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An overview of environmental forensics

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─────┤ A B S T R A C T ├─────

Environmental forensics has emerged as an important area of environmental studies over the past two decades. There are two basic aspects to any environmental investigation. The first being a conventional approach where the standard EPA (Environmental Protection Agency) methods are used to determine concentrations of selected compounds released into the environment. These methods are extremely well documented and widely used, but only provide information on specific target compounds. Whilst this information may be useful for monitoring purposes it is of little use when trying to determine the source of a spill or contaminants in the environment. If the purpose of an investigation is to determine the source of a contaminant, or point of release, then it is necessary to use a wide variety of analytical techniques and integrate all of the resulting data into one comprehensive data set. It may not always be possible to obtain a unique answer, particularly in the case of groundwater contaminants where there might only be one compound, for example MTBE or PCE. In that case if there are multiple possible sources in the area it may be difficult to narrow it down to a specific source. Furthermore fingerprinting tools that may be useful with complex mixtures may not be directly applicable to single component mixtures. The purpose of this paper will be to provide a brief overview, along with some recent examples of the type of information that is typically obtained in an environmental forensic investigation and how this information may be interpreted. It should be noted that all these examples are related to organic contaminants in the environment since that is the major area of focus at this time. Examples will involve hydrocarbons, chlorinated solvents, and MTBE and BTEX compounds. Techniques will include gas chromatography (GC), gas chromatography-mass spectrometry (GCMS), stable isotopes both bulk and gas chromatography-isotope ratio mass spectrometry (GCIRMS). There are other techniques being used but in a paper of this length we will limit ourselves to these widely used techniques and those applications mentioned above since space does not permit a comprehensive review of all of them.

KEYWORDS | **Environmental forensics. Organic contaminants. Analytical techniques.**

INTRODUCTION

Environmental forensics is a rapidly growing area primarily directed towards determining those responsible for releasing contaminants into the environment (Mudge, 2009; Murphy and Morrison, 2007). There is a wide range of contaminants that are continually being released into a large number of environments. Not only will the nature of the product and environment determine what actually happens to the product but they will play an important role in evaluating the time it may take for the environment to be cleansed, particularly if natural attenuation is the major means for remediating the environment. So in general the majority of environmental issues require a number of basic questions to be addressed:

What is the product? Where did it come from? How long has it been there? Is it degrading?

As illustrated in Figure 1 this can be a very complex problem since there may be multiple sources of the same product, comingling of the same product from different sources, mixing of degraded and non-degraded products and a multitude of other possibilities. Weathering aspects also need to be considered along with the length of time the spilled product has been in the environment. As noted below these investigations cannot depend upon the standard EPA (Environmental Protection Agency) monitoring methods but rather conventional techniques, such as gas chromatography (GC), gas chromatography-mass spectrometry (GCMS) and gas chromatography-isotope ratio mass spectrometry (GCIRMS), specifically tailored to the problem being investigated. No one of these techniques should be used individually but even so it is still not always possible to provide precise answers to these questions. It is still important to use all of the data in an attempt to answer these questions which are basically directed towards finding the responsible parties who should ultimately be required to clean up and remediate the contaminated sites.

The nature and format of this paper will be somewhat different than a regular research or review paper which could be expected to provide case histories of one type or other. This paper will provide some information and examples related to the way in which each individual question is addressed. Many of the fingerprinting concepts currently being used in environmental forensics, particularly for oil spills or spills of refined hydrocarbon products were originally developed for the petroleum industry. The techniques were originally developed for correlating oils with their suspected sources and evaluating the nature of organic matter in source rocks responsible for crude oil generation. There is little to be gained by re-discovering the wheel –many of the analytical techniques and applications have already been developed and are widely used in these other areas and directly applicable to environmental forensics. Practitioners of environmental forensics would do well to research these areas to see the wealth of information already available to them.

Furthermore as mentioned above this paper will not discuss the widely used EPA methods since the purpose of these methods is somewhat different than what is needed in environmental forensics. Many of the methods and applications in these areas are routine and described on many of the EPA web sites (www.epa.gov/osw/hazard/testmethods/-sw846/online/index.htm). The majority of the EPA methods are of little use in environmental forensics. These methods were set up for routine determination of concentrations of specific target components in air, soil and water matrices and specific
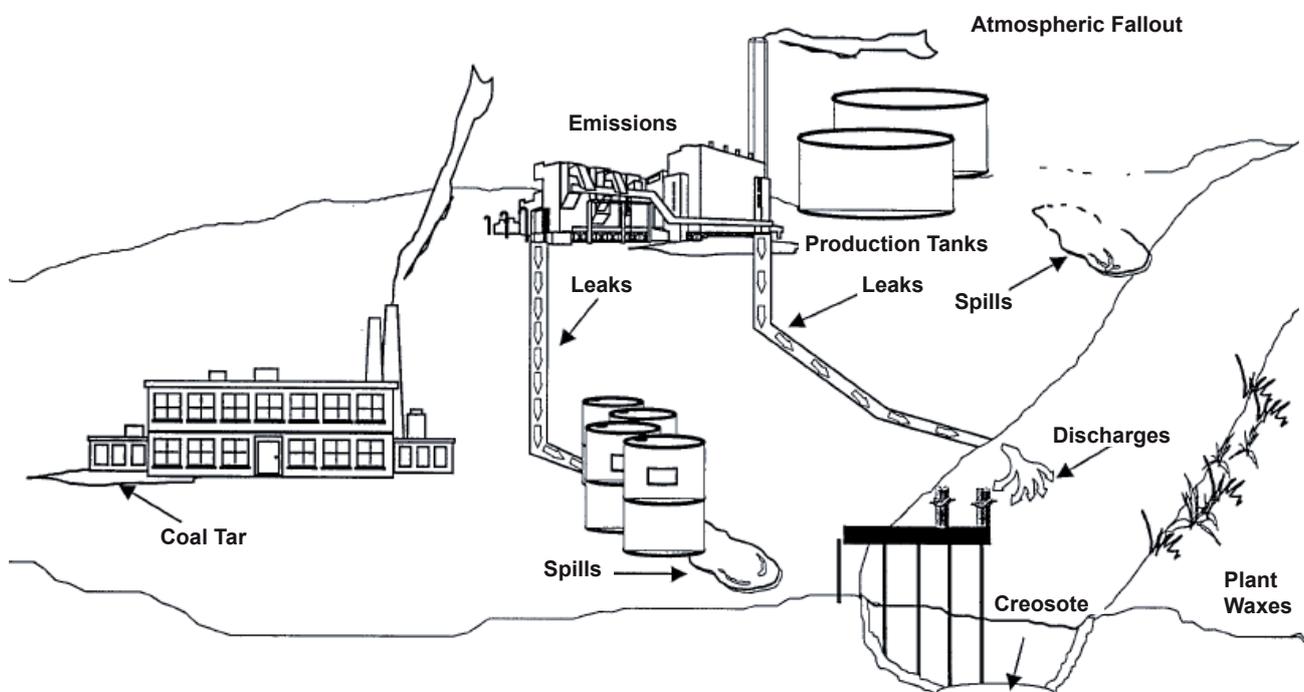

