

FORENSIC TOOLS FOR Petroleum Hydrocarbon Releases

Dawn Zemo – Zemo & Associates LLC

Subsurface releases of petroleum hydrocarbons (crude oils and refined products) are one of the most frequent causes of groundwater contamination in the United States, and the subject of billions of dollars spent in investigation, remediation, and litigation. Forensics is frequently applied to petroleum hydrocarbon releases because of factors related to: 1) the chemical complexity of petroleum; 2) its weathering in the environment; and 3) frequent commingling of plumes. Many forensic tools are available for petroleum investigations; several have been used for decades and others are now more widely used due to improvements in laboratory analytical capabilities.

The best tools to apply to a particular case depend on the questions posed, so clarity about the ultimate objective of the forensic work is important from the start. For example, a focus on product identification or source attribution is usually quite different from age-dating the release. Crude oil and refined products are complex mixtures of hundreds to thousands of constituents that can have widely varying physio-chemical properties, and some forensic tools are better suited to certain constituents than others. In addition, the sample media, which may be pure petroleum product, soil, dissolved-phase constituents in groundwater, or vapors, also must be considered.

Forensic interpretations regarding petroleum releases must also incorporate impacts of environmental weathering (by evaporation, biodegradation, or solubilization) and impacts of changes in crude oil sources or refinery processes because these factors greatly influence the composition of the mixture. All of these sources of variability differentiate forensic investigations of petroleum from those focused on discrete constituents such as trichloroethene, perchlorate, or nitrate.

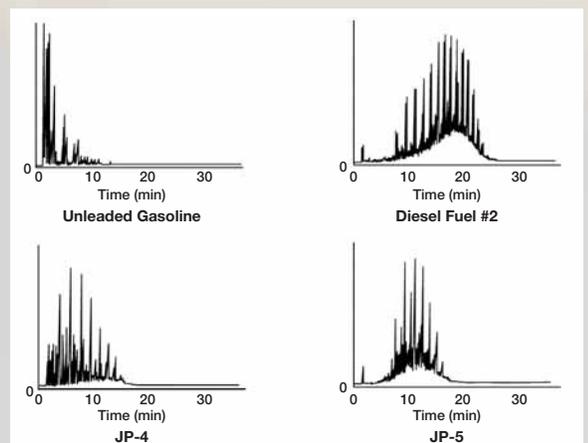
Presently, the most commonly used forensic tools for petroleum releases are: 1) chromatogram pattern matching; 2) analyses of discrete constituents or families of constituents; 3) analyses of additives or blending agents; 4) biomarkers; and 5) stable isotopes. All of these tools have wide acceptance in the forensics community, and the peer-reviewed literature provides many examples of their application.

Because most petroleum constituents have low effective solubilities in water, the dissolved phase of crude oil and most products are similar and limited to relatively few constituents. Therefore, many of the classic forensic tools that were developed for crude oil or

refined products can have utility for soil samples, but are not as useful for dissolved-phase groundwater plumes.

Gas Chromatogram Pattern Matching

This tool has been used for many decades for product-type identification. Its foundation is high-resolution gas chromatography, which separates constituents within a sample based primarily on boiling point. This forensic technique relies primarily on matching the boiling range (carbon range) and the pattern of the peaks or “humps” on the chromatogram of the unknown to known standards (see figure below). The boiling ranges and general chromatographic character of



Example chromatograms for four fuels. Vertical axis is the detector response.

most refined fuels or lubricating oils is widely agreed upon by forensic experts, and multiple examples exist in the literature. The chromatographic character changes with environmental weathering of the petroleum, but in predictable ways. Chromatograms can also show a mixture where multiple products have been released.

