

Resolution of Suspected Tank Release of Diesel Fuel Using Diagnostic Compounds and Biomarkers

Jun Lu, Deborah Dees Kowalewski

AECOM, Long Beach, USA

Email: Jun.Lu@aecom.com, Deborah.Kowalewski@aecom.com

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Abstract

During a routine inspection in a petroleum product terminal, hydrocarbon staining was found in soil along the perimeter of a diesel fuel tank. As the observation was made a few days after a magnitude 5.1 earthquake in the general area of the terminal, the hydrocarbon staining in the soil was suspected to be a result of a leak from the tank. The observation triggered an immediate tank inspection, which included examination of tank exterior, piping and connections; pressure testing; wall thickness gauging; and an inventory check. Results of the initial inspection suggested that there were no integrity issues with the tank. Before more vigorous and more disruptive inspections were conducted, chemical fingerprinting was conducted to assess the nature of soil staining and potential connection with the "suspected" tank leak. Samples were collected from the site, including a diesel fuel sample from the tank, a light non-aqueous phase liquid (LNAPL) sample from the monitoring well in the immediate vicinity, and representative soil samples from the perimeter of, and beneath, the tank. A tiered laboratory analytical approach was taken, which included initial gas chromatography-flame ionization detector carbon chain analysis and final gas chromatography-mass spectrometry or detailed fingerprint analyses. Based on the results of initial inspection, knowledge of LNAPL mobility in response to earthquake seismic waves, and chemical fingerprints of representative samples, it was determined that the soil staining was not a result of suspected tank release but remobilization of hydrocarbons from the historically impacted soil beneath the tank to the soil along the perimeter of the tank.

Keywords

Tank Leak, Seismic Wave, LNAPL Mobility, Diagnostic Compounds, Biomarkers, Source Identification and Correlation

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1. Introduction

On a routine site inspection of a petroleum product terminal, hydrocarbon staining was observed in soil along the perimeter of a diesel fuel tank. As the observation was made a few days after a magnitude 5.1 earthquake in the general area, the hydrocarbon staining in the soil was suspected to be a result of a leak from the tank. However, the preliminary inspection did not reveal any issues with the tank. This, combined with the knowledge that oil seeps induced by earthquake seismic waves occur often in the general area, leads to a belief that the staining is likely due to seismic wave-induced soil compaction and light non-aqueous liquid (LNAPL) remobilization. Before more vigorous and more disruptive inspections were conducted, chemical fingerprinting was conducted to assess the nature of soil staining and potential connection with the “suspected” tank leak. This paper presents the approach and findings of initial site investigation and chemical fingerprinting. As the soil staining was proved not to be caused by suspected tank leak, the paper also provides a case study that demonstrates avoidance of an unnecessary remedial investigation through identification of suspected diesel source using hydrocarbon fingerprints and biomarkers.

2. Initial Investigation

According to the operating protocol of the petroleum terminal, any anomalous observation made during routine inspection of the facility needs to be investigated immediately. As the diesel fuel in the tank was suspected to be the source for the soil staining, the tank was investigated using standard procedures such as inspection of the tank exterior, piping and connections; pressure testing; wall thickness gauging; and an inventory check. Review of the gathered information suggested that there were no issues with the tank. With the findings from the preliminary inspections, it was believed that the soil staining was likely caused by the change in LNAPL mobility in response to Earthquake seismic wave and not the suspected tank leak.

Given the long history of the site as a petroleum terminal and presence of petroleum-free products in a nearby monitoring well, it was believed that the soil beneath the tank and immediate area contained saturated or residual LNAPL from historical releases. The LNAPL is immobile under normal conditions. However, it may become mobile either due to decrease of residual saturation or increase of LNAPL pore pressure in the soil [1]-[3]. The decrease of residual saturation is typically associated with water level decline because the LNAPL has higher residual saturation in saturated zone media than in unsaturated zone. Because the soil staining at the site was observed at the surface, which is more than ten feet above the water table, this mechanism does not apply. The increase of LNAPL pore pressure would be the likely mechanism responsible for making immobile LNAPL become mobile. From an LNAPL mobility perspective, in order for LNAPL to migrate, it must enter the soil pores by displacing fluids already existing there. During an earthquake, seismic wave oscillation could stress LNAPL-containing soil and drive LNAPL out from soil beneath the tank to soil along the perimeter of the tank.

