FORENSIC NAPL DETERMINATION AND PLUME DIFFERENTIATION – A CASE STUDY

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ABSTRACT

Recent developments in laboratory analytical techniques, when combined with application of multivariate statistical analyses allow differentiation and delineation of comingled NAPLs and resultant contaminant plumes. The increase in laboratory expertise and a growing body of relevant studies in case literature have made possible evaluation of petroleum impacted media through relatively standard techniques a reality, and well within the realm of economical site assessments. The application of several methods to determine the number, type, and timing of multiple NAPL releases at a commercial facility in an urban setting will be summarized. The combination of chemical, historical, and statistical techniques has allowed for a more complete evaluation of NAPL sources and release histories than was initially thought possible. In the examined case, overlapping NAPL plumes are defined, delineated, and identified; and source identifications for individual releases are completed. These evaluations resulted in identification of previously unconfirmed sources, improved characterization of the nature of NAPL present, and refined fate, transport, and feasibility evaluations for the conceptual site model.

Keywords: forensic analysis, multivariate statistics, pollution, assessment, source determination

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1. INTRODUCTION

CarriageHouse Consulting Inc. has recently completed an evaluation of the source(s), timing, nature, and extent of petroleum impacts at a commercial vehicle rental and service facility in eastern Massachusetts. The objective of this paper is to communicate the techniques and evaluations used along with the associated findings and conclusions drawn from this exercise from the point of view of the general environmental consultant and client. This paper should also compliment the broad and increasingly deep literature produced by forensic chemists, academic researchers and industry experts in this field. Accordingly, the subject is herein restricted to a case study, in which we attempted to use recently developed chemical analyses, statistical evaluations, and a detailed site history to produce a "reasonable" historical narrative which could accommodate both the historical facts and the present nature and extent of petroleum non-aqueous phase liquid (NAPL) impact at the site.

CarriageHouse Consulting, Inc. (CHCI) was retained in order to conduct additional site assessment and investigation activities, identify to the extent possible the sources, release timing, extent and distribution of the releases, and evaluate the potential for remediation of the identified NAPLs, and to evaluate and apply analytical and statistical techniques in order to support the assessment activities. To these ends, CHCI installed additional monitoring wells and soil borings, collected additional soil, groundwater, and NAPL samples, evaluated the results of various forensic chemical analyses, physical tests, and statistical appraisals, and have formulated certain preliminary recommendations thereon.

2. MATERIALS AND METHODS

In order to effectively evaluate the source(s), nature, and extent of NAPLs at the subject property, three principal tasks were completed. First and foremost, a site history was developed which contained, to the extent possible, all potential sources of petroleum impact related to the subject property, all documented releases of petroleum at or near the subject property, and an assessment of the previous remedial activities undertaken at the subject property. Secondly, soil and groundwater samples were collected and analyzed using state-mandated techniques to characterize risk to human health, safety, and the environment; and NAPL samples were collected and analyzed using forensic chemical analyses selected to elucidate the potential sources, weathering histories, and possibly ages of the released NAPLs. Finaly, graphical and statistical evaluations of some of the recent and historical analytical data were undertaken in order to fortify our understanding of the physical extent of the NAPL plume(s), identify likely NAPL sources, and refine our understanding of the potential remediation scenarios.

Analytical testing of the collected NAPL samples was performed by Alpha Woods Hole Labs of Mansfield or Raynham, Massachusetts. Each NAPL sample was analyzed for alkylated polynuclear aromatic hydrocarbons (PAHs) using a gas-chromatograph coupled with a mass spectrometer operating in selective ion monitoring mode (GC/MS-SIM), and for saturated hydrocarbons using a GC coupled with flame ionization detection (GC/FID).

2.1 Site History

The subject property is situated Boston, Massachusetts. A review of the historical files for this location indicates that the property was formerly part of Boston Harbor. The historical filling and development of this portion of Boston Harbor is documented to have occurred between the years of 1888 and 1899. In the year 1888, the location of the current property was actually a dock or platform set on piles in Boston Harbor, along which ran a 5-inch diameter "oil supply pipe". This platform, pipeline, and the property situated on the far side of an abutting street were apparently operated as a petroleum production, storage, and mixing facility.

As of 1950, the majority of the storage of petroleum was occurring on the subject property in bulk-sized above ground storage tanks (ASTs). As of 1984, the property use had changed to that of a commercial leasing, maintenance, and fueling facility.

Currently five (5) USTs and a service island area remain in use at the property. The majority of the subject property is covered by reinforced or bituminous concrete or the on-site buildings. The facility currently utilizes three (3) USTs in the storage of diesel fuel and gasoline, two (2) USTs for the storage of motor oil and used motor oil, and a series of dispensers on the service island situated on the western side of the facility building for dispensing fuel to vehicles.

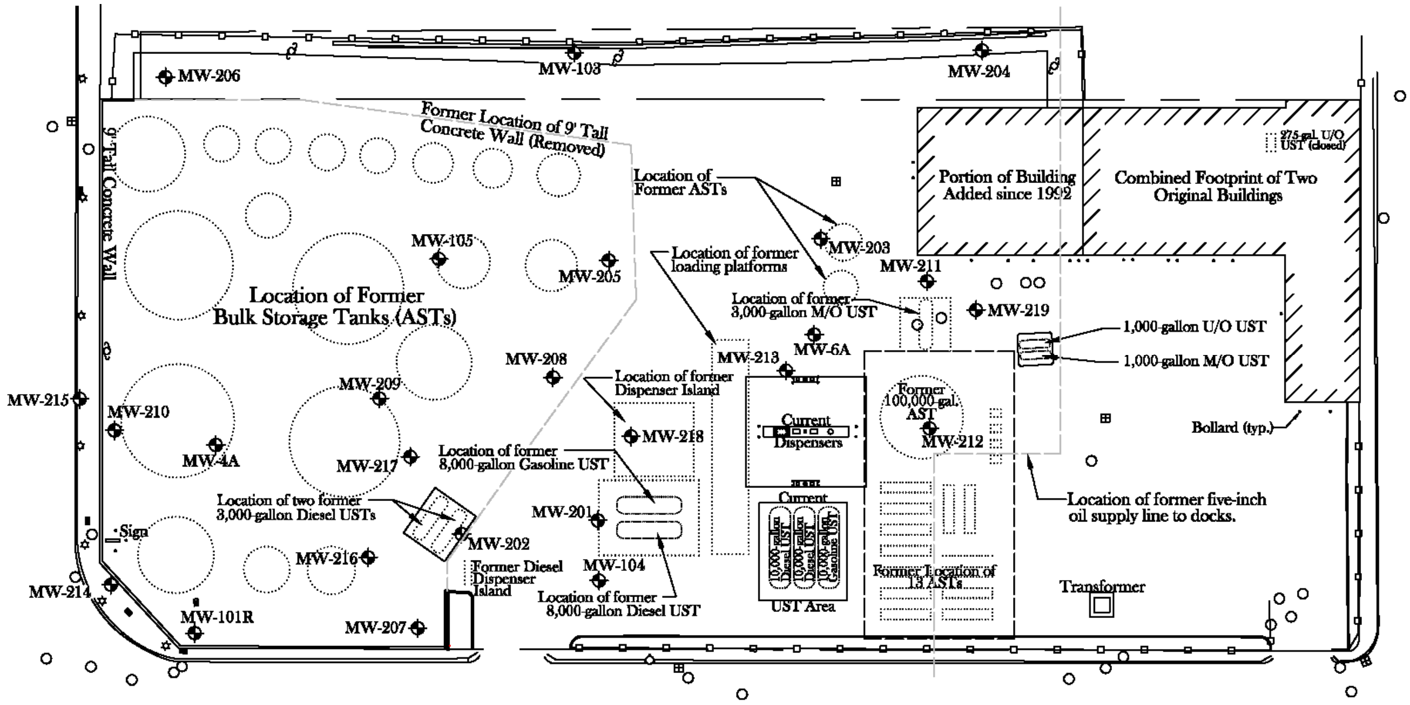

Figure 1. Abbreviated plan showing the location of former and current potential NAPL sources, monitoring wells, and property structures.

