An investigation of the applicability of oil fingerprinting as a tool in soil contamination in Flanders

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Abstract

From inspection of the literature it is clear that sufficient analytical instruments for the application of oil fingerprinting on soil contamination problems are available. However well defined requirements have to be fulfilled. Among these prerequisites are the availability of unique oil signatures and sufficient variation within the different fuels on the Flemish market. On behalf of the Public Waste Agency of Flanders (OVAM), it was investigated if these constraints are met and consequently if sufficient analytical instruments are available enabling the linking of a suspected contamination source to an observed soil contamination. Particularly gas chromatography enables one to determine very specific characteristic patterns for the contamination and the source. However weathering alters these patterns drastically, complicating further comparison. Characteristic ratios are available for polycyclic aromatic hydrocarbons and persistent biomarkers like isoprenoids. In distillates from crude oil like most fuels, these chemicals are only present in limited amounts. Consequently application of such ratios is not always possible. Other interfering factors are changes in the composition and the limited specificity of the fuels circulating on the Flemish market. The diagnostic ratios in diesel fuels are not always unique and in some cases the differences between diagnostic ratios of different diesels is too small, not allowing to link the contamination source to the observed soil contamination. Chromatograms of soil samples do not always enable determination of the diagnostic ratios. Improvement of the detection level and the chromatographical resolution might solve this problem. For gasoline fuels differentiation was carried out based on specific chromatograms for the alkanes and the monocyclic aromatic hydrocarbons since biomarkers were not present. Concentrations of methyl-t-butyl-ether and benzene were used additionally. Also, for gasoline the link between source and contamination could not be determined unambigously.

Keywords: oil fingerprinting, soil contamination, gasoline, diesel, weathering.

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1 Introduction

Because oil and related products have an important place in nowadays society, a not uncommon issue in environmental forensics is the release of oil of unknown sources in soil. Often this occurs due to accidental discharges. The inventory of contaminated sites in Flanders showed that 70 to 80 % of all oil contaminations was due to leaking storage reservoirs. Most of the used refined petroleum products are diesel (22,6 %), domestic fuel oil (26,4 %) and gasoline (11 %) [1]. For that reason this article will mainly focus on those sources as potential spills.

The liability associated with even a small volume oil spill warrants that a thorough chemical characterization of the spilled oil will be conducted by potentially responsible parties in order to defensibly determine the source of the site contamination. However the similarity or difference between the spilled oil and the candidate source is not always obvious. Petroleum hydrocarbons released into the environment are subject to a range of chemical, physical and biological processes together known as weathering, resulting in a change of the composition. The degree of weathering is of course strongly dependent on environmental factors such as air circulation, oxygen, water and the presence of bacteria. Photochemistry can also alter the composition of a spilled oil, but biodegradation is the major pathway of degradation [2, 3]. Consequently these changes make the unambiguous identification of the link between source and contamination a real challenge.

Ratios of chemicals that degrade at the same rates retain the initial oil signature until they can no longer be detected. These ratios are termed ‘source’ ratios and can be contrasted to ratios that change substantially with weathering which are termed ‘weathering’ ratios. This is the so called ‘source and weathering ratio approach’ [4]. Such an approach is useful for biomarkers like n-alkanes (n-C_{17} and n-C_{18}) and isoprenoids (pristane, phytane, norpristane). Their ready degradation makes them very useful for fresh and slightly weathered oil spills - particularly diesel and domestic fuel oils - but less reliable for moderately to heavily degraded samples [5, 6]. In such cases analysis of less degradable polycyclic aromatic hydrocarbons particularly two- to four-ring compounds including benzothiophenes are particularly useful because they are present in petroleum and many of its refined products at suitable concentrations. Their relative concentrations vary among different oils making them source specific. They can also be measured using routine analytical methods. In addition some of the ratios remain relatively constant over wide concentration ranges and weathering states. One has to realise that the suite of biomarker and polycyclic aromatic hydrocarbons indices is neither all inclusive nor appropriate for all oil spill studies. Thus maintaining flexibility in the selection of diagnostic indices for a given study is important [4, 6, 7].

The objective of this study is to evaluate the applicability of diagnostic biomarker and polycyclic aromatic hydrocarbon ratios for determining correlation between diesel and gasoline spills on contaminated sites to candidate contamination sources. In order to achieve this target the attention will first be focussed on the way the Flemish fuel market is regulated. In the second step it

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will be investigated in how far diesel and gasoline fuels can be uniquely characterised by means of diagnostic ratios and if this can be linked to a soil contamination.

2 Materials and methods

The fuel market with regard to the specifications of the refined fuels was analysed based on the information supplied by the Belgian Petroleum Federation and the communications of Total Fina Elf [8].