Oil or LNAPL remobilization associated with earthquakes has been well documented. In the same general area, USGS [4] observed a new oil seep flowing in the Northern Ojai Valley, approximately 60 miles away after the magnitude 6.7 Northridge Earthquake in 1994. Divers also described accounts of seepage changes in Santa Barbara Channels after the 1971 San Fernando Earthquake (California Offshore Oil and Gas Seeps Map). During a study of another petroleum-impacted site, the author also learned that not long after the earthquake LNAPL was detected in a monitoring well in which LNAPL was not previously present for long time.

Based on the results of the tank inspection and knowledge of the LNAPL mobility in relation to an earthquake, it appears that the soil staining is not caused by the suspected tank release. To further rule out the possibility, chemical fingerprinting was conducted to provide an additional line of evidence before disruptive inspections such as draining the tank and inspection of tank interiors were conducted.

3. Chemical Fingerprinting Analysis

Chemical fingerprinting is a forensic technique that uses patterns of compounds and their ratios to determine the nature of the products. This technique is widely used in petroleum hydrocarbon source identification and correlation. At the site, possible impacts on the media from the “suspected” tank leak include 1) stained soil along the perimeter of the tank, 2) potentially impacted soils beneath the tank, and 3) LNAPL in the shallow aquifer (*i.e.*, the first aquifer at the site). Chemical fingerprints of hydrocarbons in the above media would provide forensic information to meet the objective of determining if the hydrocarbons from stained soils along the tank perimeter are a result of the potential leak of the diesel fuel tank.

3.1. Sampling and Laboratory Analysis

Based on the initial investigation, it was believed that the impact would be shallow even if the tank had leaked. Hand augering appears to be the most efficient way to collect soil samples. The sample locations are shown in **Figure 1**. For the perimeter area, the auger was advanced vertically down to 9 feet below ground surface (bgs) with samples collected at surface, at 4 feet bgs and 9 feet bgs. Five locations were sampled in this perimeter area, three in stained soil area and two in an un-impacted area. For the soil beneath the tank, the auger was advanced at three locations with an angle of approximately 45 degree. An equivalent vertical interval of sampling was conducted from surface down to the bottom of the bore holes. A total of 24 soil samples were collected from five borehole locations. A sample of the LNAPL was collected from the nearby monitoring well MW-A with a dedicated Teflon bailer and a sample of diesel fuel was collected from the tank.

Upon their collection, the samples were immediately placed in laboratory supplied pre-cleaned sample containers, labeled, packaged in appropriate sized coolers, and chilled to approximately 4°C. Corrugated cardboard and bubble wrap were placed under and around sample containers to minimize the possibility of breakage. Chain-of-custody forms were filled out for the sample coolers, inserted in sealed plastic bags, and placed inside the coolers. The samples were then shipped to designated laboratories following standard shipping protocols.

A tiered laboratory analytical approach was taken using gas chromatography-flame ionization detector (GC/FID) carbon chain analysis for screening to minimize the number of samples for detailed fingerprint analyses. Based on carbon chain analysis, the general distribution of hydrocarbons may be revealed to gain some preliminary understanding of types of products in the media [5]. Given the known fuel in the tank (*i.e.*, diesel), samples with hydrocarbons that are not source related to the diesel or in low concentrations can be disregarded for further analysis.

An example of carbon chain analysis is shown in **Table 1** and on **Figure 2**. As can be observed, no individual compounds are identified in the analysis; instead all compounds are integrated into a broad array of hydrocarbon ranges (C₇-C₈, C₈-C₉, C₁₃-C₁₄, etc.). For a diesel fuel, the hydrocarbons typically range from C₈ to C₂₅.

Table 1. An example of results of carbon chain analysis.

