INTRODUCTION

Environmental policies in various industries are based upon comprehensive analysis of air, water and soil pollution and aim to protect the environment. Regulatory bodies, such as the United States Environmental Protection Agency (USEPA), ensure that industry complies with regulations before considering to issue permits for the facilities and activities. The central concepts driving the new policy direction are that pollution releases to each environmental medium (air, water and soil) have the potential to impact all other environments, leading to a need for comprehensive assessment and management strategies.

Figure 2.1: Illustration of the close relationship among the air, water and earth environments with each other and with living systems, as well as the tie-in with technology.
Environmental strategies must actively identify and address these interrelationships by designing policies for the "whole" facility.

The iron and steel industry produces iron and steel mill products, such as bars, strips, and sheets, as well as formed products such as wires, rods, and pipes. Blast furnace products also include coke, coke gas and products derived from chemical recovery in the coking process such as coal tar and distillates. In the by-products recovery process, volatile components of the coke oven gas stream, such as naphthalene, ammonium compounds, crude light oils, and sulphur compounds, are recovered. Coal tar is a heterogeneous mixture of various classes of compounds, as illustrated in Figure 2.2, where the compounds of most frequent occurrence in coal tar is shown. These compounds can be divided into two groups:

- LNAPLs [Light Non Aqueous Phase Liquids] containing compounds such as benzene, ethyl benzene, toluene and xylenes.
- DNAPLs [Dense Non Aqueous Phase Liquids] containing compounds such as the PAHs and alkyl-PAHs

The analysis of these compounds is important because of their toxicity and the wealth of information that can be obtained from the quantitative results of the PAHs and their alkyl homologues. The most frequent interpretative uses of the analytical results include advanced chemical fingerprinting and hazard identification. The production and transportation of coal tar and light oil in the steel industry has been subject to many accidents involving spills. Experts see the cokemaking process as one of steel industry's areas of greatest environmental concern.

Figure 2.2: Compounds of most frequent occurrence in coal tar

Benzo[a]pyrene, benzo[b]fluoranthene and dibenz[a,h]anthracene are individual PAHs that occur in coal tar related products and are listed as part of the “Top 20 Hazardous Substances” by the ATSDR/USEPA. The focus in this study is, therefore, to investigate the analytical methods that can be used to analyse DNAPL components in soil and water samples and the usefulness of the analytical data obtained for interpretative methods.

The DNAPL problem

Due to continuous spills over a few decades the DNAPLs will form pools or "toxic blobs" of coal tar in the geosphere. DNAPLS also have been called "sinkers" because they are heavier than water and sink until they hit an aquitard, a change in soil type or density. DNAPL movements are directed more by gravity than the flow of groundwater. If the base of the aquifer slopes in one direction, then the DNAPL will flow in the same direction seeking the lowest point. Once they reach the low point of their descent, these pools of toxic waste will slowly dissolve in the surrounding water in the form of small contamination plumes. Since DNAPLs have low solubility points, they can continue releasing small quantities of contaminants into the groundwater for centuries. What makes DNAPLs so dangerous is the fact that they all degrade to other compounds, which might be even more insidious. The formation of DNAPL pools is illustrated in Figure 2.3.

Warning signs of a DNAPL problem

Although all forms of NAPLs share low solubility points to varying degrees, only DNAPLs are heavier than water, which make them very difficult to find and to effectively remediate. Typically, the first indication that a site may have a potential DNAPL problem occurs during a phase 1 site assessment. A key element of a Phase 1 assessment is a detailed review of the site's history and use, including a record of all chemicals that may have been released on the site (see Figure 2.13). Even after a determination is made that DNAPL compounds were released, the likelihood of a DNAPL groundwater problem will still depend on such factors as the total quantity of the release, the period of time over which the release occurred, and the make-up of the saturated soils. If the site history reveals significant releases of DNAPL compounds, then the next phase of site characterisation should include actual soil and groundwater tests to determine if DNAPLs are present in the soil. Once a determination has been made that a DNAPL problem appears likely, then more invasive procedures are required to measure the severity and extent of contamination. The most common techniques include borings and drilling of monitoring wells at various strategic points and at different depths on the site. Computer modelling of groundwater and contaminant flows at the site and "behavioural" characteristics of the DNAPL can assist in estimating the location and migration of the pool and resulting plume without additional invasive testing. Modelling also helps to further focus sampling efforts to intersect the most likely pathways of contamination and perhaps even to locate the pools of DNAPL. The LNAPLs (light non-aqueous phase liquids) are also useful for modelling purposes and contain compounds such as benzene, toluene, ethyl benzene and xylenes (BTEXs).