FIGURE 1. The complexity of the problem faced by the environmental forensic scientist is illustrated in this diagram showing the potential for multiple sources as well as interference frombackground sources.

types of environments. The information obtained by these methods should not be ignored but the data should not be over interpreted. Environmental forensics revolves around fingerprinting contaminants and often the concentrations of certain components present in the fingerprint may provide valuable supplementary information. However the fact that a compound has the same concentration in two different samples does not mean the two samples are related.

In the monograph "Environmental Forensics" (three editions of this book have now been published) Douglas *et al.* (2007) have discussed a tiered approach for use in environmental forensic studies (Fig. 2). The concept is based on the idea of characterizing samples using basic techniques initially and then progressively using more complex techniques in order to obtain a comprehensive picture of the composition of the source material and its possible relationship to the spilled product. At this point it is very important to make very clear that source refers to the point of release not the manufacture of a particular product. This is very important since there were papers published many years ago that tried to use certain isotopic characteristics of products made by certain manufacturers and use those properties to determine whether a particular spilled product was produced by that particular company (Beneteau *et al.*, 1999). In other words, just suppose compound A made by company X had an isotopic composition of -28 per mil and then compound A was found in a groundwater sample with an isotopic composition of -28 per mil. That does not mean that compound A in the ground water was made by company X. In many cases the feedstocks used in the manufacture of these compounds varies on a daily or hourly basis and as such, one can expect the characteristics, including the isotopic composition, of these products also vary. However if the compound at the point of release had an isotopic composition of -28 and the compound in the water was also -28 per mil then there would be a strong possibility that they could be related.
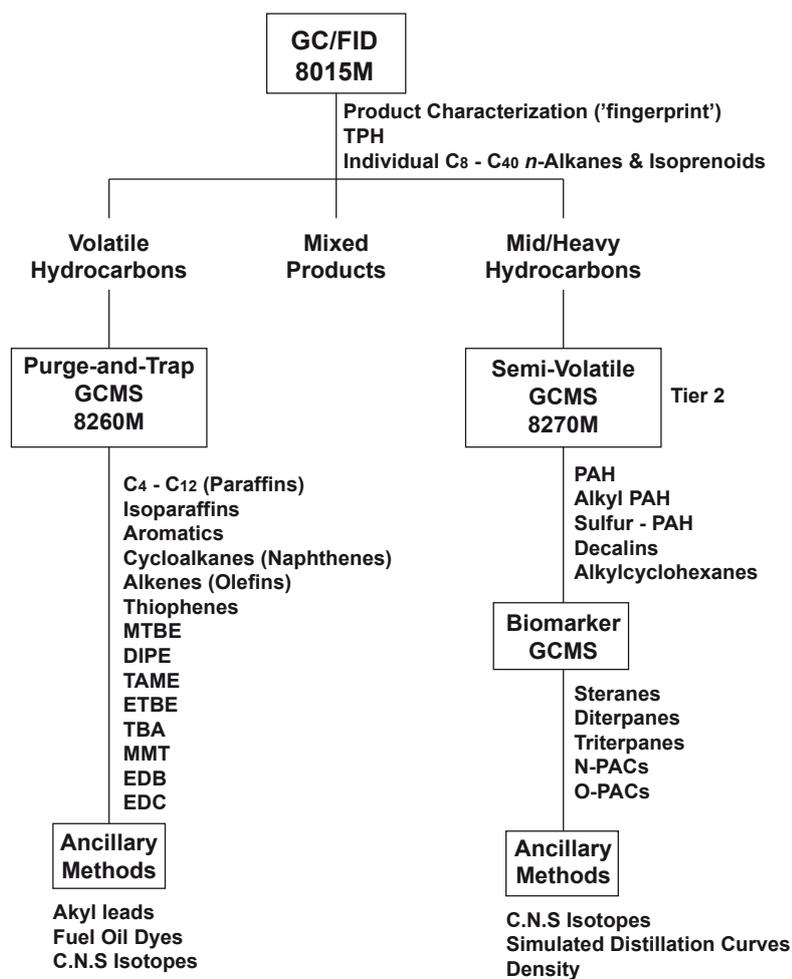

FIGURE 2. A schematic of the tiered analytical approach described by Douglas *et al.*, 2007.

