Chapter 9

SOURCE IDENTIFICATION AND THE DEVELOPMENT OF DIAGNOSTIC RATIOS

INTRODUCTION

Groundwater is a source of potable water for many households and communities. Its possible contamination by DNAPL releases into soils has become a serious environmental problem in areas adjacent to industrial sites. The development of techniques that can determine the pollution source is motivated in part by the cleanup costs, legal fees, and fines incurred by the polluter.

The potential of using GC/MS data for tracing underground DNAPLs to suspected sources is recognised by many workers in the field of hazardous waste management. The discriminatory power, sensitivity, selectivity and specificity of GC/MS were also illustrated in the previous chapters. Selective extraction techniques for spill identification have been developed in this study and the advantages of SPME as an alternative extraction method, were shown. The results (target analyte data listed in **Table 2.1**) obtained by these various methods were used to develop interpretative methods, which can be used to trace contamination in the environment to its source. The analyses of data were based on the following principles:

- Each source has a unique chemical composition
- Each source has a unique analyte distribution pattern
- Information from the GC/MS spectra can be encoded in such a way to be resistant o chemical noise
- Source ratios can be developed that stay constant during weathering changes and are relatively insensitive to changes in the overall GC profile
- Ratios can be developed that will constantly change during weathering and serve as weathering indicators

DETECTION AND OCCURANCE OF PAH ISOMERS IN TYPICAL SAMPLES

The detection and identification of data obtained with GC/MS was investigated with the following objectives:

- To develop diagnostic ratios that can be determined with good accuracy. Typical source ratios are C_1-D/C_1-P, C_2-D/C_2-P and C_3-P/C_3-D. Typical weathering ratios are C_2-N/C_1-P, C_3-N/C_2-P and C_2-P/C_2-C.
- To establish typical PAH distribution patterns in soils and sediments (compare with petrogenic and pyrogenic profiles).
- To investigate the evidence of weathering in typical soil samples

The occurrence of alkyl-PAH isomers in soil samples

The ASE-GC/MS method described in **Chapter 7** was found to be suitable for the application of advanced chemical fingerprinting. The HSSPME-GC/MS was not found suitable for this purpose. The results of alkyl substituted isomers in typical soil samples, obtained with the ASE-GC/MS method, are shown in **Figures 9.1 – 9.4**.

