated in the form of logarithmic star plot. The best fit CORAT plots are illustrated in Figure 3. Petrogenic reference products demonstrated a characteristic bell-shaped distribution profile $C_0<C_1<C_2<C_3$, and all homologous PAH series indicated parent ion dominance with inhibited bioavailability of the alkylated isomers demonstrating relative high abundances compared to the petrogenic isomers of the same species. This inhibited bioavailability of the alkylated isomers is common feature of complex refractory coal matrix effects found in pyrogenic sources[8].

Naphthalene **Dibenzothiophene**



Phenanthrene **Fluorene and Chrysene**

Figure 4 *CORAT star plots for the normalised ratio distribution of the alkylated homologues series of naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene for S-1 compared to the best fit reference products. This demonstrates the pictorial power of CORAT in forensic fingerprint interpretation.*

3.4 Normalised USEPA Priority Pollutant PAH Distribution Patterns.

Petrogenic PAHs generally have lower proportions of unsubstituted compounds, like fluorene, phenanthrene, or chrysene, compared to certain alkylated substituted homologues. Pyrogenic PAHs, from combustion sources such as lubricant oil, domestic coal, road tar, South American crude bitumen and Jeyes fluid all used in this study have higher molecular weight four to five ring PAHs and relative greater concentrations of the unsubstituted compounds[8]. The distribution of the USEPA priority pollutant PAHs were normalised and the percentage of the individual PAH concentrations were calculated to the sum of the analytes and the results for each reference product distribution was pictorially compared using CORAT to S-1 (Figure 5).

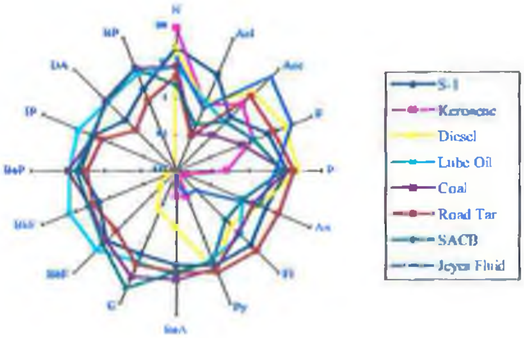


Figure 5 *CORAT star plot of normalised distribution profile of individual PAHs in the reference products compared to S-1.*

Each product has its own characteristic distribution of PAHs and CORAT analysis was used for its power to visually distinguish between each pattern which allowed for the "best fit pattern" to be determined from the reference products to S-1. Figure 6 demonstrates the best fit comparison which was found in this study.

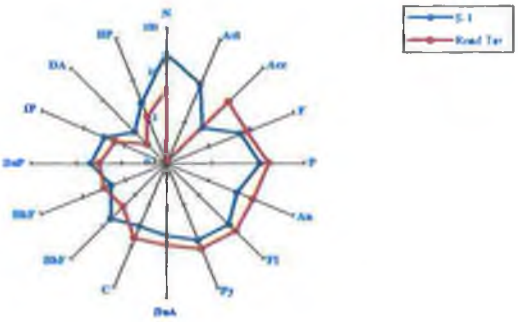


Figure 6 *CORAT "Best Fit" star plot of pyrogenic road tar vs. S-1.*

3.4 USEPA PAH Ratios

Three ring alkylated PAH compounds are used for source identification markers because their concentrations vary among products making them source specific[13]. In this study, PAH ratios are made of reference source products and compared to S-1. Numerous quantitative diagnostic ratios[6 - 8] have been defined to differentiate pyrogenic PAHs from other hydrocarbon sources, including phenanthrene/anthracene (Ph/An), phenanthrene/methylphenanthrene (Ph/m-Ph), fluoranthrene/pyrene (Fl/Py), benzo(a)anthracene/chrysene (BaA/Ch), phenanthrene/phenanthrene+anthracene (Ph/(Ph+An)), indeno[1,2,3-cd]pyrene/indeno[1,2,3-cd]pyrene+benzo[ghi]perylene (IP/(IP+BP))[7,8]. Figure 7 illustrates a CORAT plot of a number these ratios between two PAHs or ratio distributions between PAH homologues for each reference product compared to S-1.

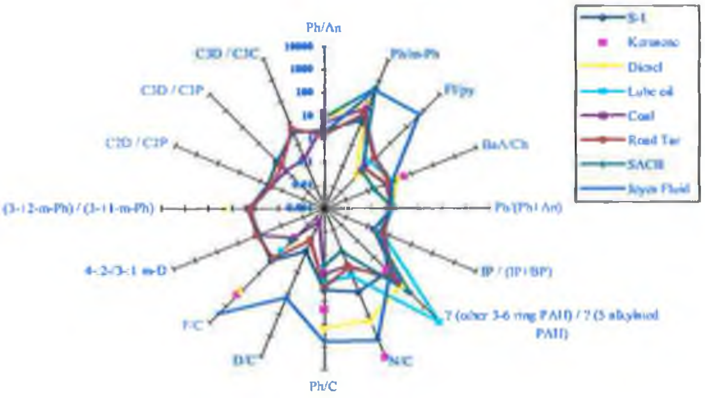


Figure 7 *CORAT logarithmic statistical analysis using multi PAH ratio star plot of reference products compared to S-1.*

A number of comparisons between the pyrogenic reference products coal and petrogenic diesel were noted and this confirms that these products may be present in S-1, however, the best fit for all of the diagnostic ratios was the pyrogenic road tar reference product (Figure 8).