As mentioned above, the so-called tier approach basically starts with relatively unsophisticated techniques that may include visual observations and also depend on the nature of the incident and product that has been released. Clearly a groundwater contamination problem will not yield a lot of useful information from the visual examination if the product is water soluble and present in low concentration. However if a free product is present as LNAPL (light non-aqueous phase liquid) or DNAPL (dense non aqueous phase liquid), such a simple observation can immediately rule out certain potential sources in the area. Similarly, release of hydrocarbon products, refined or crude oils, can often provide a general indication of the nature of the product and some preliminary information on the point of release. For some problems (i.e. vapor intrusion studies) visual observations will provide absolutely no information. The message to be learn at this point is that every investigation is going to be different and there is no one set of rules that can be applied to every problem. Each problem will have its own set of properties and the investigation has to be tailored to the nature of the environment, the product(s) that have been released, the timing of the release and a number of other related conditions. Another important issue to consider at this point is: what is the nature of the problem to be solved? Sounds like a simple question but poor planning and a poor understanding of the problem at hand can lead to expensive mistakes later in the investigation. The two major questions that normally have to be considered are related to whether or not it is a source determination issue or a natural attenuation issue. Determination of the nature of the problem will influence the number of samples to be collected, type of samples, and frequency of sampling. For example, if it is a source determination problem then one set of samples may suffice. However if natural attenuation is being studied then samples may need to be collected quarterly over several months or years. Again each problem is different and it is certainly not the intent of this paper to summarize all the possibilities but rather alert the reader to the care needed in the detailed planning of any such project.

Let us assume the project has been correctly defined, appropriate samples have been collected and preliminary characterization of the samples completed. The next step will be the extraction and, possibly, fractionation of the extract. These processes will again be sample dependent and related to the nature of the questions to be answered. Once again sample preparation is the key to good data essential to any successful environmental investigation. Volatile organic compounds (VOCs) in aqueous samples will be extracted by purge and trap, solid phase micro extraction (SPME) or simple headspace extraction. A vapor intrusion project will require desorption of samples from adsorbent tubes. As already mentioned many times above,

each project is different and careful planning is required to optimize the extraction techniques. Methods are well documented and many of these extraction techniques are described in the EPA guidelines, and that provides a useful source of additional information if needed. VOCs are generally not going to require any fractionation prior to analysis and characterization. Semi-volatile organic compounds (SVOCs) such as crude oils, refined products, or coal tars may require additional fractionation prior to analyses (Wang and Stout, 2007; Mudge, 2009; Philp and Kuder, 2008; Murphy and Morrison 2007;). While many samples can be analyzed as total extracts without fractionation, relationships between samples may ultimately depend on components that are present in relatively low concentrations and additional fractionation will lead to increased relative concentrations of these key components. A simple example of this would be a crude oil –a very complex mixture of thousands of components (Fig. 3). Fractionation by thin layer chromatography (TLC) of high performance liquid chromatography (HPLC) will separate a crude oil into saturate and aromatic hydrocarbons plus polar compounds. Further separation of the saturate fraction into n-alkanes and branched/cyclic hydrocarbons can be achieved through the use of molecular sieves to achieve separation as illustrated below simply using gas chromatography (Fig. 4). The following sections will discuss a few of the significant developments in the analytical techniques used in the subsequent stages of the tiered approach, namely gas chromatography (GC), gas chromatography-mass spectrometry (GCMS) and chromatography-isotope ratio mass spectrometry (GCIRMS).

ANALYTICAL TECHNIQUES

Gas Chrppmatography (GC)

Gas chromatography is probably the most basic and widely used analytical technique in environmental forensics

Whole crude oil chromatogram
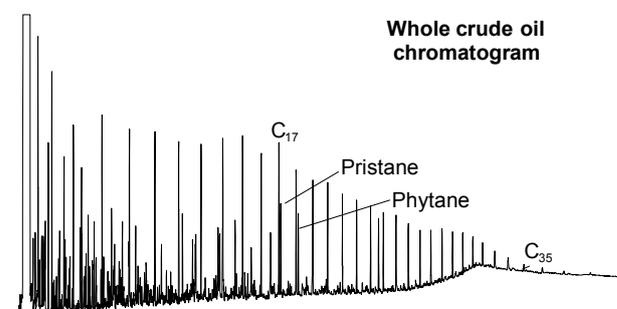
C$_{17}$

Pristane

Phytane

C$_{35}$

FIGURE 3. A typical crude oil chromatogram showing the distribution of the n-alkanes extending from C1 to approximately C40.
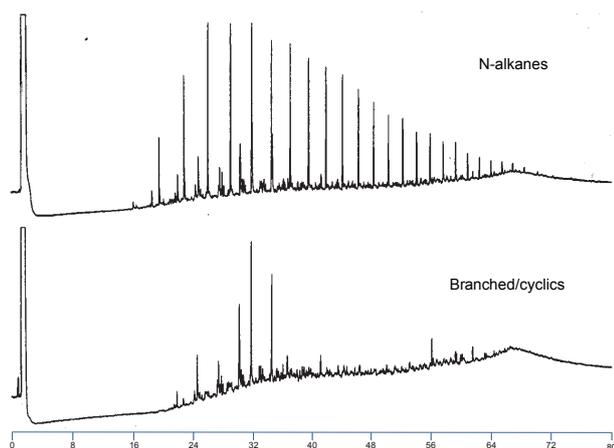
FIGURE 4. Fractionation of the crude oil into saturate and aromatic fractions can increase the compounds of interest. Further fractionation can be achieved through the use of molecular sieving to obtain the n-alkanes and the branched/cyclic fractions as illustrated here.

today and has been a standard analytical technique in many areas for the past 50 or 60 years. Chromatography initially involved two liquid phases but in their classic paper Martin and Synge (1941) suggested the concept of gas liquid chromatography leading to the development of this new tool which was described by James and Martin, (1952). Martin and Synge received the Nobel Prize for Chemistry in 1952 for their work and development of the concept of GC which is now used in virtually every analytical laboratory in the world. Since those early days, gas chromatography has come a long way although most of the major changes have involved column technology and development of new and more sensitive detectors. However the basic concept of a gas chromatography requiring an injector, detector, oven and column has remained unchanged after more than 50 years. Good chromatography is the key to the success of environmental forensics.