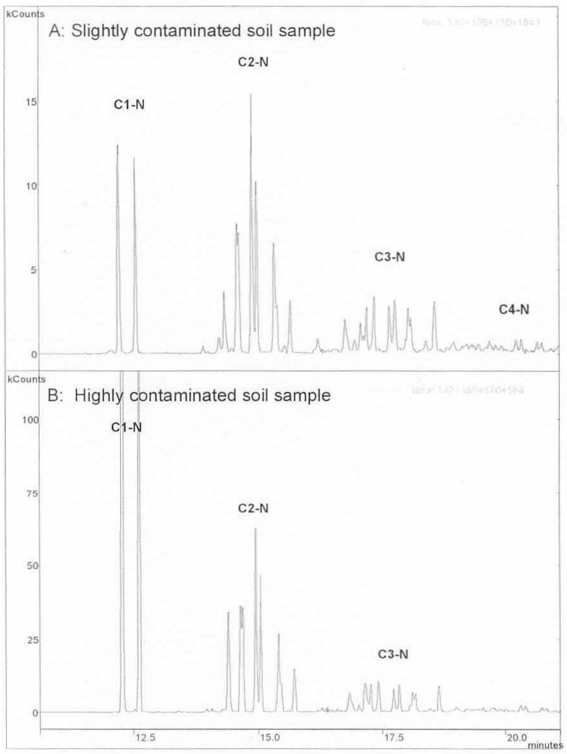

Figure 9.1: Selected ion chromatograms for the naphthalene isomers in soil

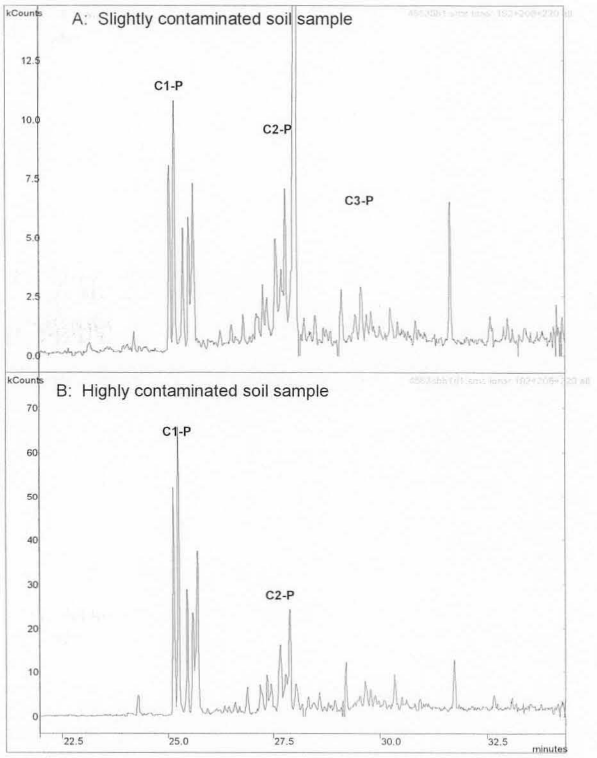

Figure 9.2: Selected ion chromatogram for the phenanthrene isomers in soil

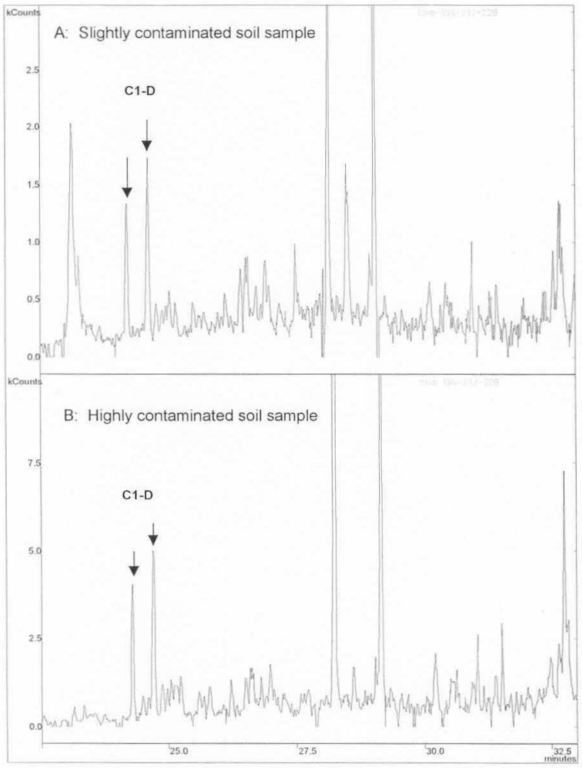

Figure 9.3: Selected ion chromatogram for the dibenzothiophene isomers in soil

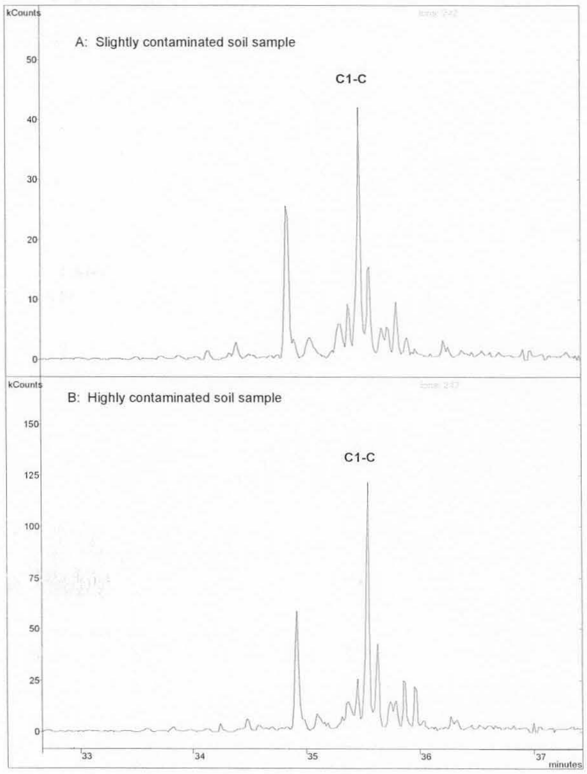

Figure 9.4: Selected ion chromatogram for the C1-chrysene isomers in soil

These results illustrate the sensitivity of the method and abundance of naphthalene, phenanthrene, dibenzothiophene and chrysene isomers. In each case the data of two samples, namely (A) a slightly contaminated sample and with a total PAH concentration of < 3.3 mg/kg and (B) a highly contaminated sample with a total PAH content of > 1550 mg/kg, are shown. The objective was to develop ratios that can be used down to low levels of contamination. As expected from a pyrogenic profile the isomer abundance decrease in the order:

$C_1 > C_2 > C_3 > C_4$.

The following isomers were found in detectable quantities:

C_1-N, C_2-N, C_3-N, C_1-P, C_2-P, C_1-D and C_1-C.

The following isomers could not be detected:

C_3-P, C_2-D, C_3-D, C2-C and C_3-C.

Although C_2-P peaks could be detected, considerable interfering peaks from co-extracted compounds were observed in the chromatogram.

The occurrence of alkyl-PAH isomers in groundwater samples collected at or nearby a steelmaking industry

It was concluded in **Chapter 5** that the sensitivity of the solvent extraction method was not good enough for the detection of isomers in alkyl homologues. The SPME-GC/MS method described in **Chapter 6** was found to be the preferred method for the analysis of PAHs in water samples, due to low detection limits that the method can achieve. The occurrence of PAHs and alkyl-PAH isomers in a total of 581 groundwater samples, which were collected on-site and in a radius of about ten kilometers from three different iron and steelmaking plants, were investigated. These samples were analysed for PAHs in our laboratory over a period of two years, using the technique of SPME-GC/MS. The chromatograms of alkyl-PAHs that are typically found in groundwater samples are shown in **Figures 9.5 – 9.6.**

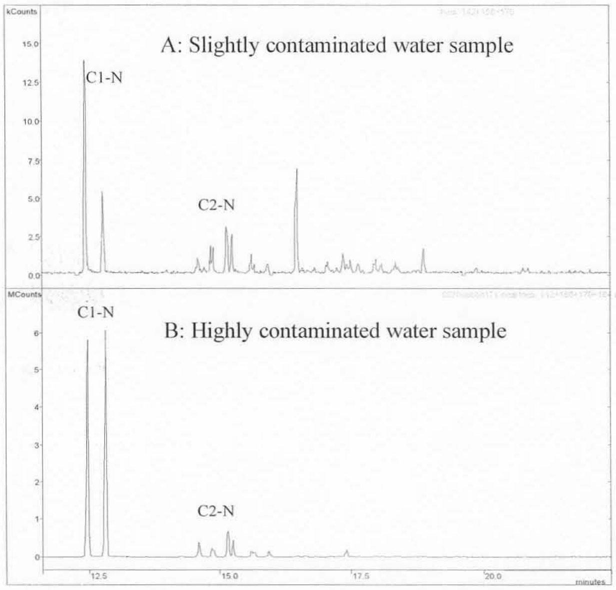

Figure 9.5: Selected ion current of naphthalene isomers (m/z = 142+156+170) in water

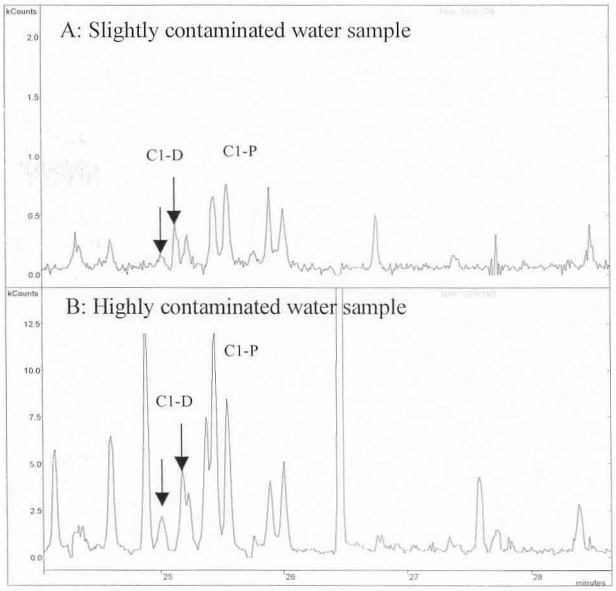

Figure 9.6: Selected ion current for C1-dibenzothiophene and C1-phenanthrene isomers in water. (m/z = 192+198)

The extent of PAH contamination in these sample were divided into 3 groups, namely highly contaminated, slightly contaminated and not detected. The number of samples that were found in each group, relative to the total number of samples, are shown in **Figure 9.7**.

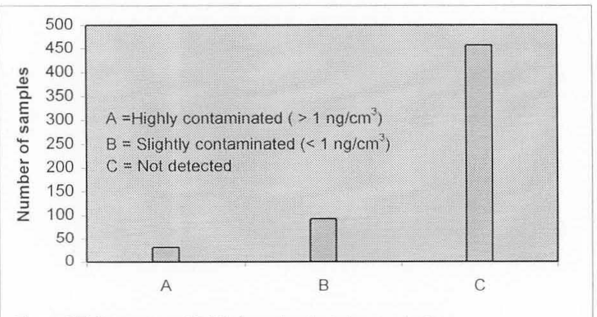

Figure 9.7: Occurance of PAHs in contaminated groundwater

The occurrence and distribution of PAHs in each group can be summarised as follows:

GROUP A: The naphthalenes were the most abundant PAHs. The PAH distribution pattern in these samples does not resemble the composition of coal tar, but rather resembles the solubility profile of PAHs. This is illustrated in Figures 9.8 (a) – (c) and shows that the occurrence of PAHs in severe coal tar contaminated water samples is mainly influenced by the PAH solubilities. The figures compares (a) the PAH distribution pattern of a typical sample, (b) the PAH solubility profile and (c) a typical coal tar profile. Only trace levels of fluoranthene and pyrene (0.004 ng/cm^3) were found in this group of samples and the C1-phenanthrenes and C1-dibenzothiophenes occurred at levels close to the detection limit (0.001 ng/cm^3). The other four- or five-ringed PAHs could not be detected at all. Similar profiles were obtained for most of the samples that were classed as severely contaminated. Other chemical properties, degree of weathering and the concentration of PAHs in the source(s) of contamination can influence PAH concentrations to a lesser degree.