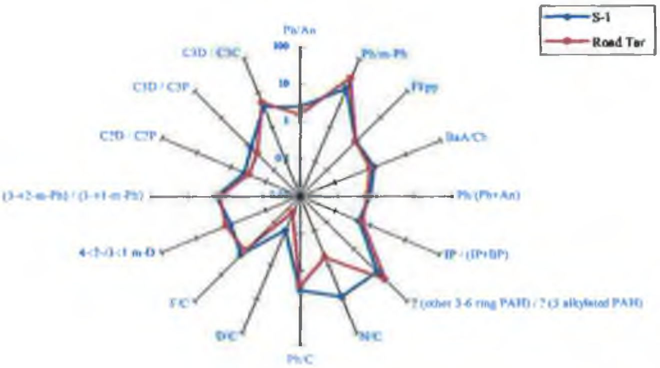


Figure 8 *CORAT star plot of logarithmic statistical analysis of multi PAH ratio plots of reference product road tar compared to S-1.*

The double ratio plots of alkylated PAH homologues, C2D/C2P versus C3D/C3P, can be used for identification and differentiation of petroleum product sources which has **been** developed and extensively used in the 1989 Exxon Valdez oil spill[14]. C3D/C3P and C3D/C3C have been defined as source ratios and weathering ratios[2]. All of these ratios have been used to help identify the possible source of S-1 in this study.

The relative distribution of phenanthrene isomers is subjected to little interference from weathering in short-term or light weathered products[3]. This information can be used to identify environmental factors. The phenanthrene distribution patterns in both the reference road tar and S-1 show a close relationship which gives indication that the sample was inhibited from microbial degradation.

The relative distribution of dibenzothiophene isomers have been reviewed in this study and used to successfully identify a possible pyrogenic source contamination. It was noted that the reference product diesel did not contain significant amounts of dibenzothiophene, which allows for the hypothesis that the sample S-1 was contaminated prior to 2000 when most commercial diesel contained higher amounts of sulphur-based compounds[7].

Combustion favours the less stable kinetic isomer over the more stable thermodynamic isomer of the same molecular mass[12]. The Ph/An and Fl/Py ratios were reviewed in S-1, and the relationship was similar to pyrogenic road tar. A method using the ratio Ph/An <10 and FL/Py >1 was used to identify contamination sources of a combustion process[12], with the ratio of S-1 for these PAHs falling within the range which may indicate a combustion source for the test sample.

The 1994 mobile Burn study[8] found that pyrogenic index can be used to differentiate pyrogenic and petrogenic PAHs. This relationship was reviewed for S-1 and it was found to be pyrogenic.

Enhancement of chrysene relative to other PAH series and significant decrease in the relative ratios of the sum of naphthalene, phenanthrene, dibenzothiophene and fluorenes to chrysene can be indicative of a pyrogenic source[8]. The distribution in S-1 was very similar to that of road tar, with the exception of naphthalene/chrysene. This discrepancy indicates a secondary source of naphthalene input, which confirms the hypothesis of the possible pyrogenic Jeyes fluid contribution to the contamination.

4 CONCLUSION

Statistical logarithmic star plots were generated from all sets of data to give a pictorial representation of the comparison between S-1 and the reference products. The study successfully characterised S-1 as being significantly contaminated with a coal tar feed stock, and clearly demonstrates the future role of compound ratio analysis technique (CORAT) in the identification of possible source contaminants.

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Is this Diesel mine...?
Advances in Forensic Identification Using Source Specific Markers of Petroleum Releases into the Environment

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Introduction

Recent developments in forensic hydrocarbon fingerprint analysis have enabled specific markers found in diesel to be characterised and identified. Fingerprinting and data interpretation techniques include the recognition of distribution patterns of hydrocarbons which include the alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene, chrysane and phenol isomers; analysis of 'source-specific marker' compounds, individual saturated hydrocarbons, including n-alkanes (n-C_8 through n-C_{40}), alkylcyclohexane homologues series, and the recalcitrant isoprenoids, pristane and phytane; the determination of diagnostic ratios of specific petroleum and non-petroleum constituents, and the application of various statistical and numerical analysis tools[1-5]. A spill sample was analysed to identify the possible source and origin of the petroleum contaminant (diesel). Samples were subjected to analysis by gas chromatography utilising both flame ionisation and time of flight mass spectral detection techniques (TOF-MS) in comparison to known reference materials. The analysis showed the diesel came from the suspected source. This allowed the regulator to prosecute.

The study follows the forensic investigation into the source identification of home heating fuel accidentally spilled when delivered to a domestic house. It was suspected that the homeowner was adding a petroleum product to the spill area to increase the value of the insurance claim. A sample was taken from the tank and compared to soil samples taken in the spill area.

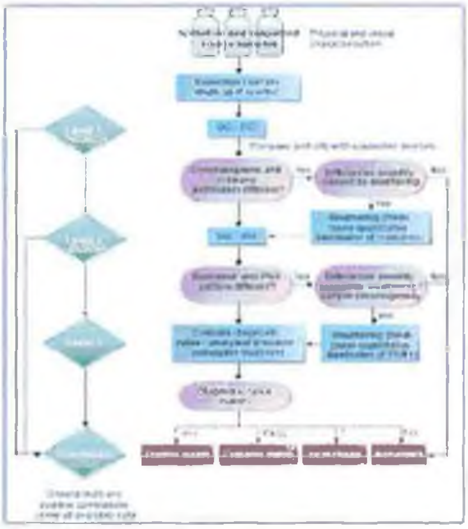
Analytical Approach

Hydrocarbon fuels and derivatives found in the environment are often characterised by gas chromatography/flame ionisation detection (GC/FID). The identification and interpretation of GC fingerprints is largely qualitative and subjective, as it is dependant upon the skill and expertise of the interpreter. It is for this reason that a tiered approach is adopted to give a quantitative and objective interpretation of the analytical data using the following[6]:-

Level 1 – Chemical Fingerprinting by GC-FID
Level 2 – Detailed Analysis by GC-TOF/MS
Level 3 – Statistical Analysis of the Data

Prior to analysis by gas chromatography the soil sample was coned and quartered and an aliquot was submitted for moisture content and a further aliquot was submitted for solvent extraction. This extract was analysed using the tiered approach (Figure 1)[6].