The fingerprinting methodology as described by Wang and Fingas [9] was applied on seven diesel and eight gasoline fuels with the intention to investigate its applicability for determining similarity or difference between fuels. This methodology was preferred since the outcome of the analysis includes the determination of the total petroleum hydrocarbons which can be used in the risk assessment of contaminated sites [10].

Total petroleum hydrocarbons are analysed by Gas Chromatography Flame Ionisation Detection (GC-FID). Identification is carried out by means of GC-FID and Gas Chromatography Mass Spectrometry (GC-MS) including two fractions:

- saturated hydrocarbons
- aromatic hydrocarbons

Separate chromatograms are generated in the GC-MS analysis on the basis of selected ions for alkanes, isoprenoids, steranes, triterpanes, monocyclic and polycyclic aromatic hydrocarbons. Chromatograms corresponding with different m/z-values were generated and compared to each other. Diagnostic ratios were estimated from the observed peak heights in the chromatograms.

A typical sample preparation includes the extraction of the soil sample with 1:1 aceton/hexane using accelerated solvent extraction (ASE). The extract is then filtered and concentrated. The total extracted material can, if desired, be determined by gravimetry. The extraction is followed by a clean-up and further fractionating using a silica-column. Three fractions are collected:

- a hexane fraction, containing the aliphatic hydrocarbons
- a 1:1 benzene/hexane fraction, containing the aromatic hydrocarbons
- a methanol fraction, containing polar compounds.

A sample of a contaminated soil was offered by a refinery and analysed by GC-MS. The soil sample was first weighted and spiked with an internal standard and subsequently fractionated in an aliphatic and an aromatic part. The extracts were diluted prior to analysis in order to avoid overload of the column. Diesel samples were diluted with hexane and followed the same fractionation procedure.

3 Results and discussion

3.1 The fuel market in Flanders

Of utmost importance in oil fingerprinting is the availability of a source ratio unique for a particular source. This means that the truly unique fingerprint has to vary widely in different oils. The specificity of petroleum products in Flanders is lost in three ways:

- Crude oil coming from all over the world is transported via ships or pipelines. Depending on the supply and demand a distributor can decide to buy barrels from an independent federation or a competitor. The origin is than lost.
- In refineries the barrels of different origin are mixed in order to obtain the best mixture with the lowest refining cost (e.g. mixing of sulphur-poor with sulphur-rich oil to keep down the costs for the desulphurisation) and the best specifications for refined products. In Flanders the refineries produce more or less similar products since they have to satisfy Belgian specification requirements. These specifications are depending on the season.
- After refining the fuels are stored in depots. These fuels are then put on the market by the producer himself or depending on the supply and demand by a competitor. In these depots additives are added just before filling the fuelcars according to the desires of the distributor.

As a consequence of this it is hardly possible to assign the origin of fuels using hydrocarbon fingerprints and even less the soil contamination by these fuels. Thus oil fingerprinting can only be applied for recent site contaminations in which a link between contamination and source has to be proved.

3.2 Diesel fuels

Comparison of the chromatograms (not shown here, for details see [1]) enables evaluation of similarity or difference of diesel fuels. An overview of the most important features with regard to oil fingerprinting is given in table 1. Key parameters in the fingerprinting are the isoprenoid-ratios. Table 1 shows the results of the applied diagnostic ratios for the isoprenoids in diesel fuels from different origin. Very commonly used ratios in fingerprinting studies of diesel are n-C_{17}/pristane, n-C_{18}-phytane, pristane/phytane and norpristane/phytane. The different depletion of n-alkanes (n-C_{17} and n-C_{18}) to isprenoids (pristane, phytane, norpristane) is useful as an indicator for weathering represented by the weathering ratios n-C_{17}/pristane and n-C_{18}/phytane. Pristane, norpristane and phytane are about equally depleted. Thus these are possible candidates for source ratios represented by pristane/phytane and norpristane/phytane in the ‘source and weathering ratio approach’.

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Two from the investigated diesels (Q8 and FINA) were similar as witnessed by the hardly different ratios (Q8: n-C_{17}/pristane = 4,12, n-C_{18}/phytane = 3,21, pristane/phytane = 0,89 and norpristane/phytane = 0,92; FINA: n-C_{17}/pristane = 3,89, n-C_{18}/phytane = 3,29, pristane/phytane = 0,90 and norpristane/phytane = 0,88). As can be concluded from the observed ratios, the other diesel fuels were significantly different. Important parameters are the weathering ratios n-C_{17}/pristane and n-C_{18}/phytane for which clear differences are observed (maximum difference n-C_{17}/pristane = 3,49 and for n-C_{18}/phytane = 1,83). Less differentiation is observed for the source ratios pristane/phytane (maximum difference = 0,60) and norpristane/phytane (maximum difference = 0,10). The differences of the latter two ratios is too small making their use for fingerprinting with regard to soil contamination hardly useful, since the differences between source and contaminant due to weathering will probably be much greater then the differences between two potential sources. But also these ratios are sensitive to degradation asking for an approach via more persistent chemicals.