Sources and occurrence of PAHs in natural waters

The discharge of coal tar products, refined petroleum products and lubricating oils into the environment is among the common anthropogenic sources that have degraded the quality of water and sediment, impacting on health and biota. As indicated previously, coal tar contains a wide variety of chemical components that can pollute the hydrosphere.
The concentration of coal tar components in aqueous samples is often in the low part per billion (ng/cm³) to part per trillion (pg/cm³) range due to the low solubility of heavy PAHs and partitioning of all PAHs back into stream sediments. Certain aromatic compounds have the potential to damage resources at low levels and can affect the health of animals and humans in a contaminated area. The European Community directive 80/778/EEC states a maximum level for PAHs in drinking water of 0.2 ng/cm³. Fluoranthene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene were used as indicators to arrive this standard. This is a generic figure that is used for overall assessment of contaminant levels to identify a hazard, but it cannot be used as such for health risk assessments. For that purpose the individual levels of PAHs must be known because individual PAHs each has a different relative potency.

CHEMICAL ANALYSIS TECHNIQUES

During the past decade environmental laboratories have put considerable effort into the development of analytical methods for the determination of PAHs in environmental soil and groundwater samples, and the use of the analytical chemical data in interpretation techniques. These methods mainly rely on a solvent extraction step to isolate the target analytes from the soil or water matrix, followed by a concentration step and finally an instrumental analysis technique. High Performance Liquid Chromatography (HPLC) methods are often preferred for the determination of low levels of PAHs in water samples, due to the sensitivity of the method. A disadvantage of the EPA HPLC method 8310 is its dependence on retention time for compound identification. Another technique that is frequently used by the USEPA is the Infrared Spectroscopy Method 418.1 (EPA, 1983), which is designed to determine the Total Recoverable Petroleum Hydrocarbons, using Soxhlet or sonication extraction. Douglas and co-workers³ reported that negative method bias may result when samples are analysed by this method.
because of:

- Poor extraction efficiency of freon for high molecular weight hydrocarbons
- Loss of volatile hydrocarbons during extract concentration
- Differences in molar absorptivity between the calibration standard and product type
- Fractionation of soluble low-IR-absorbing aromatic hydrocarbons in groundwater during water washout
- Removal of 5- to 6-ring alkylated aromatics during silica cleanup procedure
- Preferential biodegradation of n-alkanes

They also showed that other EPA methods are used for identifying and quantifying certain hydrocarbons present in petroleum products. EPA method 602 (EPA, 1983), 624 (EPA, 1983), and 8240 (EPA, 1986) for analysing volatile hydrocarbons are adequately sensitive, but identify only a limited number of components in petroleum, thus making it difficult to identify the source. To be suitable for advanced chemical fingerprinting, the method must also include the identification and quantification of compounds that are target specific indicators.

Many laboratories have modified EPA and American Society for Testing and Materials (ASTM) protocols to be better suited for the chemical fingerprinting of environmental samples. The combined technique of high-resolution capillary GC and MS is normally ideal for this purpose and is discussed below.

### Gas Chromatography/Mass Spectrometry

Sauer and Boehm showed that the identification of a single PAH compound, using EPA Method 8270, is difficult when petroleum hydrocarbons are present in the sample. The method also lacks chemical selectivity (i.e. types of constituents analysed) and chemical sensitivity (i.e. analytical detection limits). These deficiencies yield a larger problem, namely the inability to interpret the data for scientifically defensible environmental damage assessments. Detection limits of 10 pg/cm³ for individual PAHs are normally required for chemical fingerprinting. Douglas reported an improvement in the detection limit of USEPA Method 8270 from parts per million to the parts per trillion level, by basically:

- using the mass spectrometer in the single ion monitoring (SIM) mode
- concentrating the final extract to 250 µl
- increasing the sample size.

