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Dec. 28, 2020

Mr. Greg Cassidy South Carolina Department of Health and Environmental Control 2600 Bull Street Columbia, SC 29201

Subject: Forensics Analysis of NAPL, Sediment, and Soil Samples Collected from the Former Bramlette MGP Site and Surrounding Areas Former Bramlette Manufactured Gas Plant 400 East Bramlette Road, Greenville SC VCC 16-5857-RP

Dear Mr. Cassidy:

Please find enclosed two hard copies and one electronic copy on compact disk of the referenced report. The report details the results of forensics analyses of non-aqueous phase liquid, soil, and sediment samples collected from the Bramlette MGP site including the Reedy River.

If you have any questions, please contact me at (980) 373-2663 or at <u>Richard.powell2@duke-energy.com</u>.

Sincerely,

Richard C. Powell

Richard E. Powell, P.G. Lead Environmental Specialist

cc: Kevin Boland, CSXT Daniel Schmitt, Esq., CSXT Ty Houck, Greenville County William W. Brown, Legacy School Properties, LLC



Forensic Analysis of Non-Aqueous Phase Liquids (NAPL), Sediment, and Soil Samples Collected from the Former Bramlette Road Manufactured Gas Plant (MGP) Site and Surrounding Areas

Prepared for

Duke Energy Carolinas, LLC Charlotte, North Carolina

Prepared by

Corporate Environmental Solutions LLC Pittsburgh, Pennsylvania

CES Project No. 10613

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Executive Summary

Corporate Environmental Solutions (CES) was requested to conduct a forensic analysis of data collected on samples of NAPL, sediment, and soil collected from areas near the former Bramlette Road MGP site. A total of 28 individual samples were submitted for forensic testing. The samples were collected between 3/26/19 and 10/27/20. Analysis was performed by Alpha Analytical of Mansfield, Massachusetts. Parameters analyzed included PIANO Volatile Organics, Total and alkylated Polynuclear Aromatic Hydrocarbons (PAHs), and Saturated Hydrocarbons (SHC). One sample identified as MW-06A NAPL was also analyzed for viscosity and specific gravity (density).

The results of the forensic analysis revealed PAHs from multiple sources present in the samples. MGP tar was observed in several NAPL samples collected on the former site and in some sediments collected in an area identified as Ditch 4 and in one soil sample in and area identified as Ditch 2. Samples collected from Ditch 5 were shown to contain PAHs resulting from a mixture of petroleum and combustion sources, not related to MGP operations. Samples collected in the Reedy River had PAHs primarily from urban runoff. No Reedy River samples showed PAHs indicative of MGP operations. Urban runoff and natural runoff were also observed in samples collected from background and other areas. The remainder of this report discusses the MGP processes that produce tar residuals, how forensic investigation of MGP residuals are generally performed, and gives the basis for the conclusions presented in the preceding sentences based on the available data.



1.0 Introduction

Corporate Environmental Solutions (CES) was requested to conduct a forensic analysis of analytical results from samples of NAPL, sediment, and soil collected from areas near the former Bramlette Road MGP (Site).

The purpose of this evaluation is to refine the understanding of the source, nature and extent of PAHs identified at the former Bramlette MGP site. Identifying potential sources of PAHs can improve the conceptual site model and provide important information prior to developing potential remedial strategies.

Objectives of this evaluation are to:

- Determine characteristics of PAHs identified in soil and sediment samples collected from location within and near the Site. Examples of PAHs characteristics include pyrogenic versus petrogenic and degree of weathering.
- Determine potential sources of PAHs identified in soil and sediment samples collected from locations within and near the Site.
- Determine the extent of PAHs potentially sourced from former operation of the MGP.



2.0 Background Information

2.1 Site Setting and Description

The former MGP is located at 400 East Bramlette Road, Greenville, SC. The Site is comprised of five parcels that cover approximately 30 acres. The Site is bounded generally by the CSX Transportation (CSXT) railroad corridor to the north, west, and south, and by West Washington Street, the Legacy Charter Elementary School (Legacy Elementary), and the City of Greenville Sanitation Department to the east. The Reedy River and Swamp Rabbit Trail define the western boundary of the Site. Figure 2.1shows the Site layout.

Topography at the Site is relatively flat and low-lying and includes delineated wetlands. Parcels 2, 3, 4, and 5 are located within the 100-year flood plain of the Reedy River. Parcel 1 is relatively flat and gently sloping from the north (938 feet) to south (932 feet). The debris piles on Parcel 2 (946 feet) and the Vaughn landfill on Parcel 3 (elevation of 942 feet) are the points of highest elevation at the Site. Parcels 4 and 5 are generally flat with elevation ranging from 920 feet to 925 feet.

Surface water features within and adjacent to the Site include drainage ditches, jurisdictional wetlands, and the Reedy River to the west of the Site. Extensive soil coring confirmed the presence of alluvial deposits within the bounds of the floodplain, including a laterally extensive coarse sand deposit. Since most of the Site is located within a 100-year flood plain, the man-made drainage ditches were presumably constructed to improve drainage on all the five parcels.

Historical aerial photographs show a network of ditches that appear to have been associated with MGP operations (Figure 2.1). Because these ditches were present during MGP operations, they are an important aspect of the conceptual site model. Aerial images were georeferenced to develop a set of coordinates in order to:

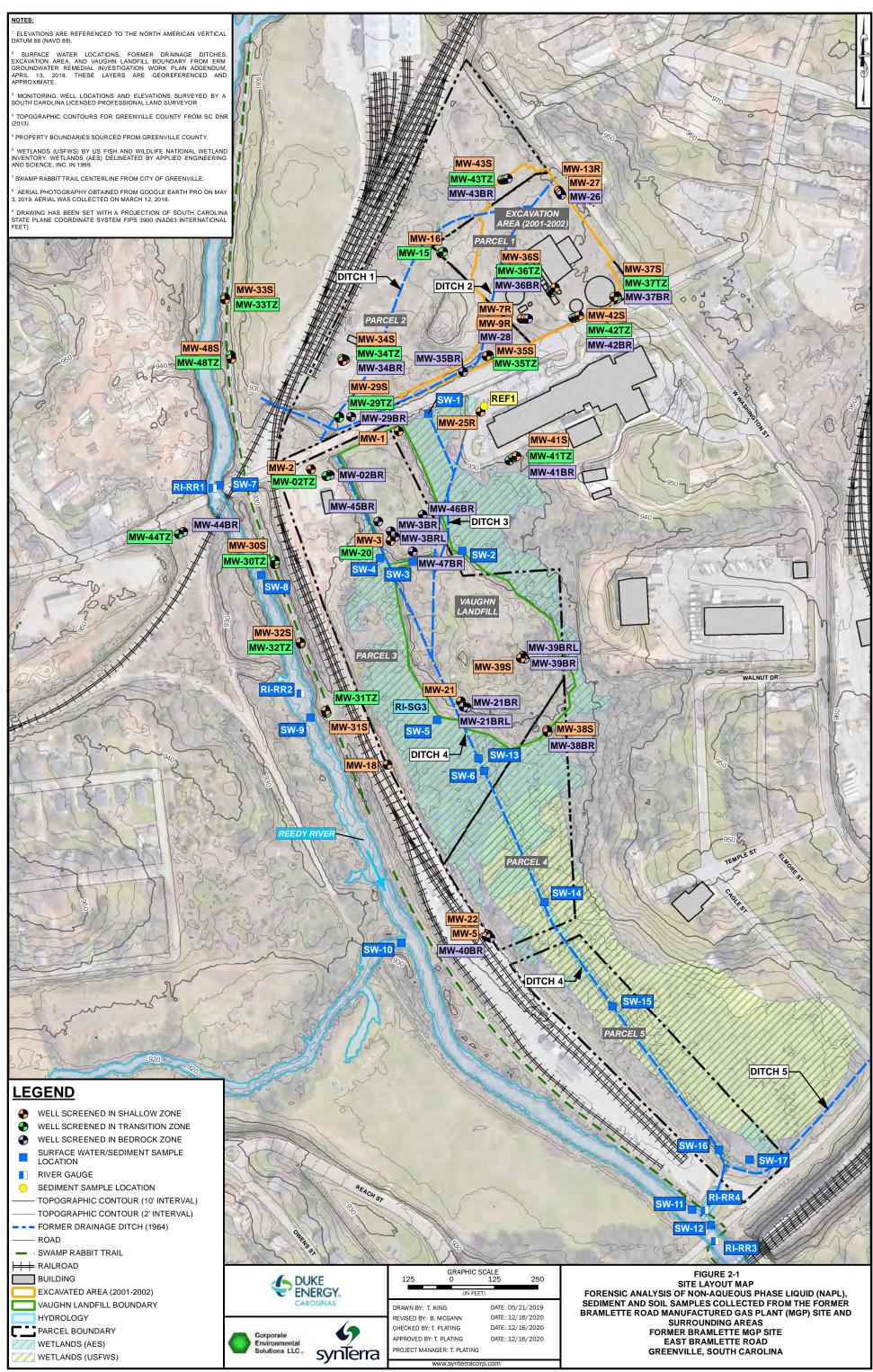
- Locate existing drainage ditches.
- Determine which ditches existed during MGP operations.
- Determine which ditches were added after MGP operations ceased.
- Identify locations of ditches that no longer are visually apparent.

Prior to sample collection, stakes were placed at 100-foot intervals along the length of an identified ditch. Characteristics of the ditches are summarized below:

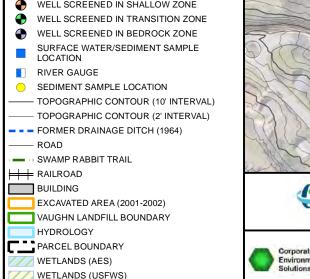
• Ditch 1 originates on Parcel 1 near the coal pile for the MGP. The ditch flowed to the west and then south a distance of approximately 984 feet. The ditch discharged to a larger ditch flowing southeast at Bramlette Road. This ditch is no longer apparent and does not convey surface water flow.



- Ditch 2 is located on Parcel 1 and Parcel 2 and originates at a culvert from West Washington Street. The ditch flows approximately 763 feet through Parcel 1 to the southwest and parallels Bramlette Road before entering a culvert that conveys flow to the southeast toward Parcel 3. This ditch conveys wet weather storm water flow.
- Ditch 3 is associated with the wetlands area between the Vaughn Landfill and Legacy Charter Elementary School. The northern portion of Ditch 3 was previously assessed. Surface water flow from the wetlands enters a culvert and flows southwest through an incised ditch that bisects the Vaugh Landfill. The approximate length of ditch planned for assessment is 139 feet. The southern portion of the wetlands is routinely inundated. Depth of water present can range from approximately 1 foot to 3 feet.
- Ditch 4 transects Parcel 3, Parcel 4, and Parcel 5. The portion of Ditch 4 planned for assessment begins at the south end of the Vaughn Landfill and flows approximately 1,637 feet prior to discharging into the Reedy River. This ditch conveys storm water drainage and during dry periods continues to flow with drainage from wetlands areas on Parcel 3.
- Ditch 5 conveys storm water flow from West Washington Street along Willard Street. The ditch segment to be assessed begins at Cagle Street and flows southwest 469 feet where it discharges to Ditch 4 described above. This ditch conveys wet weather storm water flow.









2.2 MGP Processes and Characteristics of Tar Residuals

The general term used for NAPL byproducts produced during the manufacture of gas and coke from MGP processes is tar. There were three primary processes used to manufacture gas that produced tar. These processes were coal carbonization, carbureted water gas (CWG), and oil gas. In the U.S., coal gas plants began operation in 1816 and operated by filling retorts or ovens with bituminous coal, although other types of coal were used. The ovens were sealed from ambient air and vents conveyed gases from the coal as it was heated to a temperature between 600°C and 800°C. As the retort gas cooled by water quenching, larger hydrocarbons condensed into tar while the gases stabilized. The tar consisted of aromatic hydrocarbons (benzene and PAHs) mixed with lower proportions of coal distillate and particulates (feedstock).

The CWG process was patented in 1875 by Thaddeus Lowe and the United Gas Improvement Company purchased the patent in 1882. The CWG generator directed air and steam in alternating cycles through a bed of red-hot coke or coal to produce water gas or blue gas primarily composed of hydrogen and carbon monoxide. The coke or coal in the generator was combusted in part to produce ash and slag. The water gas travelled to a carburetor where petroleum was sprayed onto hot refractory brick and cracked into light hydrocarbons. This process raised the BTU value of the gas from approximately 300 BTU/ft³ to 530 BTU/ft³. Water quenching of the hot gas condensed CWG tar, which was enriched in aromatic hydrocarbons (benzene and PAHs) mixed with lower proportions of unreacted feedstock (gas oil range saturated hydrocarbons). CWG tar is lighter than coal tar and contains little to no tar acids (e.g., phenols and cresols) and bases (e.g., pyridines, anilines, quinolines, and carbazoles) due to the fact that the gas oil feedstock typically contained relatively little oxygen and nitrogen when compared to bituminous coal. CWG tar also lacks amorphous carbon that is present in coal tar and has a higher water content.

Oil gas production began in 1889 in western United States cities with limited access to coal and easy access to petroleum. The process resembled the carburetion portion of the water gas process with custom processes for cracking crude petroleum and residual fuel oil. The cracking temperature ranged from 690°C to 1100°C, depending on the plant configuration. The oil gas process yielded more tar at the lower temperatures and more lampblack at the higher temperatures. High BTU oil gas plants were constructed beginning around 1945 during the transition from MGPs to natural gas. During this time existing CWG equipment was sometimes changed by retrofitting the generators with high temperature refractory brick. As such, oil gas tar will resemble CWG tar to some extent, however, the differences in feedstocks and temperature produce subtle differences in chemical composition that allow for a forensic analysis to distinguish the two types.

The term coal tar has been used extensively to qualitatively describe NAPL from MGP sites. But, as the discussion above shows, true coal tar is only generated during coal gasification or coke production. CWG and oil gas processes produce a petroleum tar generated from the cracking of the carburetion fluids.



2.3 Former Bramlette MGP Operational History

Southern Public Utilities built the MGP on East Bramlette Road in 1917. Duke Power Co. assumed ownership and operation of the MGP in 1939 and sold the property and operations to Piedmont Natural Gas in 1951. Property transactions from 1963 to 1967 transferred ownership of the five parcels to Seaboard Coast Line Railroad Company, also known as CSX Transportation, Inc.