Three releases of NAPL have been identified over the operational history of the subject property. All three releases reportedly occurred within the last 25 years, and while the potential certainly exists for other unreported historical releases prior to this period, wholesale removal and replacement of much of the site soil, and the confounding effects of the three releases described below, have served to render them difficult to identify.

Between 1984 and 1989, site development activities resulted in the discovery of two major NAPL releases. NAPL-impacted soil was discovered in the area of the former motor oil UST, then located adjacent to the former onsite building no more than twenty feet from where current wells MW-211 and MW-219 exist. Estimates of the volume of motor oil released vary, but gauging and bailing activities at MW-211 have indicated NAPL thicknesses up to approximately 3 feet. Additionally, during the removal of the former diesel and gasoline USTs, west of the current USTs, NAPL and petroleum impacted soil and groundwater were encountered in the area of MW-201 and MW-202.

In April 1998, at least 50 gallons of diesel fuel was released at the current dispenser island location, proximate to MW-6A. The condition of the asphalt at the property at the time of the surface release, combined with impacted soils encountered during site facility upgrades in 2006, suggest that a substantial amount of product may have entered the subsurface as the result of this incident.

Other potential sources of NAPL at the property include the former oil pipeline, 41 former ASTs containing various petroleum products, three (3) former USTs used for diesel fuel storage, one (1) former UST used for gasoline, and smaller former USTs used for motor oil, used oil, or heating oil, as well as the many tank-related or facility-specific appurtances for petroleum storage, blending, or transfer operations such as former loading racks, former piping or dispensers.

2.2 NAPL Analyses

In 2007 and 2008, CHCI personnel collected a total of eight (8) NAPL samples from monitoring wells located on the subject property. The NAPL samples were collected using either disposable bailers or a peristaltic pump equipped with disposable tubing. The collected NAPL was bottled in an unpreserved glass vial and delivered to Alpha under Chain of Custody protocols. The NAPL volumes collected and submitted ranged from 1 milliliters (mL) to approximately 40 mL.

No pre-analysis cleanups were performed on the NAPL samples, potentially resulting in higher detection limits, potential interference from non-petroleum hydrocarbons, and non-detection results for some compounds. As described below, for the purpose of this study, the analytical results proved satisfactory provided that the conclusions reached from evaluation of the analytical results were properly constructed so as to not over-reach the applicability of the results. The intended process follows the spirit of the European Committee for Standardization (Wang 2007).

The analyses of alkylated PAHs in NAPL samples, essentially a modified version of EPA 8270C, provided quantification of 61 individual compounds, including decalins, naphthalenes, chrysenes, dibenzothiophenes, and anthracenes/phenanthrenes, fluoranthenes, and 17a(H),21B(H)-hopane. The reduced detection limits and identification of this particular list of compounds was achieved through operation of the MS in SIM mode, scanning a proprietary list of ions (m/z) developed by Alpha Woods Hole Labs. The analytical results also provided several useful compound ratios, discussed below, and a quantification of the total detected concentrations of the target compounds. The resulting list of compounds has been previously indicated to be beneficial in the evaluation of NAPL samples (Wang and Stout 2007, Murphy and Morrison 2000).

Analyses of SHCs in the NAPL samples provided quantification of up to 37 petroleum hydrocarbons, ranging from n-C9 to n-C40, and including the isoprenoids pristane and phytane.

36 of the compounds were analyzed for all eight (8) NAPL samples, and were used in the subsequent evaluations. Additionally, the SHC analyses quantified Total Saturated Hydrocarbons and Total Petroleum Hydrocarbons. The SHC analyses were conducted utilizing a GC with an FID detector, essentially a modified EPA Method 8015.

2.3 Evaluation Methods

Four primary methods of evaluation were used to derive lines of evidence to identify the sources, extents, and potential mixing of NAPLs at the subject site. Each method was used to guide the selection of additional methods, and was evaluated for its applicability in achieving the goals of this portion of the project. In general, it is important to note that success for this particular portion of the project consisted of providing a basis for the delineation of the NAPLs, identification of individual potential sources, and elucidating potential mixing events which could improve site characterization and remediation. The identification of a particular source crude oil, manufacturer, age, or owner of the individual NAPLs was not necessary.

As such, the techniques and methods used are viewed as a platform from which to potentially research other issues which may be germane at a particular site, and not as a complete catalog of the possible tools at the disposal of the stakeholders in assessment and remediation of similar sites. Some pre-processing of the data was performed prior to graphical evaluations, the Principal Component Analysis, and the Cluster Analysis. All non-detect values were assigned a value of zero, and PAH and SHC concentrations were normalized through division by the sum of detected PAH or SHC concentrations for each sample. Additionally for PCA, each component (analyte) concentration for each sample was normalized through subtraction of the mean value.

2.3.1 Laboratory Data Evaluation

The initial method of evaluation of the NAPL analyses consisted of a review of the laboratory reports, which included quantitative analytical results, chromatograms, charts of alkylated PAH concentrations, and library standards of petroleum products, including gasoline, motor oil, and diesel fuel. Inspection of the GC/FID chromatograms indicated that at least three types of product could be tentatively identified within the site NAPLs. Samples collected from MW-6A, MW-202, MW-208, MW-218, and MW-101R each appeared on GC/FID analysis to be similar to weathered mid-range distillate fuels, potentially diesel. The sample from MW-6A, upon inspection of normalized SHC data, showed a decreasing abundance of n-C9 through n-C13. Only samples collected from MW-6A, MW-202, MW-208, and MW-218 exhibited detectable concentrations of n-alkanes from C9 through C18.