Through this approach the contaminants from petroleum and coal tar sources (PAHs and volatile aromatic hydrocarbons) can be quantified at very low (ppt) levels. Analysis by GC/MS is necessary to enable analysts to focus on complex PAH patterns and to determine concentrations of specific PAHs, including their alkylated homologues and isomers. The complexity and uniqueness of these compounds that contain a wealth of “finger printable” information at trace levels can only be studied using a more selective and sensitive analytical method, such as GC/MS.

### Solid Phase Microextraction (SPME)

The technique of SPME was introduced by Pawliszyn in 1989 and has shown advantages such as solvent free extraction, relatively short analysis turnover time and possibilities for automation. Typically a fused silica fiber, coated with a thin layer of polymeric stationary phase, is submerged into a water sample or in the headspace of a soil sample to extract the analytes. Once the analytes are adsorbed the fiber is inserted into the injection port of a gas chromatograph for thermal desorption. Phases such as polydimethylsiloxane (non-polar) and polyacrylate (polar) are currently commercially available. Applications of these phases for the analysis of a variety of
volatile components, including PAHs, have been reported. Liu et al. and Zhang and Pawliszyn showed the potential of applying headspace SPME for analyzing organic compounds in a variety of matrices, including soils and sludges. PAHs can be extracted from aqueous samples with SPME using a non-polar phase fiber such as the 100μm polydimethylsiloxane. The technique has since been developed for a variety of compound classes and has earned a reputation for its simplicity, speed, high sensitivity and selectivity. The extraction of organic compounds using the SPME technique eliminates most drawbacks to extracting organics and detection limits in the pg/cm³ range can be achieved. SPME is suitable to extract PAHs directly from a water matrix or in the headspace of a soil sample. A schematic diagram of the technique is shown in Figure 2.4.

The basic theory behind SPME has been detailed in previous publications. It has also been reported that the distribution coefficient (K) of alkyl substituted compounds vary with different degrees of alkylation. This is because PAHs with side chains are more soluble in the hydrophobic stationary phase, improving the partitioning into this phase. This is an advantage for chemical characterization purposes because it will result in an increase in the detection limits of alkyl-PAHs, which is ideal or the purpose of this study. Due to the absence of standards, however, the quantification of alkyl-PAHs is complex, especially when using an equilibrium technique such as SPME. This is due to the differences in extraction efficiencies with a single extraction step, which will introduce errors when using the parent PAH response factors and internal standards. Typically, an enhanced profile will be obtained for compounds with a higher degree of alkylation. It is possible to overcome this problem by using the technique of multiple extraction MESPE. This technique calculates the total area of an analyte in solution by using the data of two consecutive extractions and, therefore, allows for differences between the extraction efficiency of parent and alkyl-PAHs.

**SPME Device for GC Application**

[SPME device diagram]

**Figure 2.4**
Accelerated Solvent Extraction

Pressurised Liquid Extraction (PLE), also known as Accelerated Solvent Extraction (ASE™), is a relatively new extraction technique. The method is based on the principle that a solvent is pumped into an extraction cell that contains the soil sample, which is then brought to an elevated temperature and pressure. A schematic diagram of the technique is shown in Figure 2.5. This method replaces the traditional Soxhlet extraction technique. The advantages of PLE are the use of less solvent, convenience, efficiency and analysis speed. Typically, a 10 gram sample can be extracted in about 15 minutes with a total solvent consumption of about 15 cm$^3$. PAH recoveries are reported to be equivalent to traditional methods and meet the requirement for the extraction of solid waste as described in USEPA$^{15}$ method 3545. Following the extraction step, the extract is transferred from the heated cell to a standard collection vial for clean-up, pre-concentration and analysis. For a quantitative determination of individual PAHs, the extraction step is then followed by a GC/MS analysis.