Gas was manufactured at the Bramlette Road MGP from 1917 to 1952. Based on review of historical information including Brown's Directories of Gas Companies (1887-1957), estimates of production quantities can be made for this MGP. A total of 5.5 billion cubic feet of gas was produced at the Bramlette Road MGP, with 99 percent being coal gas. The carbureted water gas (CWG) process was used in a limited capacity beginning in 1945. Both coal tar and CWG tar were produced and sold as a marketable byproduct. A total of 4 million gallons of tar was produced from 1922 to 1952, with 99.7 percent being coal tar (0.3 percent CWG tar). Tar residuals would have been a part of MGP process effluent flow. Effluent from coal gas production was 99 percent of the total effluent during the period of 1922 to 1952. The trend follows gas production with effluent peaking at the end of the 1940s at just over 6,000 gallons per day(gpd). As a perspective, a flow rate of 6,000 gpd equates to about 4 gallons per minute (gpm), similar to the flow from two kitchen sinks.



3.0 Sampling Methods

Soil and sediment samples were collected using stainless steel bowls and trowels or by stainless steel hand auger in general accordance with SynTerra's sampling standard operating procedures (SOPs) employed by SynTerra (QAPP Appendix B, SynTerra 2018) and U.S. Environmental Protection Agency (USEPA) Science and Ecosystem Support Division (SESD) Operating Procedure SESDPROC-200-R3 (August 21, 2014). NAPL samples were collected from MW-3BR following routine groundwater monitoring procedures in accordance with standard operating procedures (SOPs) employed by SynTerra (QAPP Appendix B, SynTerra 2018) and directly into sample jars from the abandoned well screen of MW-06. Samples were placed in ice-filled coolers and managed under chain-of-custody protocols for submittal to Alpha Analytical Laboratory.

Samples collected were analyzed for paraffins, isoparaffins, aromatics, naphthenes, and olefins (PIANO), total and alkylated PAHs, and saturated hydrocarbons. Analyses and laboratory analytical methods are summarized in the table below.

Analysis	Laboratory Analytical Method
PIANO	USEPA Method 8260B/5035 High-Resolution sampling and analysis
Total and Alkylated PAHs	USEPA Method 8270D-SIM
Saturated hydrocarbons	USEPA Method 8015D-modified



4.0 Approach to Forensics Analysis

4.1 Forensic Analysis of Tar

As discussed in Section 2, forensic analysis of tar is based on differences in the chemical composition resulting from the use of different feedstocks and differences in reaction temperatures. While seemingly straightforward, once these materials are released into the environment, the process of identification becomes much more difficult. Processes such as evaporation, dissolution, oxidation, biodegradation, photolysis, adsorption, etc. can produce significant changes in the appearance of the original tar. Comingling with other combustion materials, urban background, soot, road tars, or creosote can make identification even more difficult.

Source identification of liquid tar can usually be done with volatile and semivolatile fingerprinting if little to no weathering has occurred. In more weathered material, the semivolatile organics, particularly PAHs are the most useful for source identification. That is because they are the most abundant material in tar and show a greater resistance to degradation at the higher molecular weight. As such, PAH fingerprints and diagnostic ratios have become one of the primary means for distinguishing tar from petroleum spills and for differentiating between the different types of tar.

4.2 Different Forms of PAHs

PAHs can be classified into one of three general types: petrogenic, pyrogenic and diagenetic.

Petrogenic PAHs are those derived from petroleum and include crude oil, fuels, and lubricants. The key feature of most petrogenic materials is a regular series of normal alkanes along with cyclic alkanes. These are seen as a progression of evenly spaced individual peaks in a GC total petroleum hydrocarbon (TPH) or saturated hydrocarbon (SHC) chromatogram. In addition, the GC chromatogram normally shows a "hump" in the baseline. This "hump" is referred to as an unresolved complex mixture (UCM) resulting from thousands of compounds in petroleum that cannot be adequately resolved by the chromatograph.

When plotted on a histogram, the PAH pattern for a petrogenic material resembles a bell-shaped curve, with lower amounts of the parent PAH and higher amounts of the alkylated PAHs. The appearance of a petrogenic PAH signature would indicate a source other than an MGP tar or a combination of sources.

Pyrogenic substances are those created from oxygen depleted high temperature processes, including incomplete combustion, pyrolysis, cracking, and destructive distillation. All MGP tars are pyrogenic in nature, regardless of which process was used. When plotted on a histogram, the PAH pattern would show a sloped pattern with greater amounts of the parent PAH compounds and decreasing amount of the alkylated PAHs. As the temperature increases, the sloping pattern becomes steeper. Figure 4.1 shows example PAH histograms of petrogenic and pyrogenic materials.



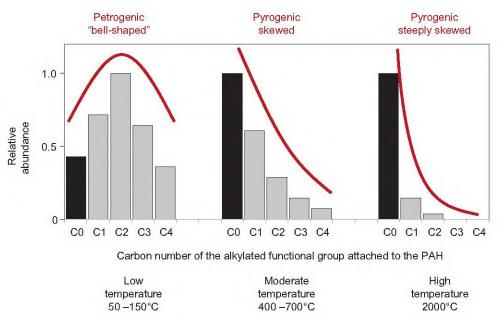


Figure 4.1 – Petrogenic and Pyrogenic PAH Patterns

Diagenetic PAHs are formed from natural sources, such as plants and buried organic materials in their early stages of maturation. Two examples of diagenetic PAHs are retene and perylene.

4.3 PAHs and Urban Background

PAHs are a group of semivolatile constituents that are nearly ubiquitous in sediments worldwide (Battelle, 2003). The term urban background denotes the variety of nonpoint sources of PAHs in the environment. Common nonpoint sources include atmospheric (soot) particulates and dripped/leaked petroleum washed from the surrounding urban roadways, parking lots, and structures during rainfall events. Other nonpoint sources include general surface and stormwater runoff. Stormwater runoff is probably the largest chronic contributor of background PAHs to urban sediments. A typical PAH profile for sediments impacted by urban background sources is shown in Figure 4.2. Please note that this is not absolute for all urban background. During a forensic investigation background samples should be collected and analyzed to determine the typical urban background for the site.



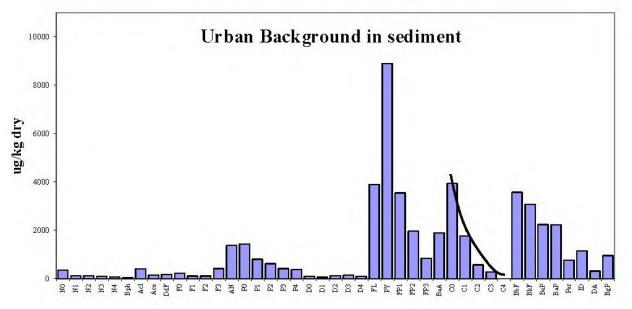


Figure 4.2 – Histogram of Typical Urban Background PAHs in Sediment

The most abundant PAHs are high molecular weight (4- to 6- ring) compounds, particularly the fluoranthene and pyrene isomers. Very few low molecular weight (2- and 3- ring) PAHs are present. The PAHs are consistent with pyrogenic sources; however, the pattern is distinct and very different from MGP tars. The SHC chromatogram of urban background is characterized by a late eluting UCM which takes the form of a hump in the chromatogram. An example of a SHC chromatogram of urban background is given in Figure 4.3.

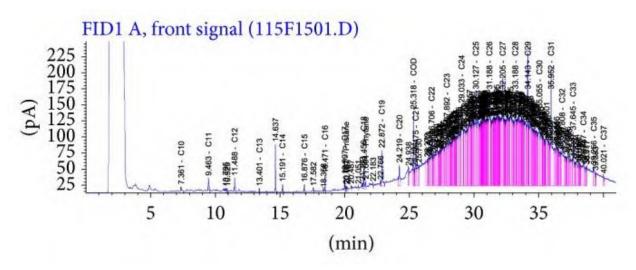


Figure 4.3 – Example of SHC Chromatogram of Urban Background



4.4 Effects of Weathering on PAH Source Signatures

Two key effects on PAH signatures from weathering are common:

- Levels of low molecular weight (2- and 3- ring) PAHs are reduced, thereby increasing the proportion of 4-to 6- ring PAHs; and
- Levels of non-alkylated PAHs are reduced, thereby increasing the proportion of alkylated PAHs.

The PAH weathering rank (PWR) provides a semiquantitative approach for gauging tar weathering. The PWR is calculated using the concentrations of naphthalene, phenanthrene, pyrene, chrysene, and benzo(a)pyrene. Using naphthalene as an example, the PWR would be calculated by taking the naphthalene concentration and dividing by the sum of all five PAH compound concentrations. The process is repeated with the other compounds. The PAH with the highest rank determines the weathering.

- PWR 1 Dominant naphthalene indicates light PAH weathering
- PWR 2 Dominant phenanthrene indicates moderate PAH weathering
- PWR 3 Dominant pyrene indicates heavy PAH weathering
- PWR 4 Dominant chrysene indicates severe PAH weathering

A heavy or severely weathered tar could possibly take on the characteristics of urban background. If severe weathering is suspected, other diagnostic techniques (e.g., interpretation of geochemical biomarkers) are used to help with the identification.

4.5 PAH Diagnostic Ratios

Forensic investigators have developed numerous (hundreds) ratios that are used to help identify PAH sources in the environment. Petrogenic PAH ratios emphasize differences among PAH analytes that are more abundant among fossil fuel products. For example, benzo(e)pyrene concentrations relative to alkylated benzo(a)anthracene/chrysene concentrations are higher than the same ratio using benzo(a)pyrene in sediments near petroleum refineries. In one case, an investigator showed that the urban background chromatogram from a site showed equal amounts of petrogenic and pyrogenic PAHs. This was used in a case study with potential tar impacts to show that urban background alone could not account for sediment impacts and that tar was a contributing factor.

Pyrogenic PAH ratios emphasize differences among PAH isomers that are more abundant among combustion and carbonization products. The ratios of fluoranthene/fluoranthene + pyrene and benzo(b)fluoranthene + benzo(j) and benzo(k)fluoranthene / benzo(b) fluoranthene + benzo(j)and (k)fluoranthene + benzo(a)pyrene are particularly effective at differentiating PAHs from different pyrogenic sources.



Some PAH ratios are sensitive to pyrolysis while others are thermodynamically stable. Other ratios help separate samples with heavier petrogenic sources. A simple ratio test for distinguishing between coal tar and water gas tar was used by the Electric Power Research Institute (EPRI) in its 2000 report on chemical source attribution at MGP Sites. In this report, CWG tars had a fluoranthene to pyrene ratio of between 0.5 and 0.9 while coal tars had a ratio between 0.87 and 1.46. Another ratio was the dibenzofuran/fluorene ratio. Coal tars had a ratio between 0.39 and 1.11 while CWG tars had a ratio between 0.12 and 0.46. Dibenzofuran is much more prevalent in coal tar because of the higher oxygen content of the coal. Many other ratios are used as well.

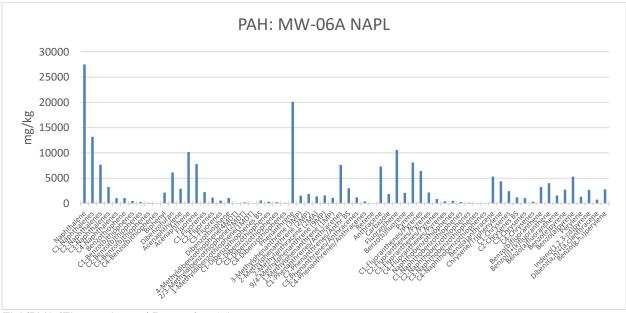
In the end, the choice of what ratios to use are based on a knowledge of the site history, potential PAH sources to the environment, a well-defined urban background, and an understanding of potential weathering at the site. There is no one set of ratios that will necessarily work in all instances, therefore while useful in unweathered single source samples, the ratios may be altered in mixtures and highly weathered samples.



5.0 Parcel 3 Forensics Evaluation

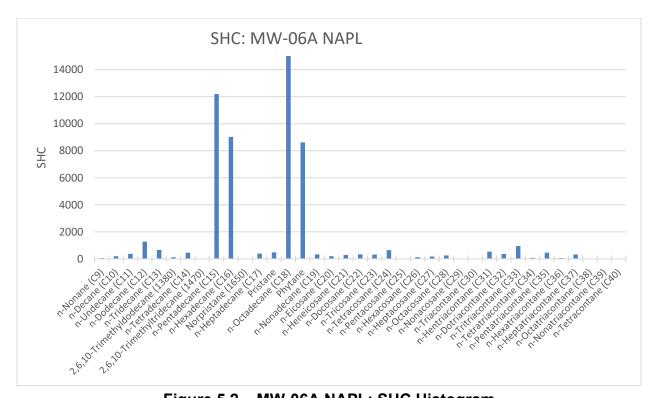
5.1 MW-06 NAPL

Monitoring well MW-06 has been abandoned and was formerly located with the MW-21 monitoring well cluster in the southwest portion of the Vaughn Landfill (Figure 2.1). The sample was collected from NAPL that had accumulated within the well screen. The sample was analyzed for PIANO volatiles, Total and Alkylated PAHs, viscosity and specific gravity/density. For forensic analysis purposes, the data from the PAH and SHC analyses were plotted on histograms and the SHC chromatogram was reviewed. Fluoranthene/pyrene and dibenzofuran/fluorene diagnostic ratios for PAHs were calculated as a first pass evaluation. These histograms and chromatogram are shown in Figures 5.1 through 5.3. The SHC histogram plots hydrocarbons C9-C40. PIANO constituents were examined but not plotted on a histogram as pattern recognition is not used in the interpretation of this data.

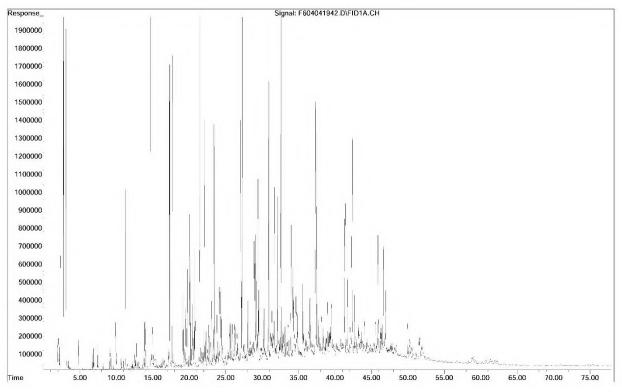


FL0/PY0 (Fluoranthene / Pyrene) = 1.3 DF/F0 (Dibenzofuran/Fluorene) = 0.79

Figure 5.1 – MW-06A NAPL: PAH Histogram and Diagnostic Ratios











The PIANO analysis reveals primarily heavier ends of the volatile range with some benzene present.