Figure 1 Tiered Three Level Approach[6]



Level 1 - Chemical Fingerprinting by GC-FID

Identification of the product type in contaminated samples is the single most important stage in any environmental forensic investigation as it frequently forms the foundation on which many of the relevant conclusions are derived. Among the analytical methods used to identify a wide range of contaminants are those that focus on specific hydrocarbon classes, such as alkanes and alkylated polycyclic aromatic hydrocarbons (PAHs). This screening Level 1, allows for the general characterisation of the sample for volatile petroleum hydrocarbons (VPH) in the carbon ranges n-C_5 to n-C_9, n-C_{9} to n-C_{12} and extractable petroleum hydrocarbons (EPH) in the carbon range n-C_{10} to n-C_{40}. The tank sample was characterised for both VPH and EPH (Figure 2). The EPH characterisation of the contaminated soil sample located around the spill site revealed a fingerprint profile indicating a bimodal unresolved complex mixture (UCM) profile (Figure 3). The observed carbon range n-C_{10} to n-C_{27} is characteristic of kerosene and diesel[illegible].

Figure 2 VPH and EPH Characterisation - Tank

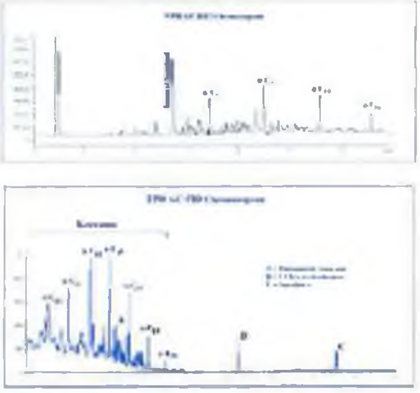
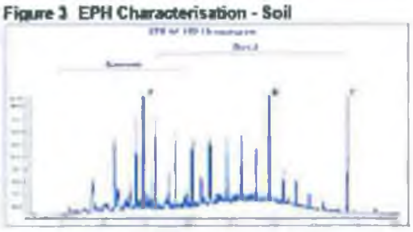


Figure 3 EPH Characterisation - Soil



Level 2 – Detailed Analysis by GC-TOF/MS

The next analytical "level" involves analysing the extracts and candidate source samples by Time of flight GC/MS (Figure 4). This helps determine the content and profile/distribution of a suite of petroleum or source specific alkylated PAH target analytes. The unique power of the time of flight mass spectral investigation involves the use of its deconvolution software combined with retention time locking (RTL) allowing for reduced risks of false positives[11].

Chemical analysis of source-characteristic and environmentally persistent source specific markers generates information to determine the possible source of spilled products, differentiating products, monitoring degradation and weathering under a variety of conditions. In the past decade, these fingerprinting techniques were used to study spilled products has greatly increased, and been playing a prominent role in almost all spill work[illegible]. In general qualitative chemical analysis and visual comparison of chromatograms of a contaminated soil sample by GC/FID or GC/MS determined in **Levels 1** and **Level 2** with suspected candidate source, may sufficiently meet the needs of most forensic investigation. Diagnostic information was obtained by examining the chromatographic data from the tank and soil samples using selected alkyl homologues of the primary PAHs. In addition, sulphur containing compounds such as dibenzothiophene and its alkyl derivatives were used to access the source[illegible]. Table 1 lists the alkylated PAH compounds, the number of benzene rings in each compound and the selected ion monitoring (SIM) mass to charge (m/z) ions used during this investigation[11].

Figure 4 TOF-GC/MS[11]

Table 1 Alkylated Polycyclic Aromatic Series[illegible]

Compound	Ring No	m/z
Naphthalene Series		
C_0-naphthalene	2	128 m/z
C_1-methylnaphthalene	2	142 m/z
C_2-dimethylnaphthalene	2	156 m/z
C_3-trimethylnaphthalene	2	170 m/z
C_4-tetramethylnaphthalene	2	184 m/z
Phenanthrene Series		
C_0-phenanthrene	3	178 m/z
C_1-methylphenanthrene	3	192 m/z
C_2-dimethylphenanthrene	3	206 m/z
C_3-trimethylphenanthrene	3	220 m/z
C_4-tetramethylphenanthrene	3	234 m/z
Dibenzothiophene Series		
C_0-dibenzothiophene	3	184 m/z
C_1-methyldibenzothiophene	3	198 m/z
C_2-dimethyldibenzothiophene	3	212 m/z
C_3-trimethyldibenzothiophene	3	226 m/z

However, when the chemical similarity/difference between spilled product and suspected source is not obvious, or a large number of sources are involved, or where the spilled product has undergone a degree of weathering, or significant alteration in its chemical composition, the quantitative approach can be difficult, and therefore the qualitative analysis of degradation-resistant PAH compounds should be performed[illegible].

Naphthalene Alkylated Series

Figure 5 depicts the TOF-GC/MS analysis of the tank sample selecting the m/z ions for the naphthalene alkylated series along with the chemical structure of naphthalene and its methyl naphthalene isomers. The individual isomers are targeted and the depletion of these isomers can be used to assess the degree of weathering or biodegradtion[12]. The fragmentogram indicated minimal depletion of the series[12].