Figure 2.5: ASE Schematic Diagram
CHEMICAL CHARACTERISATION
The development of Chemical Fingerprinting Techniques

In the following paragraph a review about hydrocarbon fingerprinting, which was published by Page et. al.16, is discussed. They indicated that most work conducted in organic geochemistry before the 1960s focused on the exploration of fossil fuels. Petroleum chemistry and hydrocarbon fingerprinting developed further in the 1970s with the passage of certain environmental regulations in the US (e.g. the clean water act). GC was one of the earliest techniques to examine alkane distributions in fresh oils. The application of alkane fingerprinting was very limited because the GC patterns changed over time due to the effects of evaporation, biodegradation, dissolution and photo-oxidation. Although GC analyses of alkanes are still in use, they represent only part of fingerprinting methodology. The GC methods have since been replaced by more advanced techniques such as GC/MS, which focus on other classes of compounds, especially the alkyl-PAHs. Fingerprinting of hydrocarbons is made possible by the variety of individual PAH compounds found in hydrocarbon sources and in the great variability in the relative abundances of these compounds among different sources. PAH analyses were first applied to oil spills to determine the composition of the more toxic fraction of petroleum and to examine the weathering of hydrocarbons. After the Exxon Valdez tanker incident on the 24th of March 1989 and the release of 11 million gallons of oil into Prince William Sound, a need existed for advanced method of chemical characterisation. It was necessary to investigate the rates of weathering of the oil, the changes that occurred during these weathering processes and to differentiate between petroleum sources and coal tar sources.

Chemical Fingerprinting objectives

The interpretation methods that were developed during the Exxon Valdez investigations17, serve as a basis for environmental pollution characterisation. Hydrocarbon fingerprinting involves the comparison of specific chemical patterns that will distinguish potential sources from each other and from background levels. For example, conventional gas chromatograms of diesel fuel, lubricating oil, crude oil and coal tar can reveal the presence of PAHs in all cases, but they exhibit different chromatographic profiles. Chemical mixtures that leak into the water leave behind a characteristic pattern. A suit of sampling, chemical analysis and data interpretation strategies enables chemists to identify specific contaminant sources and to link a wide range of pollutants to their sources. Advanced chemical fingerprinting is the appropriate technique for land-based and aquatic site contamination assessment and cost allocations for remediation of problems associated with crude oil releases. This approach employs chemical analysis technology to identify the constituents of complex chemical mixtures, and/or unique chemical markers, then matches the patterns of those constituents against chemical patterns of potential sources. As indicated in the review by Page et.al.16, chemical fingerprinting has, over the last two decades, evolved into a science by which original source(s) of complex chemical mixtures (e.g. petroleum or coal tar) can often be identified. They showed that the relative abundance of key individual compounds (especially two to four ring PAHs, and three ring heterocyclic dibenzo thiophenes) forms a chemical pattern that can be used for source identification. There are two major objectives5 in the chemical characterisation of contamination in environmental samples:

Short-term: To characterise the hazard and to determine the concentration of the environmentally important hydrocarbon constituents in the contaminated samples. These constituents include those that are immediately toxic to organisms and those
that would be considered carcinogenic to organisms. The intent is to determine the potential toxicity of the coal tar components as it is transported in the water and to help estimate what components would be available to affect a particular habitat.

Long-term: The application of advanced chemical fingerprinting to determine the concentration of major hydrocarbon constituents that would be valuable as source indicators and of the fate and weathering of the coal tar in the environment. Concentrations of key individual components or reference compound are used to evaluate the coal tar's behaviour and its toxicity as it persists in the environment. The following advances in chemical fingerprinting techniques have been reported:

Source discrimination based on the hydrocarbon distribution pattern

The compounds that are commonly measured for these studies include the 16 U.S. EPA priority pollutant PAHs, their associated alkylated homologues and selected heterocyclic compounds. A list of analytes and abbreviations are given in Table 2.1. The method used for source discrimination involves profiling the alkyl substituted homologous series, e.g. C0 - C4 naphthalenes, C0 - C4 phenanthrenes, C0 - C4 fluorennes and C0 - C4 chrysenes. The results are normally presented as an analyte profile histogram and accurate quantitative data for each alkyl homologue is necessary for this purpose. The parent PAH is accurately quantified with the help of internal standards and the alkyl homologue concentrations are then calculated, assuming the same response factor for each respective molecular ion signal. All the isomers within an alkyl homologue are grouped together for this purpose. The fundamental differences in the distributions of PAHs are used to distinguish between different sources. The characteristic profiles of various sources of pollution, which were obtained from Ad Little Inc, Acorn Park, Cambridge, are illustrated below:

Petrogenic hydrocarbons (Figure 2.6): These sources are characterised by their distributions of alkylated homologues of naphthalene (N), fluorene (F), phenanthrene (P), dibenzothiophene (D) and chrysene (C), where the parent PAH for each series is least abundant18.

Pyrogenic hydrocarbons (Figure 2.7): These sources are combustion related that produce PAH distributions dominated by the parent compounds of two to four ring PAHs and containing large quantities of fluoranthene (FL) and pyrene (PY)18. The characteristic profiles are used to establish chemical matches between one “suspect” oil and the petroleum in an environmental sample, and to distinguish between petrogenic and non-petrogenic sources3.

Degraded oil (Figure 2.8): The profile of degraded oil is typical petrogenic and dominated by phenanthrenes, dibenzothiophenes and chrysenes. A build-up of heavy PAHs and C3 - C4 alkyl PAHs is observed in degraded samples. The build-up of C4-P > C3-P > C2-P can, for example, be observed in the figure. It is also evident that the C1- to C4-chrysenes are very resistant towards weathering as only a slight change in the relative abundances of alkylated chrysenes can be observed.

Diesel oils (Figure 2.9): The characteristic profile of typical diesel oil is dominated by phenanthrenes, dibenzothiophenes and chrysenes. A build-up of heavy PAHs and C3 - C4 alkyl PAHs is observed in degraded samples. The build-up of C4-P > C3-P > C2-P can, for example, be observed in the figure. It is also evident that the C1- to C4-chrysenes are very resistant towards weathering as only a slight change in the relative abundances of alkylated chrysenes can be observed.

Atmospheric deposition (Figure 2.10): A characteristic profile is mainly dominated by heavy PAHs (four to six ring structures). Atmospheric deposition normally occur near airports or industry where aerosols fall to the ground.

Creosote (Figure 2.11): Anthracene, phenanthrene, chrysene, fluoranthene and pyrene dominate the profile (naphthalenes and other light PAHs are absent).
Table 2.1: Analytes measured for source discrimination based on hydrocarbon distribution patterns showing abbreviations

