5-2019

Saturated Hydrocarbon Analysis of Liberty State Park Soils

Matthew Chi-Hymn Cheung
Montclair State University

Abstract

Contaminated soils have been a concern in New Jersey since the Industrial Revolution (Gallagher, 2008). One site in particular has a variety of contaminants and is near the coast of Jersey City in Liberty State Park. Liberty State Park has been impacted by three significant changes. It was first a wetland in the 1600s, then became a New York dump site, and finally a railyard for the Central Railroad of New Jersey (Stanislaw, 2013). The whole land mass has mixed contaminants, including trace elements, heavy metals, organic wastes, and organic compounds. Currently, most of the state park has been dredged out and filled with "reclaimed landfill". Only 102 out of the park's 490 hectares were left unremediated and this is the area that is under research. Even with this site still being highly contaminated, it has abundant plant life that has followed a relatively normal succession. In normal conditions, one might expect that contaminants would interfere with plant growth because they would impede different enzymatic functions of the plant. The goal of this study is to find out what contaminants are present in the LSP soils. There are four subplots and a reference site that my research group studied: HMF, 146, 43, 25F, and 25R. HMF or Hutcheson Memorial Forest is a natural preserve that Native Americans used for agriculture. The sites 146, 43, 25F, and 25R are in different locations within the restricted, unremediated section of Liberty State Park (LSP) and have different levels of contamination and plant life. This thesis reports on a category of organic compounds called saturated hydrocarbons. Depending on how contaminated each individual site is, the abundance of the specific saturated compounds may vary. The numerous findings prove that HMF is a natural site by having fewer hydrocarbons, as revealed by gas chromatography-mass spectrometry (GCMS). It also

proves that 25R is the most organically contaminated site by its highest abundance of hydrocarbons out of all of the sites.

- Chapter 1 (Introduction): presents the background of the two site (HMF and LSP) and prepares the reader for the complex topics discussed in the following chapters and describes the significance of this study.
- Chapter 2 (Environmental Forensics): explains techniques used to investigate specific chemical compounds, how they relate to biotic processes, and how the chemical compounds affect the ecosystem.
- Chapter 3: (Experimental Methods): goes into the specifics of the analytical techniques and how they apply when examining soil contamination.
- Chapter 4: (Results and Discussions): shows the results from the experiment and interprets the data.
- Chapter 5: (Environmental Toxicology/Impacts): explains the health impact of each studied category of compounds, how the compounds enrich the actual sites, and compare overall contaminants (LSP) to the uncontaminated site (HMF).
- Chapter 6: (Conclusions): draws a final picture of what all the above evidence means, what we should do next, and how does the entire study relate to the people/communities that visit the LSP park now.

Montclair State University

Saturated Hydrocarbon Analysis of Liberty State Park Soils

By

Matthew Chi-Hymn-Cheung

A Master's Thesis Submitted to the Faculty of

Montclair State University

In Partial Fulfillment of the Requirements

For the Degree of

Master of Science

May 2019

College of Science and Mathematics

Department of Biology

Thesis Committee:

[redacted]

Nina Goodey, Ph.D.
Thesis Sponsor

[redacted]

Michael Kruge, Ph.D.
Committee Member

[redacted]

Jennifer Krumins, Ph.D.
Committee Member

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Acknowledgements

First, this entire paper and the whole LSP study is done by a large team that is increasing in size. The reason for that is because this study is interdisciplinary and that means that we need expertise from more than a couple of fields, both students and professors alike. I would first like to thank Kevin Olsen and Eric Stern for introducing me to soil contamination and the benefits of doing a research project on this field. When I first got into the LSP project, the two other Ph.D. students were Bhagyashree (Shree) Vaidya and Jay Singh, and they helped me with the initial stages and stayed together through all the 2+years until I completed my thesis. Thanks also to Ella Ojinnaka for showing Shree and I the techniques that were used in Dr. Goodey's lab. After Ella graduated, the next person to help and guide me was Diane Hagmann and she was my student mentor until the end. The research advisors that I have are Dr. Goodey and Dr. Krumins and they lead me throughout my whole thesis process.

In order for our research group to expand and to be more interdisciplinary in order to answer the project's contamination question, we needed to get an NSF grant. My next thank you is the NSF RUI grant (CBET # 1603741) titled RUI: SusChEM: Increasing Soil Enzymatic Function with Targeted Microbial Inocula. One of the professors that this grant allowed us to partner with and expand our study was Dr. Kruge. Dr. Kruge brought his knowledge and experience in the oil industry and showed Diane and I different analytical and instrumental techniques to try solving the question of LSP being a contaminated site. We also benefited from the environmental forensic and analytical expertise of Dr. José Luis R. Gallego and Dr. Azucena Lara-Gonzalo, from the Area of Mining Prospection and Research, Mining Exploitation and Prospecting Department,

Mieres Campus at the University of Oviedo in Spain. Much of the analytical work was performed by the Oviedo group, for which I am very grateful. Lastly, since my degree program is not within this field of study, I want to thank my original major advisor, Dr. Bologna. Dr. Bologna helped me by advising me throughout my master's thesis academic process by choosing and approving courses; and filled out paper work right away! In all, everyone that was in the research group helped me mature as a well-equipped scientist.

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1. Chapter 1: Introduction

One of the pivotal locations where the American Industrial Revolution in the United States first began in 1792 was in Paterson, New Jersey (National Park Service, 2018). The dominant source of power that drove the revolution was coal because of its abundance (Averitt et al., 1960). One of the sources was around the Appalachian Mountain region, where coal was very abundant. Before the 1800s, the United States had not expanded out to the west yet so the only ports for commerce were on the East Coast. Since for most of the entire period, the waste products of industries were not regulated. The reason for this was because the U. S. Environmental Protection Agency (EPA) was not established until the 1970s. Coal combustion produced a lot of hazardous gases and other waste products, and since there were no regulations yet, businesses could make products nonstop without any care for the environment or the residents around them. On top of that, companies also produced other chemically hazardous compounds. These included chemical products for household and military use, plastics, as well as metals. The various products can affect humans and other organisms in negative ways. An example is a infamous toxic defoliant that was manufactured in New Jersey, called "Agent Orange". It got to the point where the physical building structures became contaminated as well. New Jersey also became a famous port for the import/export of resources, specifically Jersey City, particularly after the locomotive had become the number one mode of transportation.