Gas chromatography has some limitations. The chromatograms provide us with a fingerprint of the compounds present in the soil, water, or free product. With various levels of fractionation diaromatic hydrocarbons can be separated from triaromatic hydrocarbons, or n-alkanes from branched and cyclic hydrocarbons (West *et al.*, 1990) or isolate sulfur-containing compounds (Hegazi and Andersson, 2007). However gas chromatography does not unambiguously identify the compounds observed in the chromatograms.

A very significant advance that has taken place in gas chromatography over the past few years has been the development of 2D gas chromatography (GC x GC). 2D GC provides a mechanism for taking cuts from the chromatogram as it is separating in the first dimension and

then analyzing these cuts on a second column or second dimension (Fig. 5). This approach is generally combined with a time of flight mass spectrometer which permits rapid characterization of the separated components. It is a very powerful tool for complex mixtures and provides far greater separation than conventional gas chromatography. At the same time it provides far more information than is generally needed for most environmental forensic studies.

Gas chromatographic fingerprints are useful even if the information is limited since they provide an indication on the nature of the spilled product. For example, with some (limited) experience it is possible to tell whether the spilled product is a gasoline, or lubricating oil, or PCB mixture, etc. Furthermore, specific detectors can be used that will help identify the presence of certain compound types. For example, the flame ionization detector is a universal detector but use of a flame photometric detector will identify sulfur containing compounds; an electron capture detector will identify the chlorinated compounds. These are but two examples but the point is that even at this level these additional pieces of information can be very useful in getting a preliminary indication of the nature of the spilled product. Gas chromatography is going to be a prerequisite to any of the other analyses that are in the upper levels of the tiered approach such as GCMS and GCIRMS which will be discussed in the following sections.

Gas chromatography-mass spectrometry (GCMS)

As most people will know GCMS came into commercial use in the early 1970s and associated data systems came a little later. This powerful combination not only permits the separation of compounds present in a mixture but also identification of the separated compounds. It is not the goal of this paper to discuss all of the different types of mass spectrometers since they all have the same basic goal and that is to identify compounds. An ancillary GCMS technique that is exceedingly important is that of single ion or multiple ion detection. In this approach, specific ions that are characteristic of a specific compound or compound class are monitored. In certain environmental forensic studies, GCMS may not be necessary if one is looking for specific target compounds in groundwater samples. If the GC is calibrated correctly and the retention times of the target compounds are known, then GC may be sufficient. However there are certain applications particularly those involving crude oils or refined products where one is attempting to relate the spilled product with the point of release where GCMS is essential primarily using multiple ion detection.

There have been many attempts in the environmental forensic area to use biomarkers but they have certainly not been fully exploited to the extent they have been
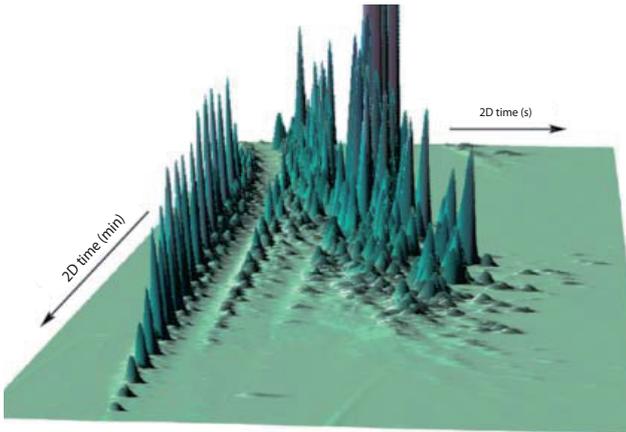
FIGURE 5. 2D Gas chromatography (GC) combined with time of flight mass spectrometry has become an important tool for separating very complex mixtures as illustrated by a crude fraction that has been characterized by 2D GC in this example.

in petroleum geochemistry (Wang and Stout, 2007; Philp and Kuder, 2008). The Biomarker Guide by Peters and Moldowan (1993) and then a totally revised version of this text by Peters, Walters, and Moldowan (2005) provide a comprehensive documentation of the utilization of biomarkers in petroleum related studies. Advances continue and most of the developments that have occurred in the biomarker field since publication of those texts can be found in journals such as Organic Geochemistry, and to a lesser extent Chemical Geology, and Environmental Science and Technology. Other papers of historic interest that should certainly be reviewed include Breger (1963), Calvin (1969), Blumer (1973), Mackenzie *et al*. (1982).

The major classes of biomarkers used in petroleum exploration are equally applicable to environmental forensics. These include n-alkanes, isoprenoids, sesquiterpanes, tri-, tetra-, and pentacyclic terpanes, steranes, and a variety of other compounds, such as diamondoids and S-containing compounds, although not strictly biomarkers can be used in a similar manner. Not every class of biomarker will be present in every type of hydrocarbon product spilled into the environment, with the exception of crude oils which contain all the classes of biomarkers. For example, diesel, containing hydrocarbons in the C_{10} to C_{24} carbon number range will not contain steranes or pentacyclic terpanes in most cases since these occur in the carbon number range beyond C_{24}. Gasoline contain few of the classical biomarkers since it is too volatile for most of these compounds to be present.