Analyte	Method 8015B—Gasoline Range Organics (GRO) (GC)				
	Result	Qualifier	RL	MDL	Unit
C7-C8	1400	J	2000	980	mg/Kg
C8-C9	1800	J	2000	980	mg/Kg
C9-C10	1500	J	2000	980	mg/Kg
C10-C11	1600	J	2000	980	mg/Kg
C11-C12	1000	J	2000	980	mg/Kg
C12-C13	ND		2000	980	mg/Kg

Analyte	Method 8015B—Diesel Range Organics (DRO) (GC)				
	Result	Qualifier	RL	MDL	Unit
EFH (C13-C14)	2000		50	25	mg/Kg
EFH (C15-C16)	1100		50	25	mg/Kg
EFH (C17-C18)	870		50	25	mg/Kg
EFH (C19-C20)	480		50	25	mg/Kg
EFH (C21-C22)	280		50	25	mg/Kg
EFH (C23-C24)	140		50	25	mg/Kg
EFH (C25-C26)	83		50	25	mg/Kg
EFH (C27-C28)	50		50	25	mg/Kg

Notes: GC = gas chromatography; RL = reporting limit; MDL = method detection limit; J = estimated result; EFH = extractable fuel hydrocarbons; mg/Kg = milligrams per kilogram.

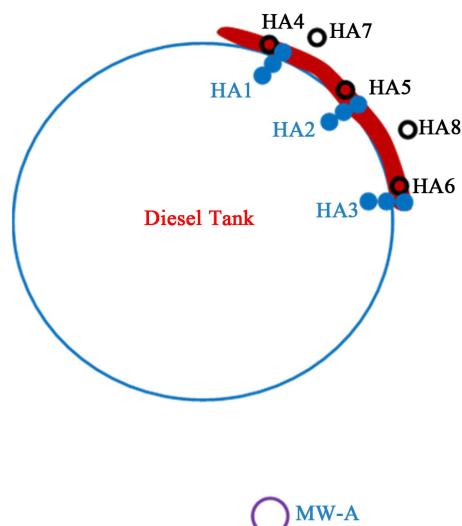


Figure 1. Sample locations relative to the suspected leaking tank (diameter is 150 feet). Area in red is hydrocarbon-stained soil. Black circles are for vertical hand auger sampling boreholes and blue dots are slanted sampling boreholes beneath the tank. MW-A is the monitoring well with LNAPL.

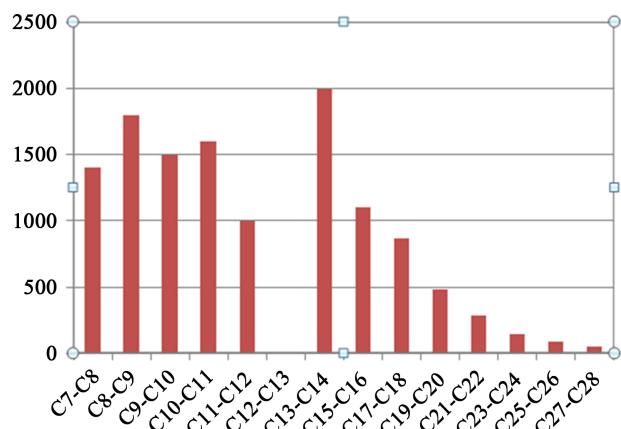


Figure 2. Pattern of GRO and DRO compound distribution.

On chromatograms, diesel fuel has a bell-shaped pattern [6] [7]. In this case, from diesel range organics (DRO) analysis, the right half of the bell is observed in which the hydrocarbons peak at C13-C14 and taper away at C27-C28. The gasoline range organics (GRO) part is not as straight forward because of the weaker solvent, less efficient extraction and higher report limits. For sample screening, DRO analysis is of primary importance. Based on the potential presence of diesel, this sample was retained for further analysis. Using this approach, the original 24 soil samples were reduced to eight for further analyses.

A total of ten samples (eight soil samples and two product samples) were sent to specialized laboratories for chemical fingerprint analyses. In a typical chemical fingerprint study, GC/FID method is often conducted before more advanced method such as gas chromatography-mass spectrometry (GC/MS). However, given the objective of this investigation and nature of potential source (*i.e.*, diesel), GC/MS was conducted to obtain the information necessary.