This important port was located on the current site of Liberty State Park, NJ. The site was originally called Communipaw Cove (Stanislaw, 2013). During the early

colonization of North America in the 1600s, it was a tidal wetland (Fig. 1 and 2A). This tidal wetland became the outlet for the Morris Canal into the Hudson River, and was called the Morris Canal Basin (Rutgers, n.d.). In 1866, the meatpacking industry in the U.S. was in its infancy, so Midwestern livestock were taken by rail to the Communipaw Abattoir and then shipped across the Hudson River to be slaughtered in New York City (Rotenstein, 2012) (Fig. 2B). Jersey City was in the midst of big changes. One company that set the stage for expansion by dredging in the tidal wetland, was the Central Railroad of New Jersey or CNJ, from about 1880 to 1916 (USACE 2005, Fig. 2C). In Figure 3 there is a term called "historic fill", which is a synonym for unearthed artifacts such as "glassware, domestic items, and 12-inch oyster shells" (Zavian 2014).Various railroad companies began claiming the tracks in Jersey City/Communipaw Terminal or JCT around the same time (Fig. 3). These companies were: Lehigh Valley, Baltimore & Ohio, and the Reading Railroad. The railyard was mainly divided into four sections: passenger, miscellaneous, stockyard, and coal. The passenger section had three main railroad routes: Jersey City, NJ to Phillipsburg, PA, New York, NY to Newark, NJ, and Newark, NJ to Elizabethport, NJ (JCRHS, 2015). It was also where the ferries crossed the Hudson River going into the New York boroughs (Baxter and Adams 1999). The miscellaneous section was directly opposite Ellis Island. The stockyard section is where the Communipaw Abattoir was relocated. Lastly, the coal section was transported principally from Pennsylvania to the New York Boroughs for heating fuel (Anderson, 1985). The rise of automobile and the use of petroleum instead of coal, among other changes, resulted in the abandonment in 1967 of the entire railyard (National Parks Service, 1983). The abandoned site became an unregulated dump site soon after even though the town's

sewage plant was close by (Fig. 2D). In 1965, Jersey City took ~63 ha. of land (in a move by Morris Pesin) from the Statue of Liberty National Monument (The Jersey Journal, 2001). He complained about having to go to NYC to take a ferry just to get to the Statue of Liberty, from New Jersey (The Jersey Journal). Finally, in 1976, Morris Pesin's dream came true with the opening of the entire Liberty State Park (LSP) (Fig. 2E) (The Jersey Journal).

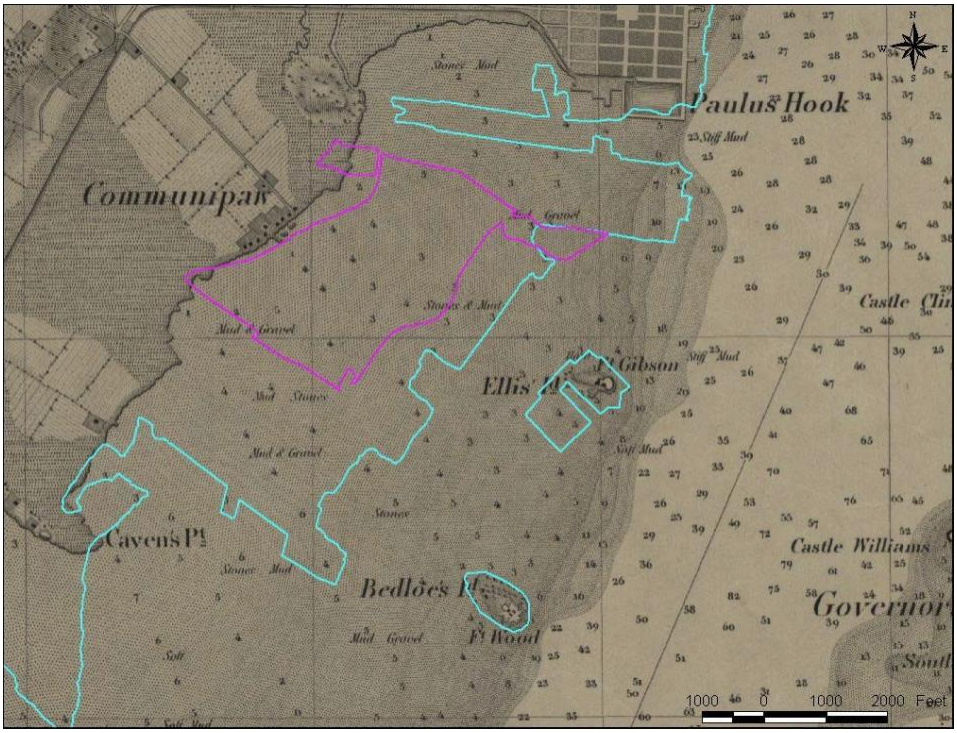

Fig. 1: Pre-1845 bathymetric map of Communipaw Cove region with outlines of two expansion time events. (USACE 2005).

Fig. 2: History of Liberty State Park (LSP). (A=NJCU; B=History Sidebar; C=French, 2002; D=Andrew Bologovsky, used by permission; D=Maplets).

