



CERCLA's Petroleum Exclusion and the Use of Chemical Forensic Methods

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Legacies of Refineries and Petroleum Terminals

In the early 1980s, the increase in crude oil production in the U.S., Saudi Arabia, and elsewhere coupled with the low demand for gasoline in the U.S., resulted in what was known as the "oil bust" of the 1980s. One outcome of this "oil bust" was the closure of one-third of U.S. refineries. These closed (and abandoned) refineries were at different stages of contamination at the time of their closure. Today, many of these former refinery sites are the focus of CERCLA cleanup actions. Additionally, many of the leaks and spills that occurred from the operation of fuel terminals over the past decades resulted in contamination of adjacent river sediments. The declaration of these rivers as Superfund Sites subjected the bordering terminals to CERCLA actions, as part of multiple responsible parties.

In all of these cases, the presence of contamination from some sources is not much in doubt, but the sources of petroleum may be in question, and the liability under CERCLA may also come into question because of what is known as the petroleum exclusion. This discussion will cover the latter issue. To incur liability under CERCLA, a release of a hazardous waste into the environment must have occurred. However, under 42 U.S.C. §9601(14) the definition of hazardous waste excludes "petroleum, including crude oil, or any fraction thereof which is not specifically listed or designated as a hazardous substance". Therefore, for CERCLA to be applicable to an abandoned refinery site or a petroleum terminal, the contamination has to have been impacted by a hazardous waste.¹ Determining the origin of contamination (whether petroleum-excluded material, hazardous waste, or a mix) requires careful application of forensic methods including, but not limited to, chemical fingerprinting techniques.²

¹ Note that many cleanups, while managed by the U.S. Environmental Protection Agency (EPA) under CERCLA, involve state statutes where there is no petroleum exclusion. This article does not cover jurisdictional and regulatory conflict issues.

² Other lines of evidence to support a petroleum exclusion case include, for example, operational histories, cleanup histories, release reconstruction, and hydrogeology.

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In this issue, we present the chemical analytical tools that can be used to differentiate crude oil and petroleum products from hazardous wastes to ultimately determine whether a site is subject to CERCLA's petroleum exclusion clause.

What Is a "Hazardous Waste?"

Under RCRA, 40 CFR Part 261, EPA defines hazardous waste as characteristic waste and listed waste.

- A **characteristic hazardous waste** meets one or more of the physical characteristics of ignitability, corrosivity, reactivity, and toxicity. These physical characteristics are defined by specific parameters (e.g., corrosivity has $\text{pH} < 2$ or $\text{pH} > 12.5$), which can be determined through waste analysis. Once a hazardous waste no longer exhibits the characteristic that caused the waste to be defined as hazardous, it is no longer labeled as a hazardous waste.
- A **listed hazardous waste** is a waste that appears on one or more of the specific lists of hazardous waste in 40 CFR Part 261, Subpart D (e.g., EPA hazardous waste number K052 is for "tank bottoms (leaded) from the petroleum industry"; see Table 1).

Table 1.
Example EPA listed hazardous wastes

Industry and EPA Hazardous Waste No.	Hazardous Waste
K048	Dissolved air flotation (DAF) float from the petroleum refining industry
K049	Slop oil emulsion solids from the petroleum refining industry
K050	Heat exchanger bundle cleaning sludge from the petroleum refining industry
K051	API separator sludge from the petroleum refining industry
K052	Tank bottoms (leaded) from the petroleum refining industry
K169	Crude oil storage tank sediment from petroleum refining operations
K170	Clarified slurry oil tank sediment and/or in-line filter/separation solids from petroleum refining operations
K171	Spent hydrotreating catalyst from petroleum refining operations, including guard beds used to desulfurize feeds to other catalytic reactors (this listing does not include inert support media)
K172	Spent hydrorefining catalyst from petroleum refining operations, including guard beds used to desulfurize feeds to other catalytic reactors (this listing does not include inert support media)



Photo source: Assenmacher T. MK-II fuel tank cleaning. Available at: http://www.alberg37.org/Project%20DB/Fuel_Tank_Cleaning/Fuel_Tank_Cleaning.htm.

Tank bottom sludge

Chemical compounds in many of the listed hazardous wastes are also present in crude oil and petroleum products. Examples include many of the polycyclic aromatic compounds, benzene, lead, phenols, and MTBE, among other chemicals. Therefore, the mere presence of these common chemical constituents in a site's soil or groundwater media does not, in itself, indicate the presence of a hazardous waste. In these cases, using chemical forensics supported by other methods to identify the origin of the chemicals in environmental media may be extremely important in determining whether CERCLA is applicable at abandoned or operating sites.

Some of the chemicals in crude oil, petroleum products, and their additives are described below, followed by a discussion of some of the chemical forensic tools that can be used to identify the origin of contamination to environmental media.