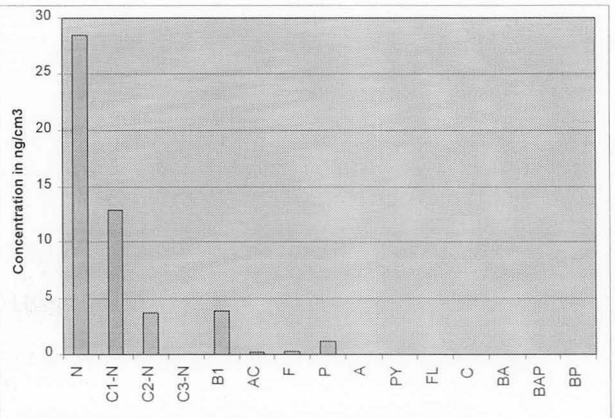

FIGURE 9.8(a): Profile of a typical Coal Tar contaminated water sample

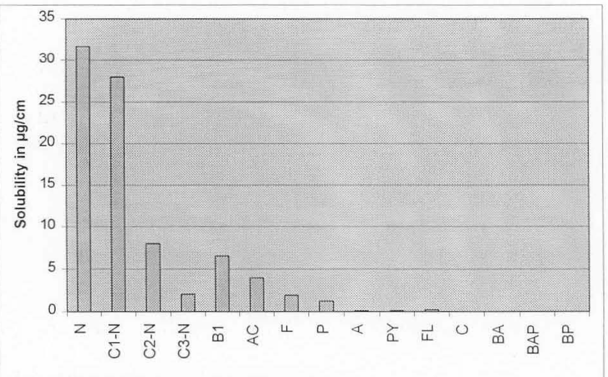

FIGURE 9.8(b): Aqueous Solubilities of PAHs

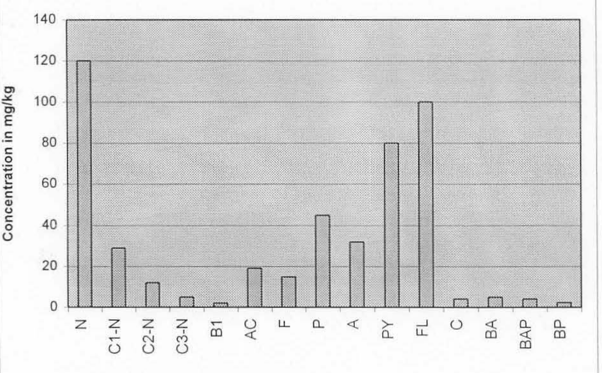

FIGURE 9.8(c): Typical Coal Tar profile

GROUP B: For the slightly contaminated samples the relative concentration of the three and four ring PAHs were much higher in comparison to the naphthalenes. Although the PAH concentrations in some samples were at trace level concentrations, C1-dibenzothiophene could still be detected. Except for fluoranthene and pyrene, the other four and five ring PAHs could not be detected.

The overall detection of PAHs in group A and B can be summarised as follows:

Detectable isomers: **C_1-N, C_2-N, C_1-D, C_1-P**
Isomers not detected: **C_3-N, C_2-D, C_2-P, C_1-C**

The detection of alkyl substituted PAH isomers in water samples were, therefore, limited due to their low abundance in coal tar and low solubilities. Detection limits of alkyl PAHs are also lower than those for parent PAHs because the total peak area of an alkyl homologue is spread over several isomer peaks. The C_1-D and C_1-P isomers could be detected in most slightly contaminated samples and very little interference from other co-extracted compounds were observed. The occurrence of these isomers generally increased with the degree of contamination, but interference from co-extracted compounds also increased. The isomers of C_1-P and C_1-D were chosen as candidates to determine source ratios because they could be detected in most coal tar contaminated water samples and have very similar chemical and physical properties. The disadvantage of this choice is that they are both compounds with a low degree of alkylation and would probably weather very quickly. The advantage is that they are ideal because of their similarity in chemical and physical properties and would dissolve to the same extent in groundwater, degrade or decompose at similar rates, partition onto the SPME fiber with similar efficiencies and behave similarly during the GC/MS analysis. Results of two typical water samples were used to illustrate the abundance of the C1-P and C1-D isomers, namely (a) a mineral oil, and (b) a coal tar contaminated water sample. These results are shown in **Figure 9.9**, where the difference in the C1-D/C1-P ratio of the two sources is evident.

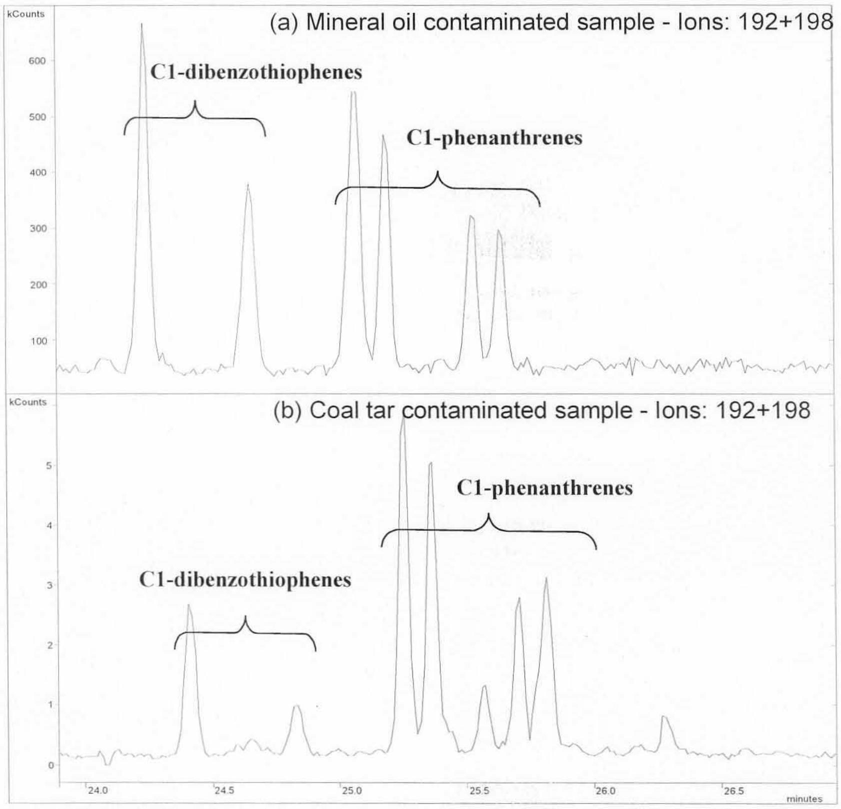

Figure 9.9: Selected ion current plots for phenanthrene and dibenzothiophene isomers in contaminated water samples

THE DEVELOPMENT OF DIAGNOSTIC RATIOS

Following the preceding studies regarding the occurrence and detection of PAH isomers is typical samples, the next step is to select appropriate diagnostic ratios (**see Phase 3 of Figure 2.13**). The principles for the selection of ideal source ratios was discussed in **Chapter 2,** for example those that have similar chemical and physical properties, i.e. the ratio stay constant during weathering and changes in the GC conditions. As shown in **Chapter 2**, the ratios of C_2- and C_3-phenanthrenes and the C_2- and C_3-dibenzothiophenes are examples of those that are considered as constant and reliable ratios. Weathering ratios are normally developed to include very sensitive, sensitive and less-sensitive ratios. In the case of a very sensitive ratio, e.g. C_2-N/C_1-P, the concentration of these isomers may degrade below their detection limits during the early stages of degradation. A less sensitive ratio, such as C_2-P/C_2-C, will be more reliable and will change at a slow rate. The selection of a specific group of isomers to be used for ratio calculations depends on a few factors, namely:

- ☐ chromatographic noise in that part of the chromatogram
- ☐ interference (peak overlap) from co-extracted compounds
- ☐ sensitivity of the analytical method
- ☐ abundance of the isomers group in the sample
- ☐ stability and rate of degradation

The determination of diagnostic ratios in water samples

As discussed earlier, recent advances[34] in chemical fingerprinting have focussed on the use the total peak area (that is the sum of all the isomer peaks in an alkyl homologue) in deriving diagnostic ratios. Various problems were, however, encountered by our laboratory using this method of quantifying the alkyl homologues in water samples. The complexity of the chromatograms is one of the concerns, which is due to the low analyte concentrations and high background levels. Certain single isomer peaks were, for example hard to distinguish in heavily contaminated samples. Another complication is that all the isomer peaks are not baseline separated. The detection of the C_1-D and C_1-P isomers was further complicated by the low signal to noise ratios that were obtained in most cases as well as interfering peaks of co-extracted compound. An example of co-extracted interfering peaks is shown in **Figure 9.10**. The peak overlap of interfering compound with the isomer peaks and poor resolution is evident from this example. This resulted in errors during the estimation of alkyl homologue concentrations and inaccurate source or weathering ratios. However, an alternative approach to hydrocarbon fingerprinting is to determine the peak area of a single isomer in an alkyl homologue, which is then multiplied by a factor to obtain the total peak area of that specific isomer group. The specific single isomer peaks that were selected for this study are shown in **Figure 9.11.** These isomers have been carefully selected based on a thorough investigation into the retention times at which interfering peaks normally elute in typical samples received by our laboratory. The selected peaks were those that had a strong signal, well isolated from other isomer peaks and where minimum interference (peak overlap with interfering compounds) could be observed. The multiplication factor used to convert single peak areas to the isomer group area was determined by averaging data that were acquired over a period of about one year. The average factors found were 3.7 for C_2-N, 2.7 for C_1-P and 2.3 for C_1-D. Diagnostic ratios, based on the method described above, were determined on selected water samples. The ratios C_2-N/C_1-P and C_1-P/C_1-D were used as weathering and source ratios respectively. These results are shown in **Table 9.1**. As previously mentioned, the dibenzothiophene isomer is very useful for source ratio calculations because its concentration reflects the sulphur content of the source and this varies widely between different oils and coal tar. The results in **Table 9.1** include water samples that were contaminated by refined oil products (samples 1 – 4) and samples mainly contaminated by coal tar (samples 5 - 30). Although the C_1-D/ C_1-P ratio is not very resistant toward weathering, these isomers could be detected in most contaminated samples down to very low levels. In the case of samples number 19 and 20 the high source ratios found were probably due to an analytical error at the low isomer concentrations. Due to their very similar chemical and physical properties, they were found to be self-normalized to changes in GC conditions resulting in ratios with a low analytical variance. The C_2-N isomers degrade at a faster rate than the other isomers and the C_2-N/C_1-P ratio are useful to determine the degree of weathering. Using the data shown in **Table 9.1**, a plot was constructed for source ratio versus weathering ratio to illustrate that double ratio plots could be used as a means of resolving multiple sources as well as differences in the extent of degradation from a single source. This plot is shown in **Figure 9.12,** which demonstrates the usefulness of the source ratio over a wide range of weathering and biodegradation for the different sources. The strategy for the successful application of these source ratios to hydrocarbon assessment studies must, however, include an initial study to determine the ratios of potential sources.

Table 9.1: Alkyl PAH concentration in groundwater samples and calculated ratios

Sample Number	C_2-N Concentration (ng/cm^3)	C_1-D Concentration (ng/cm^3)	C_1-P Concentration (ng/cm^3)	C_1-D/C_1-P Source Ratio	C_2-N/C_1-P Weathering Ratio
1.	326	21.7	23.59	0.92	13.82
2.	18.1	2.85	1.80	1.05	10.07
3.	314	3.37	3.28	1.03	95.91
4.	24.3	4.55	4.78	0.95	5.08
5.	0.04	0.01	0.02	0.34	1.80
6.	3.41	0.05	0.17	0.29	19.59
7.	2.14	0.25	0.71	0.35	3.00
8.	2.18	0.06	0.18	0.31	11.80
9.	0.16	0.01	0.06	0.13	2.70
10.	3.41	0.05	0.20	0.25	16.7
11.	3.41	0.05	0.17	0.29	19.6
12.	2.18	0.01	0.03	0.20	65.8
13.	2.18	0.01	0.03	0.25	77.9
14.	5.80	0.04	0.22	0.17	25.8
15.	50.0	0.87	11.28	0.08	4.40
16.	1.96	0.03	0.23	0.11	8.60
17.	0.04	0.01	0.08	0.08	0.50
18.	7.00	0.05	0.46	0.10	15.30
19.	0.01	0.01	0.00	4.65	3.80
20.	0.02	0.02	0.00	4.90	6.30
21.	1.75	1.37	1.35	1.01	1.30
22.	0.05	0.00	0.01	0.11	4.70
23.	239	2.07	30.1	0.07	7.90
24.	48.8	0.28	1.97	0.14	24.8
25.	0.04	0.01	0.04	0.21	1.10
26.	0.26	0.01	0.04	0.16	6.90
27.	0.21	0.01	0.10	0.09	2.00
28.	1019	11.7	124.6	0.09	8.20
29.	1.03	0.01	0.08	0.11	12.20
30.	0.02	0.01	0.05	0.14	0.40

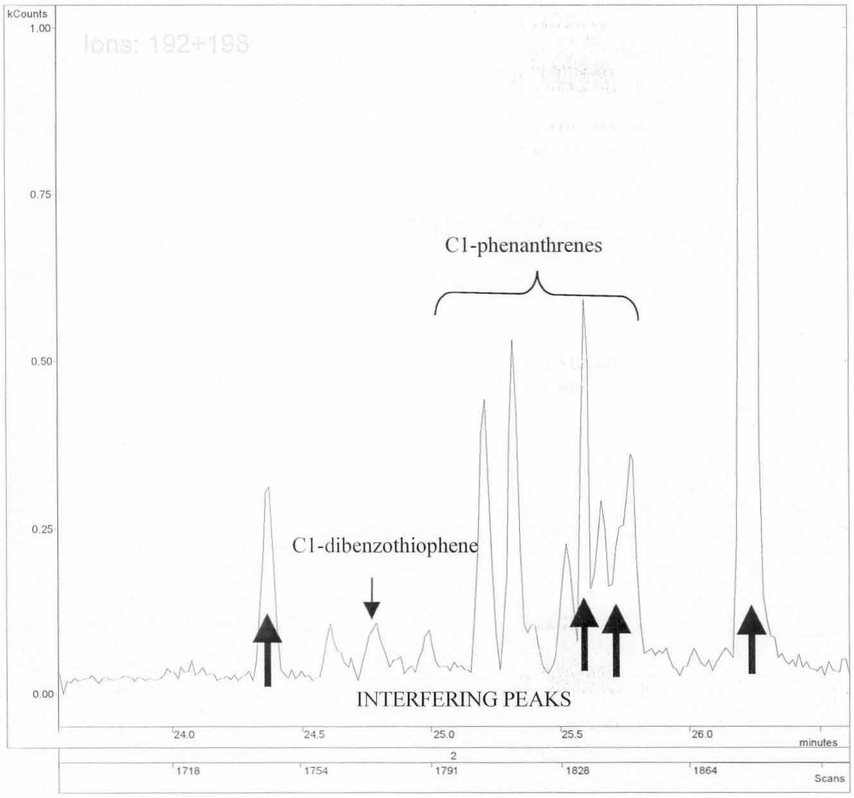

Figure 9.10: Selected ion chromatogram for the C_1-D and C_1-P isomers showing interferences