In general n-alkane fingerprints are of little use for correlation purposes since they are not specific enough for definitive correlations. On the other hand, n-alkanes can

be very useful to differentiate contemporary background from crude oil derived hydrocarbons (Wang and Stout, 2007; Murphy and Morrison, 2007). Many of the long chain hydrocarbons present in recent soils and sediments are derived from plant waxes. It was many years ago Eglinton and Hamilton (1967) and others (Bray and Evans, 1961; Scalan and Smith, 1970) documented that there is a very marked odd/even distribution of the n-alkanes derived from plant waxes reflecting the mechanism by which these compounds were biosynthesized. As organic matter is buried and becomes more mature, the odd over even predominance decreases until in a mature crude oil that value will be approximately 1. Hence, one can simply use the odd/even predominance of n-alkanes in a sediment to provide a rapid indication as to whether the alkanes at a contaminated site are derived from contemporary organic matter or a fossil fuel source and delineate the impact area of a particular spill. Recently, in N. America, there have many several significant train incidents with large quantities of crude oil being spilled from the derailed trains. Changes in the n-alkane distributions are being used in many of these spills to delineate the extent of the land contaminated by the spilled oil. It is important to mention that although the lighter hydrocarbons will be impacted by evaporation, the odd/even predominance is determined in the higher carbon number range and therefore not impacted by evaporation. It should also be noted that once biodegradation commences it will be the n-alkanes that are impacted most readily and after these have been removed then it will no longer be possible to determine this odd/even predominance.

Pristane and phytane are isoprenoids and relatively abundant in crude oils. These two isoprenoids are clearly identifiable on the GC trace but if the additional families of isoprenoids need to be determined they can easily be detected by GCMS and single ion monitoring of the ion at mass 183. The pristane/phytane ratio varies with conditions in the original depositional environment. The Pr/Ph ratio is not significantly affected by degradation and is an extremely useful parameter for correlating spilled products with their suspected source(s).

There has also been considerable interest in using the C_{17}/pristane or C_{18}/phytane ratio as a tool for age dating environmental samples based on a publication by Christiansen and Larsen (1993), some years ago, who claimed that these ratios could be correlated with age of the spill. While I have no major argument with their original paper, I totally disagree with the widespread use of the calibration chart based on the Christiansen and Larsen data to age date virtually any spill anywhere in the world. There are many reasons for this but one of the most compelling reasons is simply the fact that there is a tremendous variation in the initial ratio of C_{17}/pristane ratios for crude oils coming from different source materials. Hence, you

cannot simply assume all crude oils have the same starting value for this ratio and use the same calibration curve for every spilled oil occurrence worldwide. Furthermore, you cannot assume that all products will degrade at the same rate in totally different environments (Oudijk, 2009). With problems such as this in mind, it should be clear why the C_{17}/pristane or C_{18}/phytane ratios will vary for oils coming from source rocks at different levels of maturity and why the Christiansen/Larsen calibration diagram cannot be used to determine the age of every spill unless it has been calibrated for that particular oil and environment in which it has been spilled.

As mentioned above there are many classes of biomarkers used in the oil exploration business but only a few in the environmental arena. Two classes of biomarkers in addition to the alkanes and isoprenoids described above are the steranes and terpanes. These are very complex mixtures which means that they both produce fingerprints that are very useful for correlation purposes. In both cases GCMS is required to determine the distribution of these compounds, namely mass 217 for the steranes and 191 for the terpanes (Fig. 6).

The terpanes are present as three different families, namely tri, tetra and pentacyclic compounds. The pentacyclic terpanes are derived primarily from bacteria, tetracyclic terpanes are derived from microbial degradation of the hopanes and the tricyclic compounds are probably derived from cell wall constituents of algae. Interestingly enough the precise origin of the tricyclic terpanes has still not been unequivocally established after four decades of research (Philp, 1985; Peters et al., 2005).

The major application of these fingerprints in environmental forensics will be one of correlation of a spilled product and suspected sources. The advantage of these compounds is that they are very resistant to biodegradation and certainly over a fairly short time span, say from the present to a few hundred years, very little alteration will occur to the terpanes. n-Alkanes will disappear very rapidly following biodegradation and with increasing time we will see changes to the isoprenoids but once you move into the cyclic compounds these are very resistant to biodegradation (Wenger and Isaksen, 2002; Peters et al., 2005).

To illustrate the variability expected in terpane distributions of oils from different locations, the terpane distributions from two oils from different sources are shown in Figure 7. Without going into detail of the identity of all the individual compounds, it should be clear that these two chromatograms are very different. The differences reflect the fact that these oils are from different locations and derived from different types of

source materials. Therefore, if tankers were carrying these two crudes and there was an incident where oil was released from one tanker, it would be very easy to determine which tanker was responsible for the release on the basis of these and other biomarker fingerprints. Steranes in crude oils are relatively complex mixtures ranging from C_{20} to C_{30} with a predominance of the homologues in the C_{27}-C_{29} region (Fig. 6). Steranes are derived from sterols present in algae and higher plants and other sources of organic matter (Huang and Meinschein, 1979). For the environmental forensic scientist the sterane fingerprints provide a powerful correlation tool. A good understanding of these distributions can be very beneficial when using sterane distributions for correlation purposes.

To summarize, the above sections have provided a brief summary of the value of GC and GCMS in environmental forensic studies. It is important to emphasize that whereas a petroleum geochemist will undertake detailed interpretations of the individual compounds in these fingerprints, the environmental geochemist will think of them simply as fingerprints to establish possible relationships between different samples. At the same time, I think it is important to encourage the environmental group to expand their knowledge of biomarkers since this can provide additional insight when undertaking the interpretation of the fingerprints.

