

Environmental Forensics case studies for the non-technical person

Introduction

The need to identify, delineate, and differentiate contaminants resulting from various sources is often an important part of site investigations where knowledge of the source(s) of contamination is sought, and where an equitable settlement of the resulting remedial liability and damages is at stake.

Significant advances have been made over the last 20 years with regard to detailed compositional analysis of petroleum in the environment—often referred to as “chemical fingerprinting.”

Some of the earliest applications of chemical fingerprinting were related to marine oil spills. The *Exxon Valdez* grounding, for example, was a situation in which knowledge of crude oil or residual fuel geochemistry was applied to identify and differentiate the spilled oil in Prince William Sound and to assess its environmental impacts (Bence et al., 1996). In the past few years, continued developments in the chemical fingerprinting of refined petroleum products, such as gasoline, diesel fuel (Kaplan et al., 1997; Stout et al., 2002) and other contaminants, have aided in answering environmental forensic questions surrounding the source and/or age of contamination¹.

By combining techniques such as aerial and satellite photography and multi-spectral imagery interpretation and a determination of the first commercial availability of the contaminants of concern with analytical data collected at the site, consultants are often able to determine the timing and location of the source of the contamination. This actual application of environmental detective work draws upon divergent skills in science and engineering to find and interpret information to help interpret the results for the non-technical members of the team².

The goal of this paper is to provide specific illustrations of how the science of Environmental Forensics can be used to determine site contamination and the source of that contamination.

Examples where Environmental Forensics would be used:

- Cost allocation at a Superfund Site
- Site investigation for property transfer
- Insurance litigation
- Toxic tort
- Natural resource damage
- Site assessment
- Marine oil pollution³

¹ <http://nepis.epa.gov/Adobe/PDF/30006HLT.PDF>

² <http://www.pressomatic.com/kestrelhorizons/upload/Environmental%20Forensics-Role%20in%20Acq%20and%20Lit.pdf>

³ Introduction to Environmental Forensics, Second Edition. Edited Brian Murphy and Robert Morrison. Elsevier Academic Press Inc. 2007. Page 3.

Typical questions that environmental forensics seeks to answer are:

- Who caused the contamination?
- When did the contamination occur?
- How did the contamination occur?
- How extensive is the contamination?
- Are the test results valid? Is there evidence of fraud?
- What level of contamination have people been exposed to?
- Can environmental forensics assist in allocating remediation costs?⁴

Analytical Tools

Chemical fingerprinting data developed for such sites must provide sufficient specificity to recognize the particular type(s) of contaminant, characterize the degree(s) of weathering, and provide the diagnostic information necessary to distinguish and perhaps allocate among multiple source(s) and/or assess their likely age(s). A "turnkey" analytical program that utilizes standard methods of analysis (e.g., U.S. EPA Methods 8015, 8020, 8260, and 8270) usually will not produce the chemical detail needed to defensibly answer environmental forensic questions. The principal reason for this is that the conventional target analyte lists for compliance-driven measurement methods simply do not include the dominant and important hydrocarbon compounds that make up petroleum. For example, the PAH and BTEX target compounds measured using standard EPA 8270 and 8260 typically make up less than 5 to 8 percent of the total PAHs and volatiles in most petroleum products, and as such the data have little or no diagnostic value (Douglas and Uhler, 1993).

Instead, methods suitable for environmental forensics investigations are performance-based modifications to existing EPA SW-846-series methods that target a greater suite of compounds in contaminants that are useful for source identification and differentiation⁵.

Some of the other tools at the disposal of the investigator are:

- Site history-including documents, photographs, pass release information
- Statistical methods
- Statistical tools for ratio data
- Principal component analysis and receptor models
- Chemical fingerprinting
- Graphical methods⁶⁷

Case Study #1-Two gasoline service stations, which had the leaking tank?