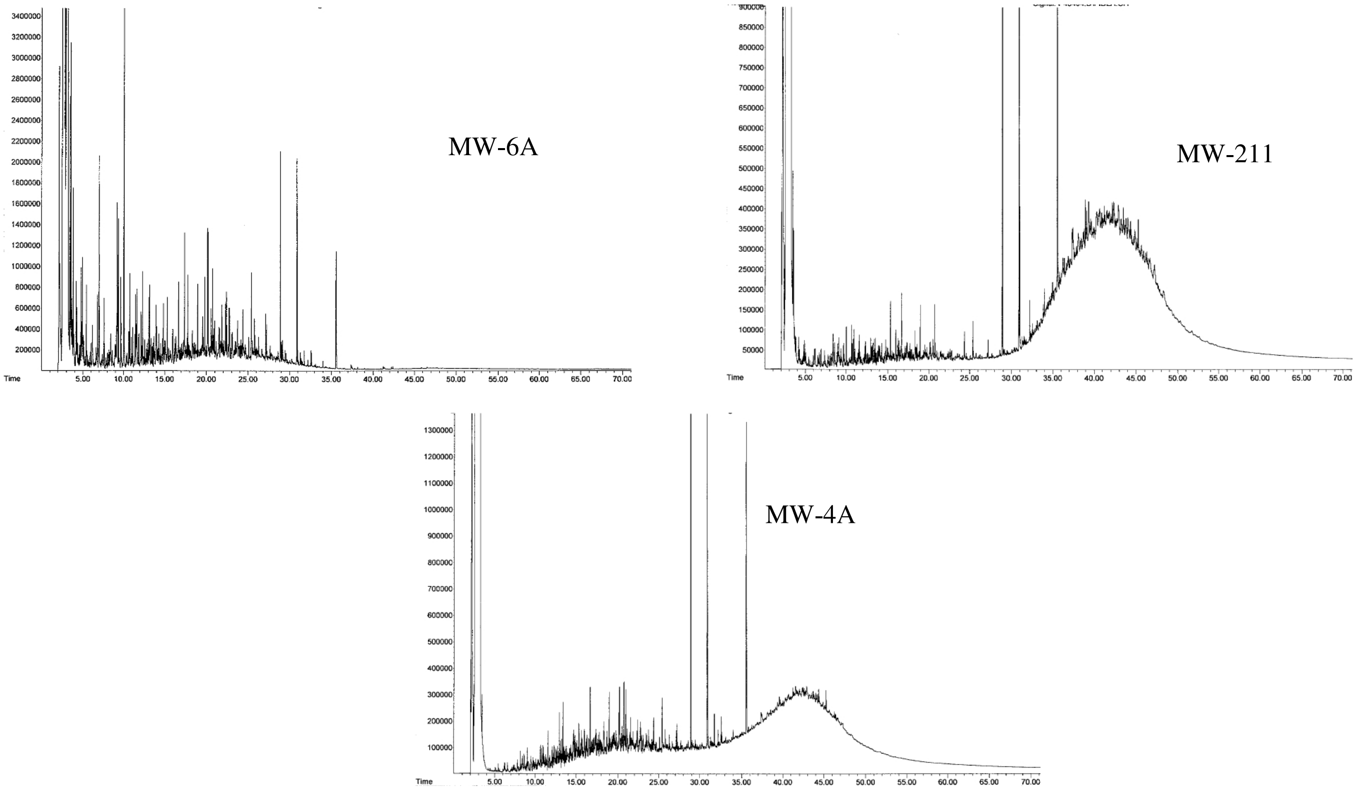

Figure 2. GC/FID Chromatograms for three NAPL samples indicating apparent mid-range distillate fuel (MW-6A), a mixture (MW-4A), and lubricating oil (MW-211).

In addition to the SHC data, PAH data was also evaluated on a percent weight basis. Evaluation of the parent and alkylated daughter products of naphthalene, phenathrene/anthracene, and decalin each indicated a parabolic trend in the abundance of the parent/daughter products, with relative depletion of the parent compound. These results have been found to indicate a petrogenic rather than a pyrogenic parent source (Murphy and Morrsion 2000). Two exceptions to this general trend were as follows. The chrysene data indicate a skewed distribution from parent to C4-chrysene in NAPL samples collected from MW-6A, MW-101R, MW-202, MW-208, and MW-218. The decalin data show the parabolic distribution from decalin through C3-decalins, but each of the samples displayed concentrations of C4-decalins such that C4-decalins/C3-decalins>1.

There were also noticeable differences in the relative abundance of different analyte groups between NAPL samples. As shown, NAPL samples from MW-211 and MW-219 were relatively lean in naphthalenes, and relatively rich in chrysenes, consistent with the GC/FID indications of a lubricating oil, rather than diesel fuel, parent source for the NAPL at these wells.

Table 1. Percent by weight distribution of major analyte groups.

	% determined by sum of parent, dimethyl-, trim ethyl, and alkylated products divided by Total PAHs			
ID	Chrysenes	Naphthalenes	Dibenzothiophenes	Phenanthrenes / Anthracenes
MW-4A	3%	10%	7%	17%
MW-6A	1%	58%	4%	17%
MW-101R	2%	46%	7%	20%
MW-202	0%	68%	6%	13%
MW-208	2%	46%	4%	21%
MW-211	22%	9%	3%	18%
MW-218	2%	55%	3%	20%
MW-219	46%	3%	1%	12%

2.3.2 Use of Diagnostic Ratios

Many diagnostic ratios for the identification, source attribution, weathering and mixing have been previously presented in the literature (*cf.* Murphy and Morrison 2000, Wang and Stout 2007). Several of these were included in the laboratory data packages from this work, and several additional potentially useful ratios were evaluated by the authors.

2.3.2.1 Dibenzothiophenes

Dibenzothiophenes are relatively common sulfur containing compounds found in crude oils from throughout the world. As a class, they can account for up to 70% of the sulfur in middle distillate fuels such as diesel (Wang and Stout 2007). They are relatively resistant to weathering, and examination of their relative abundances in NAPLs and source products can be useful for determining sources (Douglas 1996).

Table 2. Dibenzothiphene and alkylated daughter compounds.

	Concentrations in mg/kg NAPL, zero indicates non-detect				
	Dibenzothiophene (DBT)	C1-DBT	C2-DBT	C3-DBT	C4-DBT
MW-4A	76	140	230	230	140
MW-6A	280	590	600	320	97
MW-101R	160	450	520	260	95
MW-202	260	710	950	600	230
MW-208	420	790	850	470	130
MW-211	9.2	27	54	78	71
MW-218	404	658	611	295	87
MW-219	0	7.74	38	75.6	70.7

Following approach of others (Douglas 1996, Wang and Stout 2007, Murphy and Morrison 2000) we utilized the concentrations of dibenzothiophene (DBT) and alkylated daughter products in order to attempt to delineate potential source differentiation amongst the sampled NAPLs. Additionally, the ratios of DBTs to chrysenes (DBT/C) and DBTs to phenanthrenes/anthracenes (DBT/PA) were investigated in order to attempt to clarify weathering and source relationships, respectively.

Three plots were prepared. The first displays the concentration of C3-DBT to C2-DBT. As indicated, there is considerable variation between the NAPL samples, especially with regards to C2-DBT. The plot suggests that four groupings may be delineated as shown.

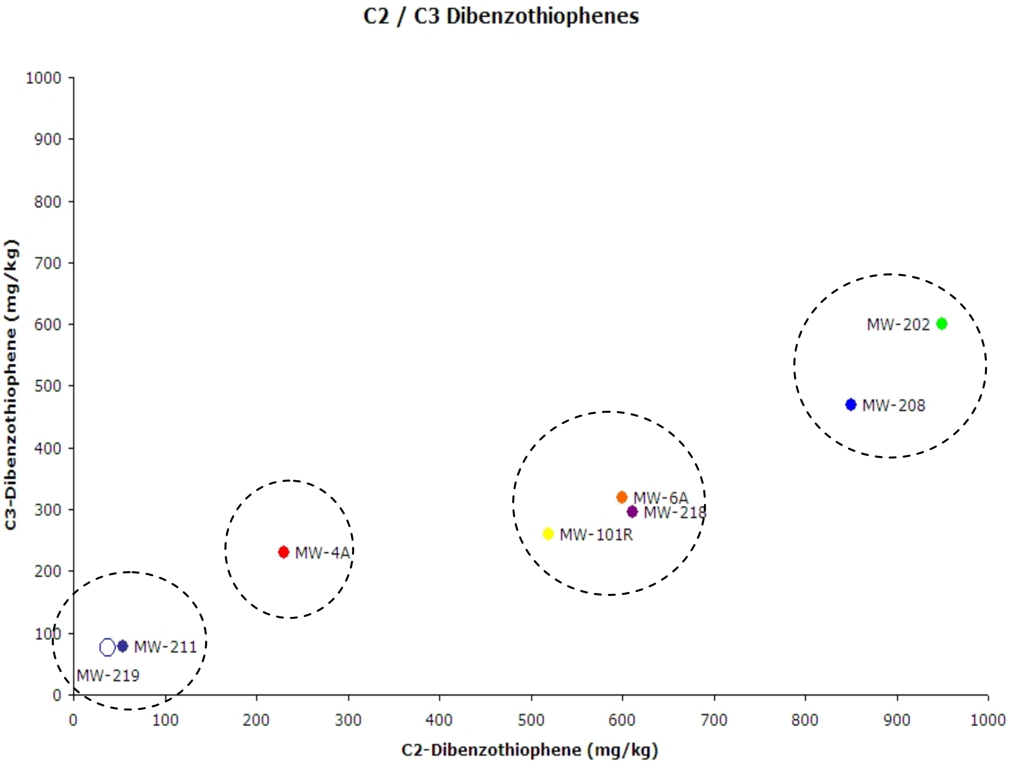

Figure 3. Plot of C3-DBT to C2-DBT. C3-DBT/C2-DBT has been used previously as a source identification ratio.