Figure 5 Naphthalene Alkylated Series – Tank

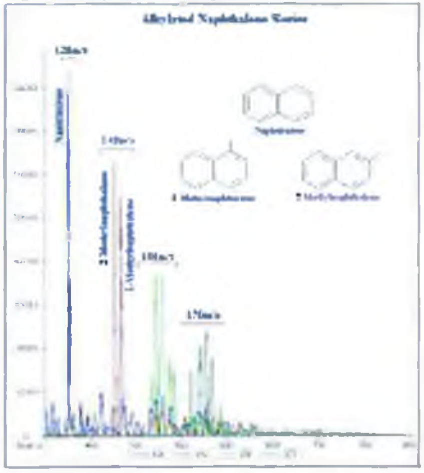
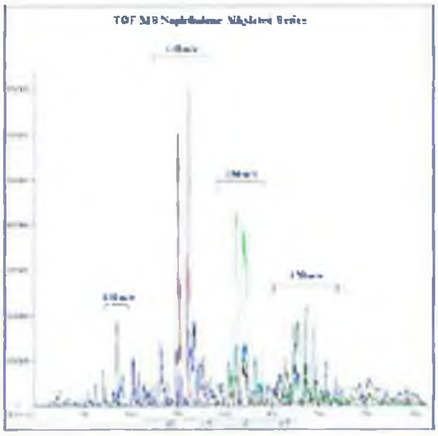


Figure 6 Naphthalene Alkylated Series -Soil



Phenanthrene Alkylated Series

A reduction in the ratio of 2-methylnaphthalene compared to the 1-methylnaphthalene isomer in the naphthalene series fragmentogram (Figure 6) indicated some weathering of the parent naphthalene ion. This indicates some alteration following the spill[12,20].

Another alkylated series is phenanthrene and its associated methylphenanthrene and dimethylphenanthrene isomers (Figure 7). The alkylated ions were monitored to target the selected ions for each phenanthrene isomer ($C_{14}H_{10}$). The presence and depletion of these isomers can give information about the degree of weathering, biodegradation or can be used in source correlation studies. The Tank sample (Figure 8) indicated the presence of no phenanthrene alkylated isomers which is characteristic of a kerosene fuel oil[illegible].

Figure 7 Chemical Structures of Phenanthrene Series

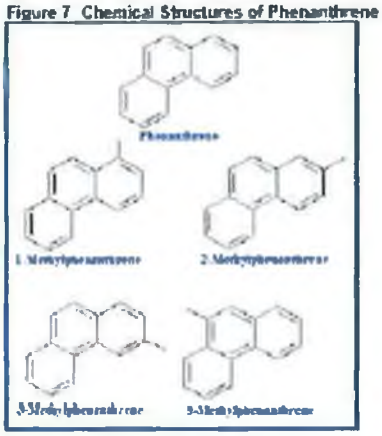
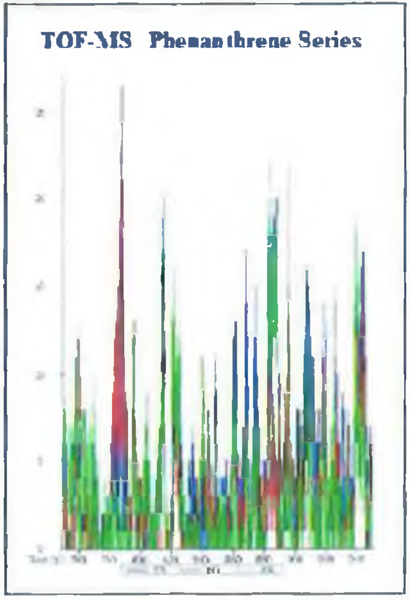
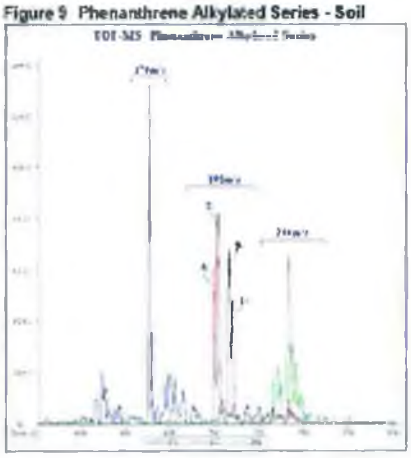


Figure 8 Phenanthrene Alkylated Series - Tank



The data obtained from the chromatogram of the soil sample was reviewed for the parent phenanthrene ion and its associated methylphenanthrene and dimethylphenanthrene isomers (Figure 9). The abundance of the series in the soil sample indicated a second source to the contaminated site which confirms the EPH bimodal chromatogram from the Level 1 investigation[4,5,8,10,12-20].

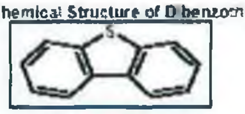
Figure 9 Phenanthrene Alkylated Series - Soil



Dibenzothiophene Alkylated Series

A similar approach was used for dibenzothiophene (Figure 10) alkylated series as for naphthalene and phenanthrene isomers[7,18].

Figure 10 Chemical Structure of Dibenzothiophene



The fragmentogram of the data obtained from the Tank sample indicates an abundance of tetramethylnaphthalene isomers (184m/z). This confirms the abundance of the naphthalene series in kerosene. The same ion is used to select the parent dibenzothiophene compound which is absent from the fragmentogram (Figure 11)[7,18].

Prior to the year 2000, diesel contained a range of sulphur compounds[7,19] the introduction of low sulphur diesel resulted in the reduction of the sulphur isomers in diesels. The presence or absence of these isomers can be used to age products as well as being used to correlate source. The abundance of the dibenzothiophene series confirms the findings of the phenanthrene series (Figure 12)

Alkylcyclohexane Series

Another group of compounds namely alkylcyclohexanes was also targeted in both samples. These compounds belong to a class of naphthenes or cycloparaffins, the most common molecular structures found in petroleum. These compounds form a homologous series similar to n-alkanes but are more resistant to biodegradation. These homologous series of compounds are present in refined oils such as gasoline, kerosene and gas oil but the profile and distribution patterns are different. For gasoline, the distribution exhibits an asymmetric rapidly decreasing pattern from methylcyclohexane to heptylcyclohexane. Kerosene is characterised by a distribution pattern in the range ethylcyclohexane to decylcyclohexane with a maximum abundance at propylcyclohexane. Gas oil exhibits a much wider range from methylcyclohexane to hexadecylcyclohexane with a maximum at nonylcyclohexane (Figure 13 and 14). The profile can be used to determine the type of product present or can be used to assess whether mixtures of products are present and the degree of weathering or biodegradation[7].