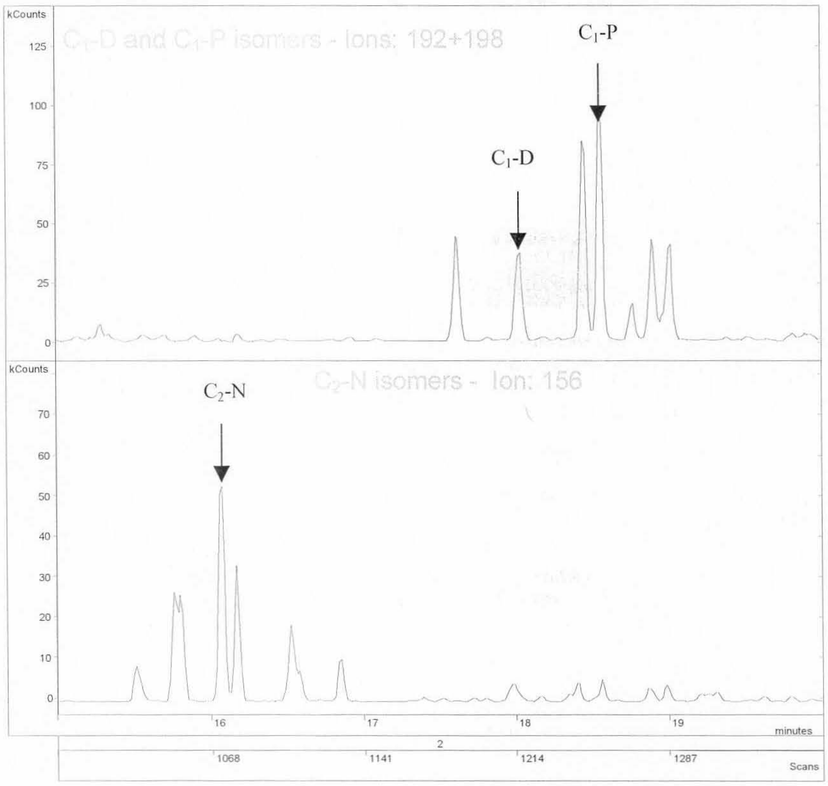

Figure 9.11: Selected ion chromatograms of PAH isomers, sowing peaks that were selected for determining diagnostic ratios

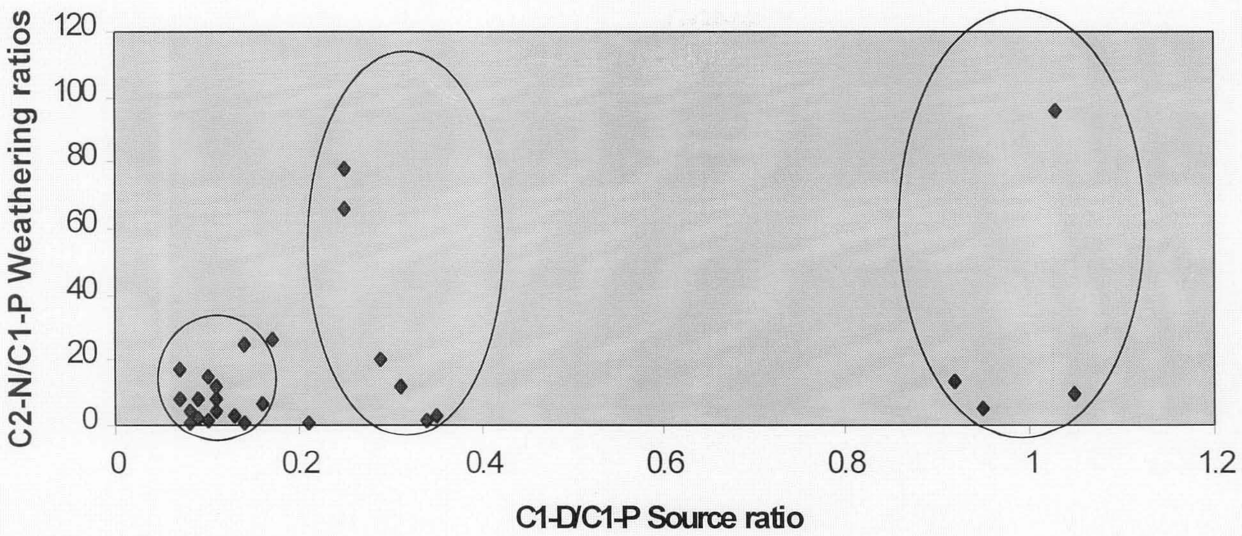

Figure 9.12: Double ratio plots of alkyl PAHs in water sample

The determination of diagnostic ratios in soil samples

Similarly to water samples, the complexity of the chromatograms of soil samples was one of the concerns during the development of diagnostic ratios. Certain single isomer peaks are for example hard to distinguish in heavily contaminated samples, especially at low levels. Examples of co-extracted interfering peaks can be seen **Figures 9.2**, **9.3** and **9.6**. The peak overlap of interfering compound with the isomer peaks and poor resolution is evident from these examples. The specific single isomer peaks that were selected for soils in this study are shown in **Figure 9.13**.

Another concern in the selection of suitable isomers was the rate of degradation. It was shown in **Chapter 2** that the rate of PAH degradation in the environment decreases with ring size, within a homologous series and with an increase in alkylation. As also indicated earlier, ideal isomers such as C_2-D, C_2-P and C_2-C were, unfortunately, either not detected in the coal tar contaminated soil samples or were present at concentrations below the reporting limits. A useful isomer that could be detected in most samples was C1-dibenzothiophene. The the C_1-D/ C_1-P ratio was , therefore, the most reliable source ratio that was found in this study, although not the most stable and resistant toward weathering. In the case of weathering ratios, C_2-N/C_1-P was found to be the most suitable ratio. The C_2-N isomers were, unfortunately, not very stable during the study and in some samples it already degraded below the method detection limit. This is evident from the results of the oil-contaminated samples (4a- 4g), which had very low concentrations of alkylated naphthalenes due to an advanced degree of weathering. The results for soil samples using the single isomer peak method, which was discussed earlier, are shown in **Table 9.2**. The results include soils which were contaminated by coal tar (samples 3a – 3 l) and soils contaminated by mineral/lubricating oil (4a – 4g).