STABLE ISOTOPES IN ENVIRONMENTAL FORENSICS

The preceding sections have discussed the conventional techniques that have been used for 4 decades in environmental forensics. In recent years, we have seen the expanded use of stable isotopes in environmental forensic
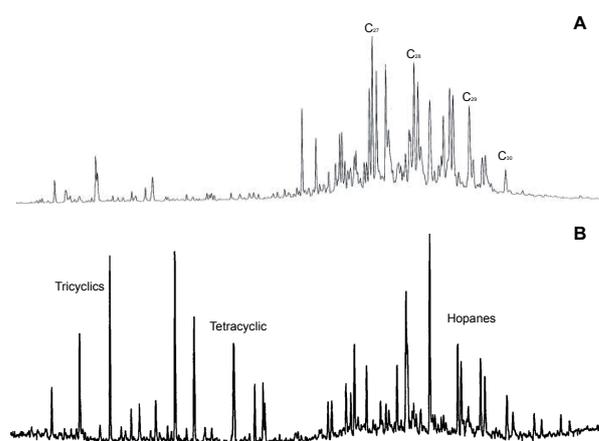

FIGURE 6. Typical sterane and terpane chromatograms following the analysis of a branched and cyclic fraction of a crude oil. These fingerprints are used for correlating spilled products with their suspected source(s): A) Steranes M/z 217, B) Terpanes M/z 191.

investigations. The use of stable isotopes can no longer be considered a new technique since it has been used in the area of environmental forensics for the past 20 years or more. The number of applications and users of this approach has continued to grow as a wider audience gains an understanding of the types of information that can be obtained from the use of stable isotopes in environmental investigations. Investigators with little experience can understand the basic concepts of GC and GCMS relatively quickly and their application to fingerprinting contaminants. The concept of stable isotopes, what they mean, how they are measured and why these values differ as a result of source differences, or from natural degradation, are topics that prove to be a little difficult to grasp for someone with little experience in stable isotopes. The situation is changing and stable isotopes are now becoming a standard item in the tool box of any environmental forensic scientist. It should also be emphasized that all of these tools should be integrated with each other since they all provide useful information in these types of investigations. No one technique should be used on a stand-alone basis except in exceptional circumstances.

Determination of stable isotopes has a long history in the petroleum industry; papers were published many years ago in the 1950s and 1960s indicating the use of stable isotopes for correlation of crude oils with each other and source rocks (Craig, 1953; Silverman and Epstein, 1958; Silverman, 1965; Fuex, 1977). These were bulk isotope values or, one stable isotope value for the total crude oil, representing a weighted average of the isotopic compositions of all the individual compounds in the oil. Stable isotopes have also been utilized very extensively for characterizing natural gas samples and determining the origin and history of natural gas, and provide a powerful tool for differentiating thermogenic and biogenic gas possibly derived from sources such as landfills (Schoell, 1983).
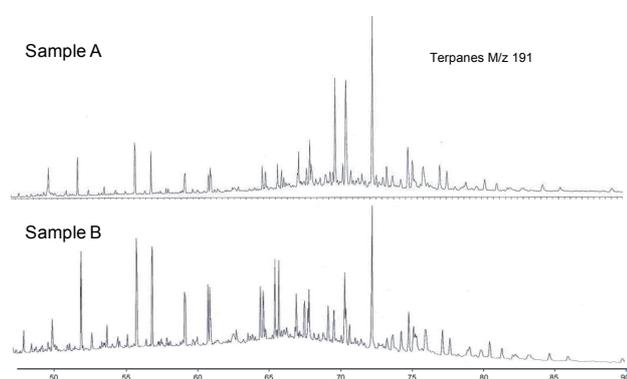

FIGURE 7. Terpane distributions from two crude oils to show differences in oils coming from different sources and as a result have different fingerprints.

Carbon exists as two stable isotopes and different compounds will have different carbon isotope distributions, depending on the extent of fractionation between the two isotopes during formation. The extent of fractionation, or the carbon isotope composition, is determined by completely combusting the material of interest to CO_2 and H_2O, removing the water, and then introducing the CO_2 into the isotope ratio mass spectrometer where the intensities of mass $45(^{13}CO_2)/44(^{12}CO_2)$ are measured relative to an international standard. The resulting ratios are converted in a $\delta^{13}C$ value as defined by the following:

$$\delta^{13}C = \frac{R_{sample} - R_{standard}}{R_{standard}}; \quad R = {}^{13}C/{}^{12}C$$

A major leap occurred in the 1970s when a system was developed that would permit determination of the isotope composition of individual compounds in complex mixtures (Mathews and Hayes, 1978; Freeman *et al.*, 1990; Hayes *et al.*, 1990; Caimi and Brenna, 1993; Merritt *et al.*, 1995; Burgoyne and Hayes, 1998). Unlike the coupling of GCMS, this was a far more complicated task. It was necessary to interface the GC with the isotope-ratio mass spectrometry (IRMS) and also completely convert the compounds to CO_2 and H_2O without the loss of any GC resolution, if C isotopes were being determined, all within a few seconds. Ultimately these conditions were achieved and GIRMS is now used as a tool to determine the isotopic composition of individual compounds in environmental forensics and many other areas. Several years later, a system capable of measuring H isotopes using a different type of interface between the GC and the IRMS system was developed. This development permitted 2D isotope measurements to be made and this was particularly useful in providing information on degradation mechanisms of many groundwater contaminants (Kuder *et al.*, 2005).

An even more recent development has been the capability to determine Cl isotope compositions of individual compounds, and to a very limited degree at this stage also Br isotopes. However the fact that for chlorinated compounds you can now measure C, H, and Cl isotopes provides a very powerful tool for both correlation purposes and studying natural attenuation of groundwater contaminants (Sakaguchi-Soder *et al.*, 2007). There have been many examples where, depending on the environmental conditions, little or no fractionation is observed for one isotope but a significant change or shift may be observed for one of the other isotopes. Hence 2D or 3D isotope measurements can be a powerful approach particularly for vapor intrusion studies where many of the compounds in the indoor air are chlorinated compounds as discussed below.