The PAH histogram reveals a pyrogenic source dominated by the naphthalenes. No petrogenic sources are indicated. Little to no weathering is indicated. The fluoranthene to pyrene ratio and the dibenzofuran to fluorene ratio are both indicative of a coal carbonization tar. There is no apparent evidence of urban background present as would be indicated by an increase in the heavier ends of the PAHs.

The SHC histogram does not show a regular pattern of hydrocarbons indicative of petroleum. There is no UCM present in the chromatogram.

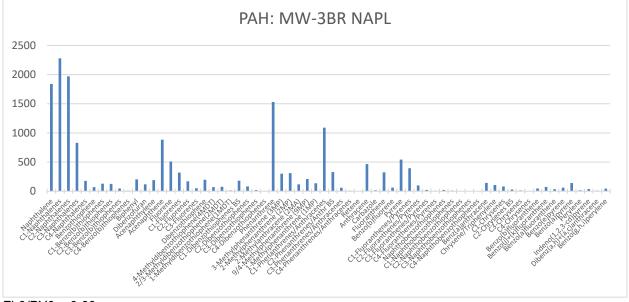
The specific gravity of the sample is 1.18 at 70F. This is indicative of a DNAPL and heavier than a CWG tar.

Based on a review of this data, the results are consistent with the NAPL being <u>a</u> tar produced by a coal carbonization process. Little to no weathering is evident.

5.2 MW-3BR NAPL

Monitoring well MW-3BR is located along the western side of the Vaughn Landfill (Figure 2.1). The sample was collected from accumulated NAPL using a peristaltic pump and low-flow sampling techniques. The NAPL sample was analyzed for PIANO volatiles, Total and Alkylated PAHs, and SHC. For forensic analysis purposes, the data from the PAH and SHC analyses were plotted on histograms and the SHC chromatogram was reviewed. The same diagnostic ratios for PAHs were calculated as for sample MW-6A NAPL. These histograms and chromatogram are shown in Figures 5.4 through 5.6. The SHC histogram plots hydrocarbons C9-C40.









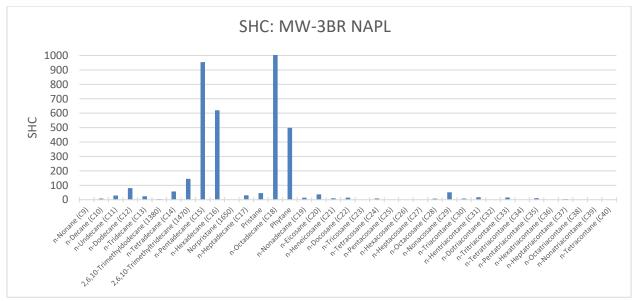


Figure 5.5 – MW-3BR NAPL: SHC Histogram



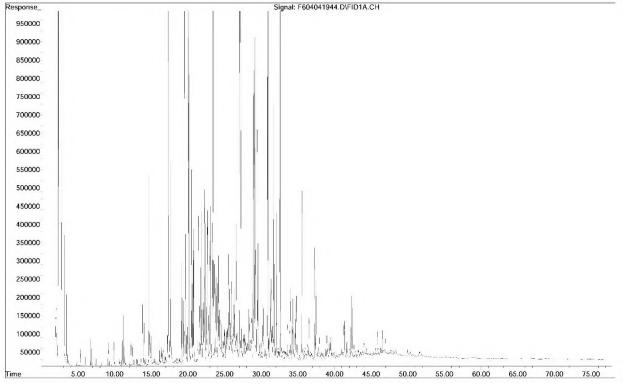


Figure 5.6 – MW-3BR NAPL: SHC Chromatogram

The PIANO analysis reveals primarily heavier ends of the volatile range with some benzene present.

The PAH histogram reveals a pyrogenic source dominated by the naphthalenes. No petrogenic sources are indicated. The loss of the parent naphthalene is indicative of weathering. The PWR for this sample is determined to be 1. Light weathering is evident. The fluoranthene to pyrene ratio and the dibenzofuran to fluorene ratio are both indicative of a CWG tar. There is no apparent evidence of urban background present as would be indicated by an increase in the heavier ends of the PAHs.

The SHC histogram does not show a regular pattern of hydrocarbons indicative of a petroleum source. There is no evident UCM present in the chromatogram.

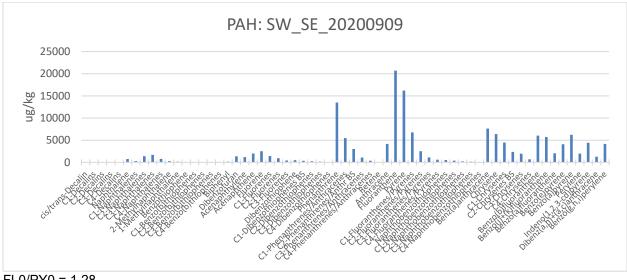
Based on a review of this data, the results are consistent with the NAPL being a tar produced by a CWG process. Light weathering (PWR =1) is evident.



6.0 Forensic Analysis of Near Site Sediment Samples

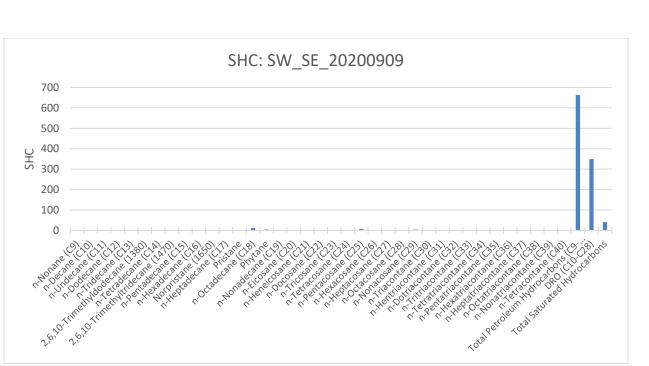
6.1 Forensic Evaluation of Sample SW-12 (SW-SE-20200909)

Sample SW-SE-20200909 was collected near the routine surface water sampling location SW-12 at the confluence of the historical drainage ditch from the Site and the Reedy River (Figure 2.1). The sediment sample was analyzed for PIANO volatiles, Total and Alkylated PAHs, and SHC. For forensic analysis purposes, the data from the SHC and PAH analyses were plotted on histograms and the SHC chromatogram was reviewed. The same diagnostic ratios for PAHs were calculated as for sample MW-6A NAPL. These histograms and chromatogram are shown in Figures 6.1 through 6.3. The SHC histogram plots hydrocarbons C9-C40.



FL0/PY0 = 1.28 DF/F0 = 0.538







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File :0:\Forensics\Data\FID6\2020\SEP\4.SEC\F609142025.D
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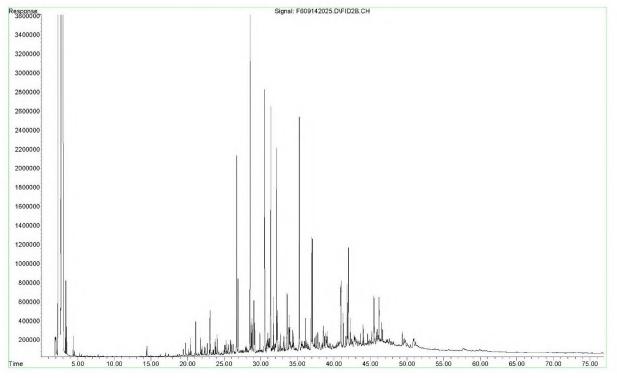


Figure 6.3 – SW_SE_20200909: SHC Chromatogram



The PIANO analysis reveals only heavy heavier ends of the volatile range.

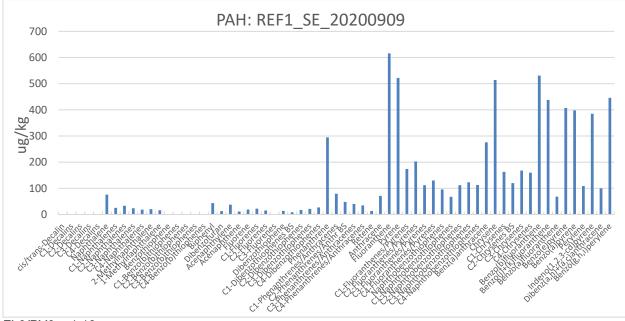
The PAH histogram reveals a pyrogenic source. Two and three ring PAH compounds have been reduced, indicating more severe weathering. No petrogenic sources are indicated. The PWR for this sample is determined to be 3. Heavy weathering is evident. The fluoranthene to pyrene ratio and the dibenzofuran to fluorene ratio are both indicative of a coal carbonization tar. There is no apparent evidence of urban background present as would be indicated by an increase in the heavier ends of the PAHs.

The SHC histogram does not show a regular pattern of hydrocarbons indicative of a petroleum source. There is no evident UCM present in the chromatogram.

Based on a review of this data, the results are consistent with the sediment sample containing <u>a tar produced by a CC process</u>. Heavy weathering (PWR =3) is evident.

6.2 Forensic Evaluation of Sample REF1-SE-20200909

The sediment sample was analyzed for PIANO volatiles, Total and Alkylated PAHs, and SHC. For forensic analysis purposes, the data from the SHC and PAH analyses were plotted on histograms and the SHC chromatogram was reviewed. The same diagnostic ratios for PAHs were calculated as for sample MW-6A NAPL. These histograms and chromatogram are shown in Figures 6.4 through 6.6. The SHC histogram plots hydrocarbons C9-C40.



FL0/PY0 = 1.18 DF/F0 = 0.681

Figure 6.4 – REF1_SE_20200909: PAH Histogram and Diagnostic Ratios

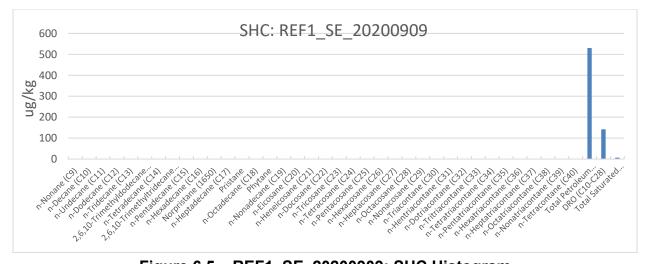


Figure 6.5 – REF1_SE_20200909: SHC Histogram

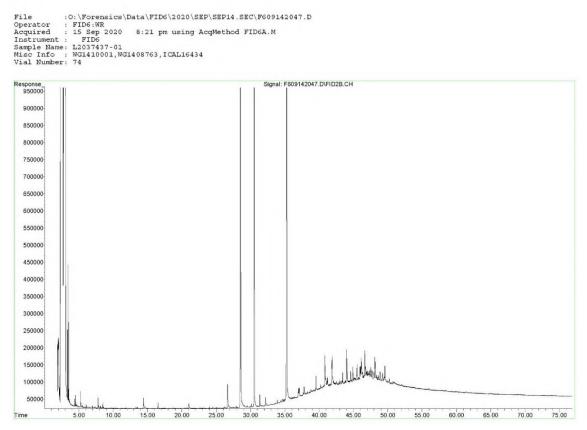


Figure 6.6 – REF1_SE_20200909: SHC Chromatogram



The PIANO analysis reveals only heavy heavier ends of the volatile range.

The PAH histogram reveals a pyrogenic source, consisting primarily of the heavy PAHs. This pattern is indicative of urban runoff as the primary source. The sample does show a somewhat higher level of naphthalenes than normally seen in urban runoff alone. As such, this sample may contain PAHs from a secondary source. Two and three ring PAH compounds have been reduced, indicating more severe weathering. No petrogenic sources are indicated. The PWR for this sample is determined to be 3. Heavy weathering is evident. The fluoranthene to pyrene ratio and the dibenzofuran to fluorene ratio are both indicative of a coal carbonization tar. The SHC histogram does not show a regular pattern of hydrocarbons indicative of a petroleum source. There is an evident UCM present in the chromatogram.

Based on a review of this data, the results are consistent with the sediment sample containing urban runoff as a primary source with the possibility of a tar produced by a CC process as a possible secondary source. Heavy weathering (PWR =3) of the tar is evident.



7.0 Forensic Evaluation of Ditch 4 and Ditch 5 Sediment Samples

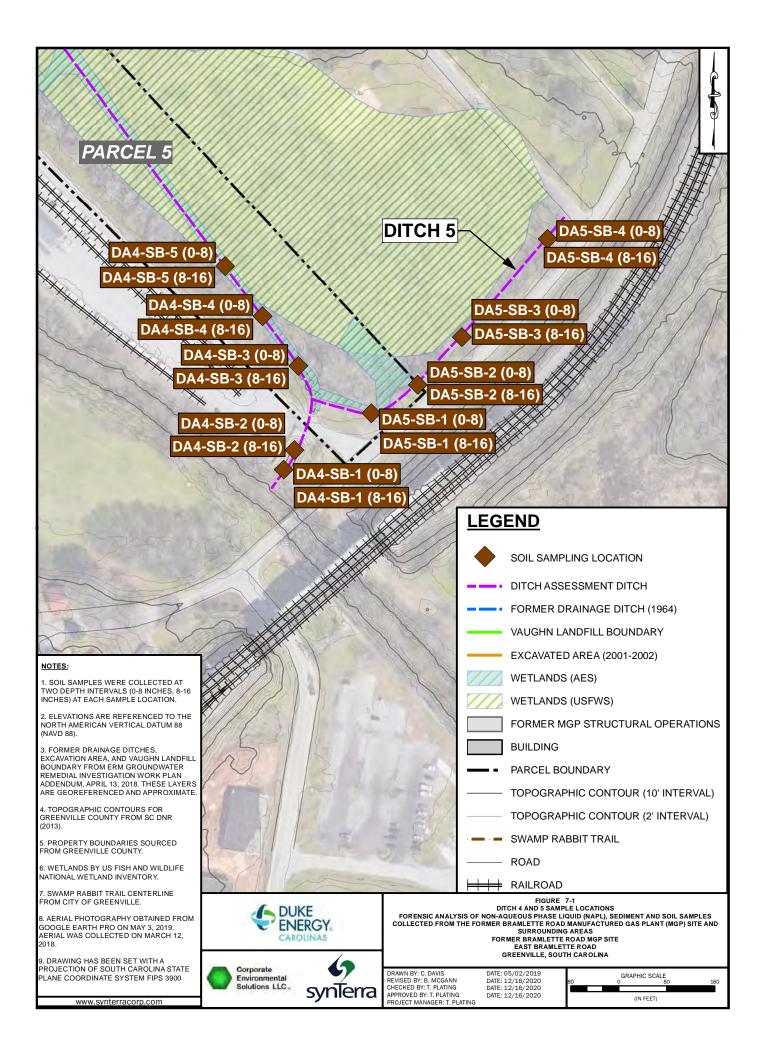
A total of six sediment samples were collected from an area identified as Ditch 4 and four samples from and area identified as Ditch 5. Figure 7.1 is a map showing the location of the samples relative to the former Bramlette Road MGP site.