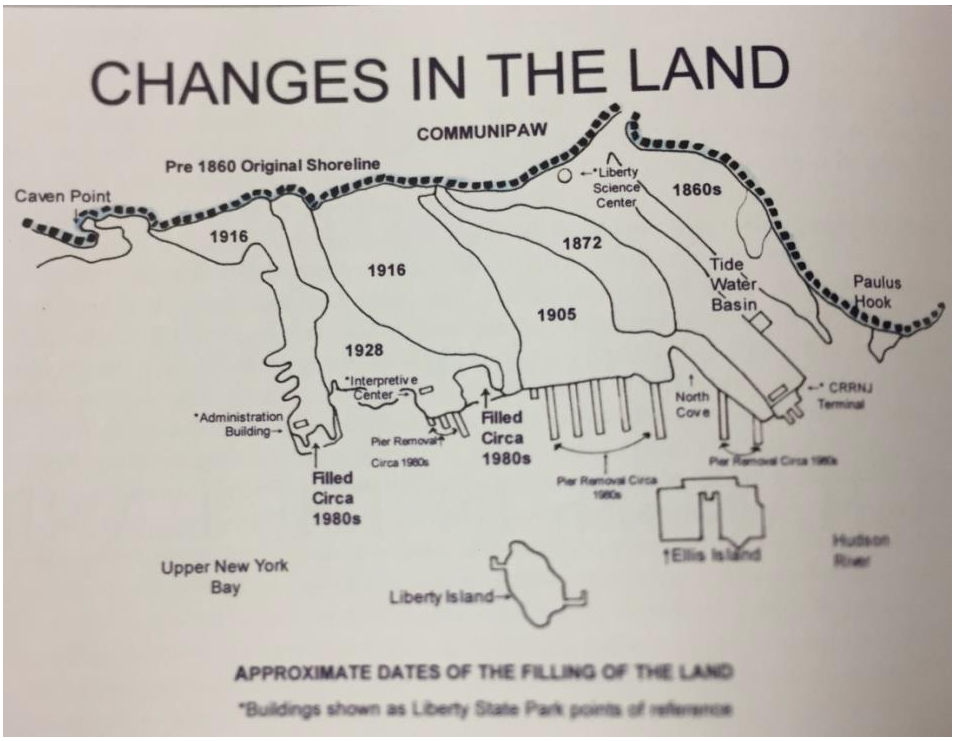

Fig. 3: Changes of the Communipaw railyard through “historic fill” from the 1880s to 1928. (Zavian 2014).

1.1 Hutcheson Memorial Forest (HMF)

Hutcheson Memorial Forest is a private nature preserve ~64 km southwest of our general study area at Liberty State Park. It is located in Franklin Township, North central New Jersey. This section of New Jersey was not affected by the main Industrial Revolution wave. The history of the park is just like LSP in that it was a Native American territory until the Dutch came over in 1701 (Hutcheson Memorial Forest Center, 2019). Other than the periodic (11th year) controlled fires by the Natives Americans until 1711, there were no anthropogenic manipulations of the land or the trees (Hutcheson Memorial Forest Center, 2019). The type of trees that this land is made up of are mainly oak and hickory; two of the oldest known living trees (Hutcheson Memorial Forest Center, 2019). Oaks are native to most of the 50 states and the largest tree genus in the U.S. (Fei et al.,, 2011). They are key components of terrestrial ecosystems providing food/shelter to animals, economic profit in the timber business, and they are also important for cultural/historical reasons (Fei et al., 2011). They represent similar qualities as the hickories do, with most species being in the Eastern U.S. (Lefland et al., 2018). As a result, these two trees are familiar to the endemic wildlife, which could indicate a healthy, mature forest. The last key factor is that Hutcheson Memorial Forest (HMF) is surrounded by agricultural activity, so this creates a “buffer zone” against any contamination coming into the park (Hutcheson Memorial Forest Center, 2019). As a result, HMF is a prime location to study undisturbed landscapes. HMF is a long-term research station for Rutgers New Brunswick with more than 250 science publications

within the university alone, and over 2,000 total publications (Hutcheson Memorial Forest Center, 2019; Google Scholar, 2019).

In this forest, there are also more than 300 species of flowering plants and more than 200 bird species (Hutcheson Memorial Forest Center, 2019). This would suggest that this forest has constant nutrient flow and a low trophic pyramid. A low trophic pyramid means that the organisms are in the lower levels of the predator/prey interaction. The final element of a terrestrial ecosystem that needs to be talked about is the pedosphere. The majority of soil types in this forest area are categorized as a silt loam (USDA, n.d). This is supported by a river running almost entirely around the whole site, since river currents can erode rocks and boulders into finer particles. The forest topography is hilly, ranging from about 91 to 304 meters in elevation and because of that floods are not frequent (USDA, n.d.). Even if there is heavy precipitation or runoff, the soil will allow the right amount of permeability for plants and animals to survive in the habitat area. These are the few reasons that our research group calls this site a reference and not a control. It is a reference site or a threshold site for minimal contamination levels in New Jersey, but it is not a control because the HMF and LSP do not exhibit similar environmental factors.

1.2 Site 146 and 43

These two sites within the LSP study plot are similar in their ecological productivity and geographical geology. They both are located in the Western-half of this contaminated plot of land, that is in the successional northern hardwood zone or SNH

(Fig. 4, Gallagher et al., 2008). This is a plant ecosystem category that was categorized based on the observable organisms around that area, even though none of the sites' ecosystems in the LSP are natural. The natural location that this plant community would be found in is most of inland Massachusetts. The plant species are highly variable, depending on the surroundings and disturbances (Massachusetts Dept. of Fish and Wildlife). If these sites were in natural conditions, the first set of colonizers would be: Aspen (*Populus tremuloides* and *P. grandidentata*), White Birch (*Betula papyrifera*), Red Maple (*Acer rubrum*), Black Cherry (*Prunus serotina*), Gray Birch (*B. populifolia*), White Pine (*Pinus strobus*), and/or Red Spruce (*Picea rubens*) (MA DFW). The second of colonizers would be: Sugar Maple (*Acer saccharum*), Red Maple (*A. rubrum*), White Ash (*Fraxinus americana*), Yellow Birch (*B. alleghaniensis*), American Beech (*Fagus grandifolia*), and Red Oak (*Quercus rubra*) (MA DFW). Since those tree species are only found in natural environments, we would expect to find less in an anthropogenic environment. In fact, there are only five tree species that match with its natural ecosystem (Anderson, 1989). As of 1988, there are plant species from 80 difference families because of ballast dumping from the Communipaw railroad period (Anderson, 1989).

One of the differences between the two sites is that site 146 is lower in elevation than site 43, by about 1.5m. This was examined with a Google Earth tool, by drawing a line between two points and looking at the elevation map that the platform provides. This elevation difference could contribute to a >2.00 total metal load difference (Salisbury et al., 2017). In an article published by Salisbury et al. 2017, site 146 had a calculated statistical value of 3.56 while site 43 has a value of 1.64, in each trace element concentration (Salisbury et al., 2017; Gallagher et al. 2008). The reason is also tied to the

coastal nature of the LSP site itself. Storm surges or runoffs can pick up metals from higher elevation and carry them down to lower elevations where they would concentrate as the water is evaporated over time. The overall plant productivity of these two sites is unusual considering the sites line up just around the south most pier, which are for shipment of coal (Fig. 5a/b & 6). This is unusual because conventional understanding of contaminated soil, in this case the contamination is coal, is that the soil would not be able to support of nurture any plant life because of the soil's chemical constraints on a plant's enzymatic processes. One of the reasons why there are fairly homogeneous biota in these sites is because maybe be that their soils are "loamy sand", in which the majority of the soil consists of sand but it still has particles of silts and clays making up a considerable percentage of the soil (Table 1; Salisbury et al., 2017). Another study reported that particle's percentage from 13 years before that shows a different set of proportions (Table 1; USACE 2004). A particle's percentage of a soil is commonly taken by using the hydrometer method in which the soil weights/percentages are calculated by suspension time and the gravity readings from a bulb (standard weight).