There are many sites world-wide with buildings that have significant plumes of hydrocarbons that have migrated underneath the building. As a result there is the potential for volatile components from the plume to migrate into the building. The problem then becomes how do you determine whether or not the VOCs in the building are coming from the subsurface or from some commercial product that is in the building? This is made more difficult by the fact that in many cases you are only looking at a single component contaminant and therefore GC and GCMS are of little use in trying to determine the source of the contaminant.

Examples of the typical ranges of values expected for a variety of indoor products containing VOCs are shown in Figure 8. Obviously this is not totally comprehensive collection but it gives some indication of the range of values that might be expected. The following figure shows the results of an indoor air study at a house over a chlorinated solvent plume (Fig. 9). The indoor air value falls in the region encompassing the commercial products. The values for the subsurface sample are considerably heavier than the indoor air value and therefore in that case the indoor

air VOC could not have been derived from the subsurface. Not all cases will be as clear as this one but it illustrates the important role that isotopes may play in this type of study.

A second example is a source related example – most chlorinated solvents are formed by chlorination of various hydrocarbons whereas chloroform is formed via chlorination of methane. The interesting point here is that if the chloroform was analyzed by GC and GCMS it would simply appear as chloroform. However if the chloroform is characterized isotopically then a totally different picture emerges since if the methane was thermogenic then the chloroform will be isotopically heavy, but if the methane was biogenic the chloroform would be isotopically lighter (Fig. 10). Not only would this be useful for potentially differentiating sources but if a manufacturer was known to have changed sources of methane from thermogenic to biogenic at a certain point in time, this could be used to age date a possible release.

A final example of using isotopes in an environmental case is related to MTBE in the groundwater. The example used here is from a gas station in California and it related to the natural attenuation of the MTBE. It can be seen
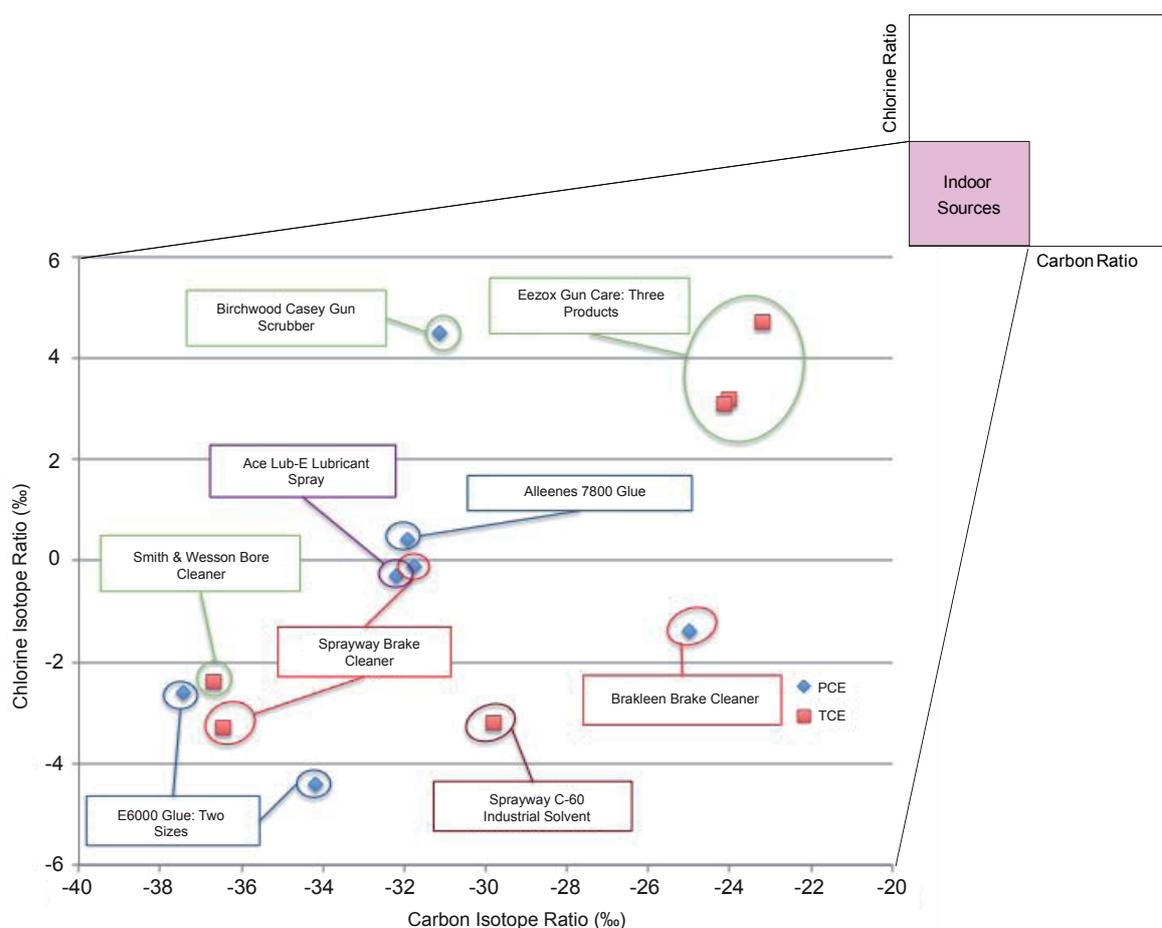

FIGURE 8. An illustration showing the range of C and Cl isotopes that may be expected for a range of household products that contain TCE.

from the isotope data in Figure 11, that there is one area at the site where the C isotope values are very heavy, indicating very extensive degradation of the MTBE. Note at the leading edge of the plume the MTBE has an isotopic composition very similar to unaltered MTBE. However by combining these isotope values and concentrations of the

MTBE in the respective wells it is also possible to estimate the amount of the MTBE that has been removed through natural attenuation.