The samples were analyzed for the same parameters and subjected to the same review as discussed for the previous samples. Histograms and chromatograms for the Ditch 4 samples are provided in Appendix A to this report. Histograms and chromatograms for the Ditch 5 samples are provided in Appendix B.

Review of the Ditch 4 samples showed two samples (DA4-SB-1 (0-8) and DA4-SB-3 (0-8)) to contain PAHs from urban runoff. No MGP impacts were observed in these two samples. Three samples (DA4-SB-2 (0-8), DA4-SB-4 (0-8), and DA4-SB-5 (0-8)) showed possible weathered CC tar (PWR 3) PAHs or impacts. Other sources (runoff) may also be present in these samples. Sample DA4-SB-3 (8-16) contains a mixture of petrogenic and pyrogenic sources. CC tar (PWR 3) PAHs or impacts may also be present in this sample.

The SHC chromatograms reveal hydrocarbons primarily in the C15-C37 range with the odd numbered hydrocarbons being dominant. This dominance of the odd numbered SHCs indicates that petroleum is not the source of the SHC. This type of pattern is common in peat and other naturally occurring hydrocarbon material.

All of the Ditch 5 samples showed a similar source pattern. All samples contain a mixture of low molecule weight petrogenic PAHs and high molecular weight pyrogenic PAHs. All samples had a high dibenzofuran/fluorene ratio (>5). Fluorene was greatly reduced in these samples compared to naphthalene. This is not consistent with general PAH weathering. The Ditch 5 PAHs are therefore classified as a mixture of petroleum and high molecular weight combustion sources. The SHC chromatograms reveal a steady pattern of hydrocarbons in the lower molecular weight ranges and the odd number dominance in the higher molecular weight range. This is consistent with the PAH data. The material in the Ditch 5 samples is not consistent with MGP tar PAHs.



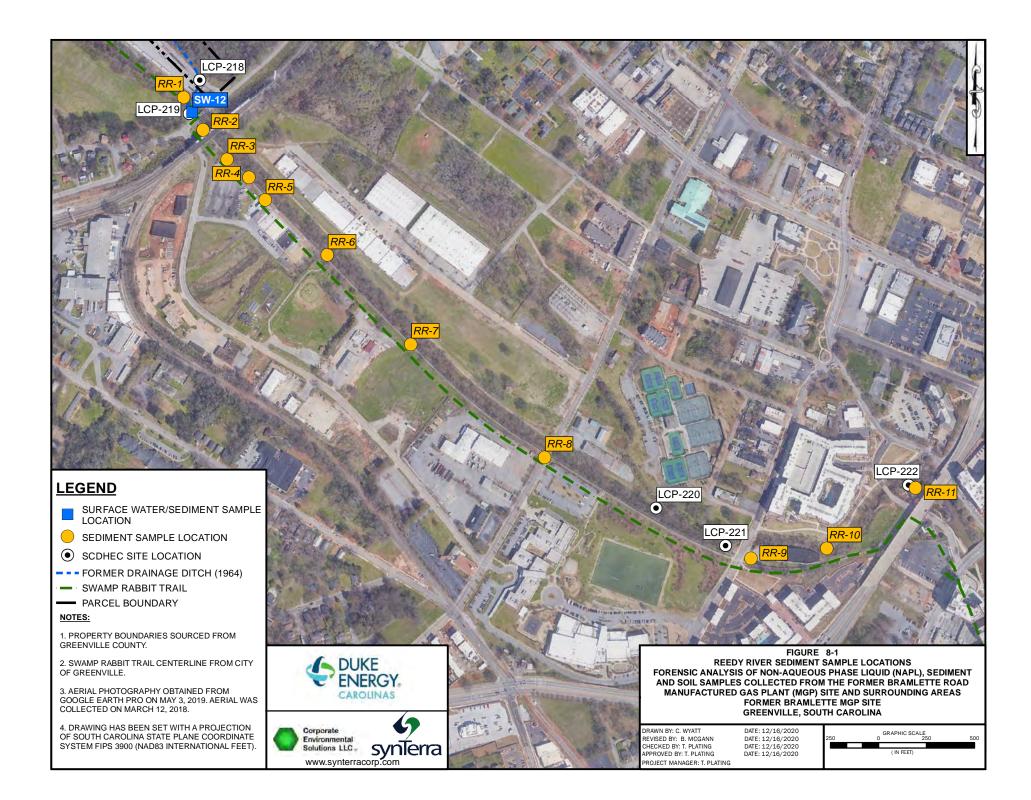


8.0 Forensic Evaluation of Reedy River Sediment Samples

A total of twelve sediment samples were collected as part of a characterization of PAHs from the Reedy River. One of the samples (RR0-SE-20201020 (0-8)) was collected upstream to serve as a background sample. The other samples were collected downstream from the former Bramlette MGP site. Figure 8.1 is a map showing the location of the samples relative to the former Bramlette Road MGP site.

The samples were analyzed for the same parameters and subjected to the same review as discussed for the previous samples. Histograms and chromatograms are provided in Appendix C to this report.

Sample RR0-SE-20201020 (0-8) was found to be consistent with natural runoff. There were no distinct patterns in either the SHC or PAH analysis. Samples RR1-SE-20201020 (0-8) through RR10-SE-20201020 (0-8) were all found to be consistent with urban runoff PAHs. The SHC chromatograms revealed the standard UCM and there is no regular pattern of SHC s indicative of any petroleum source. Sample RR11-SE-20201020 (0-8) is consistent with the material found in the Ditch 5 samples.



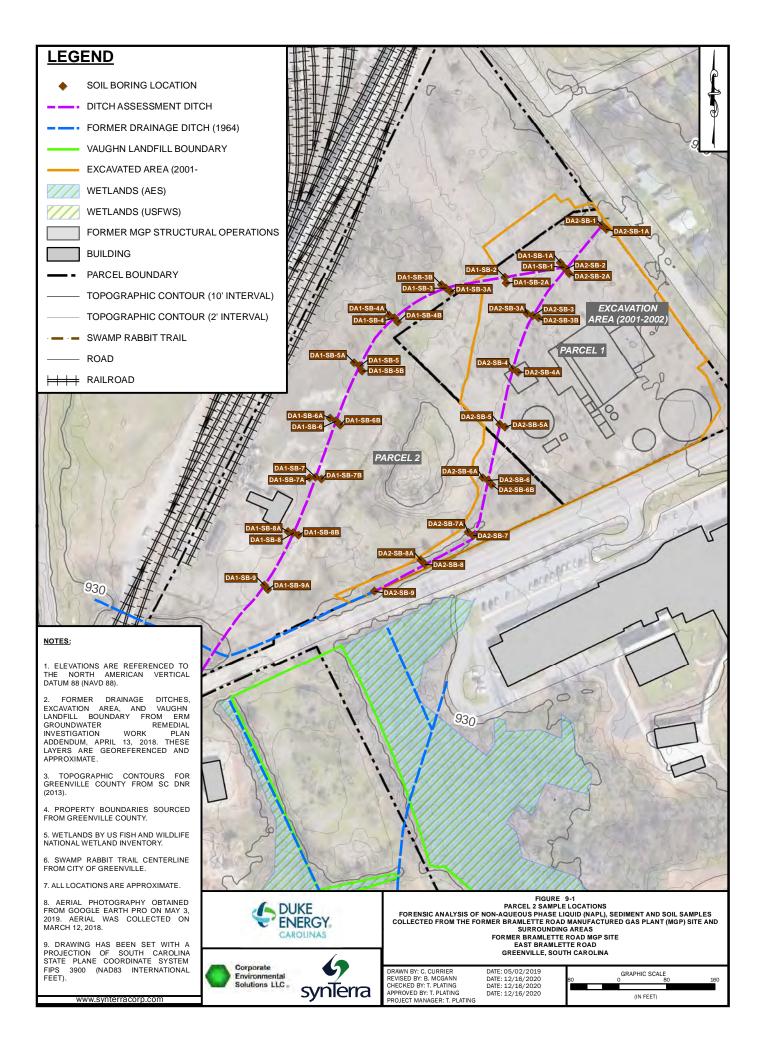


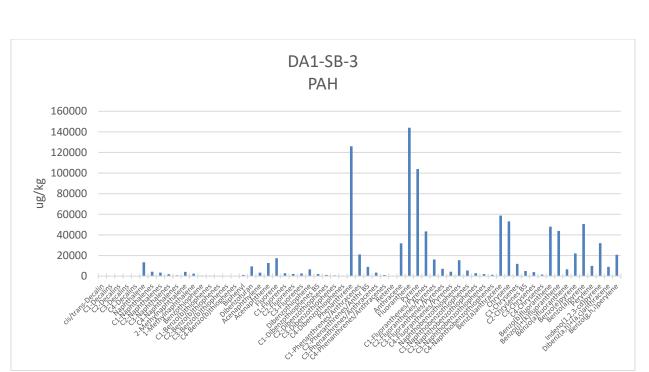
9.0 Forensic Evaluation of Parcel 2 Ditch Samples

Two soil samples (DA1-SB-3 and DA1-SB-8) were submitted from an area identified as Parcel 2. Figure 9.1 is a map showing the location of the samples relative to the former Bramlette Road MGP site.

The soil samples were analyzed for PIANO volatiles, Total and Alkylated PAHs, and SHC. For forensic analysis purposes, the data from the SHC and PAH analyses were plotted on histograms and the SHC chromatogram was reviewed. These histograms and chromatogram are shown in Figures 9.2 through 9.4 for DA1-SB-3 and 9.5 through 9.7 for DA1-SB-8. The SHC histogram plots hydrocarbons C9-C40.

Sample DA1-SB-3 was determined to contain PAHs consistent with weathered (PWR-3) coal carbonization tar impacts. Sample DA1-SB-8 was determined to contain PAHs consistent with urban runoff impacts. No MGP impacts were observed in this sample.





FL0/PY0 = 1.385 DF/F0 = 0.547



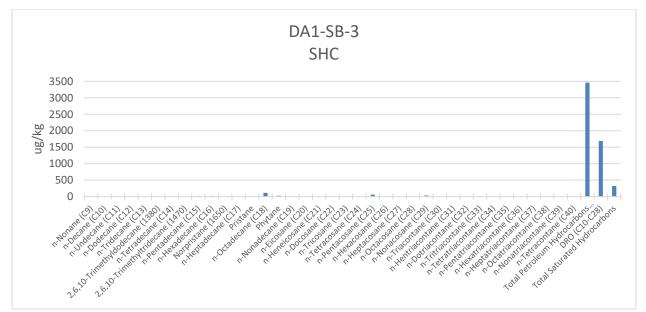
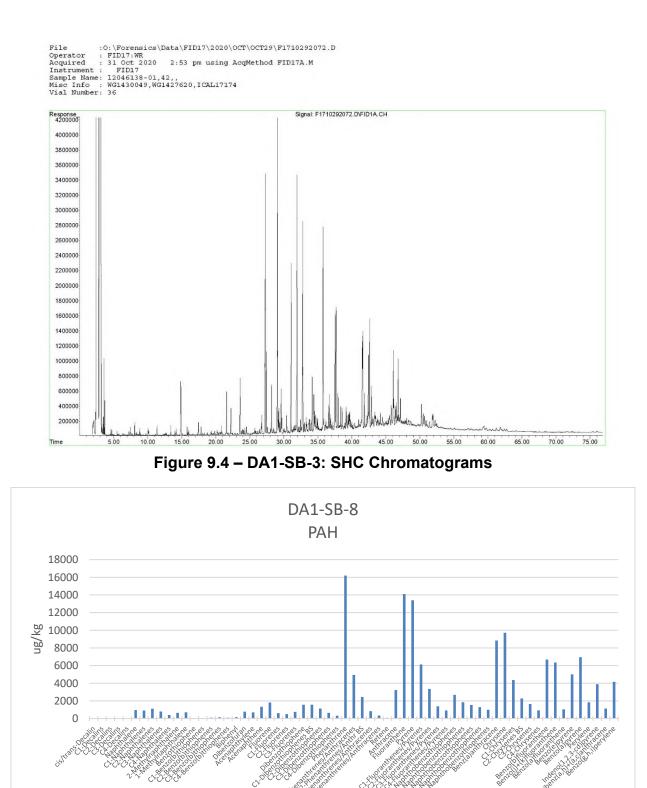


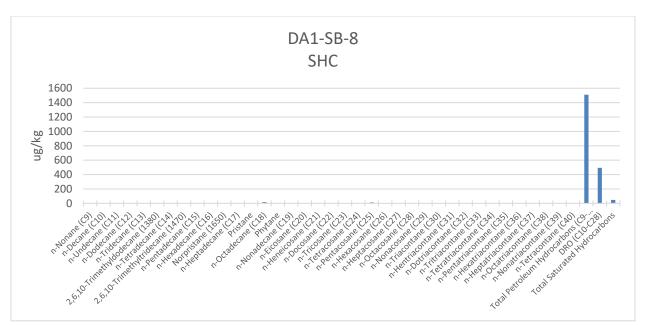
Figure 9.3 – DA1-SB-3: SHC Histogram





FL0/PY0 = 1.052 DF/F0 = 0.429

Figure 9.5 – DA1-SB-8: PAH Histogram and Diagnostic Ratios





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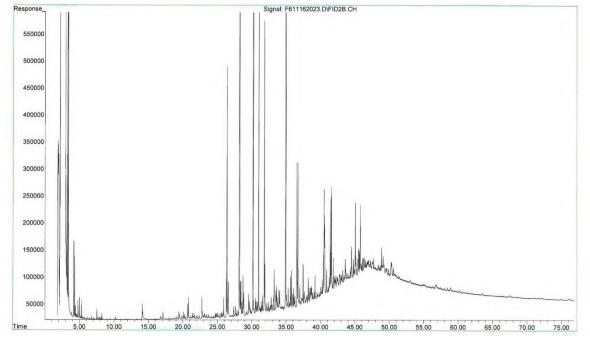


Figure 9.7 – DA1-SB-8: SHC Chromatograms



10.0 Comparison of Total Priority Pollutant (16) PAHs in Ditch and River Sediments

Forensic analytical techniques allow for the determination of low parts per billion levels of individual compounds. These low levels are scaled on histograms and chromatograms so that one can recognize patterns. As such, it is relevant to provide some discussion as to the levels of components detected. For regulatory purposes, the sixteen priority pollutant PAHs are often summed to provide a total PAH value. The sixteen compounds are naphthalene, anthracene, acenapthene, acenapthylene, benzo(a)anthracene, benzo(a) pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, chrysene, dibenzo(ah)anthracene, fluorene, fluorene, indeno(1,2,3-cd)pyrene, pyrene, and perylene.