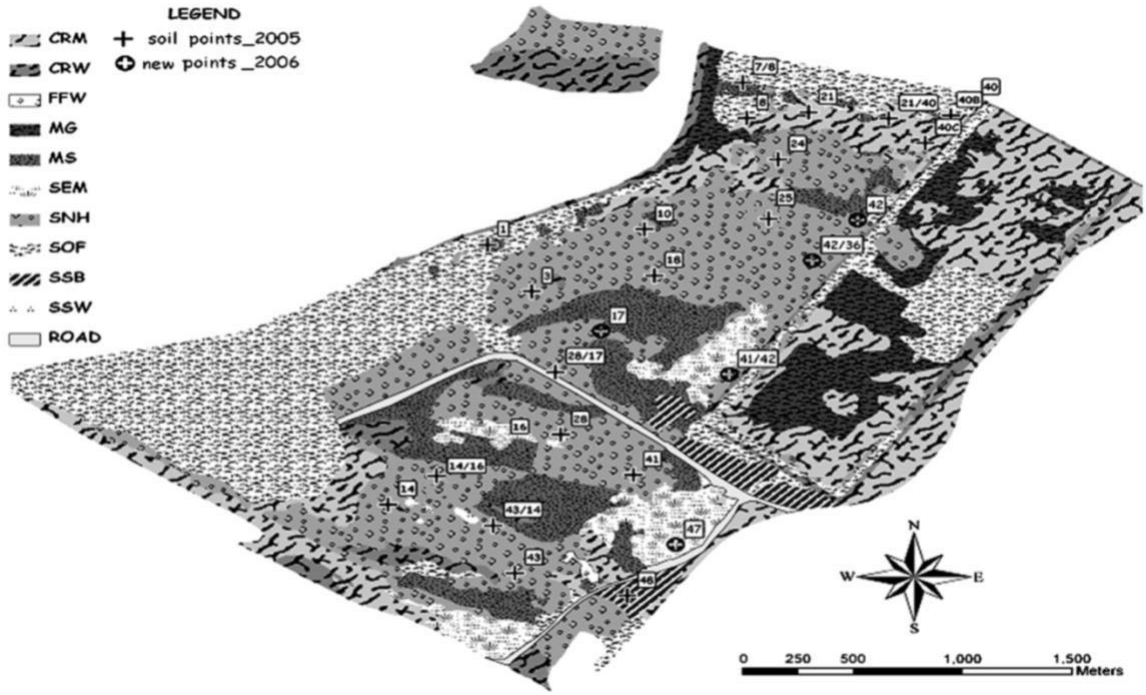

Fig. 4: The 2003 vegetation map of the study area, showing the vegetative assemblages and the soil sampling sites. (Gallagher et al., 2008).

Fig. 5a: Photograph of the habitat in site 146.

Fig. 5b: Photograph of site 43 without foliage (Photo: J. Krumins).

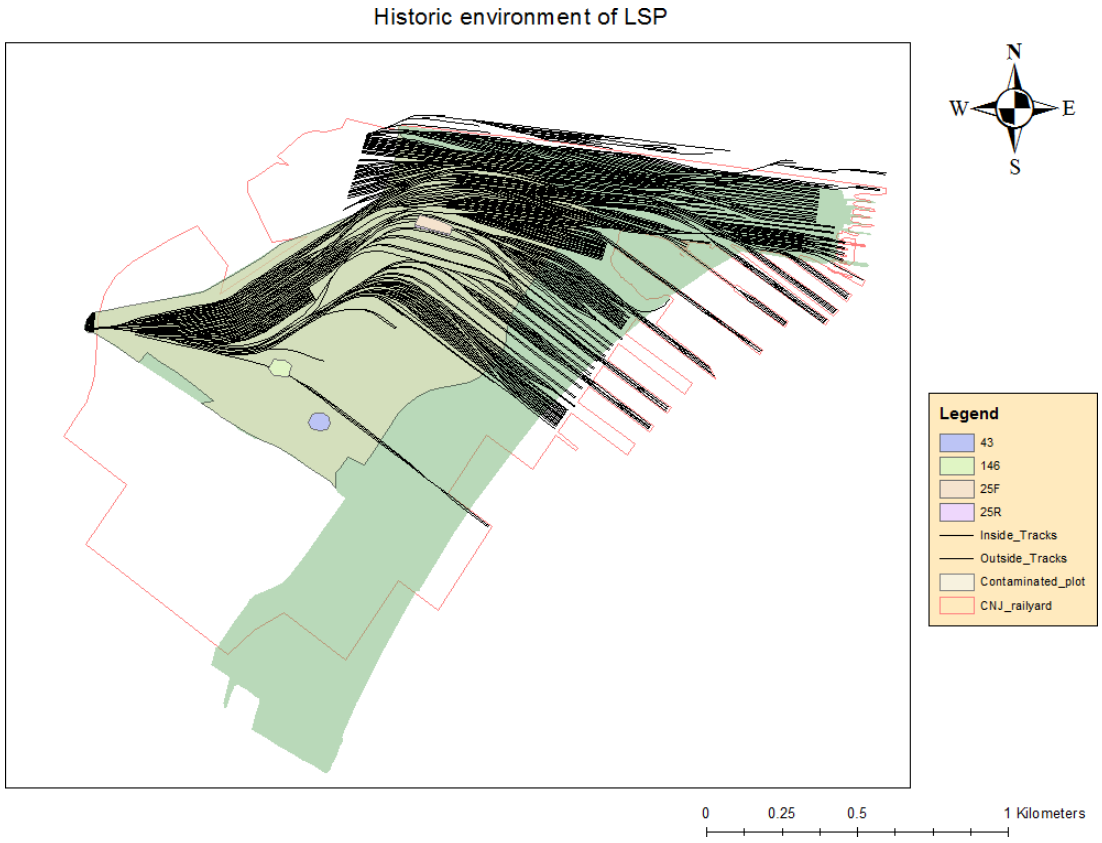

Fig. 6a: A GIS map of the Communipaw railyard laid on top of the LSP study areas.