Figure 11 Dibenzothiophene Alkylated Series – Tank

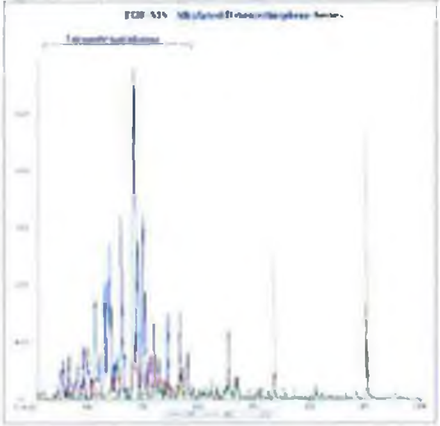
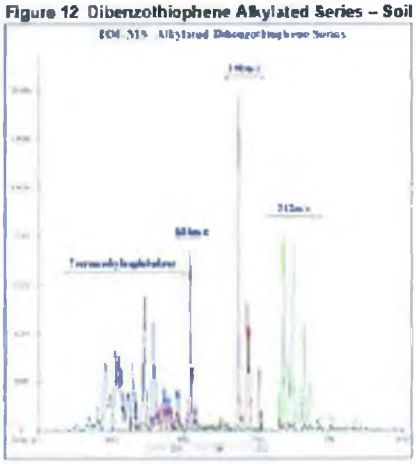


Figure 12 Dibenzothiophene Alkylated Series – Soil



The data obtained from the analysis of the Tank sample clearly demonstrates a distribution of the alkylcyclohexane series for methylcyclohexane to decylcyclohexane with a maximum at propylcyclohexane. The typical distribution for a diesel was observed for the Soil sample[7].

Figure 13 Alkylcyclohexane Series -Tank

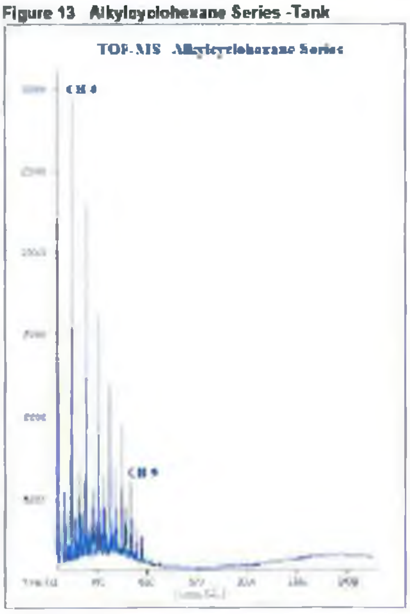
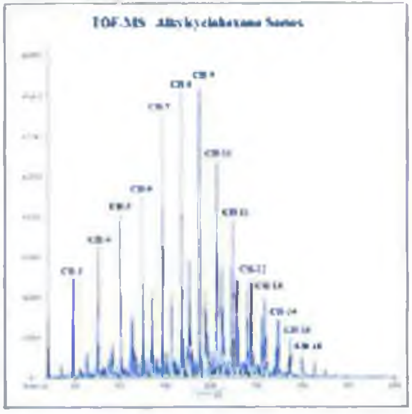
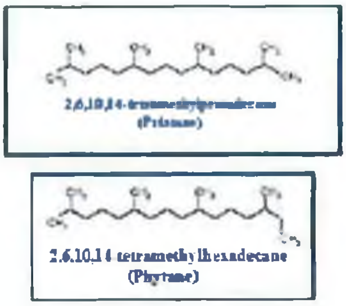


Figure 14 Alkylcyclohexane Series - Soil



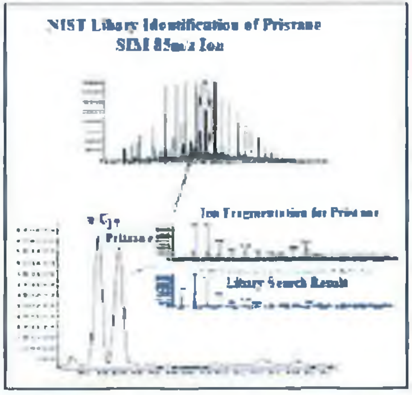
Pristane and Phytane
The source specific markers in diesel typically used in age analysis are the recalcitrant isoprenoid compounds of which the two most abundant are pristane and phytane (Figure 15). The degree of change in diesel within the subsurface environment may be measured by comparing ratios of compounds with different physical, chemical or biological properties. The n-alkanes are readily biodegraded and the pristane and phytane are recalcitrant and therefore ratios of these compounds can be used. The most common ratios are n-C_{17}/pristane, n-C_{18}/phytane and pristane/phytane[illegible].

Figure 15 Pristane and Phytane Chemical Structures



The soils sample data for the fragmentogram was reviewed for the ion 85m/z and the resulting fragmentogram was compared to the NIST library using the Time of Flight deconvolution software. The comparison indicated a 96% match to the library example of pristane (Figure 16)[7,9,10,23].

Figure 16 Pristane Identification – Soil



The presence of these markers confirms the addition of diesel to the contaminated site where the kerosene was spilled

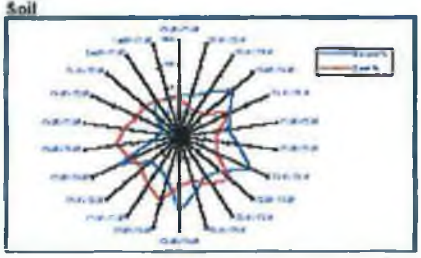
Level 3 – Statistical Analysis of the Data
Having conducted Level 1 and 2 investigations, data obtained from both these procedures can be utilised in various mathematical routines to determine the degree of similarity to reference materials, degrees of weathering and / or biodegradation. Evaluation of those diagnostic ratios

exhibiting considerable variability due to analytical variance and sample heterogeneity is determined using Compound Ratio Analysis Technique (CORAT).