Discrete Constituent Analyses and Constituent Ratios

Detailed information about the discrete petroleum constituents present in a sample can be used to distinguish between products of similar boiling ranges. For example, is the product a mixture of gasoline and jet A fuel or is it a wide-cut jet fuel such as JP-4? For the gasoline-range and jet-fuel range products, the workhorse tool is the PIANO analysis, which stands for paraffins, isoparaffins, aromatics, naphthenes (cycloalkanes), and olefins. These five families of hydrocarbon molecules have different properties and occur in products in differing proportions.

The PIANO analysis is essentially an extended EPA Method 8260, in which more than 100 hydrocarbons are quantitatively reported in the volatile range, usually up to molecules with 13 (or 15) carbons. It is usually performed by gas chromatography. For diesel-range and heavier products, the tool most frequently used is the Extended PAH (polycyclic aromatic hydrocarbon) analysis (EPA 8270 SIM modified), where typically up to 53 PAHs are analyzed.

Ratios of the various PIANO components are routinely used to compare similarity among gasolines (see top sidebar at right), and to potentially age-date products due to refining process changes that significantly impact the PIANO signature. The relative proportions of the extended PAHs are used to distinguish petroleum sources from combustion sources (for example, bunker fuel versus creosote). Certain ratios of the alkylated PAHs can be used to compare similarities among petroleum sources. These tools are useful for product and soil samples, but typically are less

useful for dissolved-phase groundwater samples. There is exciting new research into the PIANO-type analysis for forensic evaluation of vapor samples.

Age-Dating Releases via “Weathering Ratios”

A few ratios of discrete petroleum constituents have been used in an attempt to age-date petroleum releases; the theory for these approaches relies on trends in differential weathering rates. The best known examples of these are the (benzene + toluene)/(ethylbenzene + xylene) ratio for groundwater impacted by a gasoline release and the nC17/Pristane ratio for soil or product samples from diesel releases. For diesel releases this approach is based on the fact that straight-chain paraffins (such as heptadecane, nC17) are biodegraded much more quickly than the branched-chain isoparaffins (such as Pristane). These age-dating approaches have been widely disputed in the peer-reviewed literature, and many site-specific variables can affect the calculated ratios and therefore the estimated release date.

Biomarkers

During the formation of crude oil, biochemicals such as sterols are transformed to molecular fossils known as biomarkers, such as steranes. Biomarkers reflect the crude oil source and are very resistant to weathering or refining effects. They are routinely used to distinguish among petroleum sources, especially for crude oils and diesel-range or heavier products. Due to their low solubility caused by their very complex molecular structure, however, biomarkers are not useful in dissolved-phase groundwater plumes.

Additives or Blending Agents

Additives include the alkyl lead packages (TEL, TML, etc.) and lead scavengers (EDB, EDC) that were historically added to automotive gasolines, and oxygenates such as the ethers (MTBE, TAME, etc.) and alcohols (TBA, ethanol) that have

see *Petroleum*, page 35

Case Study: Whose Gasoline Is It?

Sites A and B both had gasoline releases that resulted in product floating on the water table. Product was found in a monitoring well installed in the street between the two sites, and the forensic focus of the case was to identify whose product had migrated beneath the street. Routine analyses such as TPH and BTEX were inconclusive. Product samples were collected from monitoring wells at both sites and from the well in the street; all samples were analyzed for PIANO, in addition to other forensic analyses. The PIANO results implicated Site A for the product beneath the street, as shown by the double-ratio cross plot (below).



What Is Added to Gasoline?

Alkyl lead compounds were added to gasoline to reduce the “knock” in combustion engines. In the U.S. they have been banned from use in automobile gasoline but TEL is still used in aviation gasoline (avgas).

- TEL – tetraethyllead
- TML – tetramethyllead

Lead scavengers were used in leaded automotive gasoline to reduce the adverse effects of lead oxide formation in the engine after combustion. EDB is still used in avgas.

- EDB – 1,2-dibromoethane
- EDC – 1,2-dichloroethane

Oxygenate compounds maintain high octane ratings and reduce carbon monoxide emissions from automobiles.