3.2. Analytical Results and Interpretations

GC/MS analysis generally conforms to U.S. Environmental Protection Agency 8270. On selective ion monitoring mode, the analyses provide ion profiles and concentrations of a wide range of diagnostic compounds and

biomarkers. Each profile provides a different set of chemical fingerprints and thus diagnostic information for source identification and correlation of samples under investigation.

An initial review revealed that the hydrocarbons from the ten samples fall in three groups: 1) soil beneath the tank; 2) soil along the perimeter; and 3) LNAPL from the monitoring well. To determine the source relationship with the diesel fuel from the tank, only four samples were involved, namely the diesel fuel sample, LNAPL sample, soil sample at 9 feet bgs beneath the tank, and stained surface soil along the perimeter. It was also found that among the types of chemical fingerprints obtained from laboratory analyses, m/z 85 profiles and associated data, and sesquiterpane biomarkers provided the most critical information for the source determination.

3.2.1. m/z 85 Profiles

The GC/MS full scan m/z 85 ion profiles of the four selected samples are shown in **Figure 3**. m/z represents mass divided by charge number of ions. The type of profile primarily shows characteristics of straight chain hydrocarbons [8] [9]. As straight chain hydrocarbons are typically the predominant resolved peaks in fresh diesel fuels and also most susceptible to biodegradation, depletion of these compounds relative to the more biodegradation resistant isoprenoid compounds in the environment after release provides information on degree of biodegradation and in some cases, time of release of diesel fuels.

The diesel fuel from the tank is shown on **Figure 3(a)**. The straight chain hydrocarbons starts at C₈, ramps up and peaks at approximately C₁₈, and slopes down to approximately C₂₇. The product sample from the nearby monitoring well and the soil sample beneath the tank at 9 feet bgs are shown on **Figure 3(b)** and **Figure 3(d)**. The peaks of the ion profiles are both at approximately C₁₄, which is a lot lighter as compared with tank fuel. It was noted that for these two samples, the heavier part of chromatograms (*i.e.*, from the peak to the right) look