Figure 10.1 shows a comparison of the total PAH ranges for the Ditch 4, Ditch 5, and Reedy River sediment samples.

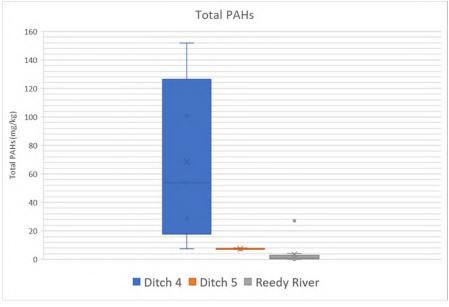


Figure 10.1 – Total PAHs (16) by Sample Area)

The Figure shows the highest levels of PAHs to be present in the Ditch 4 samples. Ditch 5 samples were fairly consistent in PAH concentration, ranging from approximately 7 to 8 mg/Kg. For the river samples, 11 of the twelve samples showed PAH concentrations less than 5 mg/Kg and 6 of 12 samples showed total PAH concentrations less than 1 mg/Kg.



11.0 Summary

Twenty-eight samples were collected on and near the former Bramlette Road MGP site in order to determine the source of PAH compounds present in the samples. Findings from the sampling and forensics analysis are as follows:

- MGP impacts were observed in site NAPL samples and in some sediments and soil in Ditch 4 and Ditch 2.
- No MGP impacts were observed in Ditch 5 sediment samples
- No MGP impacts were observed in Reedy River sediment samples.
- PAHs in Ditch 5 and the Reedy River can be attributed to urban runoff and petroleum sources not related to the MGP.
- Comparison of total PAH values show the highest concentration to be present in the Ditch 4 sediment samples with lesser amount in Ditch 5 sediments and trace amounts in the Reedy River sediment samples.



12.0 References

- Brown's Directories of Gas Companies, certain editions from the 1887 Edition (CY 1886) through the 1956-57 Edition (CY 1955), 1887-1957
- Battelle, et al, 2003, Guidance for Environmental Background Analysis, Volume II: Sediment
- Electric Power Research Institute, 2000, Chemical Source Attribution at Former MGP Sites

Morgan, J.J. 1926, Manufactured Gas: A Textbook of American Practice, First Edition

Murphy, B.L and Morrison, R.D. 2015, Introduction to Chemical Forensics

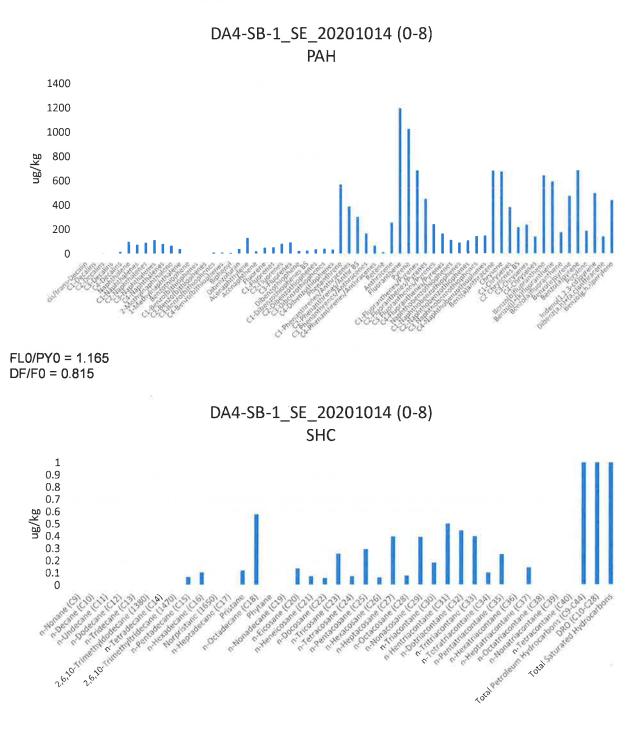
Stout, S.A. and Wang, Z. 2018, Oil Spill Environmental Forensics Case Studies

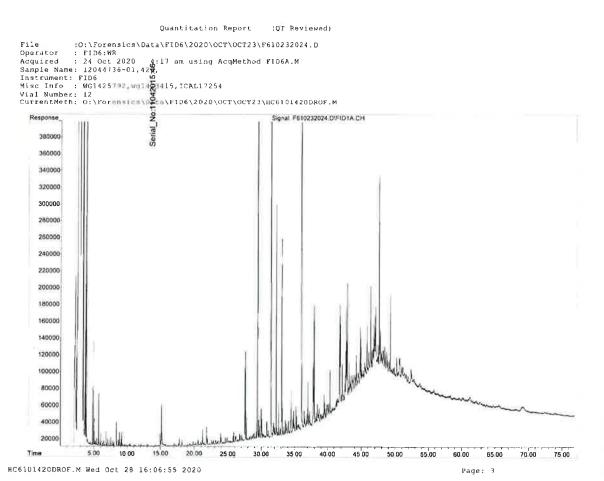
SynTerra. 2018, Quality Assurance Project Plan – Former Bramlette MGP Site



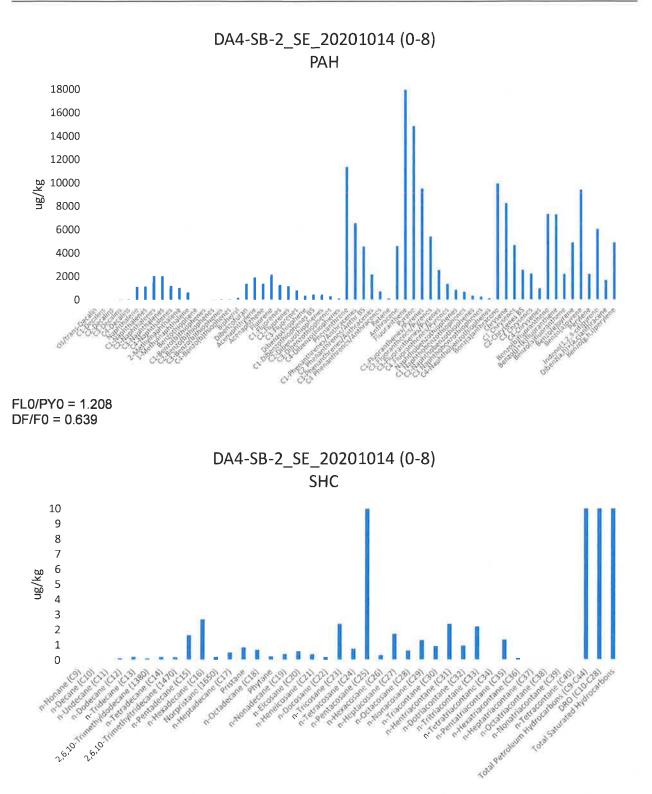
Appendix A: Ditch 4 Samples Histograms and Chromatograms



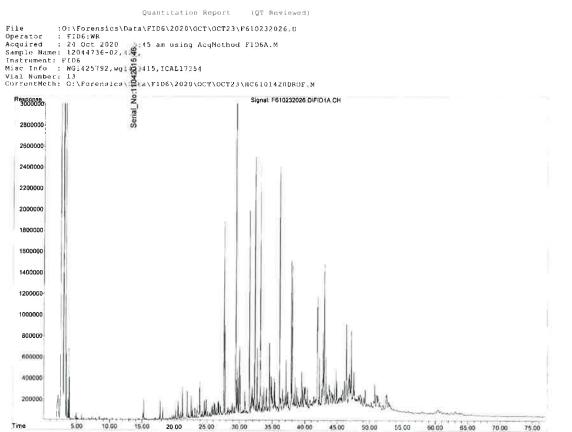




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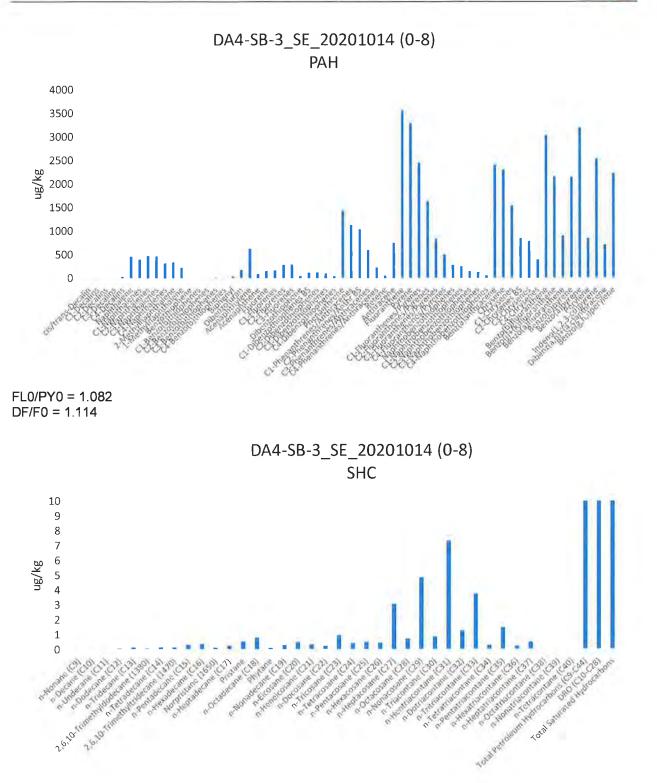


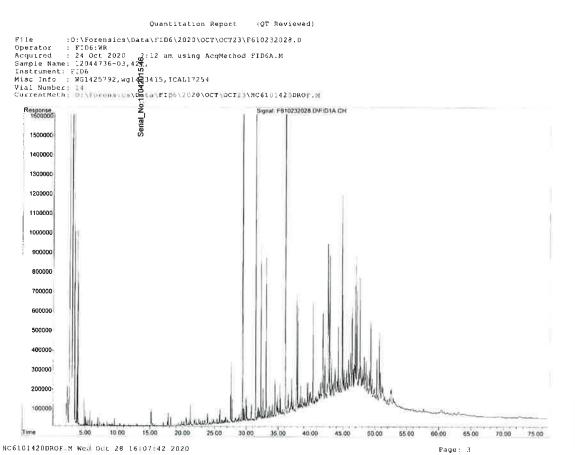
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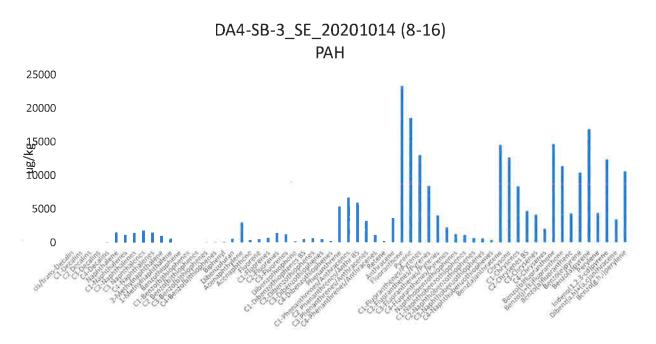




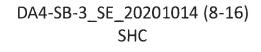


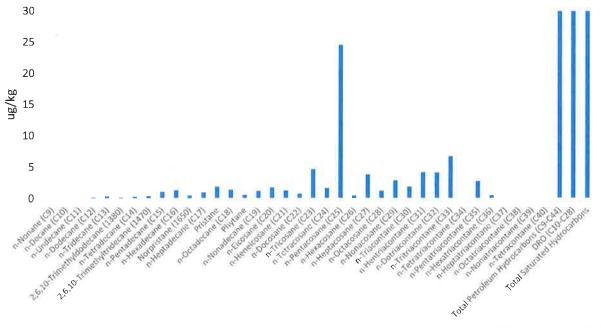




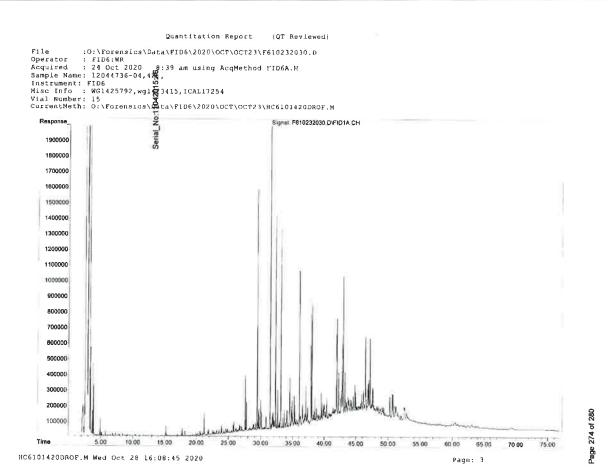


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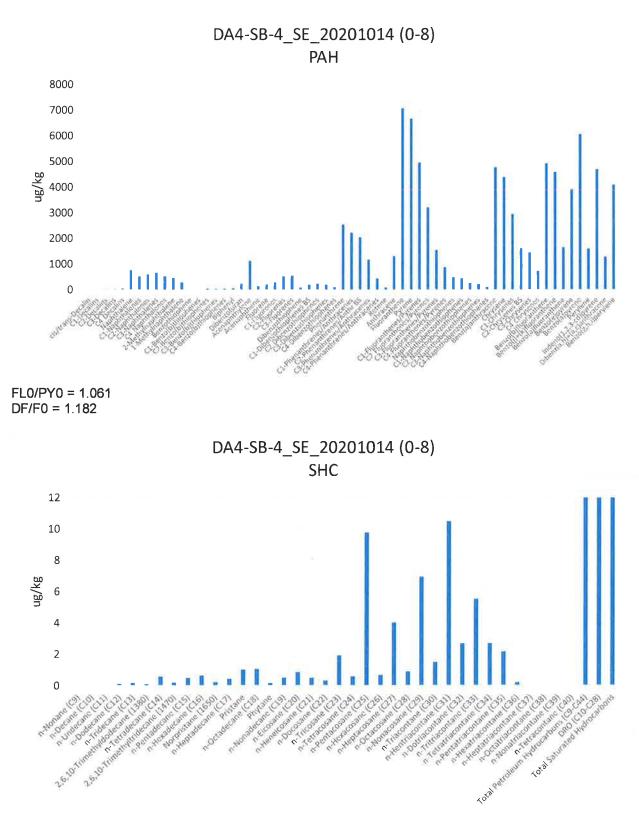