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>Naphthalene</td>
<td>N</td>
</tr>
<tr>
<td>C₁-Naphthalenes</td>
<td>C₁-N</td>
</tr>
<tr>
<td>C₂-Naphthalenes</td>
<td>C₂-N</td>
</tr>
<tr>
<td>C₃-Naphthalenes</td>
<td>C₃-N</td>
</tr>
<tr>
<td>C₄-Naphthalenes</td>
<td>C₄-N</td>
</tr>
<tr>
<td>acenaphthylene</td>
<td>AE</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>AC</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>BI</td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>DI</td>
</tr>
<tr>
<td>Fluorene</td>
<td>F</td>
</tr>
<tr>
<td>C₁-Fluorenes</td>
<td>C₁-F</td>
</tr>
<tr>
<td>C₂-Fluorenes</td>
<td>C₂-F</td>
</tr>
<tr>
<td>C₃-Fluorenes</td>
<td>C₃-F</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>P</td>
</tr>
<tr>
<td>Anthracene</td>
<td>A</td>
</tr>
<tr>
<td>C₁-Phenanthrene/anthracenes</td>
<td>C₁-P</td>
</tr>
<tr>
<td>C₂-Phenanthrene/anthracenes</td>
<td>C₂-P</td>
</tr>
<tr>
<td>C₃-Phenanthrene/anthracenes</td>
<td>C₃-P</td>
</tr>
<tr>
<td>C₄-Phenanthrene/anthracenes</td>
<td>C₄-P</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>D</td>
</tr>
<tr>
<td>C₁-Dibenzothiophene</td>
<td>C₁-D</td>
</tr>
<tr>
<td>C₂-Dibenzothiophene</td>
<td>C₂-D</td>
</tr>
<tr>
<td>C₃-Dibenzothiophene</td>
<td>C₃-D</td>
</tr>
<tr>
<td>Fluoranthenes</td>
<td>FL</td>
</tr>
<tr>
<td>Pyrene</td>
<td>PY</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>BA</td>
</tr>
<tr>
<td>Chrycene</td>
<td>C</td>
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<tr>
<td>C₁-Chrycene</td>
<td>C₁-C</td>
</tr>
<tr>
<td>C₂-Chrycene</td>
<td>C₂-C</td>
</tr>
<tr>
<td>C₃-Chrycene</td>
<td>C₃-C</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>BB</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>BAP</td>
</tr>
<tr>
<td>Benzo[ghi]pyrene</td>
<td>BP</td>
</tr>
<tr>
<td>Dibenzo[a]anthracene</td>
<td>DA</td>
</tr>
<tr>
<td>Indeno[123-cd]pyrene</td>
<td>IP</td>
</tr>
</tbody>
</table>

Figure 2.6: Typical Petrogenic Profile
Figure 2.7: Typical Pyrogenic Profile

Figure 2.8: Typical Degraded Heavy Oil

Figure 2.9: Typical Diesel Profile
Relative amounts of phenanthrenes, dibenzothiophenes and chrysenes

The relative amounts of these compounds in an environmental sample are used to differentiate among different crude oils, petroleums and refined petroleums\textsuperscript{16,19}. In crude oil, for example, similar abundances of phenanthrenes and dibenzothiophenes are found, with the chrysenes series largely absent in some cases (e.g. Exxon Valdez crude oil)\textsuperscript{16}. Major differences in the PAH fingerprints between petroleum sources have previously been found in the relative amounts of dibenzothiophenes\textsuperscript{18}. Creosote, on the other hand, contains significant amounts of five to six ringed PAHs with a low relative abundance of dibenzothiophenes. The relative amounts of phenanthrenes, dibenzothiophenes and chrysenes in creosote are shown in Figure 2.11.

The use of source ratios

A source ratio is a ratio between two characteristic analytes or group of analytes in a source, which must be ideally unique to that particular source. For the ratio to stay constant the particular compounds must degrade at similar rates and have similar
chemical and physical properties. Page et. al.\textsuperscript{16} reported that selected alkyl-PAH homologues are (1) relatively resistant to weathering influences and (2) occur in relatively different concentrations in different petroleum sources. Douglas et. al.\textsuperscript{20} reported that the ratios of C\textsubscript{2}-dibenzothiophenes to C\textsubscript{2}-phenanthrenes (C\textsubscript{2}-D/C\textsubscript{2}-P) and ratios of C\textsubscript{3}-dibenzothiophenes to C\textsubscript{3}-phenanthrenes (C\textsubscript{3}-D/C\textsubscript{3}-P) stay relatively constant, even when weathering has degraded up to 98% of the total PAHs. They have also demonstrated the stability and usefulness of the source ratio over a wide range of weathering and biodegradation of different oils using double ratio plots of C\textsubscript{3}-D/C\textsubscript{3}-C (weathering ratio) versus C\textsubscript{3}-D/C\textsubscript{3}-P (source ratio). The dibenzothiophene group of compounds (C\textsubscript{0}-D to C\textsubscript{3}-D) was found to vary the most widely in different sources, as their concentrations reflect the sulphur content of the source\textsuperscript{20}. The resistance to weathering, combined with the source specific nature of the C\textsubscript{3}-D/C\textsubscript{3}-P ratio in spilled oil, makes them especially useful for the identification of multiple sources of hydrocarbons\textsuperscript{20}.