A second method to delineate different sources of NAPL at the subject site was made by comparing the concentrations of C2-DBT / C2-PA to C3-DBT/C3-PA. As with the C2-DBT/C3-DBT evaluation, MW-211 and MW-219 NAPLs remain distinct from the other samples, owing primarily to relatively lower concentrations of DBTs. As PA have been demonstrated to degrade at greater rates than DBT (Wang and Stout 2007), this may indicate lower initial DBT abundances in these two samples. The other outlier, the NAPL sample from MW-202, also exhibited a relative paucity of chrysenes. With regards to the DBT/PA chart, the extreme groups are similar to the DBT evaluation, but resolution of the other groups seen above is more problematic.

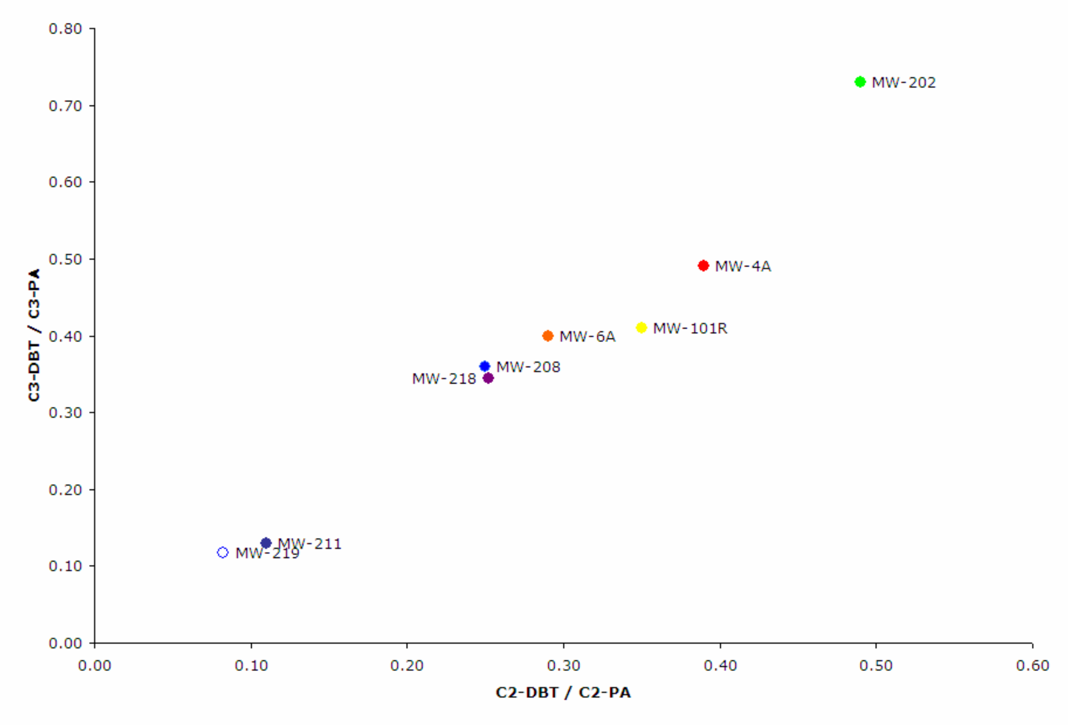

Figure 4. Diagnostic plot of alkylated dibenzothiophenes and phenanthrenes/anthracenes. DBT/PA has been previously used to indicate the degree of weathering a NAPL has undergone.

The third diagnostic plot prepared consisted of DBT and chrysene ratios. These ratios have been previously utilized to source ratios in NAPLs, impacted marines and biogenic media, and soils (Douglas 1996). Similar to DBT/PA plots, the use of ratios for each axis allows for both an evaluation of the relationship of individual sample with the remainder of the data, and also may facilitate description of the processes involved in the development of the NAPL sample. In this case, the sample from MW-202 is not originally plotted, as no C3-chrysene was detected in this sample. If one-half the detection limit (as opposed to zero) were used, the resulting coordinates of the MW-202 sample on this chart would be 40,66. For the sake of comparison, this method was used for the MW-202 sample only, as shown. Similar to the result for the DBT/PA evaluation, MW-211/MW-219 and MW-202 represent outlier groups, here potentially interpreted as two NAPLs sources. The central cluster of the remaining 5 NAPL samples may represent a set of sample with mixed provenance, or a third NAPL source, or perhaps both.

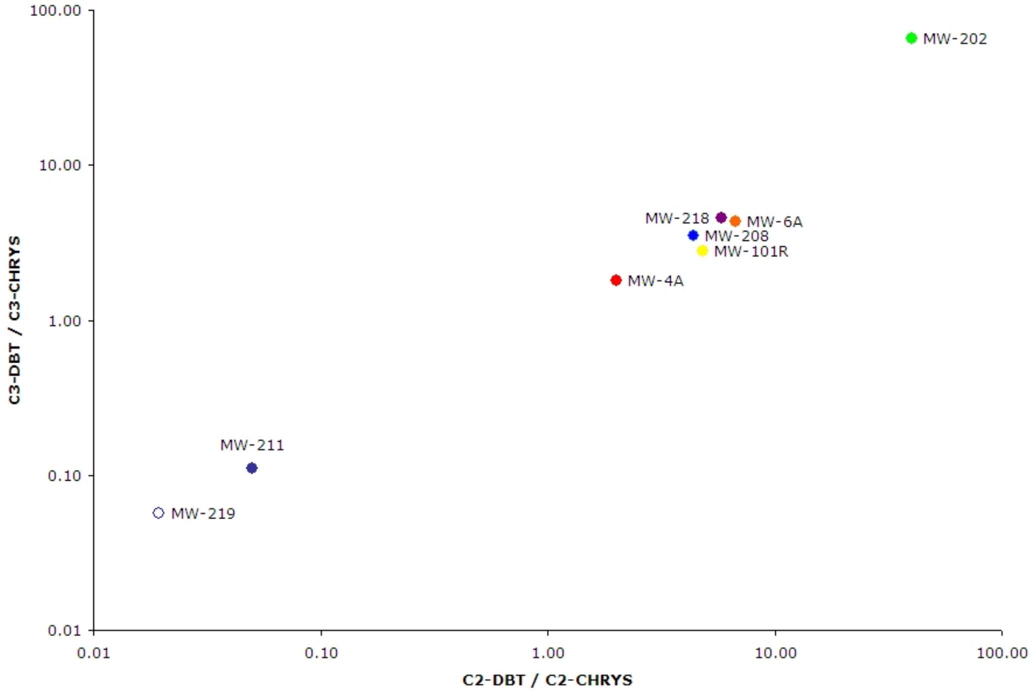

Figure 5. Plot of C3-DBT/C3-CHRYS to C2-DBT/C2-CHRYS. This ratio has been utilized to differentiate NAPL sources. MW-202 value utilized one-half the detection limit for C3-CHRYS (9) rather than zero. Note logarithmic scale.