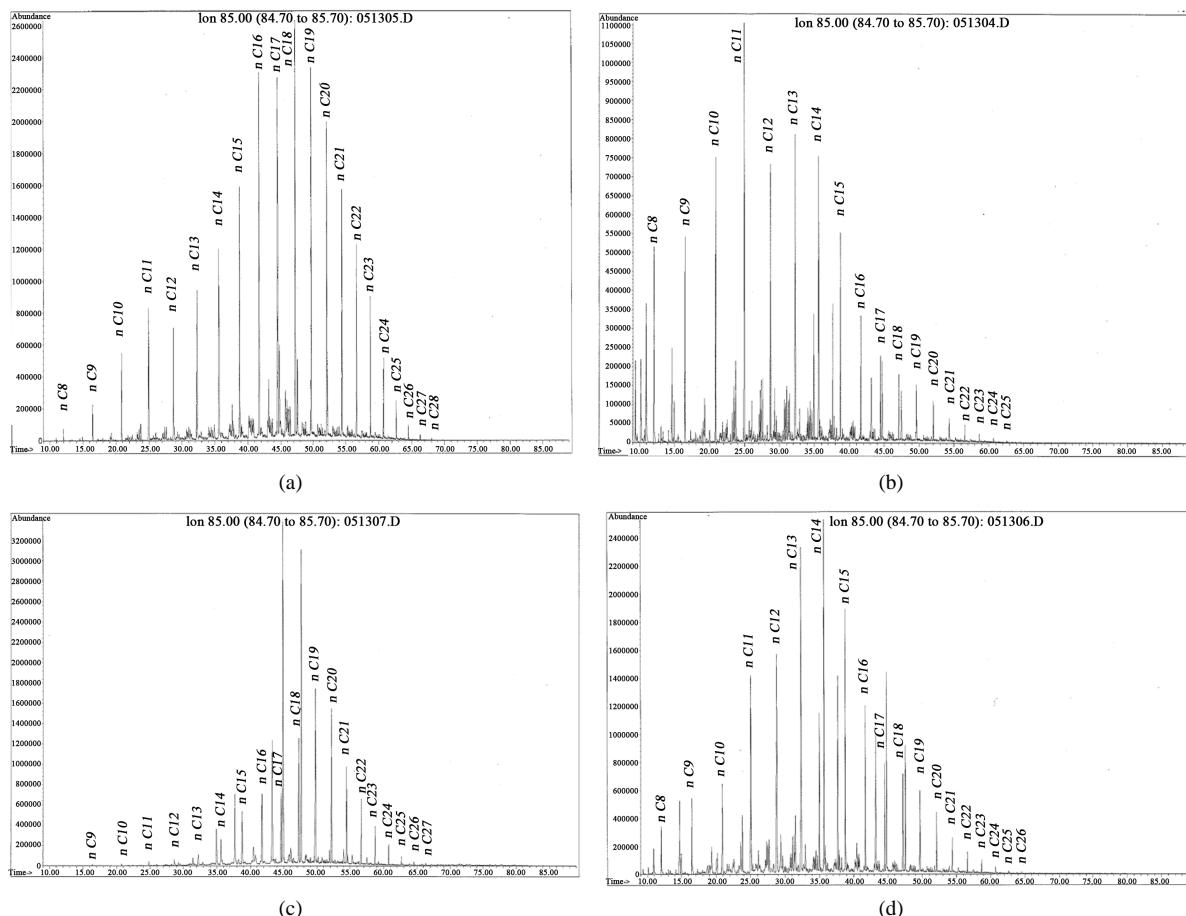


Figure 3. m/z 85 ion profiles of the selected samples of interest. (a) Diesel fuel from the tank; (b) Product sample from the monitoring well nearby the tank; (c) Stained surface soil; (d) Soil sample from beneath the tank at 9 feet bgs.

essentially identical. On the lighter part of chromatograms, the product sample contains additional component which is likely a lighter product (e.g., kerosene) that comingled with the historically released diesel fuel. The stained soil sample near surface is shown on [Figure 3\(c\)](#). The peak of the ion profile is at C₁₉, which is similar to the tank fuel sample. Differences are observed between the two samples. First, the stained surface soil sample appears to lack hydrocarbons in the range from C₈ to C₁₁. Second, the two isoprenoid compounds pristane and phytane are overwhelmingly high as compared to their straight chain hydrocarbon neighbors nC₁₇ and nC₁₈. It is possible that these differences result from evaporation and/or biodegradation. However, given the short time frame (a few days) and relatively low vapor pressures of these compounds, neither biodegradation nor evaporation is likely responsible for the differences observed.

The ratio of nC₁₇ over pristane can also provide some forensic information. Christensen and Larson model [10] presented a method of age dating diesel fuel using nC₁₇/pristane ratio. The model was critiqued by many authors, who cautioned about the validity of the assumptions including constant degradation rate and similar ratios between the sites where the method was developed and the sites of use [11]-[13]. However, many practitioners in the forensic community have also used it successfully in determining or constraining the time of releases. In this study, the ratio was calculated to be 0.2, by which the release can be interpreted to be approximately 18 years or older. It is understood that this estimation isn't necessarily completely accurate but it is clear that the release did not occur recently.

Based on all these analyses, it can be concluded that the product from the nearby monitoring well and hydrocarbons in soil beneath the tank are not source related to the diesel fuel in the tank. While the chemical fingerprints of hydrocarbons in the stained soil along the perimeter of the tank have some similarity with those of the diesel fuel in the tank, the pattern and degree of alteration of hydrocarbons suggest that these hydrocarbons are not source related to the tank diesel fuel.

3.2.2. Biomarkers

Biomarkers are complex molecules derived from formerly living organisms and have been found in crude oils with little or no changes from their parent biochemicals (*i.e.*, biogenic precursors) [8]. Given the biodegradation-resistant nature of these compounds, they are of extreme value for chemical fingerprinting. For example, even when the degradation prone compounds (e.g., straight chain hydrocarbons) are completely depleted in the products of interest, the biomarker compounds still preserve the source fingerprints so that source identification and/or correlation may be made.