Compound Ratio Analysis Technique (CORAT)

In modern forensic investigations, various analysis techniques have been developed and applied to data interpretation. The application of sophisticated statistical analysis techniques for analysis is a relatively new phenomenon of which compound ratio plotting is one such approach. This is a dynamic area of research which enhances the interpretive power of hydrocarbon fingerprinting and promises to greatly improve the identification of spill sources. CORAT is a combination of analytical and interpretive techniques that utilises "fingerprint" chromatograms of crude oil samples used in the petroleum geochemistry industry. This technique has been adapted in this study to review the compositional variations of source specific PAH markers in the Tank reference product and compared to the contaminated Soil sample to try and determine whether the origin of the source of contaminant. Since a GC fingerprint is a representation of the relative concentrations of compounds present in a sample as analysed, it can be used for the relative abundances and distribution of each compound and then plotted on a star plot diagram. This technique assesses whether or not two or more products correlate by comparing the relative abundance of selected compounds obtained from the chemical fingerprint and rationing them to each other. Values for these ratios for each sample product are plotted on a polar CORAT star plot. On such diagrams the composition of each product is represented by a star in which each point on the star corresponds to the value for a given peak ratio (Kaufman et al., 1990). Figure 17 reviews the differences between the kerosene which was found in the Tank and diesel in the soil samples which appears to be added after the initial spill. The star plots differ for the naphthalene series which suggests two possible sources of contamination at the site[illegible, 10].

Figure 17 Naphthalene Series CORAT – Tank and Soil



Conclusions

The review of the Tank and Soil samples for the naphthalene, phenanthrene and dibenzothiophene alkylated series confirmed two sources of contamination at the spill location. The identification of the source specific markers found in diesel and the EPH chromatogram indicated the presence of this petroleum product.