**The use of weathering ratios**

Ratios of compounds that change substantially with weathering and biodegradation are termed "weathering ratios". Weathering is the combined effect of dissolution, biodegradation and photo-oxidation. The bacterial degradation within a PAH homologous series is\textsuperscript{19}:

\[ C_0\text{-PAH} > C_1\text{-PAH} > C_2\text{-PAH} > C_3\text{-PAH} > C_4\text{-PAH} \]

During a study of hydrocarbon sources following the Exxon Valdez oil spill, Page and co-workers\textsuperscript{16} reported the following major compositional changes in sediments and soils:

- Pronounced decrease in naphthalenes (N) relative to other PAHs, which occurs rapidly in the first few days of exposure to the atmosphere.
- Development of a "water-washed" profile for each of the petrogenic groups so that each group has the distribution: Parent (C\textsubscript{0})<C\textsubscript{1}<C\textsubscript{2}<C\textsubscript{3}.
- Gradual build-ups in the relative abundances of the phenanthrenes, dibenzothiophenes, and chrysenes as the more soluble components are lost. The chrysenes exhibit the most pronounced relative increase because of their low solubilities in water, and resistance to microbial degradation.

In the study by Douglas and co-workers\textsuperscript{20} concerning the environmental stability of petroleum hydrocarbons, they reported that compounds that weather to below their respective detection limits during the early stages of oil degradation cannot provide reliable weathering ratios. Bence and co-workers\textsuperscript{21} developed weathering indicators of varying sensitivity for different stages of the weathering process. The ratio of C\textsubscript{3}-N/C\textsubscript{2}-P is a sensitive ratio and can for example be used for light product degradation such as diesel fuel. A less sensitive weathering ratio such as C\textsubscript{3}-D/C\textsubscript{3}-C may be used for crude oil degradation.

**The use of individual isomer distributions**

This method involves the profiling of *isomers* of a certain alkyl homologue\textsuperscript{22}, e.g. isomers of C\textsubscript{2}-phenanthrene or C\textsubscript{3}-dibenzothiophene. A typical profile for C3-dibenzothiophene isomers is shown in Figure 2.12, illustrating the differences in the relative distribution of individual isomers. For this purpose, an accurate quantitative result is not required for each isomer, but the result is presented as a single ion chromatogram, based on the major ion of the homologue, showing the relative intensities of all the isomers. Page et.al.\textsuperscript{16} have shown that the differences in the relative distribution of individual isomers within a homologous series, such as the C\textsubscript{3}-dibenzothiophene isomers, present opportunities for fingerprinting similar petroleum hydrocarbon sources.
They indicated that:

- the C₃_dibenzothiophenes as a group, represent more than 20 individual abundance's in oils from different sources
- these isomer distributions reflect the source carbon, depositional environment during formation and the existence of any diatomic sources.

Phases of an advanced chemical fingerprinting Strategy

The chemical characterisation of pollutants in the geosphere and hydrosphere is an integral part of the fingerprinting strategy. A typical Advanced Chemical Fingerprinting (ACF) project¹⁷ is a sequence of separate but strategically related steps that can be explained in the phases shown if Figure 2.13.

![Figure 2.12: Example of a Selected Ion Chromatogram of C₃-dibenzothiophene isomers – (m/z = 226 and 211).](image)
### Phase 1
- Evaluate contaminated site and adjacent sites
- Assemble a team of specialists (in-house and consultant)
- Determine all possible contributors
- Characterise sources looking for similarities and differences

### Phase 2
- Develop case-specific sampling strategy to include size, number and location of samples and stressing sample integrity and statistical replication
- Implement high quality chemical fingerprinting analyses

### Phase 3
- Develop tiered analytical strategy combining lower cost and rapid field screening methods with ACF to help select samples for ACF
- Screen samples and select subset for ACF
- Select diagnostic ratios
- Develop and implement mixing models to establish allocation

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**Figure 2.13:** Phases of an Advanced Chemical Fingerprinting (ACF) project