Table 1: Applied diagnostic ratios for the isoprenoids in diesel fuels from different origin.

Distributor	n-C_{17}/pristane	n-C_{18}/phytane	pristane/phytane	norpristane/phytane
ARAL	5,31	3,95	0,84	0,87
SECA	1,80	2,22	1,44	0,94
Q8	4,12	3,21	0,89	0,92
TEXACO	2,13	2,28	1,20	0,86
POLLET	3,40	2,88	0,90	0,90
TWINS	1,82	2,12	1,32	0,84
FINA	3,89	3,29	0,90	0,88

Consequently the use of less volatile and more persistent chemicals like polycyclic aromatic hydrocarbons, steranes or triterpanes is more appropriate. It is empirically observed that the ratio of the alkylated dibenzothiophenes and the alkylated phenantrenes remains constant. Thus this ratio is very useful as a source ratio. Since the ratio of the alkylated dibenzothiophenes and the chrysenes is sensitive to weathering, this ratio can be used as the weathering ratio. However some of these chemicals are only present in limited amounts in diesel fuels. Chrysenes were not detected. The distribution of the C_1-dibenzothiophene isomers and the ratios of some triterpane and sterane isomers could not be used due to the limited chromatographic resolution, the minor concentrations of the latter compounds in diesel distillates and the relatively high detection level. As a consequence the most important diagnostic ratio is the double ratio C_2-alkylated dibenzothiophene/C_2-alkylated phenantrene: C_3-alkylated dibenzothiophene/C_3-alkylated phenantrene noted as C_2-DB/C_2-P: C_3-DB/C_3-P. An overview of these ratios is given in table 2.

Table 2: Applied diagnostic ratios for the polycyclic aromatic hydrocarbons in diesel fuels from different origin.

Distributor	C_2-DB/C_2-P*	C_3-DB/C_3-P**
ARAL	0,67	2,36
SECA	0,55	2,14
Q8	0,57	2,06
TEXACO	0,58	2,15
POLLET	0,57	1,51
TWINS	0,62	2,91
FINA	0,58	2,19

*C_2-DB/C_2-P=C_2-alkylated dibenzothiophene/C_2-alkylated phenantrene

** C_3-DB/C_3-P=C_3-alkylated dibenzothiophene/C_3-alkylated phenantrene

Note that the conclusion based on this ratio is similar to that based on the isoprenoid-ratios. As can be observed from table 2, the ratios C2-DB/C2-P and C3-DB/C3-P for Q8 and FINA are almost the same. Also for diesel fuel from SECA and TEXACO these ratios are not significantly different suggesting that they are more or less the same. The other diesel fuels differ significantly from each other. A graphical overview is given in figure 1.

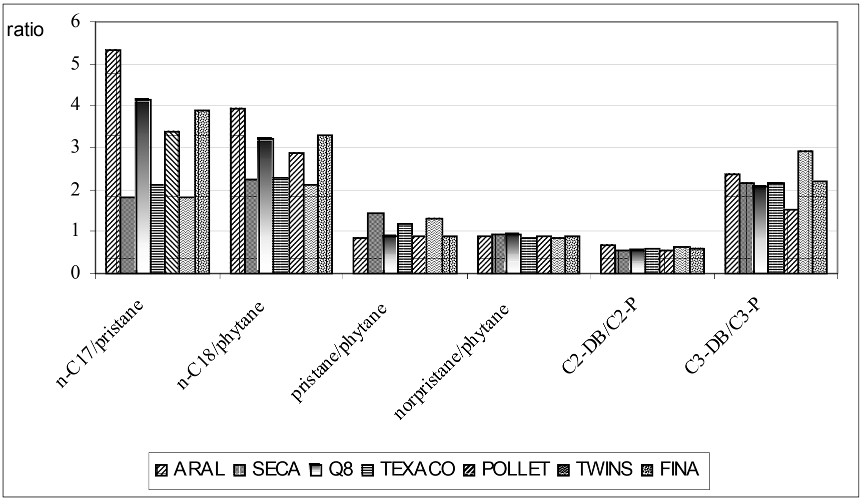

Figure 1: Overview of the diagnostic ratios in diesels.