2.3.2.2 Pristane and Phytane

Pristane and phytane are isoprenoids, common in all crude oils, derived from the source materials from with crude oils are formed (Murphy and Morrison 2000). They are relatively easy to quantify analytically, and due to structural similarities they tend to maintain a fixed ratio in NAPLs during degradation. Similarly, the related n-alkanes C17 and C18 may also be indicative of crude oil, and therefore product or NAPL sources (Wang and Stout 2007). The n-C17/Pristane ratio has also been used in the dating of diesel fuel releases (Christensen and Larsen 1993, Wade 2001).

With the exception of the sample collected from MW-219, none of the collected NAPL samples exhibited detectable concentrations of n-C17 or n-C18, this fact in addition to the hypothesis that diesel fuel and motor oil were potential NAPL sources, precluded the use of n-C17/pristane to determine the relative ages of the releases at the subject site. Pristane and phytane were, however, detected in each of the eight (8) NAPL samples, and the ratio of their concentrations (PRI/PHY) were used in and attempt to group the NAPL samples by source. The following table summarizes the isoprenoid and n-alkane to isoprenoid ratios.

Table 3. Pristane/phytane ratios, potentially indicative of differences in NAPL sources, and n-C17/Pristane and n-C18/Phytane, potentially indicative of weathering stages.

	Determined using concentrations in mg/kg, non-detect treated as zero.		
ID	Pristane/Phytane	n-C17/Pri	n-C18/Phy
MW-4A	2.55	0	0
MW-6A	3.09	0	0
MW-101R	2.52	0	0
MW-211	2.23	0	0
MW-202	2.08	0	0
MW-208	2.62	0	0
MW-218	2.65	0	0
MW-219	1.58	0.67	1.94

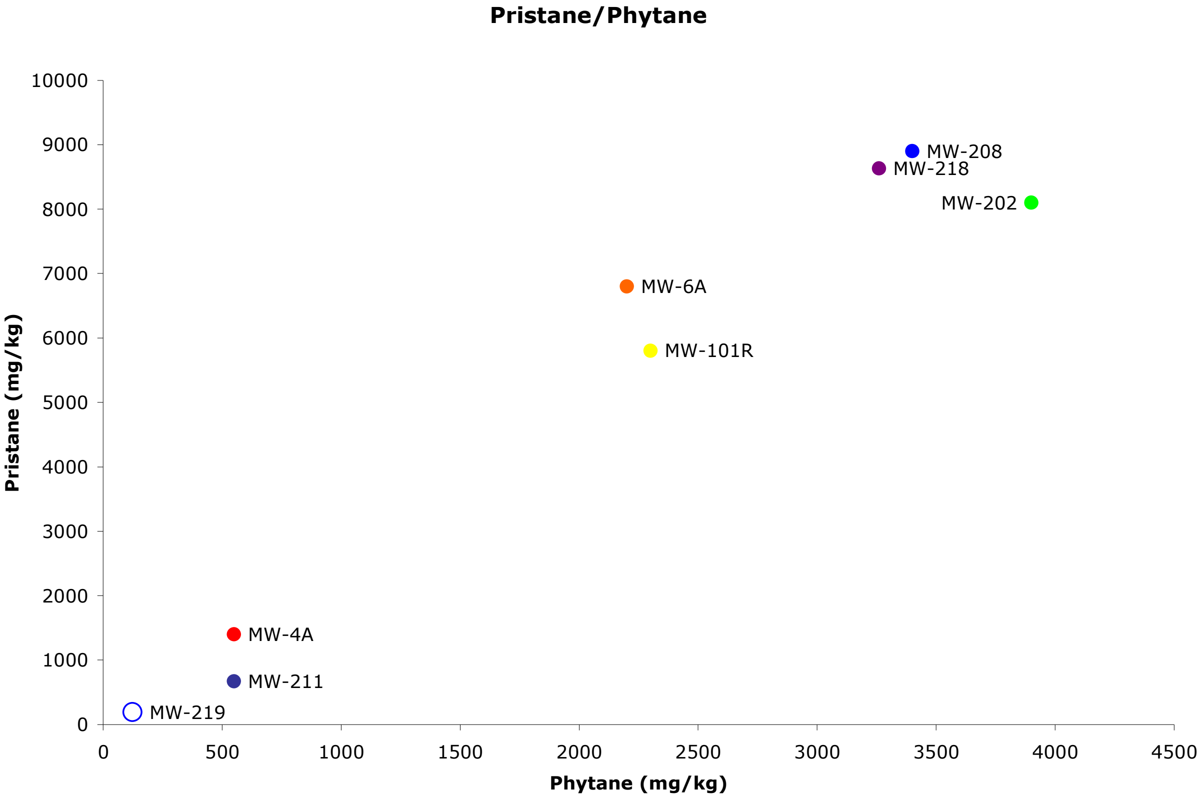

Figure 6. Pristane to phytane for the eight NAPL samples. Three distinct groupings are evident, potentially indicating three distinct NAPL sources.

2.3.3 Principal Component Analysis

The direct evaluation of GC/FID chromatograms provided evidence of three apparent NAPL types; variously weathered middle-range distillate fuel believed to be diesel, lubricating oil characterized as weathered motor oil, and one sample which clearly indicated a mix, potential of the first two types (MW-4A). The use of diagnostic source and weathering ratios had indicated that up to four distinct groups may exist, including two potential diesel sources, a motor oil source, and at least one mixed source. Unfortunately, there is no record of potential source (unweathered) NAPL samples from the documented releases at the subject site, and no evidence of sampling from all the potential sources of NAPL at the site - at least 54 potential on-site sources in the case history. Another potentially limiting factor in the quantitative evaluation of the PAH data or any data set with a large number of variables is the rapidly expanding number of potential comparisons to be made.

Principal Component Analysis is a method used in exploratory data analysis to minimize the number of parameters to be evaluated while maximizing the variability explained by each parameter. PCA uses eigenvector calculations to combine correlated variables, resulting in a set of principal components which account for the majority of the variability (*i.e.* differences) in the data. These principal components are constructed to be uncorrelated to one another, allowing for better differentiation between samples (Borradaile 2003, Murphy and Morrison 2000). In this study, PCA was conducted on the PAH and SHC using statisXL ®.