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Appendix 2

Appendix 2 Fragmentograms

Figure 3.25 Naphthalene Alkylated Series

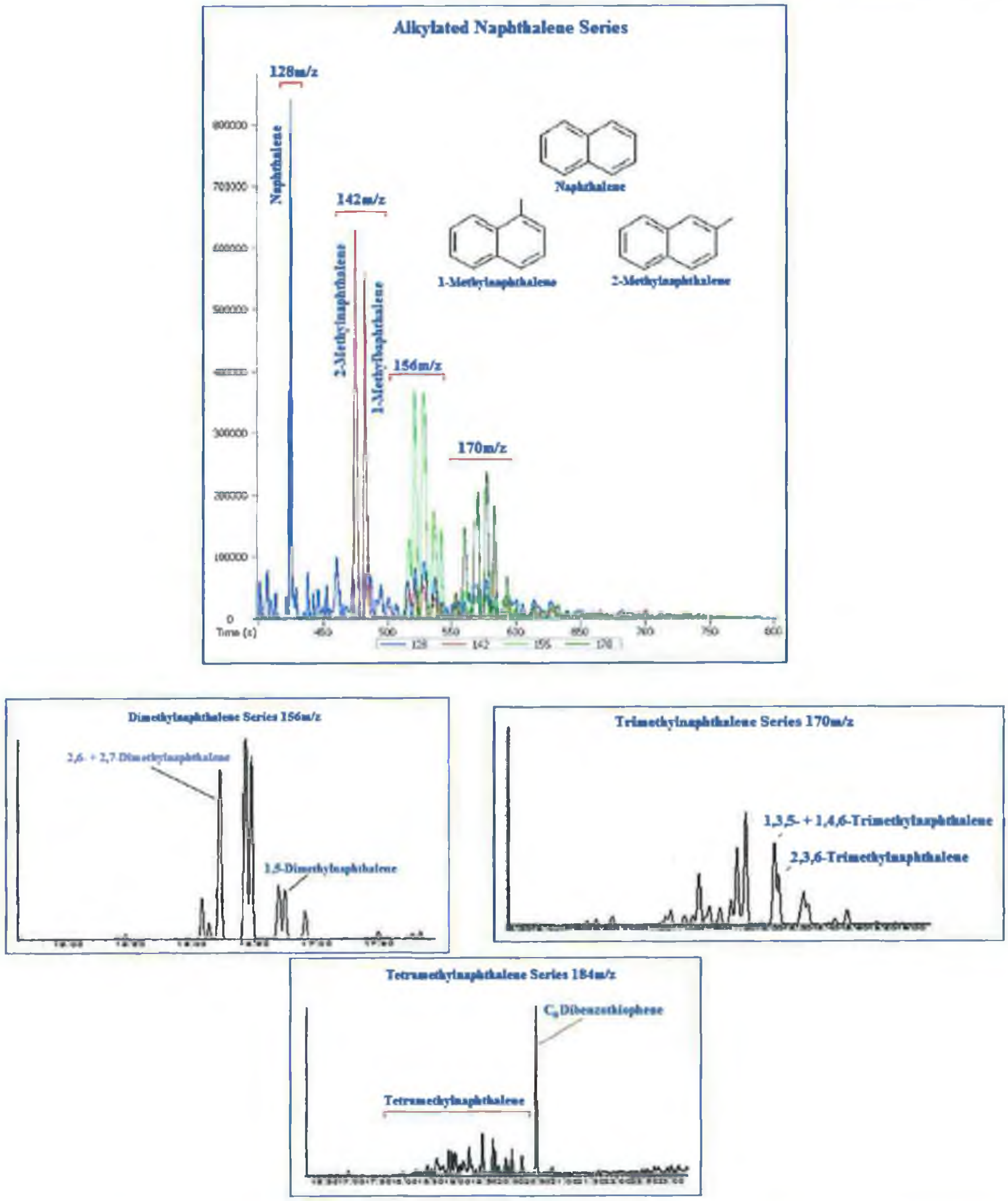


Figure 3.29 Phenanthrene Alkylated Series

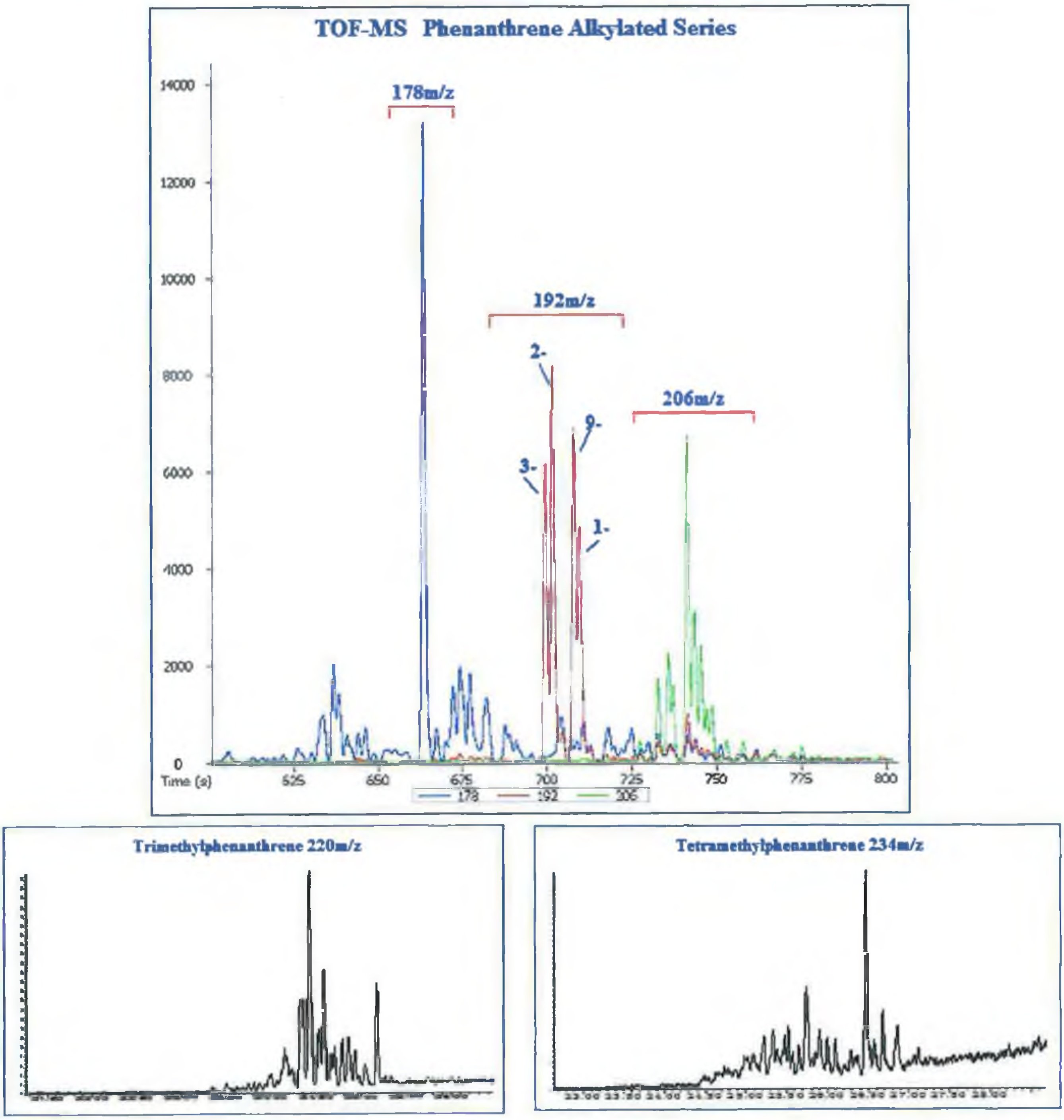