SUMMARY

This paper has attempted to highlight some of the significant developments that have occurred in the area of environmental forensics over the past four or five decades. Many of these developments initially occurred in the studies related to origin of life and the lunar missions in parallel with developments in the petroleum industry. More recently, and specifically since the mid-1980s, many of these concepts have been extended into the rapidly growing area that is known today as environmental forensics. A primary purpose of the paper is to provide information to the environmental forensic community that has been widely used in petroleum geochemistry for many years and equally applicable to environmental forensics. Some of this information is already used in this area but there is a wealth of information from petroleum geochemistry that many people working in environmental forensics are totally unaware of, but it is hoped that after being exposed to the information in this paper people working in this area will search further in the petroleum literature in order to find this information.
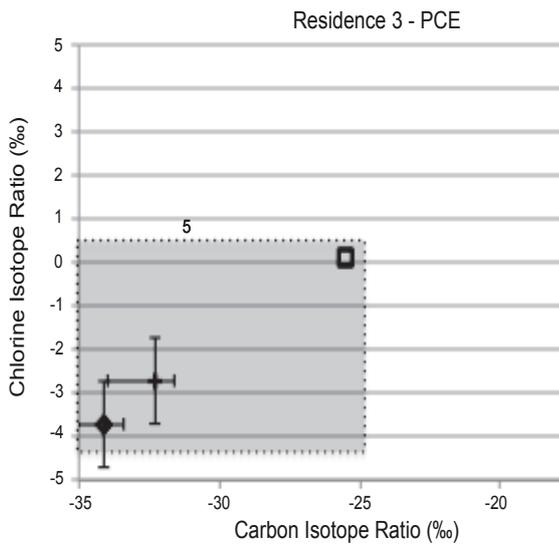

FIGURE 9. An example from the use of C and Cl isotopes in an indoor air study. The difference between the indoor air compound value and the groundwater sample, suggest that in this case the volatil organic compound (VOC) is coming from the indoor source and not the subsurface.
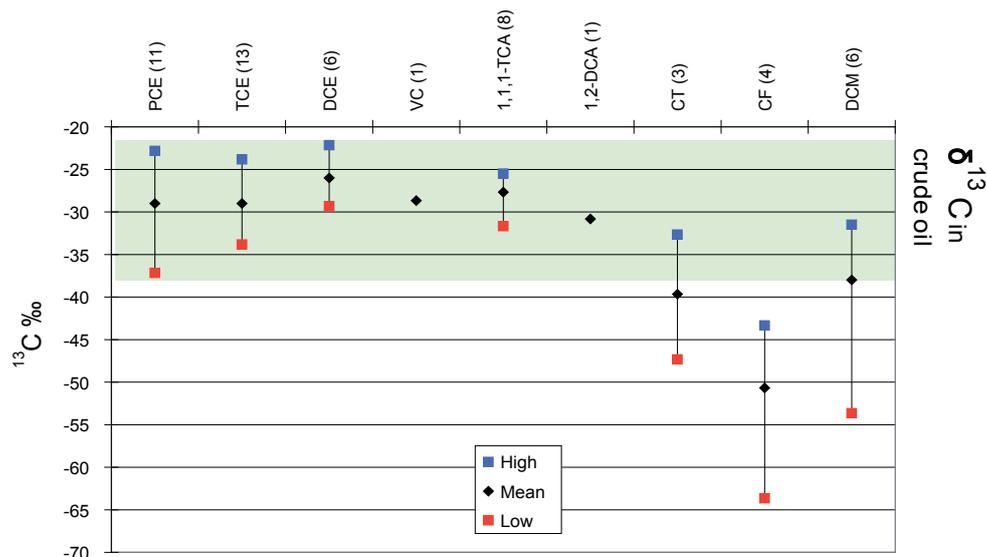
ACKNOWLEDGMENTS

FIGURE 10. A summary of the C isotope values that may be expected for different chlorinated solvents. Note the wide range of values for the chloroform as a result of the methane used in the preparation of the chloroform could be either thermogenic or biogenic.
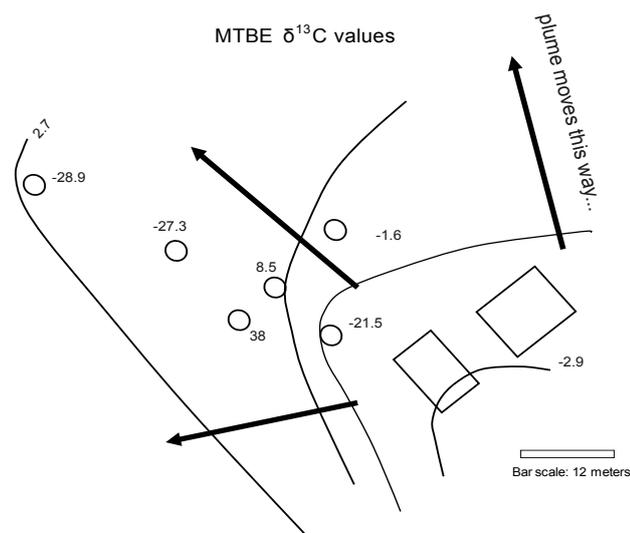
MTBE δ^{13}C values

plume moves this way...

2.7

○ -28.9

-27.3

○

8.5

○

38

○

-1.6

○

-21.5

○

-2.9

Bar scale: 12 meters

FIGURE 11. A diagram showing variations in the C isotope values of MTBE at a gas station site in California. Note the variation in the values resulting from the natural attenuation of the MTBE.

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