Background

Gasoline Fingerprinting

Automotive gasolines are complex fuels blended from a variety of intermediate refinery streams, each with different physical and chemical properties (Stout et al., 2001). Historic gasolines were blended primarily to achieve physical specifications for boiling range, vapor pressure, oxidation stability, and octane with the goal of suitable

⁴ Ibid, page vii.

⁵ <http://nepis.epa.gov/Adobe/PDF/30006HLT.PDF>, page 2.

⁶ Introduction to Environmental Forensics, Second Edition. Edited Brian Murphy and Robert Morrison. Elsevier Academic Press Inc. 2007.

⁷ Practical Environmental Forensics: Process and Case Histories. Sullivan, Patrick; Agardy, Franklin; and Traub, Richard. John Wiley & Sons, Inc. 2001.

engine performance, such as cold/hot starts, acceleration, knock, resistance to vapor lock. How these physical specifications were achieved was largely left up to the individual refiners. Consequently, historic gasoline compositions were quite variable in chemical composition. Modern reformulated and oxygenated gasolines must now meet stricter physical and chemical specifications. The latter include restrictions on the content of olefins, sulfur, benzene, total aromatic hydrocarbons, and oxygen. These specifications have reduced the compositional variability that had existed within the gasoline pool; nonetheless, on a molecular level chemical differences between different "types" of gasolines persist depending on the refining process (Beall et al., 2002; Stout et al., 2001). In this example, both gasolines (presumably) met federal RFG and ASTM and performance requirements, yet each exhibits distinct hydrocarbon distributions. It is apparent that the RFG from Refiner A achieved octane primarily from the blending of MtBE (RON 115) and iso-octane (RON 100), whereas Refiner B achieved octane from MtBE and toluene (RON 124). This probably reflects a difference in refining capabilities. For example, Refiner B does not employ an alkylation unit and must rely upon aromatics (toluene) to achieve the necessary octane. So let's see how we use this information on gasoline variability to conduct a gasoline-fingerprinting investigation.

Case Study

The objective of this investigation was to determine if contaminants encountered under a street separating two service stations was correlated to free-phase gasolines found on two adjacent service station properties. Detailed gasoline analysis was conducted on free phase product samples from each property and from beneath the street. Weathering had affected the samples differently; therefore, some differences were apparent. In spite of weathering differences, the gasolines recovered from each station revealed genetic differences related to refinery blending. Station B's gasoline contained an abundance of particular isoparaffins, namely, 2,2,4-, 2,3,4- and 2,3,3-trimethylpentane which indicate that Refiner B blended alkylate into its gasolines. Station (Refiner) A apparently did not use alkylate in production of its gasoline(s). The relative absence of these isoparaffins in the 'Street' indicated it was consistent with the gasoline from Station (Refiner) A⁸.

Case Study#2-Past and present pollution problems at a truck stop.

Background

Diesel-Fuel Fingerprinting

Diesel fuel #2, used in on-road vehicles, belongs to the distillate family of fuels. As the name implies, the production of distillate fuels involves vaporizing and re-condensing, which distinguishes these fuels from the higher-boiling-range residual fuels (e.g., fuel oil #6). With minor exceptions, diesel fuel #2 generally boils within the range of approximately 100°C to 400°C, which roughly corresponds to a carbon range of C7 to C25. The specific characteristic of any given diesel fuel #2 depends on: (a) the specific "recipe" by which it was refined and/or blended (e.g., hydrotreated versus straight-run), (b) the nature of the crude-oil feedstock (e.g., sweet versus sour crude), and (c) the intended market (e.g., onroad-versus off-road-grade diesel fuel; Stout et al., 2004). Each of these factors can introduce considerable variability in the detailed molecular composition of distillate fuels. This variability provides an opportunity for the environmental forensic

⁸ <http://nepis.epa.gov/Adobe/PDF/30006HLT.PDF>, pages 2-4.