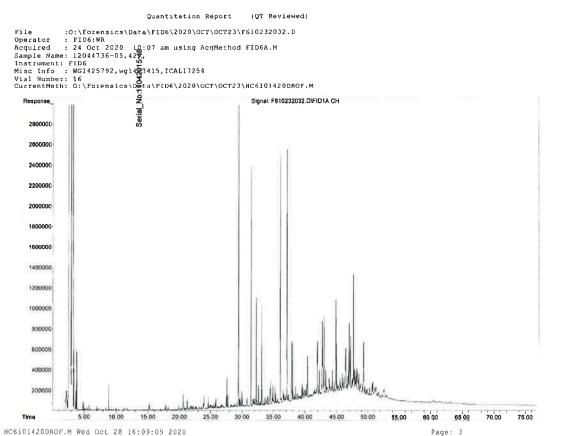








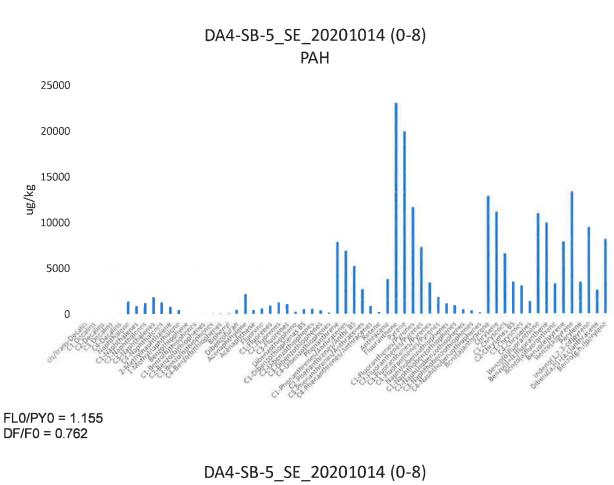




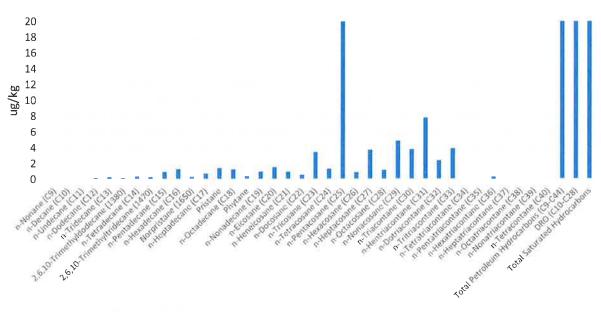
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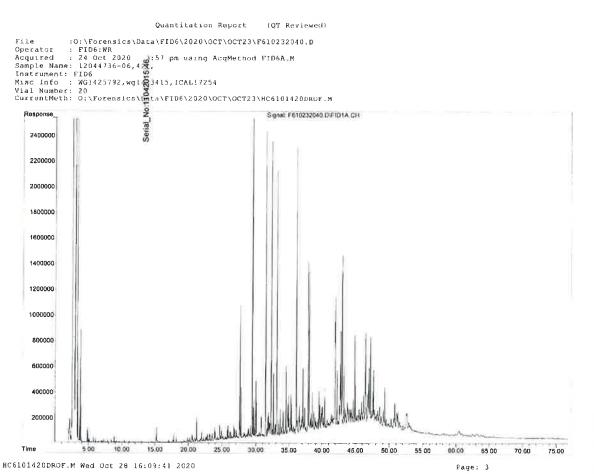
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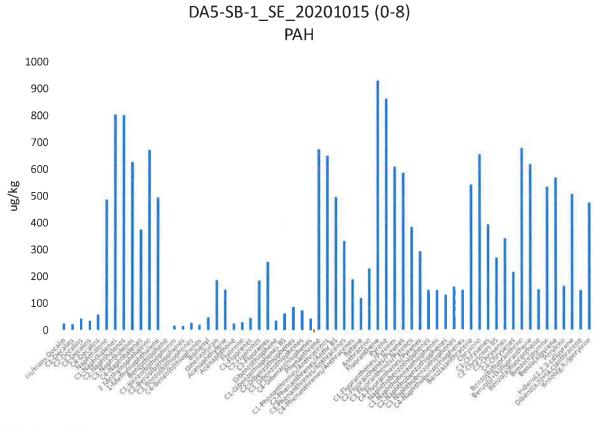




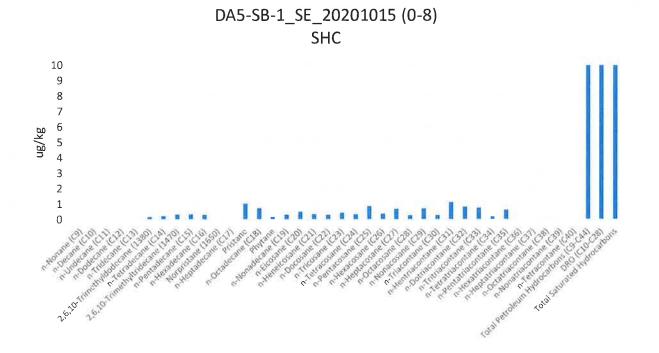


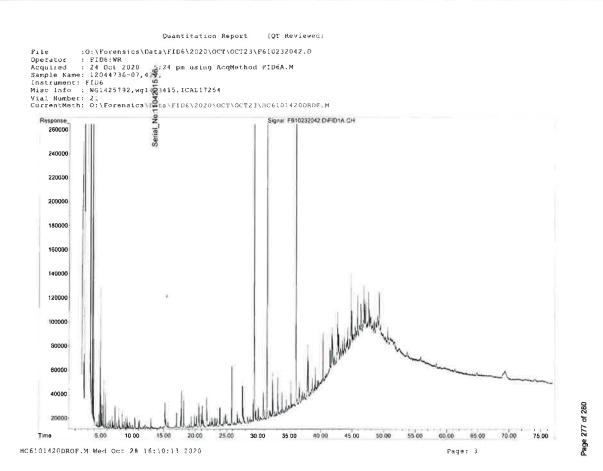
Appendix B: Ditch 5 Samples Histograms and Chromatograms





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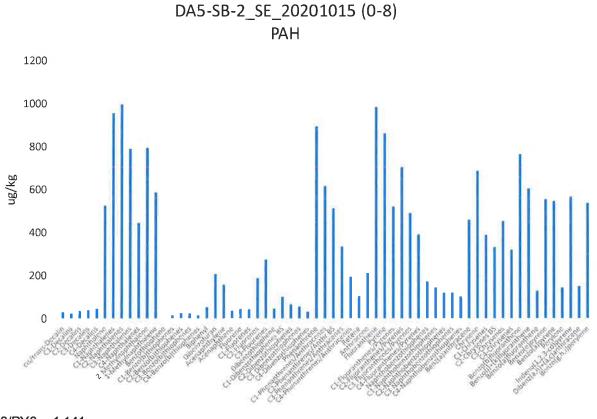




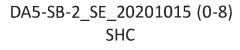
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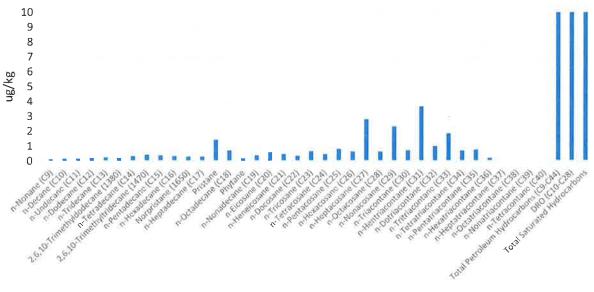


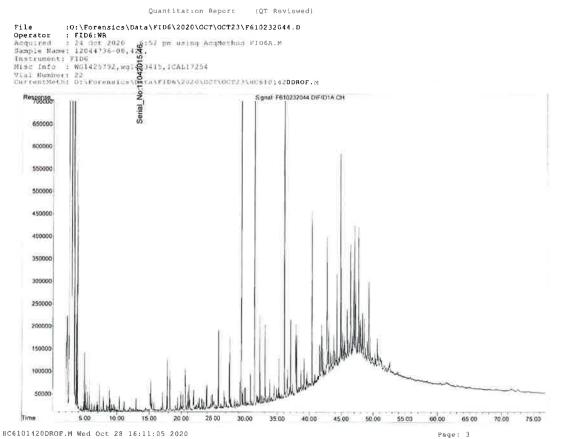




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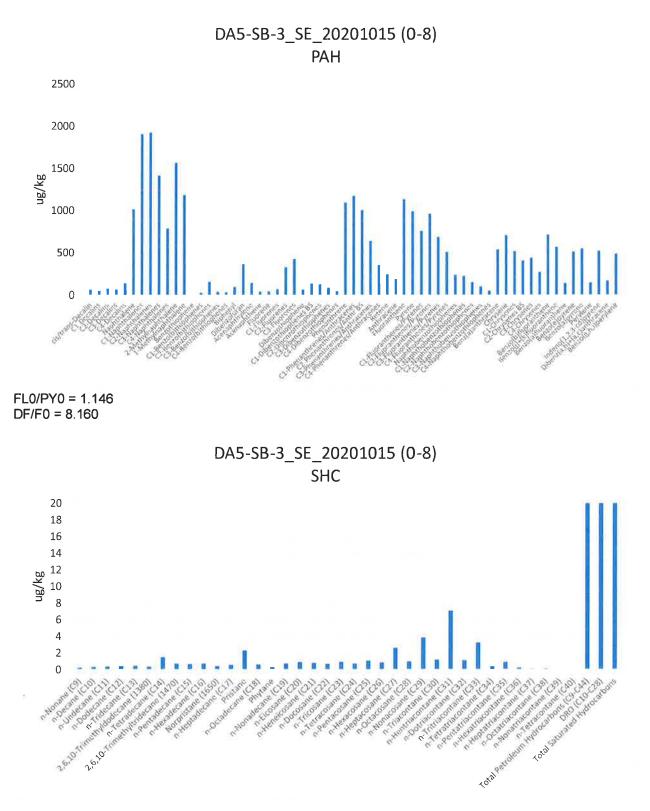