Figure 3.34 Dibenzothiophene Alkylated Series

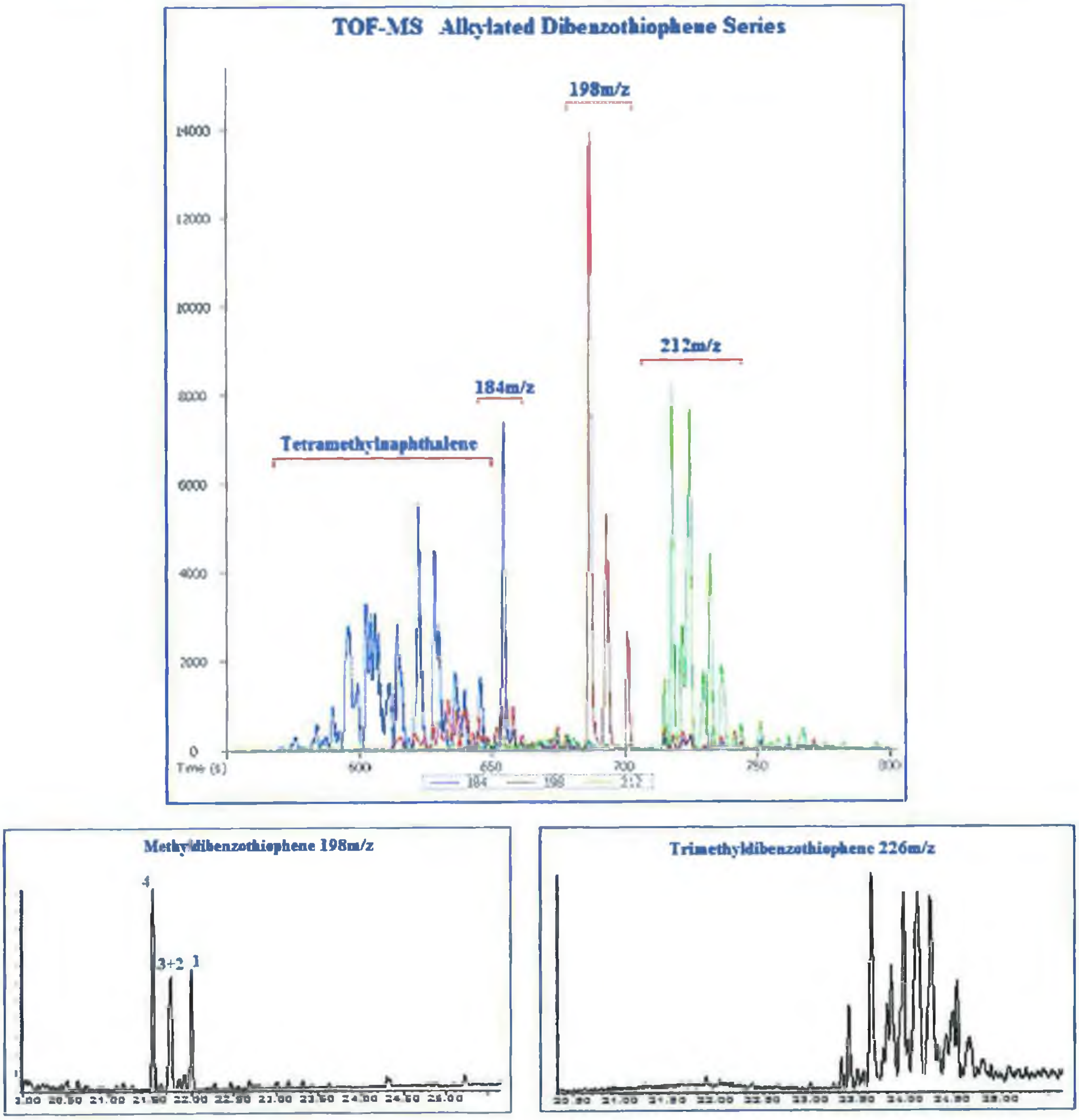
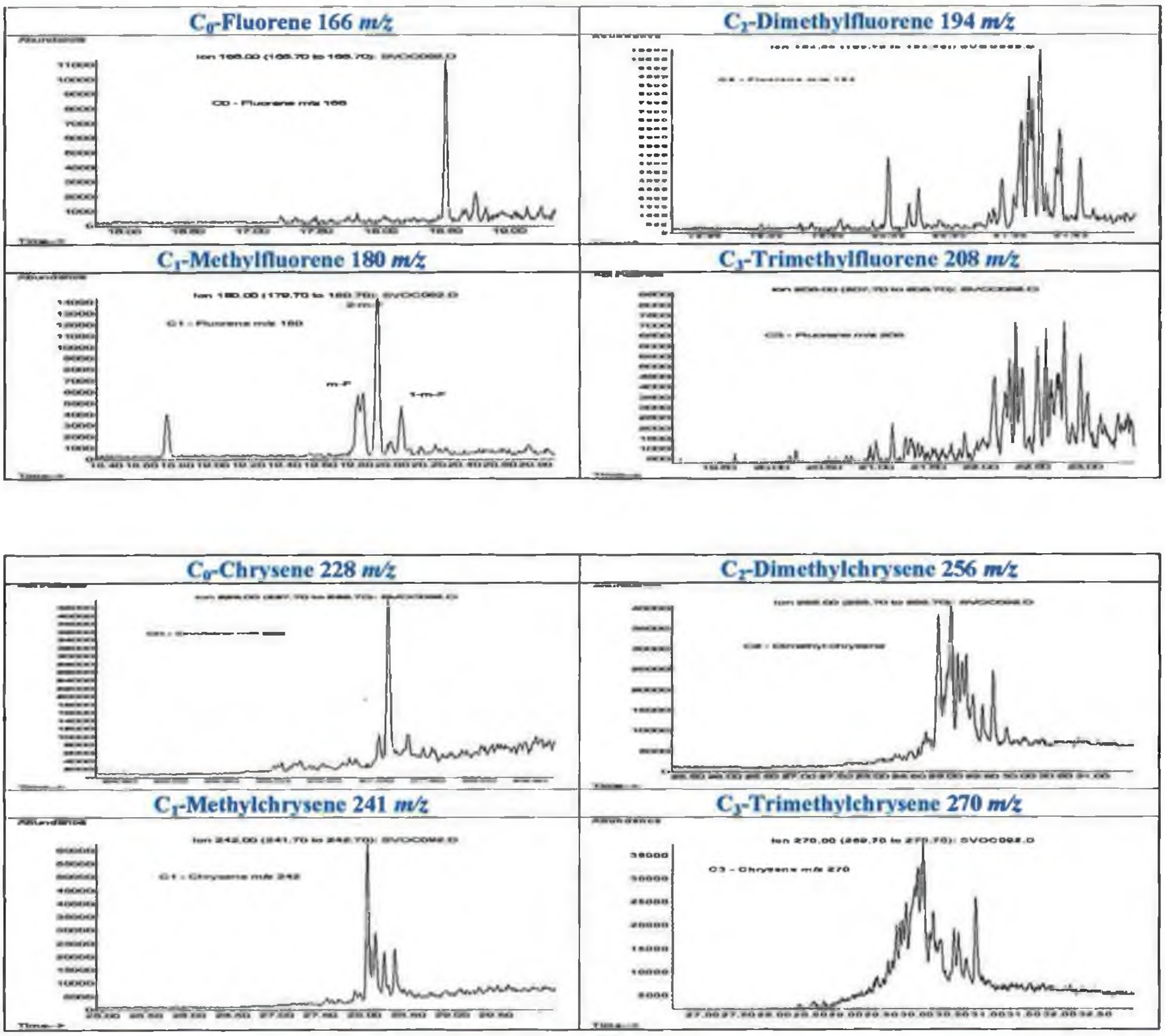


Figure 3.38 Fluorene and Chrysene Alkylated Series



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