investigator to unravel issues, such as the source(s) of diesel fuel-derived contamination. Due to the detrimental effects (e.g., corrosion, wear, deposit buildup) sulfur has on engine and furnace parts, and the implications for deleterious air quality impacts, sulfur content of most distillate fuels has been long specified (Gruse, 1967). The first U.S. specification for diesel fuel #2, dating from 1922, required <1.5 percent volume sulfur (< 15,000 ppm; Gruse, 1967). However, it was quickly learned that the higher the sulfur content, the greater were the maintenance problems encountered in diesel engines. Thus, in practice, most historic diesel fuels contained <5000 ppm sulfur. In 1993, owing to concerns surrounding air emission (not engine maintenance), U.S. EPA required that "low-sulfur," on-road varieties of diesel fuel contain < 500 ppm sulfur. Prior to 1993, on-road diesel fuels #2 contained an average of 2,500 ppm sulfur (U.S. EPA, 2000) (i.e., five times higher than the current limit). Even more stringent sulfur specifications for on-road diesel fuels are planned for the future. U.S. EPA has proposed a rule that would require refiners to further reduce the sulfur maximum in 80 percent of the on road diesel fuels sold from the current maximum, 500 ppm, to 15 ppm (0.0015 % vol) by June 1, 2006. (The remaining 20 percent of the on-road diesel would need to meet the 15 ppm limit by 2010.) This difference in sulfur content, with time, can prove useful in certain environmental forensic investigations where the "age" of diesel fuel determines liability. So let's look at how we can use this information to conduct a diesel-fuel fingerprinting investigation.

Case Study

The objective of this study was to determine the age(s) of contaminants at a truck stop that changed owners in December 1993, with the agreement that existing contamination was the responsibility of the former owner and any new contamination was the responsibility of the new owner. In 1997, NAPL thickness was observed to increase dramatically despite ongoing recovery, prompting the previous owner to suspect that a recent (post-sale) UST release had occurred. Because each operator had received diesel fuel from a variety of sources over the time of operation, the conventional fingerprinting data (e.g., isoprenoid ratios, PAH distributions, and low-boiling biomarkers), which might normally recognize distinct types of diesel, yielded ambiguous results, most likely due to the long-term nature of the release. Age-dating based on degrees of biodegradation (Christensen and Larsen, 1993) was inappropriate (the fresh-dispensed diesel fuel was erroneously estimated to be eight years old by this method). However, when the total sulfur content was measured in the NAPLs and modern dispensed samples using ASTM Method D- 4294-03, and then compared to the historic trend for diesel fuel #2 sold in the northeastern U.S., as compiled from National Institute of Petroleum and Energy Research (NIPER) annual databases, the apparent NAPL ages became clear. The evidence clearly demonstrates that most of the 25 NAPLs (M#) and all eight of the dispensed diesel fuels (D#) from the site contained less than 0.5 percent (<500 ppm) sulfur. This indicated that most of the NAPLs were consistent with low-sulfur diesel fuels produced after the 1993 regulation requiring <500 ppm sulfur. The few NAPLs containing more than 500 ppm total sulfur were likely from the area of the site where the former owner's USTs storing pre- 1993 diesel fuels were located. These results demonstrated that the increase in NAPL thickness observed in 1997 was the result of recent releases of diesel fuel, and thus the responsibility of the new owner⁹.

⁹ Ibid, pages 5-6

Conclusion

Environmental Forensics has been an integral tool for site assessments and other environmental investigations. Significant advances have been made over the past 20+ years with regard to detailed compositional analysis of various contaminants, often referred to as "chemical fingerprinting". In this article we examined that conventional EPA test methods are often inadequate for use in environmental forensics analysis. For example EPA test methods 8270 and 8260 are inadequate for forensics analysis of PAHs since this test typically makes up only 5-8% of the total PAHs and has little or no diagnostic value. In addition to analytical testing, there is a multitude of graphing and statistical methods which are employed due to the fact that most site assessments have multiple possible sources of the contaminant in question. Finally we looked at two simplified cases studies where environmental forensics was utilized to help determine the responsible party.