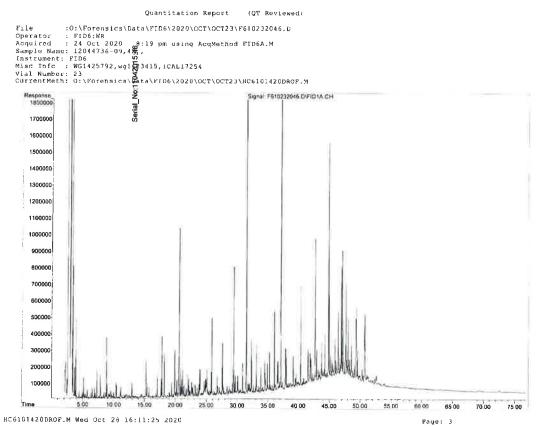




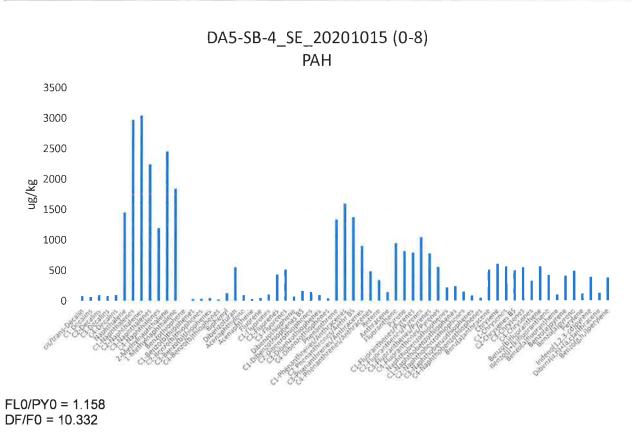


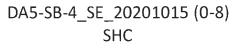


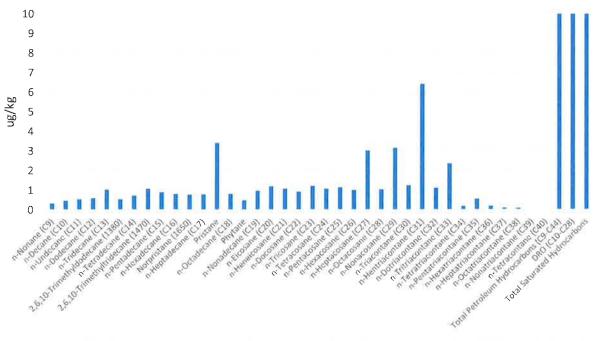






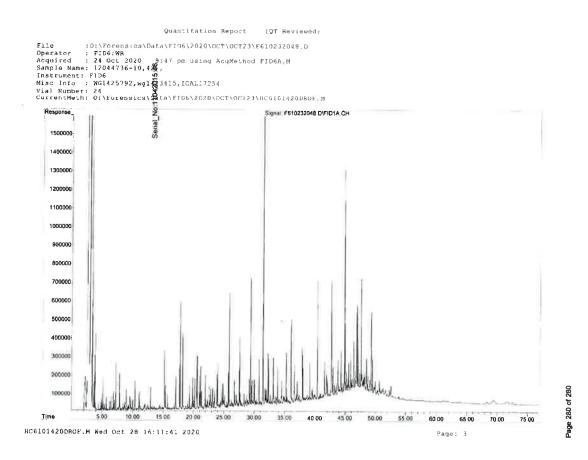






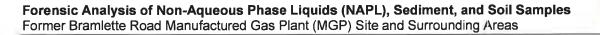


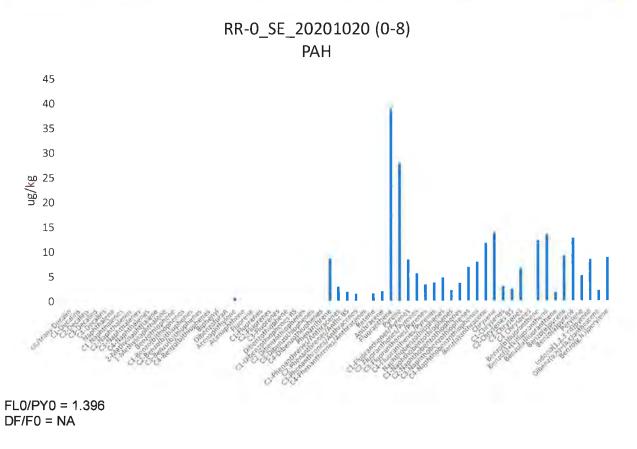


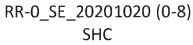


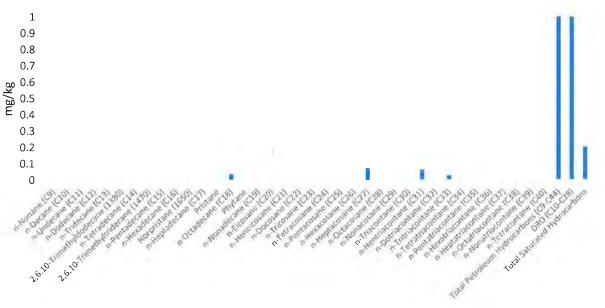


Appendix C: River Samples Histograms and Chromatograms

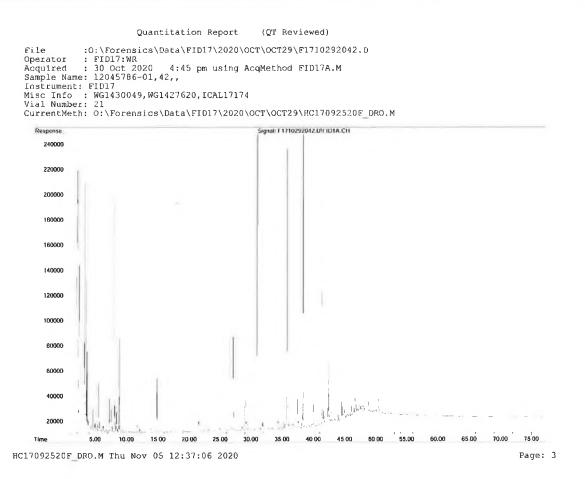






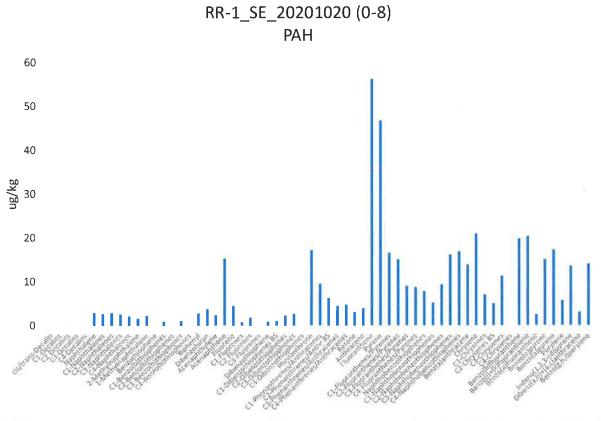




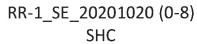


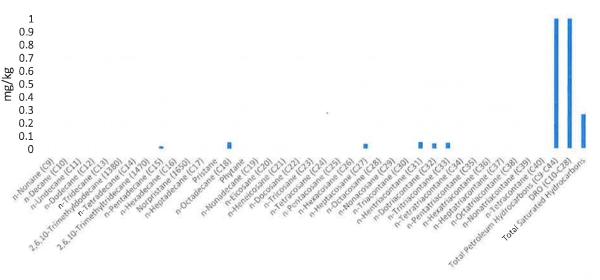
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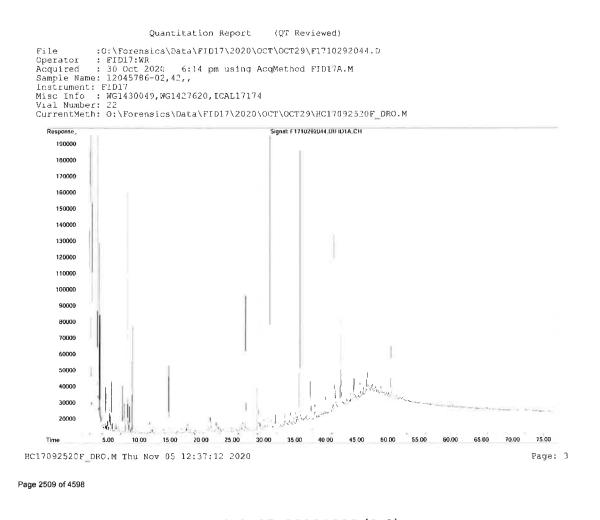


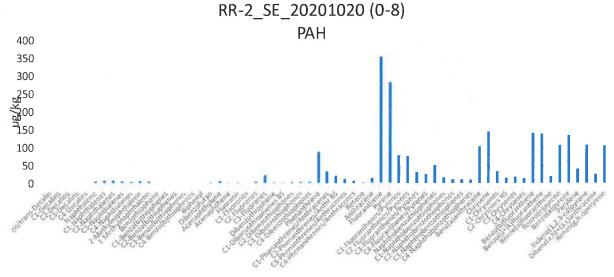
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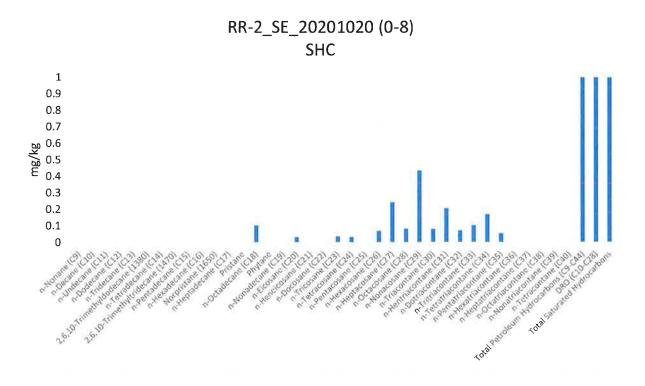




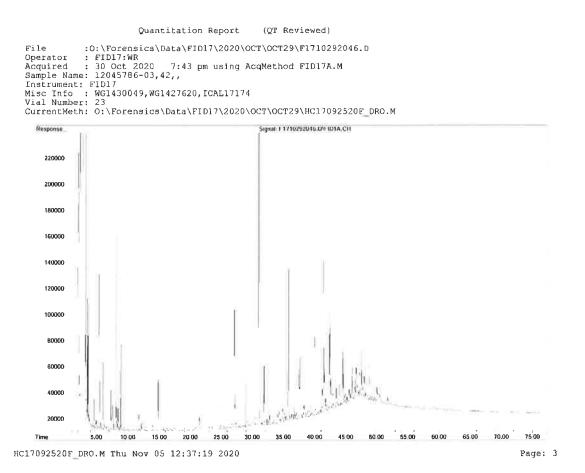


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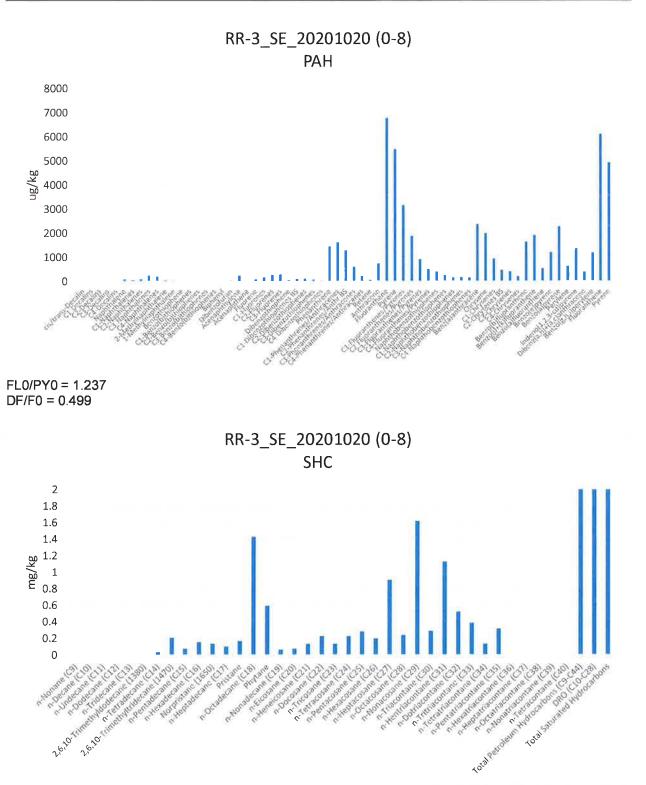






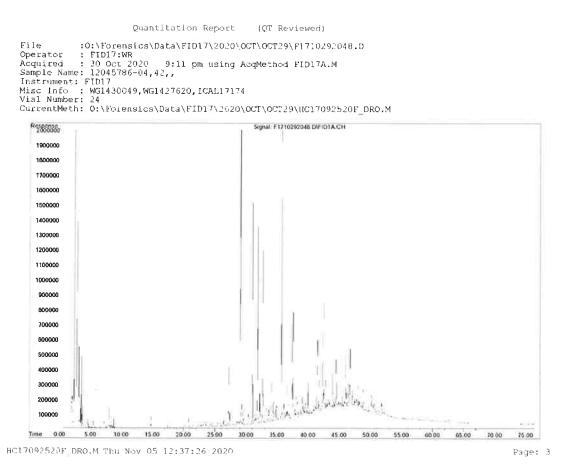


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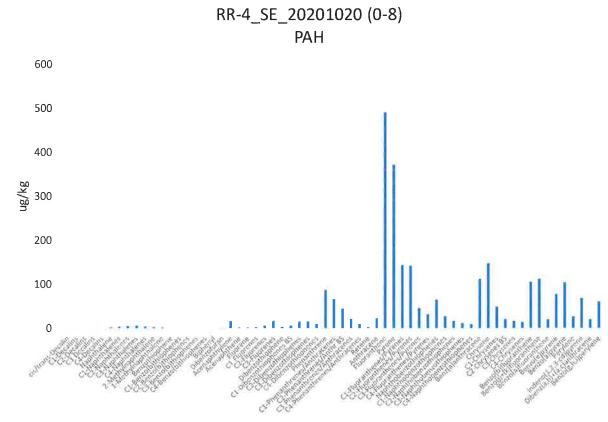




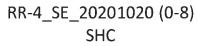


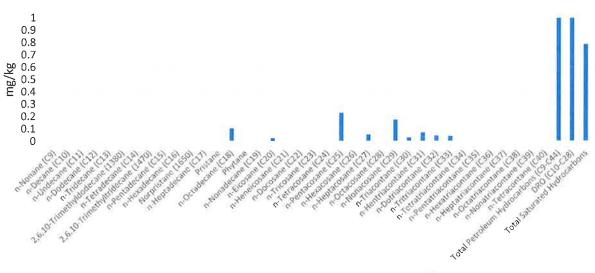
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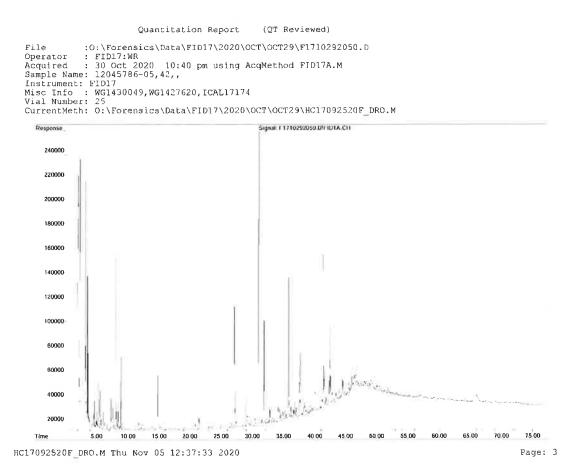


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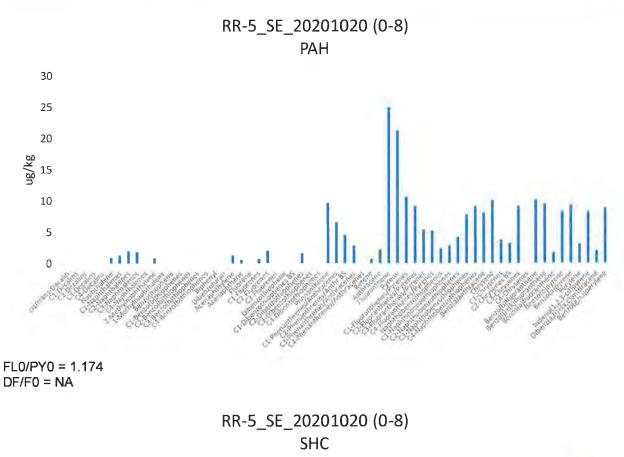


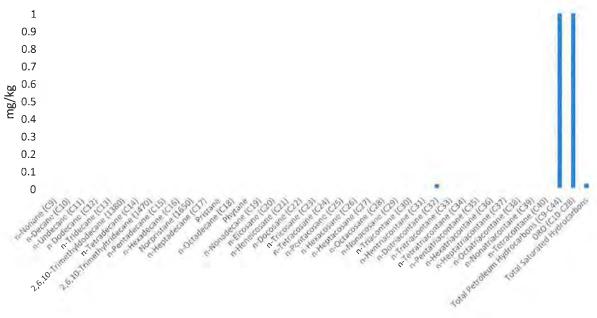




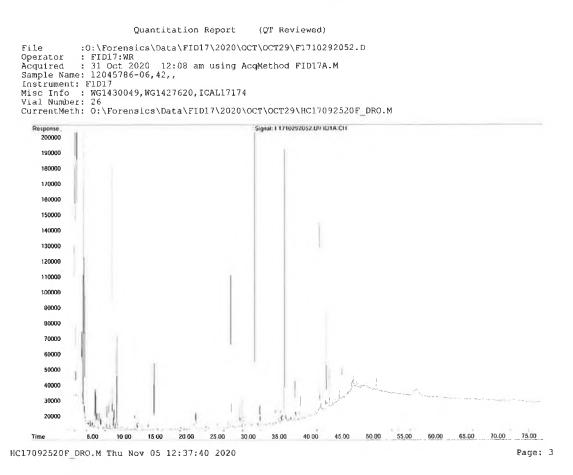


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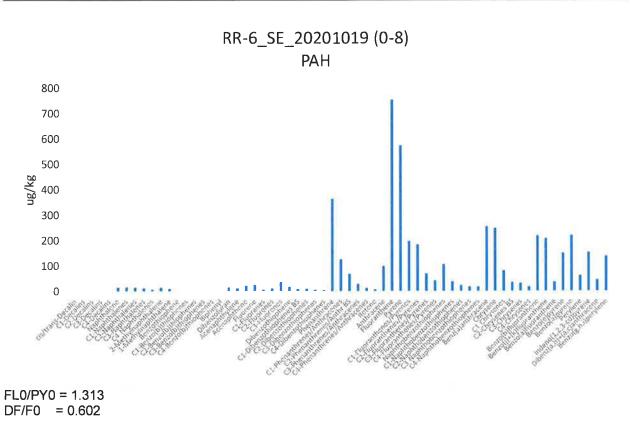