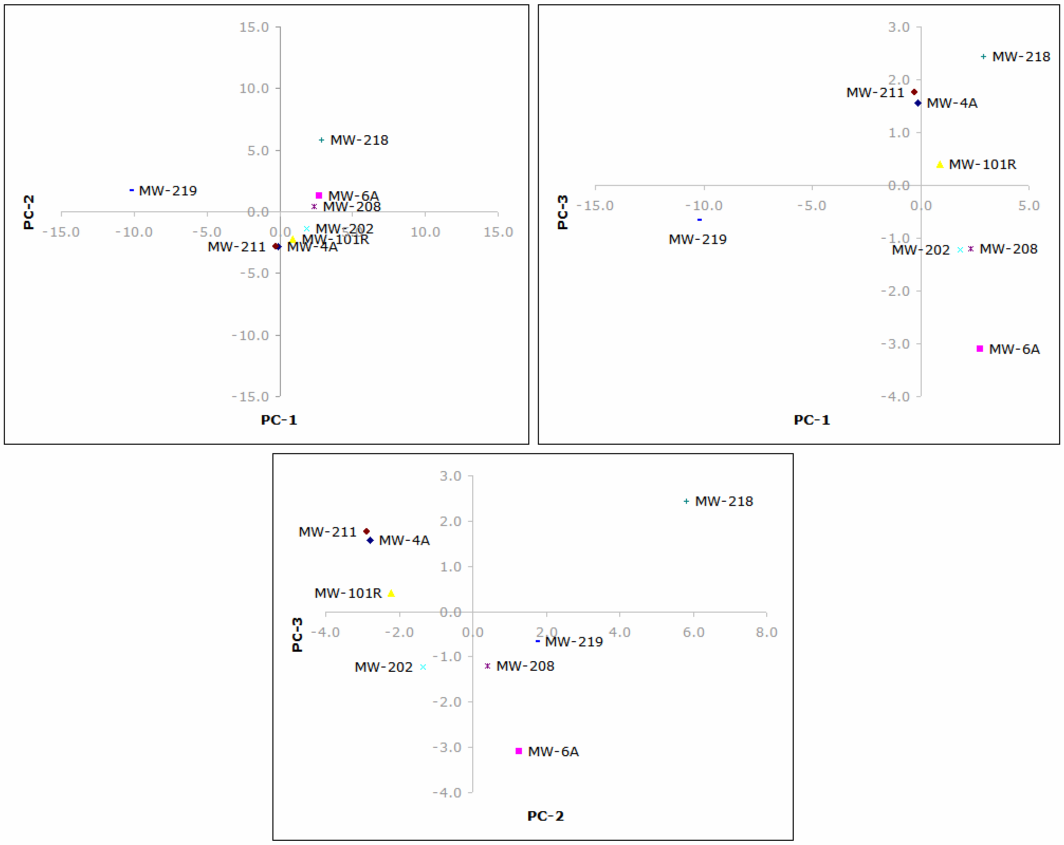

Figure 7. Results of PCA analysis for SHCs.

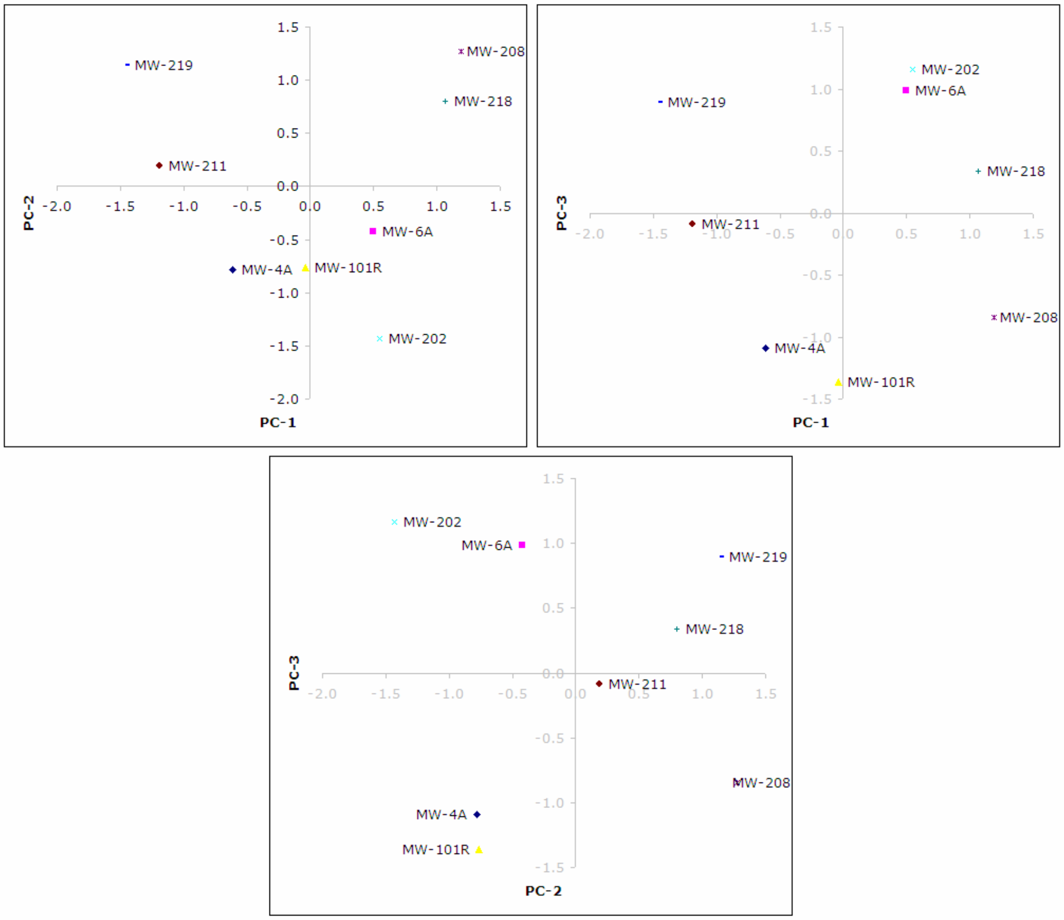

Figure 8. Results of PCA analysis for PAHs.

For each analysis, cross-plots of the first three principal components, accounting for 91.3% and 92.6% of the variability in the SHC and PAH data respectively, were used to produce cross plots of the results of the PCA. As shown in the above figures, PCA for SHCs and PAHs produce some relatively consistent groupings. In each case, MW-4A and MW-101 occupy proximate locations, negatively correlated with each of the PCs (III). Similarly, MW-6A and MW-202 also occur in the same quadrant, correspondingly correlated with each PC. The distribution of the remaining samples shows variability in both PC correlation and sample grouping.

2.3.3 Cluster Analysis

Finally, cluster analysis was utilized for both the PAH and SHC results. Cluster analysis was performed using statsiXL ®. The clustering strategy was agglomerative (Lance and Williams, 1962), exclusive (any case occurs in only one group), and with equal weighting of all analyzed compounds. Calculation of the connection distance of the clusters is Euclidean (the relationship between two attributes 1 and 2 is calculated as; $d_{12} = (S_j\ (x_{1j} - x_{2j})^2)^{1/2}/j$ where j is each attribute). The resultant dendrograms for the SHC and the PAH analyses are provided below.

Similar clusters can be discerned in both dendrograms; MW-218 and MW-208 are strongly correlated (short branches), and in both cases the second most proximate sample is MW-6A.

Cluster analysis of PAHs also shows a relatively high correlation between MW-211 and MW-219, with negative correlation to the other samples. This appears inconsistent with the GC/FID results, which indicates a motor oil-type component in NAPL at MW-4A.