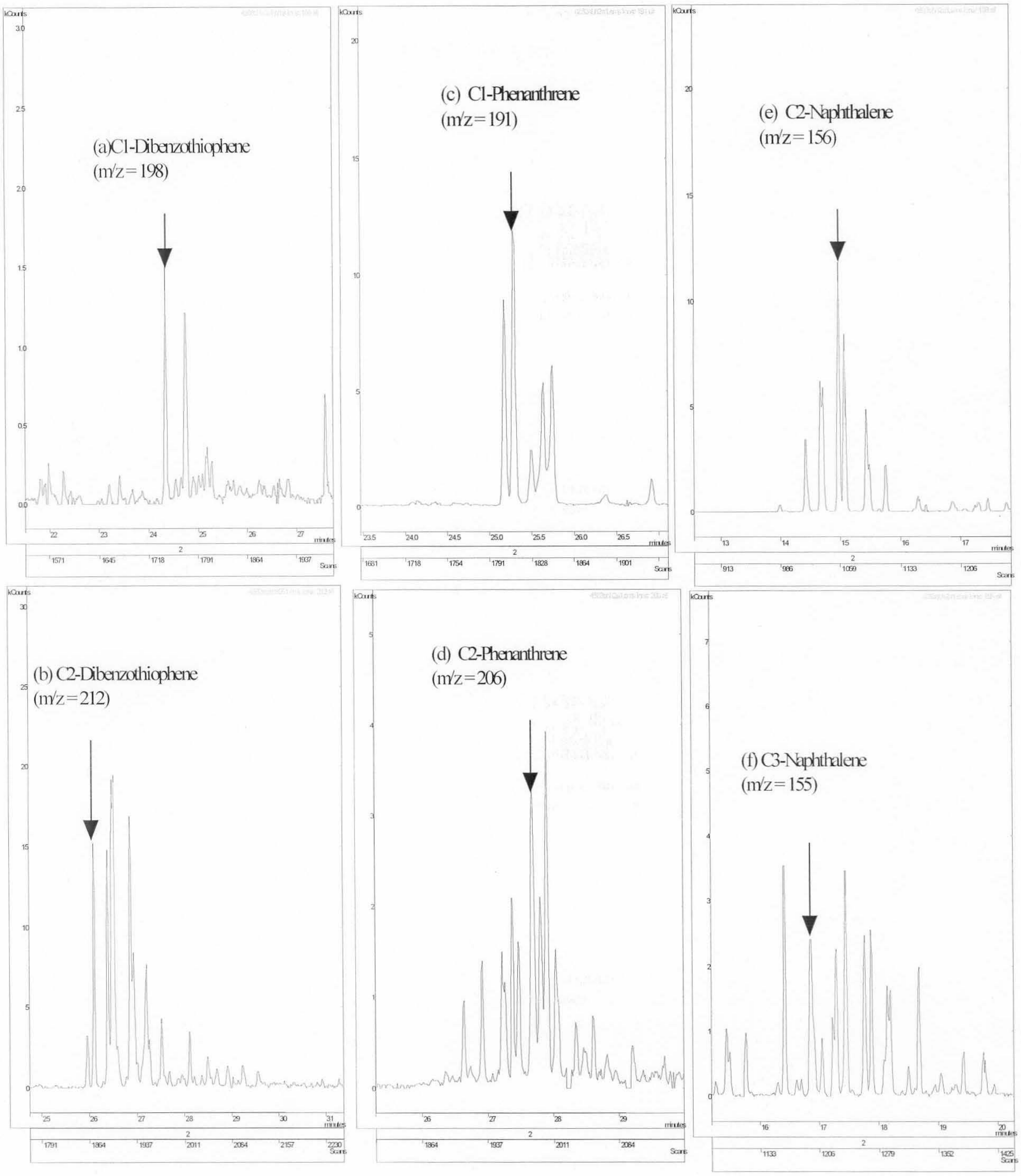

Figure 9.13: Selected ion chromatograms of PAH isomers in soil samples, showing peaks that were selected for diagnostic ratios

Table 9.2: Diagnostic ratios of selected soil samples

	Source Ratios		**Weathering Ratios**	
	Less Stable	Stable	Very sensitive	Less sensitive
	D/C1-P	**C1-D/C1-P**	**C2-N/C1-P**	**C3-N/C2-P**
No 1(a)	1.5	0.09	1.00	1.00
No 1(b)	2.22	0.81	1.06	1.32
No 1(c)	2.46	0.22	1.22	1.38
No 1(d)	-	-	-	-
No 1(e)	-	-	-	-
No 1(f)	-	-	-	-
No 2(a)	1.50	0.13	3.06	0.45
No 2(b)	1.04	0.14	1.06	0.45
No 2(c)	2.09	0.11	1.75	1.25
No 2(d)	2.32	0.19	3.83	2.46
No 2(e)	2.35	0.16	4.67	4.02
No 3(a)	1.07	0.18	0.97	0.38
No 3(b)	1.03	0.22	1.93	0.33
No 3(c)	1.15	0.21	1.04	0.38
No 3(d)	1.19	0.22	2.82	0.49
No 3(e)	0.61	0.18	0.43	0.20
No 3(f)	1.02	0.18	1.01	0.44
No 3(g)	1.19	0.16	1.42	0.82
No 3(h)	1.49	0.22	1.93	0.62
No 3(i)	1.99	0.24	2.25	0.63
No 3(j)	1.74	0.22	1.85	0.61
No 3(k)	1.50	0.18	1.84	0.96
No 3(l)	1.41	0.22	2.12	0.47
No 4(a)		0.48	0.04	0.16
No 4(b)		0.45	0.02	0.04
No 4(c)		0.46	0.08	0.21
No 4(d)		0.54	0.04	0.19
No 4(e)		0.52	0.16	0.05
No 4(f)		0.44	0.23	0.16
No 4(g)		0.54	0.31	1.04

The results shown in **Table 9.2** are also presented graphically is **Figure 9.14**. An average C_1-D/C_1-P source ratio of 0.20 was determined for coal tar contaminated soil, which was significantly lower than the average ratio of 0.49 that was found for the oil contaminated soils. The findings agree with the theoretical expectation as a higher ratio is expected in samples contaminated by lubricating/mineral oil sources because of their higher sulphur content. Weathering was evident by the relative increase of heavy PAHs that was observed in most cases. It was also observed in the disappearing of concentrations within the naphthalene homologue: C_0-N < C_1-N < C_2-N < C_3-N. Weathering could be due to bacterial degradation or dissolution in ground- or rainwater or a combination of both. The weathering ratios for the C_2-N/C_1-P isomers had a large variation between samples, which is probably due to the sensitive nature of this specific ratio. More constant ratios were found for the C_3-N/C_2-P isomers.

A plot was constructed for source ratio versus weathering ratio to illustrate that double ratio plots can be used as a means of resolving multiple sources as well as differences in the extent of degradation from a single source. This plot is shown in **Figure 9.15,** and similar to **Figure 9.12** demonstrates the usefulness of the source ratio over a wide range of weathering and biodegradation for the two sources. The strategy for the successful application of these source ratios to hydrocarbon assessment studies must include an initial study to determine the ratios of potential sources.