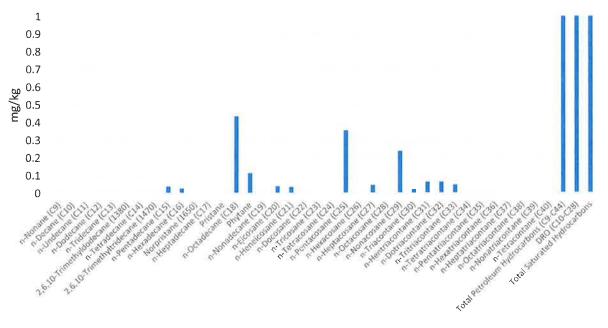




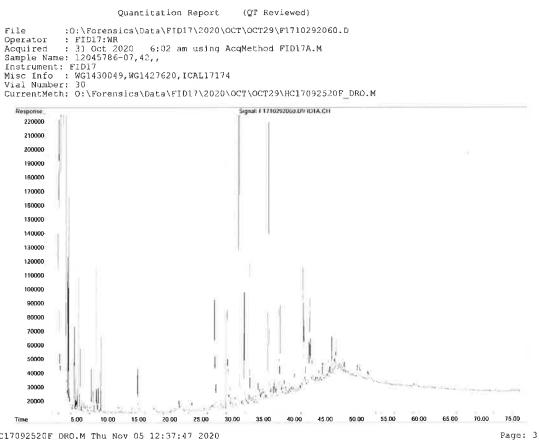
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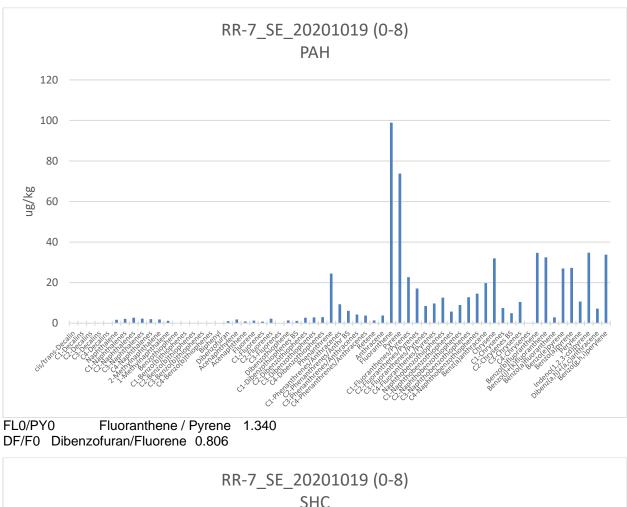


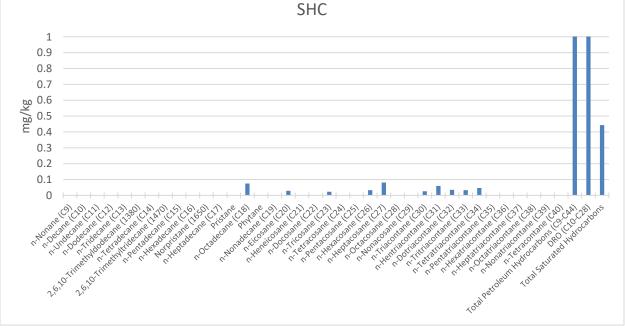




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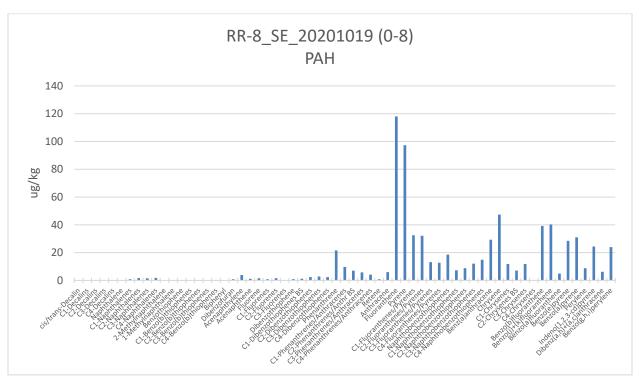




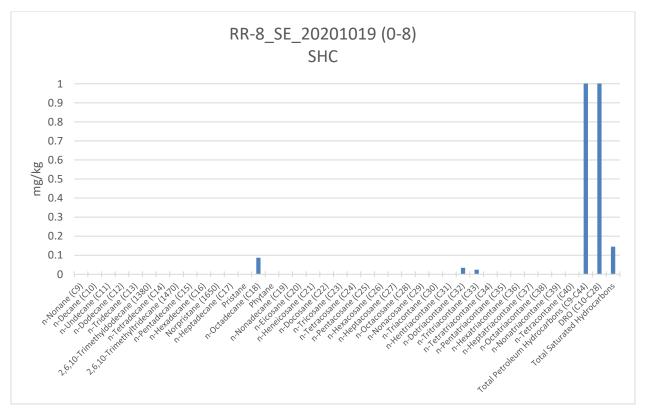


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CurrentMeth: 0:\Forenci interval Quantitation Report (QT Reviewed) CurrentMeth: 0:\Forensics\Data\FID17\2020\OCT\OCT29\HC17092520F_DRO.M Signal: F1710292062.D\FID1A.CH Response_ 200000 190000 180000 170000 160000 150000 140000 130000 120000 110000-100000 90000 80000 70000 60000 50000 40000 30000 20000 10.00 15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00 65.00 70.00 75.00 5.00 HC17092520F_DRO.M Thu Nov 05 12:37:54 2020 Page: 3

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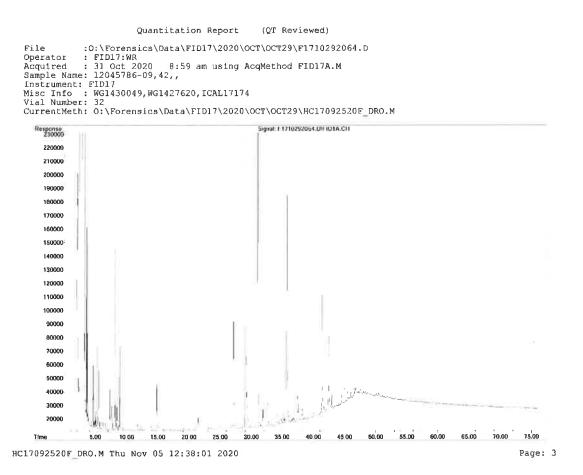


FL0/PY0 = 1.213 DF/F0 = 0.556



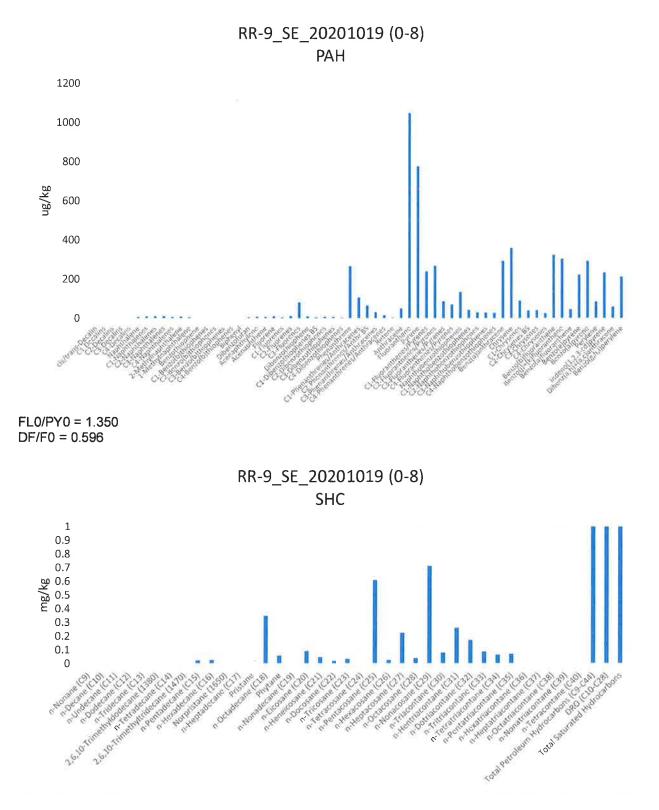




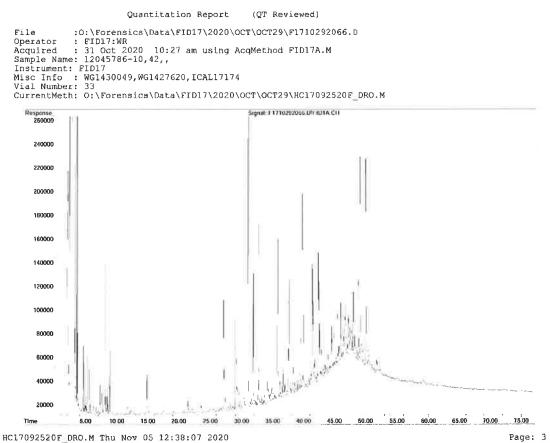


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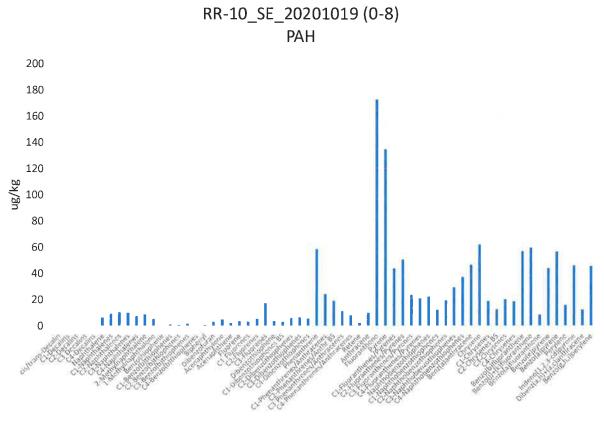




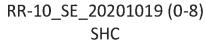


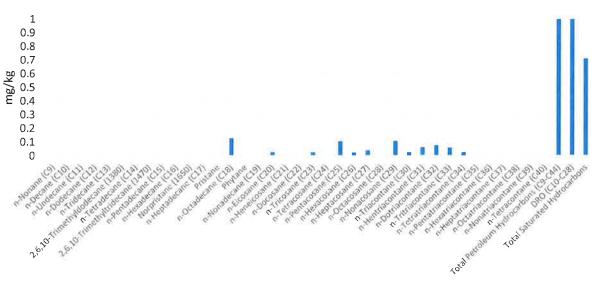
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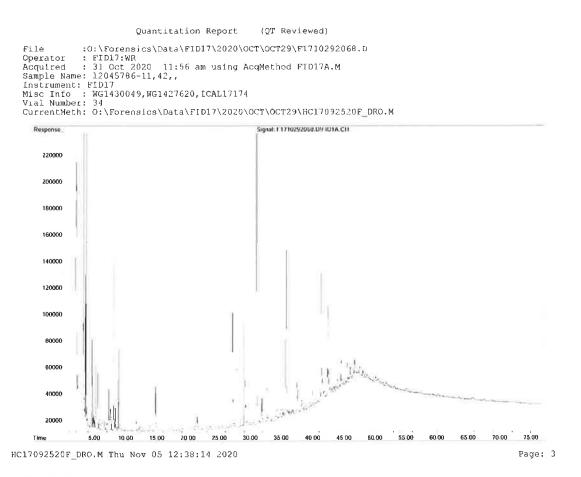


FL0/PY0 = 1.281 DF/F0 = 0.830



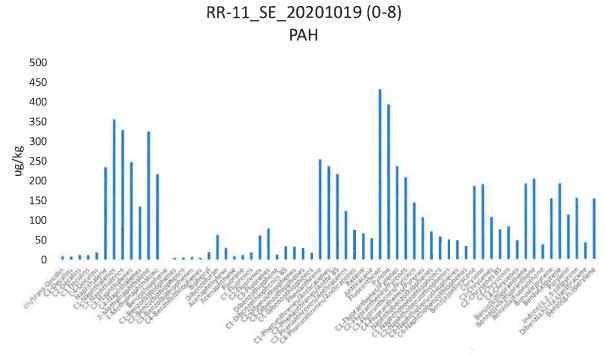






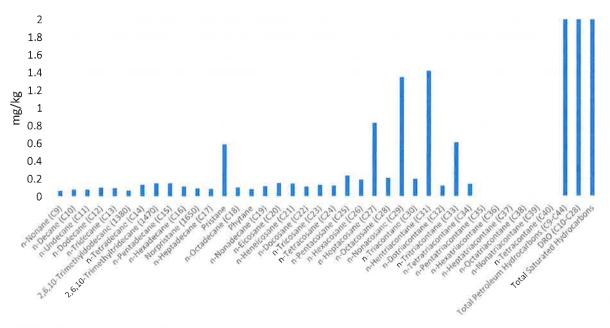
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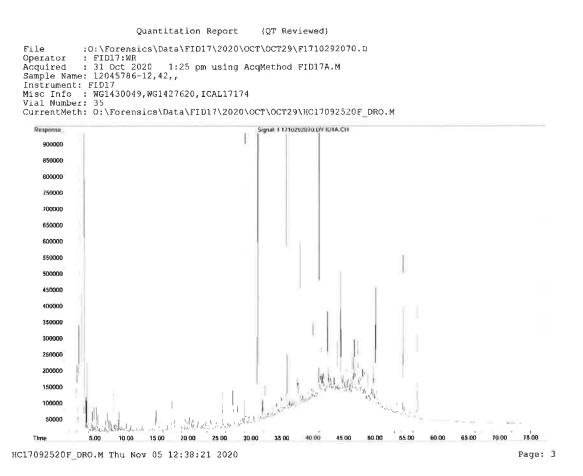


FL0/PY0 = 1.096 DF/F0 = 4.892

RR-11_SE_20201019 (0-8) SHC







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