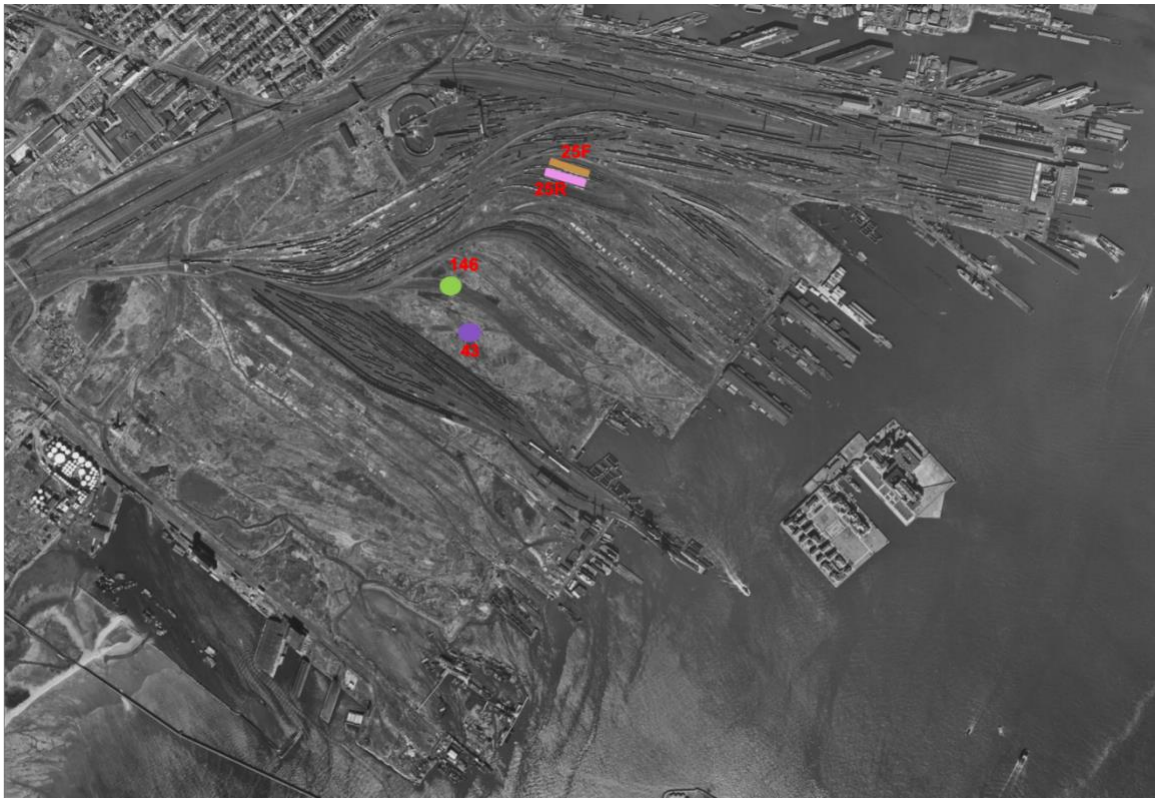

Fig. 6b: 1954 Aerial photo of CNJ railyard (USGS, 1954).

1.3 Site 25F and 25R

These two sites are located north of the middle of the rectangular imprint within the study plot (Fig. 4). In other studies, before ours the site 25F was designated as site 25 and there was not a site 25R listed. We made the distinction of 25F and 25R because they have differences in vegetation even though they share geographic and chemical similarities (Fig. 7a/b). Site 25F looks closely related to site 146 and 43 in its biotic make-up. The stark difference between the two sites is in the concentrations of the metals (Hagmann et al., submitted) and the organics (which will be presented below). A previous study ranked site 25F (TP-25) as having the most total metal load/soil measurement with an average statistical value of 4.31 (Salisbury et al., 2017; Gallagher et

al. 2008). 25R is the site that our research group, and subsequently my study, focuses on. This unique landscape is barren with not much growing on top of the soil. It aligns with a low-lying mound in between two tracks (Fig. 6 and 8). This means that 25F would be on a track line (Fig. 8), which is interesting because it has almost the complete opposite plant productivity. These extra facts about 25R and 25F complicate the reason why only 25F has mostly plant productivity while 25R has a minimal amount. As with the 146/43 section, 25F/25R also has particle's percentages from the report 13 years ago (Table 1; USACE 2004).

Fig. 7a: Photograph of the habitat in site 25F.

Fig. 7b: Photograph of habitat in site 25R.

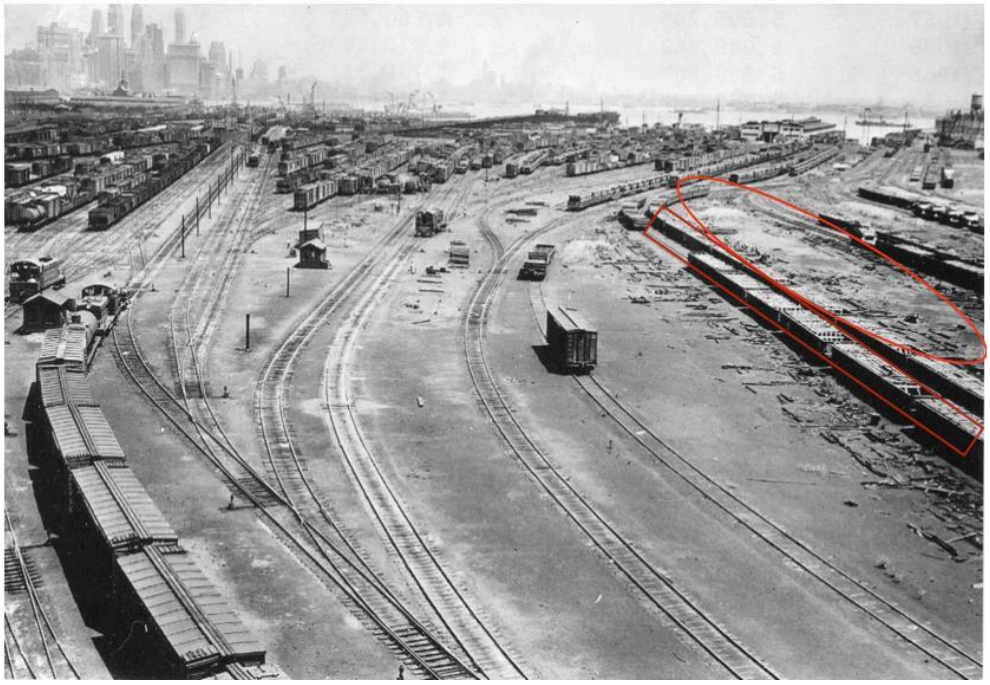

Fig. 8: Detail of sites 25F and 25R marked in the Communipaw railyard. (Photo: Andrew Bologovsky. Used by permission.)