- MTBE – methyl tertiary-butyl ether
- TAME – tertiary-amyl methyl ether
- TBA – tertiary-butyl alcohol (a metabolite of MTBE)
- Ethanol

Petroleum, continued from page 27

been blended with gasoline relatively recently (see bottom sidebar, p.27). These constituents are routinely used for age-dating gasoline releases when their use is well-constrained in time by regulatory requirements. Research has shown that alkyl leads typically degrade relatively quickly in the environment outside of the product matrix. Additives or blending agents can be present in unexpected products as a result of cross-contamination during fuel transport and storage. The lead scavengers and oxygenates are soluble, and therefore can be useful for forensic evaluation of a dissolved-phase groundwater plume.

Stable Isotopes

Stable isotopes of carbon, hydrogen, oxygen, and sulfur are forensic tools that are relatively new applications in environmental investigation settings. These isotopes are in the signature of the crude oil and therefore reflect the crude oil source. Bulk stable isotopes have been used for decades in the petroleum industry to characterize individual crude oils. Due to very recent advances in analytical techniques, we can now analyze product, soil, groundwater, and vapor matrices for stable isotopes on either a "bulk" or "constituent-specific" scale. Descriptions of forensic and remediation applications for stable isotopes now abound in the peer-reviewed literature, especially constituent-specific applications. However, caution is needed in forensic interpretations because certain isotope ratios change due to biodegradation.

Contact Dawn Zemo at dazemo@zemoassociates.com.

References and Resources.....

Hundreds of peer-reviewed publications focus on the application of the forensic tools for petroleum releases described herein. Two textbooks (below) provide an excellent summary of current knowledge and contain extensive reference lists. Also, see the International Society of Environmental Forensics' peer-reviewed journal, Environmental Forensics (www.environmentalforensics.org/journal.htm).

Morrison, R.D., and B.L. Murphy, eds., 2006. *Environmental Forensics: Contaminant-Specific Guide*, New York, Academic Press/Elsevier.
Murphy, B.L., and R.D. Morrison, eds., 2002. *Introduction to Environmental Forensics*, New York, Academic Press.

ZymaX
A DPRA Company

**Groundwater &
Environmental Forensics**

Isotope Analysis

D/H ¹³C/¹²C ¹⁵N/¹⁴N ¹⁸O/¹⁶O ³⁴S/³²S

¹³C/¹²C of Chlorinated Solvents in Groundwater and Soils

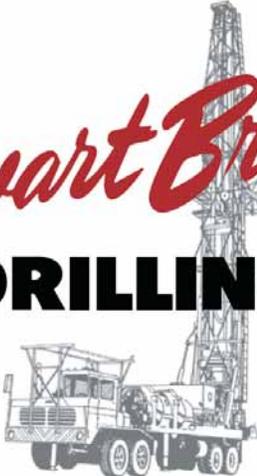
¹⁵N/¹⁴N of NO₃, NH₃; D/H + ¹⁸O/¹⁶O in Groundwater
D/H, ¹³C/¹²C, ¹⁴C of Crude, Petroleum Fuels & Gases

ZymaXisotope.com
805.544.4696 isotope@zymaxusa.com

Stewart Brothers

DRILLING CO.

*Providing Quality
Drilling Services
Since 1945*



Stewart Brothers Drilling Company
P.O. Box 2067
306 Airport Road
Milan, New Mexico 87021
(505) 287-2986
<http://www.stewartbrothers.com>

Services Include:

- Water Exploration
- Mud Rotary
- Air Rotary
- Packer Testing
- Coring
- Mineral Exploration
- Environmental



Geomatrix

SMARTER SOLUTIONS FOR A COMPLEX WORLD

- Water Resources Engineering
- Resource Forecasting and Optimization
- Climate Change Impact Analyses
- Integrated Watershed Management
- Modeling

Offices throughout the U.S.
Please visit www.geomatrix.com
for career opportunities - EOE