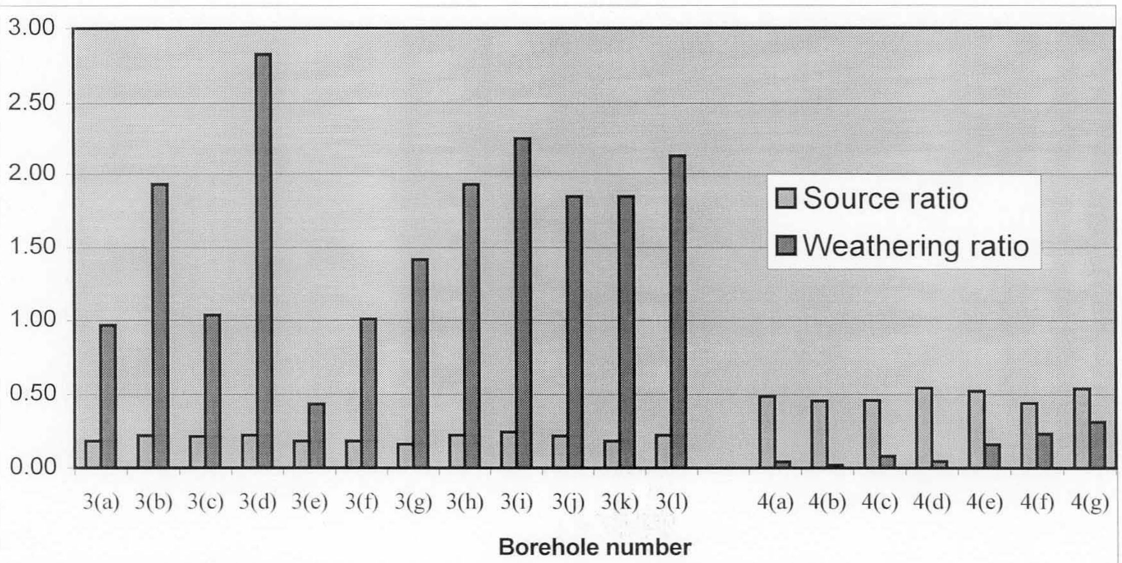

Figure 9.14: Source and weathering ratios of soil samples

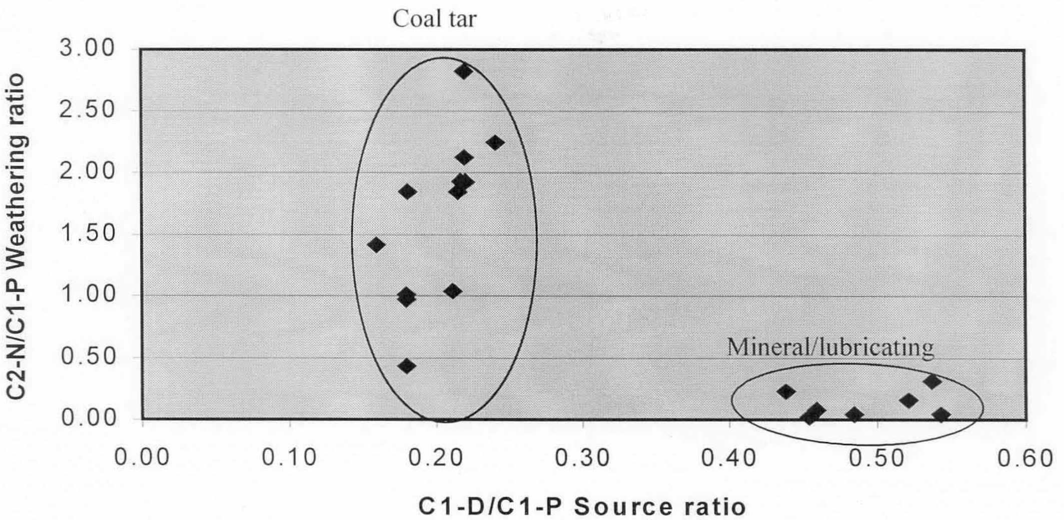

Figure 9.15: Double ratio plots for soil samples

Other analyte ratios, such as C_2-D/C_2-P, might be useful in the case of petrogenic sources. The determination of ratios in water samples was complicated by the low abundance of alkyl-PAHs in samples that are contaminated by pyrogenic sources. The concentration of parent PAHs in water samples routinely analysed by our laboratory, is normally < 10 ng/cm^3 and often < 1 ng/cm^3. Only a few samples contained PAHs in concentrations of > 10 ng/cm^3 and these were from surface water in an industrial area. The C_1-D/C_1-P source ratios that could be determined for selected water samples are shown in **Table 9.3**.

Table 9.3: Source ratios of selected water samples

	SOURCE RATIOS
	C1-D/C1-P
Coal tar contaminated samples	
No 1	0.35
No 2	0.36
No 3	0.13
No 4	0.20
No 5	0.25
No 6	0.40
No 7	0.36
No 8	0.17
No 9	0.22
No 10	0.27
No 11	0.35
No 12	0.16
No 13	0.15
No 14	0.34
No 15	0.23
No 16	0.29
No 17	0.39
Surface water samples	
No 18	0.28
No 19	0.13
No 20	0.20
No 21	0.65

Most measurements were found to be very close to the detection limit with a very low signal to noise ratio. The results are, therefore, not expected to be very accurate. This was also evident from the high analytical variance between results. The fact that the samples were influenced by multiple sources (pyrogenic and petrogenic) could also be a reason for the variance. A source ratio of between 0.15 and 0.25 was observed for some of the samples, which is similar to the source ratio found on the contaminated soil samples. Only one surface sample had a high source ratio of 0.65 (petrogenic source) and the others were in-between. The conclusion was made that the determination of C_1-D/C_1-P source ratios in groundwater samples is useful, but is limited to samples containing these isomers in concentration of > 0.07 ng/cm^3 (based on the MDL of phenanthrene with SPME-GC/MS and the number of C_1-P isomer peaks).

ANALYTE DISTRIBUTION PATTERNS IN SOILS

Fingerprinting of hydrocarbons is made possible by the variety of individual compounds found in hydrocarbon sources and in the great variability in the relative abundances of these compounds among different sources. The main objective is to distinguish combustion related sources (coal tar) from petroleum using fundamental differences in the distribution of PAHs according to the number of aromatic rings and the degree of alkylation.

Weathering can also alter these patterns as illustrated in **Figure 9.16**. Results for the drill core soil samples analysed in **Chapter 7**, using the ASE-GC/MS method, were used to illustrate the change in profile with weathering. With an increase in the depth of the sample, an increase was observed in the relative concentration of the naphthalene homologous series and a decrease in the relative concentration of the 5-ring compounds.