Site #	Publication	% Sand	%Silt	%Clay
146	a	81.8	15	3.3
	b	74	26	0
43	a	79	16.5	4.5
	b	33	80	4
25F	a	91.5	5.5	3
	b	75	25	0
25R	a	91.5	5.5	3
	b	12	65	23

Table 1: Soil components in percent from two publications. (a=Salisbury et al., 2017, b=USACE 2004).

2. Environmental Forensics – Analytical tools

"Environmental forensics focuses on the reconstruction of past contamination (pollution) events based on the evidence that is left (e.g., identifying the source and age of environmental contaminants and allocating responsibility for contamination)" (Petrisor 2014). Pollution usually is a result of anthropogenic contaminants, which was critical for our country to be more technologically advanced. These contaminants can include organic compounds, inorganic compounds, or biomedical compounds. Organic compounds include any hydrocarbons or nonmetals that are soluble in water, or any combination of those substances. These are commonly found in fertilizers, food waste, sewage sludge, or engine fuel. Depending on the amount present, these compounds can be either easily degraded or become a long-lasting contaminant. Inorganic compounds include metals and radioactive nuclei. Metals are either from industries or a byproduct of urbanization. Each kind of metal has its own limits until it becomes toxic for human health. Radioactive material has only been produced since the time of WWII with the Manhattan Project and the Hiroshima and Nagasaki nuclear bombs (Department of Energy). Every radioactive isotope has a different half-life (half of the time to decay). They can have adverse effects on human health. Different separation techniques can be combined when analyzing pollutants. This technique is used extensively, for example, in a recent in a study dealing with five different oil spills (Kruge et al. 2018).

3. Experimental Methods

I analyzed data for hydrocarbons that was collected by gas chromatography-mass spectrometry (GC-MS). The entire organic contaminant analysis was done on soils from two locations with different professors leading the labs: Our research group collected the soil, then the extractions, liquid and gas chromatography was done by Dr. Gallego's lab group, while we did everything else from the computational analysis to the right most branch in Figure 9 (thermodesorption and residue pyrolysis GC-MS) in Dr. Kruge's lab, reported elsewhere (Hagmann et al., submitted). The analysis that was done for my thesis is only on the saturated hydrocarbons (Fraction 1, Fig. 9), under the maltene group. Below I describe in detail each step of the whole analysis process until the saturates fraction. The extraction and the pre-analysis were done by Dr. Gallego's lab.

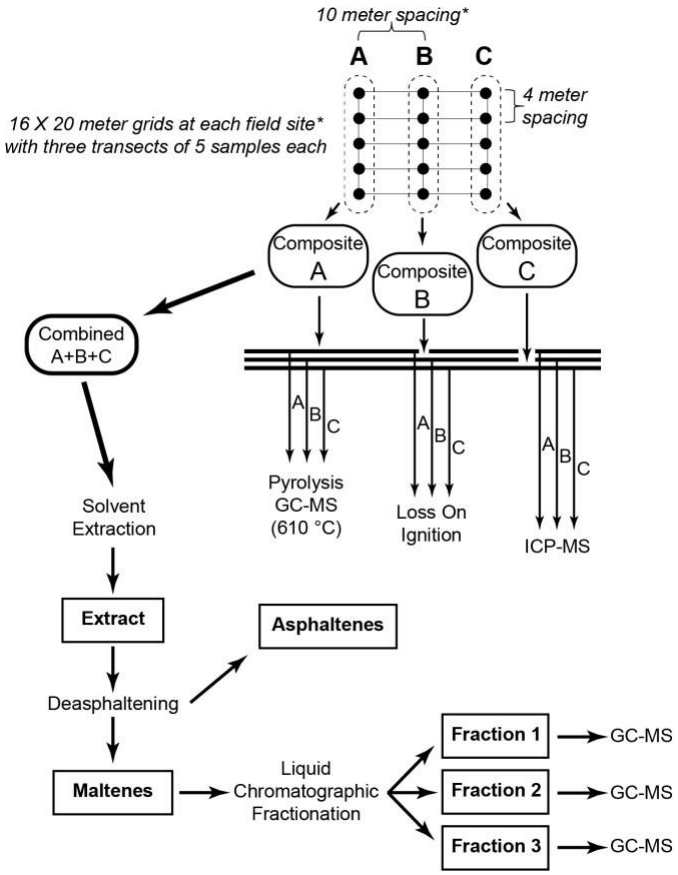

Fig. 9: Schematic of our complete experimental design/analysis (Hagmann et al., submitted).

3.1 Field Methods

Soil was collected in July 2016 form LSP sites 25F, 25R, 43, and 146 as well as the reference site HMF. Along a transect, 5 samples were collected at intervals of 4 m for this study into separate bags (depth of 10 cm below the leaf-litter). At each site, five samples were collected along three parallel transects 10 m apart. Thus, fifteen soil subsamples from a 20 X 20 m field grid, were combined into 3 composite samples (one for each transect) as seen in Figure 9a.

3.2 Initial sample handling

The samples were stored in the refrigerator (4 °C). At the lab the soils were sieved through a 2 mm sieve and equal amounts of the 5 samples along a transect were combined into one bag labelled the transect name and site (ex 43A). For each site, the composites A, B, and C were combined and submitted to the laboratories of the Área de Prospección e Investigación Minera at the Mieres Campus, University of Oviedo, Spain for analytical processing (Fig. 9).