In crude oils, various types of biomarkers are present, typically in the carbon range of C₁₀ and above.

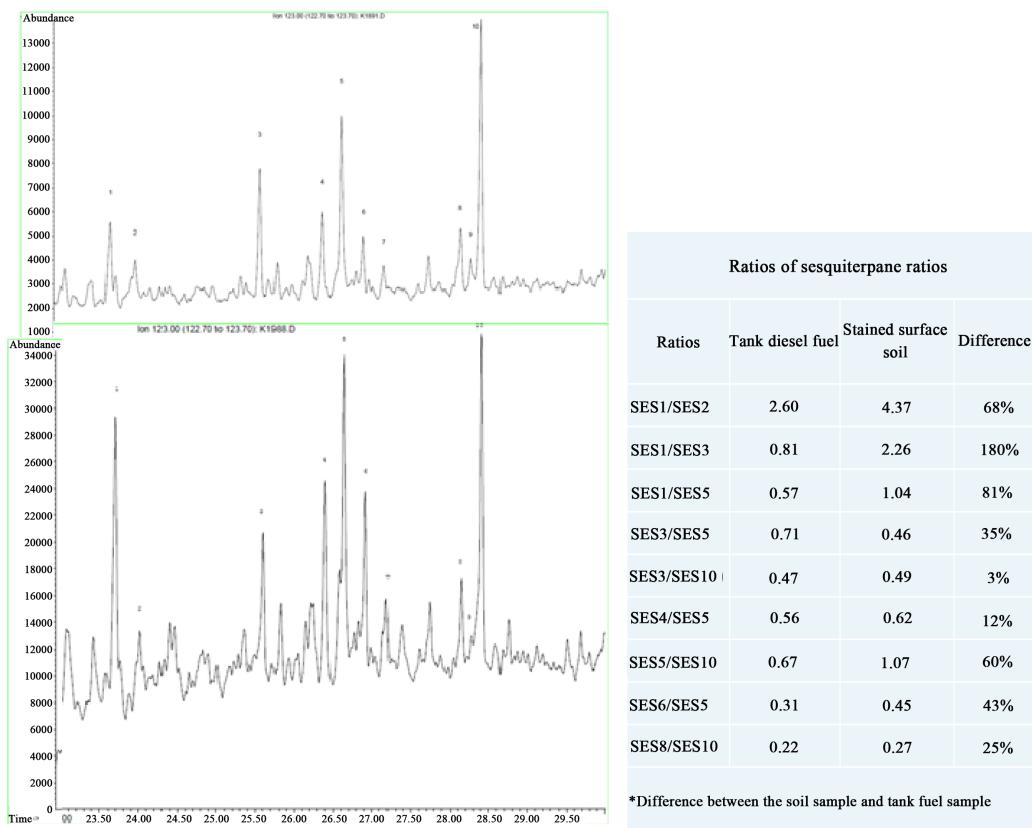
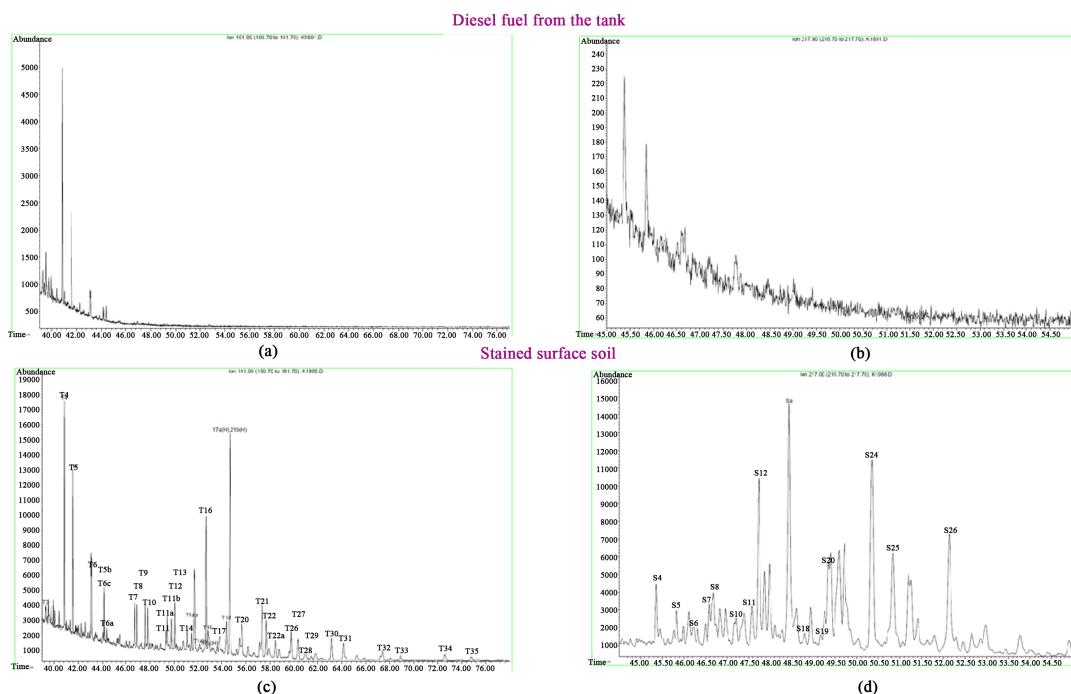
For light diesel fuels (*i.e.*, #1 and #2), sesquiterpanes are present and their patterns and ratios have been used for source identification and correlation [8] [14]. Heavier biomarkers such as terpanes and steranes are low in concentrations in light fresh diesel fuels; however, their relative concentrations can be increased during mild to severe degradation due to preferential depletion of lighter components in the products. To confirm the preliminary conclusions drawn previously, sesquiterpane, terpane and sterane biomarkers were examined for the tank diesel fuel and the stained surface soil sample.