With regard to soil contamination reasonable resolved high resolution chromatograms (not shown here, for details see [1]) can be obtained with the exception of the polycyclic aromatic hydrocarbons, steranes and triterpanes. These ratios are essential in order to link source and site contamination but are not measurable for routine analytical laboratories. Improvement of the detection level and the chromatographical resolution might solve this problem. The chromatograms showed volatile and less volatile hydrocarbons. The volatile hydrocarbons were dominantly monocyclic aromatic hydrocarbons. Also n-alkanes could clearly be distinguished. Based on the isoprenoid-ratio and comparison with other site contaminations it was estimated that the diesel spill was about 7 years old.

3.3 Gasoline fuels

Evaluation of the chromatograms of gasoline samples (not shown here, for details see [1]) was carried out by means of specific alkane and monocyclic aromatic hydrocarbon chromatograms. Inspection of these chromatograms using the alkane patterns (m/z = 43, m/z = 57, m/z = 71 and m/z = 85) showed four different groups of gasoline:

- WIT OUD-TURNHOUT, PETROS OEVEL and SECA GEEL
- AS OIL TESTELT and FINA
- ARAL
- Q8 EZAERT and VAN DE VEN OEVEL

Analysis of the monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene) did not result in further differentiation (m/z = 91, m/z = 105 and m/z = 120). Only a particular peak height at m/z = 134 for gasoline ARAL deviated significantly from the other samples. Analysis of concentrations of methyl-t-butyl-ether and benzene enabled further differentiation. AS OIL TESTELT and FINA gasoline showed to be the same. The same conclusion is also valid for Q8 EZAERT and VAN DE VEN OEVEL gasoline. Other gasoline fuels were significantly different from those two pairs.

The followed methodology enables one to distinguish similar and different gasoline mixtures. Weathering by evaporation or leaching results in important changes of the observed patterns in the chromatograms making comparison with potential sources almost impossible. Due to these reasons contaminated soil samples were not further investigated and a groundwater analysis would be more appropriate. In addition biomarkers are not present. Product additives (oxygenates) are probably a valuable alternative and are investigated at the moment in another research project. An overview of the observed concentrations of methyl-t-butyl-ether and benzene in the different gasoline samples is given in table 3.

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Table 3: Observed concentrations of methyl-t-butyl-ether and benzene in gasoline samples from different origin.

Distributor	Type	MTBE* (mg/g)	Benzene (mg/g)
WIT OUD-TURNHOUT	superplus	7,5	57
AS OIL TESTELT	superplus	55	37
ARAL	superplus	26	36
FINA	superplus	58	37
Q8 EZAERT	eurosuper	33	72
PETROS OEVEL	eurosuper	50	69
VAN DE VEN OEVEL	eurosuper	36	71
SECA GEEL	eurosuper	18	57

* MTBE = methyl-t-butyl-ether

4 Conclusions

From inspection of the literature it is clear that sufficient instruments for proving similarity or difference between fresh petroleum hydrocarbon mixtures are available. Particularly gas chromatography enables one to determine very specific patterns characteristic for the contamination and the source:

- chromatograms corresponding with different chemical classes and isomers can be evaluated using well defined peaks and peak ratios;
- ratios of specific biomarkers and polycyclic aromatic hydrocarbons can be compared;
- The concentrations of additives or well defined chemicals can be measured;

Comparison of chromatograms for weathered hydrocarbon mixtures is complicated and not always useful due to the very specific situation in Flanders. The observed patterns are drastically changed as a consequence of physical processes and biodegradation. Characteristic ratios are available for polycyclic aromatic hydrocarbons and persistent biomarkers for diesel fuels but not for gasoline fuels. The most persistent biomarkers in diesel fuels are steranes and triterpanes. However these chemicals are only present in relatively small concentrations in diesel fuels requiring a more sensitive and selective detection in order to carry out a reliable determination.

One has to realise that oil fingerprinting has only a limited applicability in Flanders due to the limited specificity of the fuels circulating on the Flemish market. This is an additional feature which makes the linking of a suspected contamination source to an observed soil contamination if not impossible at least very difficult. The diagnostic ratios (biomarkers and polycyclic aromatic hydrocarbons) in diesel fuels are not always unique and in some cases the differences between diagnostic ratios of different diesels is too small not allowing to link the contamination source to the soil contamination Chromatograms of soil samples do not always enable determination of the diagnostic ratios. Improvement of the detection level and the chromatographical resolution might solve this problem. For gasoline fuels differentiation was carried out based on specific alkane and monocyclic aromatic hydrocarbon chromatograms and the concentrations of methyl-t-butyl-ether and benzene.

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