3.3 Solvent extraction

First, dry soil samples < 2 mm (0.009 - 0.08 g_{dry}) from each of the LSP sites underwent solvent extraction as described in Lara-Gonzalo et al. 2015. Briefly, soils were extracted with dichloromethane:methanol (3:1, v/v) in a Soxtherm system (Gerhardt) (Fig. 10A). The extract was concentrated by rotary evaporation (Fig. 10B). Aliquots of the Soxtherm extract were fractionated and gravimetrically quantified by open column liquid chromatography (LC). In brief, LC was carried out in two steps: in the first one, maltenes and asphaltenes were separated by filtering through 0.45 μm filters using hexane and dichloromethane, respectively; then, in the second step, maltenes were fractionated into three fractions by LC in columns filled with silica gel and alumina (Fig. 10C) . The saturated hydrocarbon fraction (Fraction 1, Fig. 9) was eluted with hexane. This work was done in the laboratories of the Área de Prospección e Investigación Minera at the Mieres Campus, University of Oviedo, Spain. Only the saturated hydrocarbon results are presented in this thesis; the other fractions were discussed previously (Hagmann et al., submitted).

3.4 Liquid Chromatographic Fractionation

This technique is called open column liquid chromatography, which is basically separation of chemical compounds (chromatography) using various organic solvents and adsorbent materials (Fig. 11). Specifics for this procedure is that four different fractions are eluted out of a single soil sample extract. The four different fractions are: saturates hydrocarbons, aromatic hydrocarbons, polars (organic compounds with nitrogen, sulfur, or oxygen), and asphaltenes (heavier, more complex organic compounds). The first three fractions of these are all produced out of a column filled with silica gel and dried alumina (Lara-Gonzalo et al., 2015). The first thing was to separate the heavier compounds (asphaltenes) from the lighter compounds (maltenes) by precipitating each consecutive solution with hexane and then with dichloromethane (Kruge et al., 2018). Maltenes are comprised of saturates, aromatics, and polars. After that the maltenes mixture is poured into the column three times for the three different fractions with their respective solvent mixtures: Fraction 1 (saturates): hexane, Fraction 2 (aromatic hydrocarbons): dichloromethane/hexane, and Fraction 3 (polar compounds): dichloromethane/methanol (Kruge et al., 2018). This technique is different from the others above in that it is labor intensive and requires patience. Usually you turn the burette (column) flow to low speed or until only drops descend to a fraction beaker. These speeds could be hard to transition quickly, from one fraction beaker to another fraction beaker, maybe leading to an error of small amounts of one category of compounds mixing with others. After the fractions are all eluted they will each get injected separately into the GC-MS. The only difference with this GCMS procedure is that the sample is now a liquid not a solid, so a micro syringe is

needed instead of a tube. This work was done in the laboratories of the Área de Prospección e Investigación Minera at the Mieres Campus, University of Oviedo, Spain.

3.5 Gas Chromatography-Mass Spectrometry (GC-MS)

The whole setup is shown below (Fig. 10D). The analysis of the LC fractions was carried out by GC/MS. The injection of the extracts was performed on a QP-2010 Plus GC-MS (Shimadzu). A capillary column DB-5ms (5% phenyl 95% dimethylpolysiloxane; 60 m × 0.25 mm i.d. × 0.25 μm film) from Agilent Technologies was used with helium as carried gas at 1 mL/min. The initial oven temperature was 50 ºC (held for 2 min) and ramped at 2.5 ºC min^{-1} up to 310 ºC and held for 45 min. The mass spectrometer was operated in electron ionization mode (EI) at 70 eV. It was calibrated daily by autotuning with perfluorotributylamine (PFTBA) and the chromatograms were acquired in full-scan mode (mass range acquisition was performed from 45 to 500 m/z). Compounds were identified using the NIST MS library and by reference to the literature. This work was done in the laboratories of the Área de Prospección e Investigación Minera at the Mieres Campus, University of Oviedo, Spain.

3.6 Data Handling

The common manufacturers for the analytical instruments discussed above are Agilent, ThermoFisher, and Shimadzu. Each of these manufacturers uses their own specific modifications when constructing their instruments. Even though they all perform essentially the same function, all the files are written in different code and therefore have different extension. This could be a problem if you need to transfer files to another

company's program to read it, or if you cannot purchase the compatible program reader to begin with. Regardless, all these programs have similar interfaces with the left side bar to search different files, top half for the overall gas chromatograph, and the bottom half for the individual mass spectra under each molecular peak (Fig. 12). The programs are called data acquisition or DAQ systems (Dabrowski 2015).

On the other hand, you have Free of Charge programs or FoCs, which are open source software that can be downloaded from the internet in order to read any analytical file extension. These kinds of programs are not so well known in the analytical community but can bring an educational benefit to students or new researchers (Dabrowski 2015). For any educational programs, it is better if you can take it home or use it anywhere, which these FoC programs allow people to do. Usually with DAQ systems they are connected directly to the instrument in the lab or placed around a lab setting. Although FoCs have all these benefits, the only downside is that the program interface layouts are different and may even have the same functions under different commands.

Whether a DAQ system or a FoC program is used, they both need an external mass spectrum library for the chromatographic programs to correctly identify different chemical compounds. The two common mass spectra libraries that are known are NIST (https://webbook.nist.gov/chemistry/) and Wiley (https://sciencesolutions.wiley.com) . NIST stands for the National Institute of Standards and Technology and it is a federal agency under the U.S. Department of Commerce. This agency develops all different types of measurement standards in science. It makes the mass spectra library more trusted because it is backed by rigorous testing at the government level. Wiley, on the other

hand, is more commercial. It is an academic publishing and materials company. There are online libraries as well for the chromatographic programs, but they are not downloadable and underdeveloped (Milman and Zhurkovich 2016).