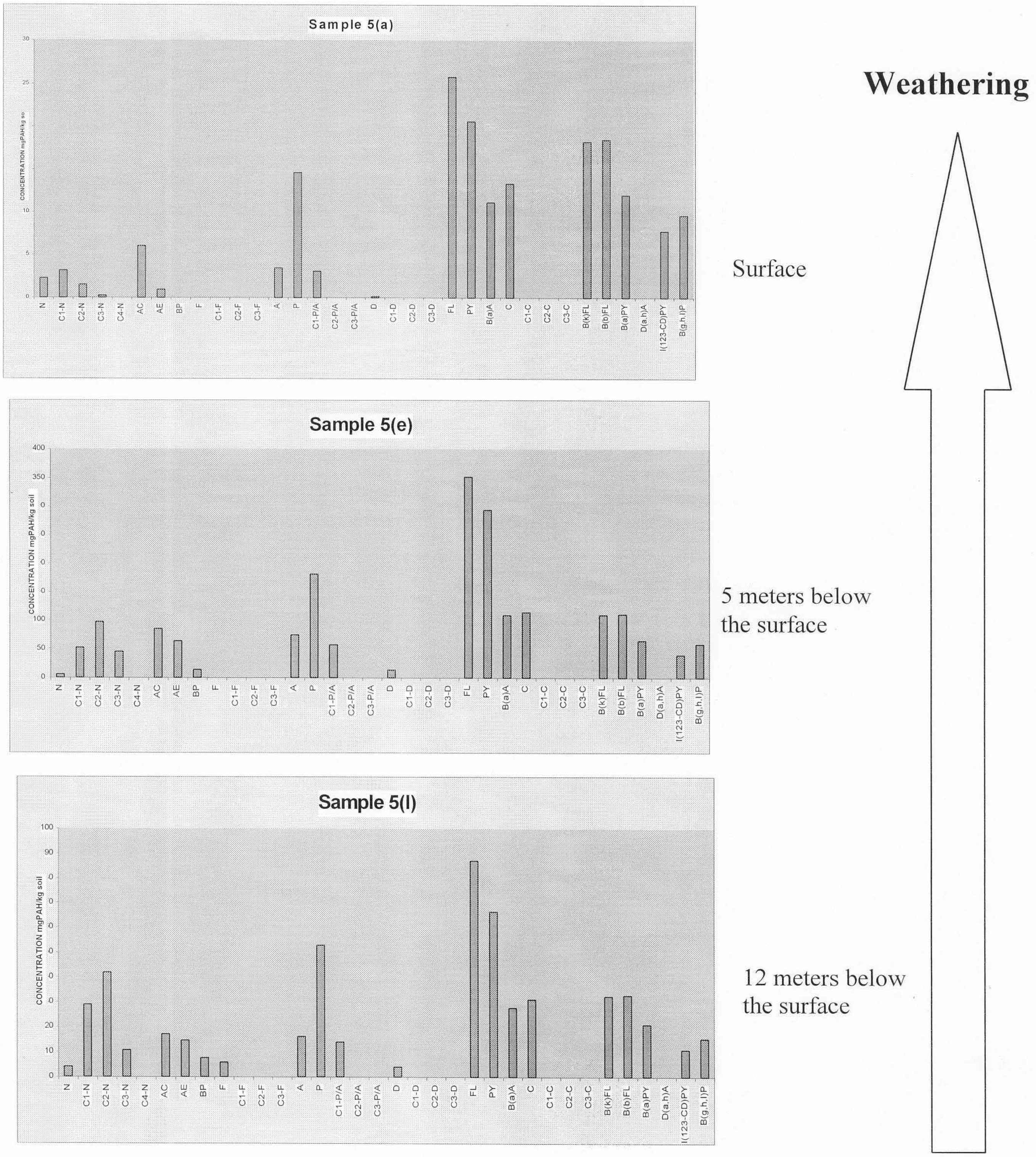

Figure 9.16: Weathering of coal tar with depth

Analyte distribution patterns were also used to identify the pollution source of soil samples contaminated with coal tar and mineral oil respectively. The fingerprints of these samples are shown in Figure 9.17. This example illustrates that the fundamental differences in the distributions of PAHs according to the number of rings and degree of alkylation, is effective to qualitatively determine the type of hydrocarbon pollution. The two soil samples used in this example were specifically chosen because they were contaminated to the same degree but with different distributions. The total PAH concentration found in these samples were < 25 mg/kg. The coal tar contaminated sample was characterised by a relatively high abundance of fluoranthene, pyrene and the 5- and 6-ring structures, with a low dibenzothiophene to phenantrene ratio. The mineral oil contaminated sample was characterised by a relatively high abundance of naphthalenes, phenenthrenes, dibenzothiophenes and chrysenes, with a high dibenzothiophene to phenantrene ratio. However, a more quantitative technique is needed to allocate the contribution of the two sources to the PAH contaminated soils, such as the double ratio plots illustrated in Figure 9.15.

CONCLUSIONS

The quality of PAH data generated with respect to accuracy and precision is critical for the successful determination of diagnostic ratios. The simplified method that was developed to determine source and weathering ratios by using only one isomer peak in an alkyl homologue, was found to be accurate and precise enough for this purpose. In the case of soil samples investigated in this study, the relative abundance of alkyl-naphthalenes (C_1-C_3), alkyl-phenanthrenes (C_1-C_2), alkyl-dibenzothiophenes (C_1-C_2) and C_1-chrysenes were found in high enough concentrations to develop source ratios based on these isomers. Substantial differences were also found in source ratios between petrogenic and pyrogenic sources to allow the ability to distinguish between different sources. These differences were further enhanced when a double ratio plot of C_2-N/C_1-P (source ratio) versus C_3-N/C_2-P (weathering ratio) is used.

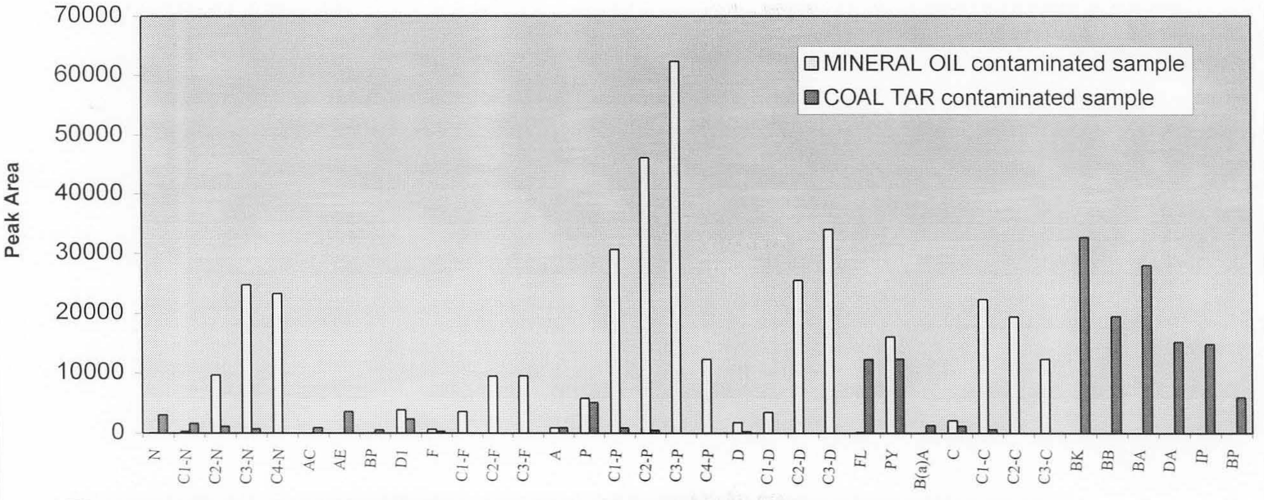

Figure 9.17: Analyte distribution patterns obtained for coal tar and mineral oil contaminated soil samples

This plot is also a useful indicator of weathering and degradation.

The determination of source ratios in water samples is subject to some inherent limitations:

- **Limited data:** The abundance of alkyl-PAHs in water samples was generally found to be lower than the detection limit.

- **Weathering:** Source ratios based on parent PAHs are inaccurate because these compounds weather rapidly at different rates losing their fingerprint. Ratio calculations can be useful in the case of fresh and unaltered pollution.

- **Lack of repeatability:** Interferences from co-extracted compounds complicated the determination of certain isomers. The manual integration of analytical data further limited the repeatability.