Composition of Crude Oil, Petroleum Products, and Their Additives

Crude oil and petroleum products naturally contain a complex mixture of many organic compounds classified chemically by their structure. Some of these compounds include:

- BTEX, the collective name for benzene, toluene, ethylbenzene, and xylenes.
- Polycyclic aromatic hydrocarbons (PAHs), including naphthalene, 2-methylnaphthalene, acenaphthene, anthracene, fluorene, fluoranthene, pyrene, phenanthrene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, chrysene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene.
- Metals that are indigenous to crude oils, including antimony, arsenic, barium, beryllium, cadmium, cobalt, copper, lead, manganese, mercury, nickel, selenium, silver, vanadium, and zinc, among other metals.



Additives that were used to improve the performance of petroleum products may be present in some product samples. Depending on the circumstances, these additives could be subject to the petroleum exclusion. Some of the additives include:

- Phenolic compounds (used as antioxidants), including amino phenols, and other ortho-alkylated phenols, and tert-butyl-p-cresol
- Alcohols, glycols, amides, amines, organophosphate salts (used as anti-icing agents)
- Some halogenated hydrocarbons, such as dichloroethane and ethylene dibromide (to improve flow under cold weather conditions)
- Tetraethyl lead and other organic leads (used as anti-knock additives)
- MTBE (used as an additive to gasoline to reduce carbon monoxide emissions and increase fuel octane).

Chemical and Related Forensic Methods to Determine the Type and Source of Contamination

Ideally, a chemical fingerprinting program starts by collecting a set of samples representing crude oil and petroleum products from the refinery or terminal, waste samples, and background soil samples, which themselves can contain significant quantities of many naturally occurring metals (e.g., arsenic). In some cases, petroleum products can be found in pipelines that may still exist onsite. Waste material samples may be obtained from waste lagoons or waste-carrying pipes. Background samples can be collected from locations not impacted by the former site operations. These samples represent the potential “end-member” sources to contaminated areas. In addition to the source samples, contaminated areas will have to be sampled.

After sample collection, a laboratory analytical program is designed to focus on chemical characterization of the samples. Once analytical data are generated, several techniques can be used to determine the origin of contamination at the locations in question. Some of these techniques include:

- Gas chromatograms can be analyzed to determine the general hydrocarbon composition (e.g., crude oil or petroleum products like gasoline or diesel).
- Statistical analysis tools (e.g., Principal Component Analysis) can be used to analyze metals and other chemical groups’ data. These tools compare the chemical composition of different sample groups to determine whether the samples in question resemble waste, petroleum excluded material, background, or a mix.
- Chemical diagnostic ratios (used to determine the concentration of one chemical compound divided by another, indicating relative amounts of both in a sample) are used in the published literature to characterize and identify contamination sources to a sample. For example, the lead to arsenic ratio was used to differentiate contamination sources from background sources of these metals in one study.

- Tracking chemical characteristics along a plume of light, nonaqueous phase liquid (LNAPL): Crude oil and refinery products along an oil plume beneath a former refinery site preserve their chemical fingerprint characteristics. If an LNAPL plume traveling under a waste unit is impacted by hazardous waste, there may be a change in the fingerprint (for example, the GC chromatogram, or the PAH and metal ratios). Comparison of LNAPL samples collected upstream and downstream from a waste unit could provide clear evidence of hazardous waste impacts to the LNAPL plume, if any.

The ultimate goal of these environmental forensic techniques is to track chemical characteristics specific to wastes. For example, settling sludges in tank bottoms are typically associated with wax crystals and asphaltene material. Gas chromatograms can identify the presence of such compounds to determine whether a sample is impacted by sludge wastes. Also, some chemicals concentrate in hazardous wastes at levels higher than their typical ranges in crude oil, petroleum products, and background. Statistical techniques can analyze chemical concentration ranges in a sample to evaluate whether that sample has been impacted by a hazardous waste.

Challenges and Difficulties

In abandoned sites, petroleum products and wastes may no longer be available for sampling. In these instances, a forensic chemist has to rely on older chemical data that are not likely to be of fingerprinting quality. Depending on the available historical chemical data, some of the chemical fingerprinting analysis techniques can still be used for evaluating whether hazardous wastes had impacted the site samples, and for deciding the applicability of the petroleum exclusion. For example, statistical techniques can be used to determine whether the historical metals data for the site's soils exhibit a pattern similar to that of crude oil, petroleum products, and/or background versus hazardous wastes. Also, forensic evidence (e.g., operational histories, cleanup histories, historical practices, aerial photographs) in addition to the chemical evidence will be significant in determining the presence of hazardous wastes and ultimately the applicability of the petroleum exclusion to those abandoned sites.

Knowledge of the chemical characteristics of wastes generated from refinery process units and petroleum terminals, an understanding of historical processes, and detailed knowledge of chemical fingerprinting tools are all required for successful determination of sources of contamination to environmental media. ●●●

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Please contact Tarek Saba or Paul Boehm at Exponent if you would like additional information on this issue of our Environmental Forensics Notes.

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