Sesquiterpanes are bicyclic paraffins containing approximately 15 (sesqui) carbons [14]. In the two samples of interest, their patterns are shown in [Figure 4](#). It is apparent that sesquiterpane profiles (*i.e.*, patterns) of both samples are different. Ratios were also calculated for quantitative comparisons and shown in [Figure 4](#). As can be observed, among nine ratios, five are different by 35% to 180%.

Terpane biomarkers are in a wide carbon range from C₁₉ to C₃₅ and the characteristic compounds are reflected on the GC/MS *m/z* 191 profiles. As for sterane biomarkers, the carbon range typically spans from C₂₀ to C₃₀. GC/MS profiles *m/z* 217 and *m/z* 218 are characterized by these compounds respectively. In the samples of interest, the terpane and sterane biomarkers (*i.e.*, *m/z* 191 and 217) are shown in [Figure 5](#). Differences are apparent as there are no biomarkers present in the tank fuel sample while both types of biomarkers are present in the stained soil sample. Lack of the heavier biomarkers in the fresh diesel fuel is due to low concentrations. As the stained soil is moderately to severely weathered, the heavier biomarkers are relatively enriched and therefore become detectable. These pieces of information are consistent with the previous analysis.

4. Conclusion

The fingerprint data collected, GC/MS full scan *m/z* 85 ion profile and associated diagnostic compounds and

**Figure 4.** Sesquiterpane profiles and ratios.**Figure 5.** m/z 191 and 217 ion profiles of the selected samples of interest. (a) Terpane biomarkers of diesel fuel from the tank; (b) Sterane biomarkers of product sample from the monitoring well nearby the tank; (c) Terpane biomarkers of stained surface soil; (d) Sterane biomarkers of soil sample from beneath the tank (at 9 feet bgs).

sesquiterpane biomarkers provided critical lines of evidence for differentiation between the hydrocarbons in the soil and the fuel in the tank. In conjunction with other information, it was determined that the soil staining was not a result of suspected tank release, but remobilization of hydrocarbons from the historically impacted soil beneath the tank to the soil along the perimeter of the tank. This case study demonstrated elimination of unnecessary remedial investigation through diesel source identification and correlation using knowledge of LNAPL mobility in response to earthquake seismic wave and chemical fingerprinting.

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