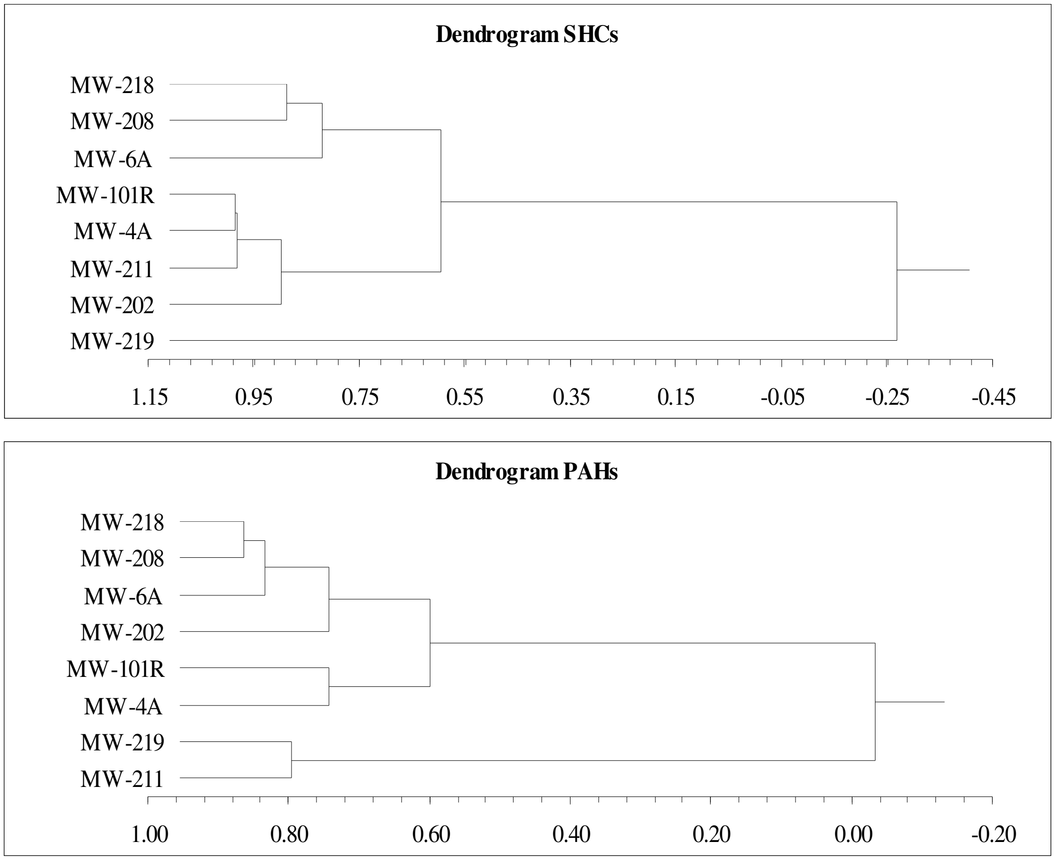

Figure 9. Dendrograms of SHC and PAH analyses. Common attributes include tight grouping of MW-208 and MW-218, followed by MW-6A, MW-101R and MW-4A are coupled in both dendrograms, and MW-219 is negatively correlated in both cases.

3. RESULTS AND DISCUSSION

Evaluation of the analytical results in this case is complicated by several factors. The first is a lack of source product analytical data. Access to chemical analyses of source material can prove very helpful in attempts to delineate and define different, especially overlapping areas of NAPL impact. The results of the chemical analyses and the forensic evaluations demonstrated the influence of multiple types of NAPL, but did not establish the relationship between NAPLs in light of the conceptual site model. If only GC/FID chromatograms were provided for visual review, one reasonable interpretation may be that there is a diesel release originating near MW-6A, a motor oil release near MW-211, and that these two plumes have mixed near MW-4A. Additional PAH data, however, indicates a potential fourth area of impact, defined variously as MW-202, MW-208, and/or MW-218. PCA of the data suggests even more differences, variously emphasizing the relative uniqueness of MW-219, MW-202, MW-208, and MW-6A. These results taken together initially confounded the investigators of this site. In order to assist in the separation of sources, and to elucidate potential transport or mixing scenarios, CHCI attempted to combine the analytical and historical data for the subject property in a meaningful and reasonable narrative.

The history presented above indicated that sources for the diesel fuel and motor oil signatures seen in GC/FID chromatograms for the NAPL samples did exist on site. The documented motor oil release in the area of MW-211 and MW-219, combined with the current NAPL occurrence at these wells, serves as a reasonable source for this NAPL. At least two known diesel fuel releases could be responsible for the weathered diesel fuel signatures observed in GC/FID chromatogram for NAPL samples collected at MW-4A, MW-6A, MW-101R, MW-202, MW-208, and MW-218. Here site history and hydrological information aids in clarifying the situation. The average depth to the water table at the property ranges from approximately five to ten feet below grade. The water table tends to exhibit a slope in the general direction from MW-212 towards MW-101R, exhibiting an average gradient of approximately 0.005. A study conducted in 1993 did not indicate any tidal influence to groundwater.

Two known diesel fuel releases are documented to have occurred at the site, the first one found in 1989 when petroleum-impacted soil and NAPL were encountered during diesel UST removal activities approximately 120 feet from the current dispenser islands and approximately 150 downgradient of MW-6A, in the area of MW-202. The second known release is the surface spill which occurred in 1998. The NAPL sampled from MW-6A exhibited detectable concentrations of n-alkanes, which are among the first petroleum compounds to degrade (Kostecki et al. 1988), this seems to indicate that the USTs removed in 1989 may not be the source of this NAPL.

Assignment of the NAPL sampled at MW-101R, MW-4A, MW-202, MW-208, and MW-218 was the next step. Based on the source ratios of C3-CHRY/C3-DBT, C2-CHRY/C2-DBT, C3-DBT/C2-DBT, and PRI/PHY, the most consistent separations observed are MW-6A versus MW-202. This is consistent with the historical information indicating a diesel release in the area of MW-202 from the 1989 UST removals. MW-101R, MW-4A, MW-208 and MW-218 are all potentially impacted by NAPL from the area of MW-6A, and considering the documented groundwater flow conditions, MW-101R and MW-4A could plausibly be impacted by a NAPL source in the vicinity of MW-202. Resolution of these potential relationships appeared to require an additional method of evaluation. As a supplementary approach to elucidating the NAPL sources and potential mixing, we produced a ternary plot of three source ratios discussed above, C3-CHRY/C3-DBT, C2-CHRY/C2-DBT, and PRI/PHY.

In an effort to improve the delineation of the different NAPLs and semi-quantitatively estimate the amount and type of mixing of NAPLs at the sample monitoring wells, we utilized ternary plotting of those ratios whose applicability has been previously demonstrated for the separation of NAPL sources. Similar ternary charts have long been used in the geologic literature for the characterization and classification of rock types (Streckeisen 1974), and have been used with measurements of monoaromatic petroleum compounds to differentiate between sources of petroleum-impacted groundwater, and to elucidate transport and attenuation processes in aquifers. (*cf.* Stevens 2003, Wade 2001, Lipson & Siegel 2000, Morrison 2000, Yang, et al. 1995, and API 1994.)

For the purpose of source delineation, it is necessary that the compounds involved be present in the source material at measurable concentrations, be relatively resistant to degradation, and be present at an actual or normalized concentration different for different source materials. It is in this case assumed that, because the involved compounds are relatively resistant to biodegradation (DBTs, chrysenes) and/or degrade at approximately equal rates (PRI/PHY), that the location of the sample on the ternary diagram is indicative of the source NAPL composition, and that relative Euclidean positions between the plotted sample locations serve as proxy for the source similarity of the NAPL samples. We also suggest that the degree of mixing (percentage contribution) of different NAPLs to the material evident at a sample location can be semi-quantitatively estimated by observing the distance between the endpoint NAPLs and the potentially mixed specimen. This evaluation does not by itself provide any information on the NAPL source type (crude oil, middle-range distillate fuels, gasoline, etc.).

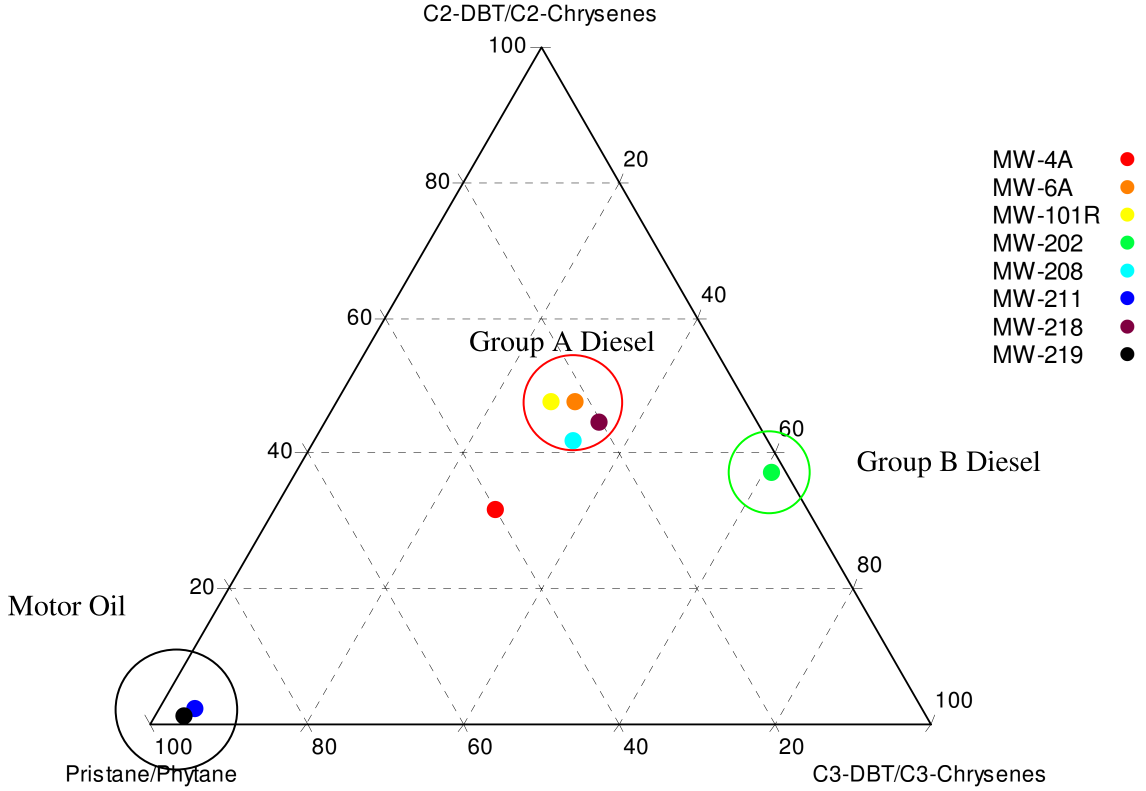

Figure 10. Ternary diagram of the PRI/PHY, C2-DBT/C2-CHRY, C3-DBT/C3-CHRYS 'system'. The location of each point is taken to be indicative of initial NAPL source composition, and the distance between points is taken as a proxy for source similarity.

As indicated in the figure, MW-211/MW-219, MW-202, and MW-6A/MW-101R NAPL samples delineate an area in this ternary space, and as the extreme values, may indicate three different source types; including one motor oil type NAPL, and two distinct diesel NAPLs. Given the site geometry and hydrogeology, it seems reasonable to designate MW-6A, rather than MW-101R as the source area of the 'Group A Diesel' NAPL. Similarly, MW-202 may potentially be designated as the 'Group B Diesel' NAPL. These sources, combined with the 'Motor Oil' source represented by MW-211 and MW-219 NAPL samples, appear to account for the remaining NAPL samples. MW-4A, as supported by the GC/FID chromatogram, is apparently a NAPL consisting of 'Motor Oil' and 'Group A Diesel' NAPLs. Using the distance proxy described above, it is estimated that the MW-4A sample may consist of approximately 80% 'Group A Diesel' and 20% 'Motor Oil'. Similarly, MW-101R NAPL may be inclusive of some 'Motor Oil' NAPL, albeit to a lesser extent than MW-4A. MW-208 NAPL appears to be a

'Group A Diesel', potentially mixed with 'Group B Diesel' or 'Motor Oil', although quantifying the mixing is problematic. MW-218 NAPL may indicate a mix of 'Group A Diesel' and 'Group B Diesel', a possible composition considering the site history and site hydrogeology.

One primary factor in determining the mobility, transport, and fate of NAPL is kinematic viscosity. Given the relatively high measured viscosity of the 'Motor Oil' NAPL (151centistokes at 70°F), a question raised is as to how the 'signature' of this NAPL is present in the GC/FID chromatogram of the MW-4A NAPL sample, and the potential influence on the NAPL compositions of samples collected from MW-208 and MW-101R. A suggested possibility is that there is an interface of 'Motor Oil' and 'Group A Diesel' NAPLs. It is suggested that the mixing of NAPLs resulted in a lowering of the 'Motor Oil' NAPL viscosity, allowing increased transport velocity.

The suggested narrative is put forward; the 'Motor Oil' and 'Group B Diesel' NAPLs were released prior to site upgrade activities in 1989. 'Motor Oil' NAPL remained in the general vicinity of MW-211 and MW-219 until a later time. During site excavation and extraction activities, the original distribution of NAPL may have been distorted due to increased and directionally different transport velocities resulting from increased water table gradients imposed by pumping, and/or through excision by excavation activities. The resulting NAPL source areas then supplied NAPL and dissolved contaminants for transport by groundwater flow following the primary hydraulic gradient. The 'Group A Diesel' release then provided an additional NAPL to the subsurface, apparently in the area of MW-6A. This new factor may have served as the mechanism for the increased transport velocity of the 'Motor Oil' NAPL, resulting in a 'mixed' NAPL signature at MW-4A and MW-101R.

4. CONCLUSION

In the studied case, the use of recently commercially available analytical techniques, defined, refined, and improved by many practitioners in the field of chemistry, petroleum geology, laboratory analyses, and environmental studies allowed the authors to make considerable progress in recognizing, identifying, and classifying different NAPLs present on the subject property. The application of PCA and cluster analysis was invaluable for data exploration, and allowed for a refinement in the recognition of multiple NAPL sources, estimates of the degree of similarity of the different NAPL samples, and guidance towards the identification of 'endpoint' NAPL compositions and thus potential mixing or interference effects.

The authors concluded that the use of ternary diagrams was essential to identifying three distinct NAPL groups and a progressive step in determining the relative amounts of the different NAPLs at other sampling points. The ability to present the incremental variables using a third axis in this unique situation provided enough Euclidian disparity among the separate groupings to better understand the relationship among the various NAPLs at this site. This understanding directly benefitted the conceptual site model and the evaluation of migration and exposure potentials, while establishing a higher degree of certainty on where the mixing zones for the different groupings existed.

The authors further hypothesize that the technique demonstrated herein may be equally as effective when applied with source-indicative, degradation-resistant petroleum compounds such as diamondoids, biomarkers, or metallic compounds to confirm corollary relationships. The ability to confirm stronger corollary relationships between various types of NAPL present on-site using this method may well serve as the basis for establishing the degree of scientific certainty required to render professional opinions on the same. Thus, we consider ternary analyses of source-specific compounds in this manner to be a useful complement to the analytical and statistical toolbox so far available.

The intrinsic value of furthering the source identification process in hazardous waste site assessment and cleanup is self-apparent, so the presence of petroleum NAPLs at hazardous waste sites offers a unique opportunity to obtain factual data for use in multivariate analyses to confirm information from other site research to obtain imperative and defensible information on source or parent materials.

The authors contend that the costs to use of forensic NAPL analyses in Site Characterization work can no longer be viewed as disproportionate to the resulting benefits, which are now as valuable as accurate site history information and scaled property and feature plans for any given release location. In this specific case, the costs required to complete the multivariate analyses reported herein represented less than 1% of the current expenditures for this site, and less than 0.5% of the overall projected life-cycle costs for this case. The results, however, will influence all aspects of the assessment and remediation process, from confirming or refuting parent source identification, to assisting with evaluation of categorical feasibilities for remediation or recovery of NAPLs.

Finally, the authors conclude that the multidisciplinary approach to site assessment and characterization should reflect, whenever and wherever possible, basic scientific principles proven in the multivariate analyses during typical forensic NAPL analyses first to confirm the nature and source of contamination being assessed, and then to establish conclusions imperative to correctly identifying the accuracy of the site history used to develop the conceptual model. The use of multivariate statistical analyses in this manner for NAPL, or even for large and potentially incongruous data sets, is invaluable in establishing and confirming the intrinsic fundamental relationships among contaminants at a site and their potential parent sources.

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