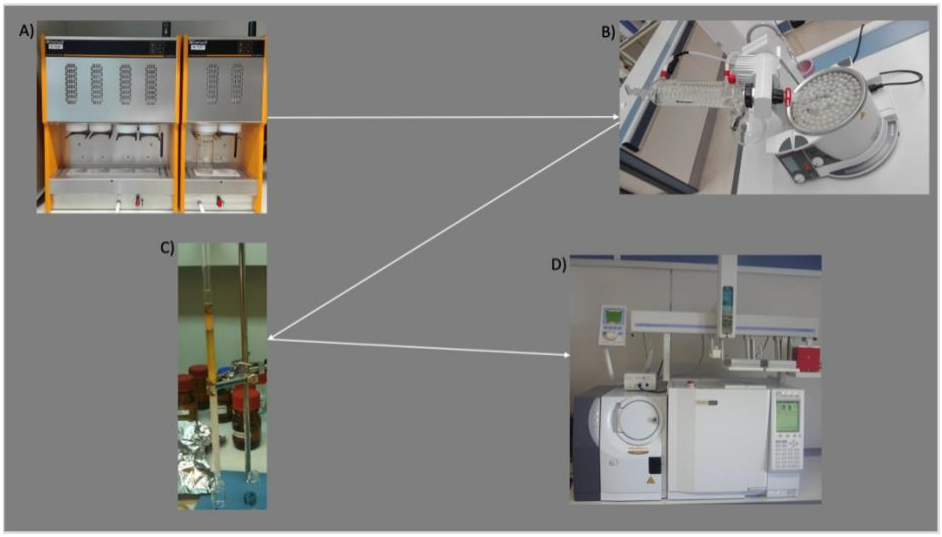

Fig. 10: Photograph of equipment used in the solvent extraction process. (Photos: J.L.R. Gallego)

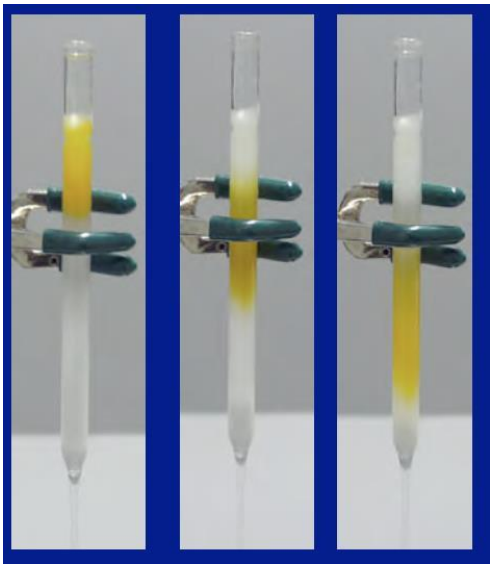

Fig. 11: Photograph open-column liquid chromatography in operation.

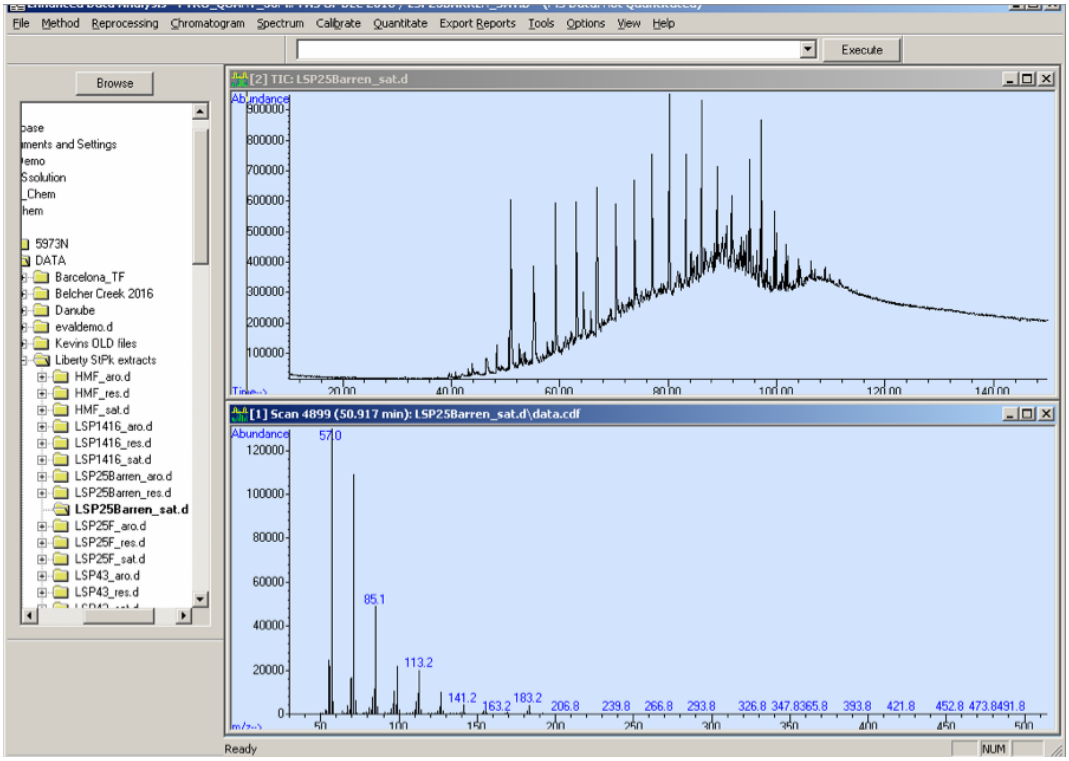

Fig. 12: Agilent GC-MS software screen layout as used in this project.

4. Results and Discussion

4.1 Saturated Hydrocarbons – General Remarks

The individual "line graphs" are called chromatograms. Each chromatogram shows the distribution of saturated hydrocarbons, as detected by the GC-MS, which had previously been fractioned by chromatography. The site's chromatogram of HMF (Fig. 13A) represents a reference site to the background "normal" soil condition in the LSP geographic region, which is the Piedmont. There are *n*-alkanes C_{17}-C_{37} along with diploptene (peak B2) and an amyrin isomer or derivative (peak B6) which are living biomass biomarkers. Immediately in the next chromatographs of all of the LSP sites (Fig. 13B-E), the intensity of the biomass biomarker peaks is lowered below some of the *n*-alkanes. A phenomenon that takes place in the biomass biomarker peaks being lower in Fig. 13B-D is called OEP or odd-even predominance. All these attributes will be discussed in further detail, but each Figure shows a particular attribute more pronounced than the rest. Figure 13 highlights the UCM or unresolved complex mixture, which indicates resistant compounds after microbial biodegradation (Peters et al., 2005). When biodegradation occurs, usually the microbes prefer to break down fewer complex molecules such as aliphatics, aromatics, and NSOs seen in (Hagmann et al., submitted). Depending on the size of the UCM it can conclude the extent of the biodegradation and how long has it been since newly petroleum/oil was spilled. UCM is also a way to track petroleum/oil contamination, since the most contaminated site out of our samples is 25R and the least contaminated site is HMF.

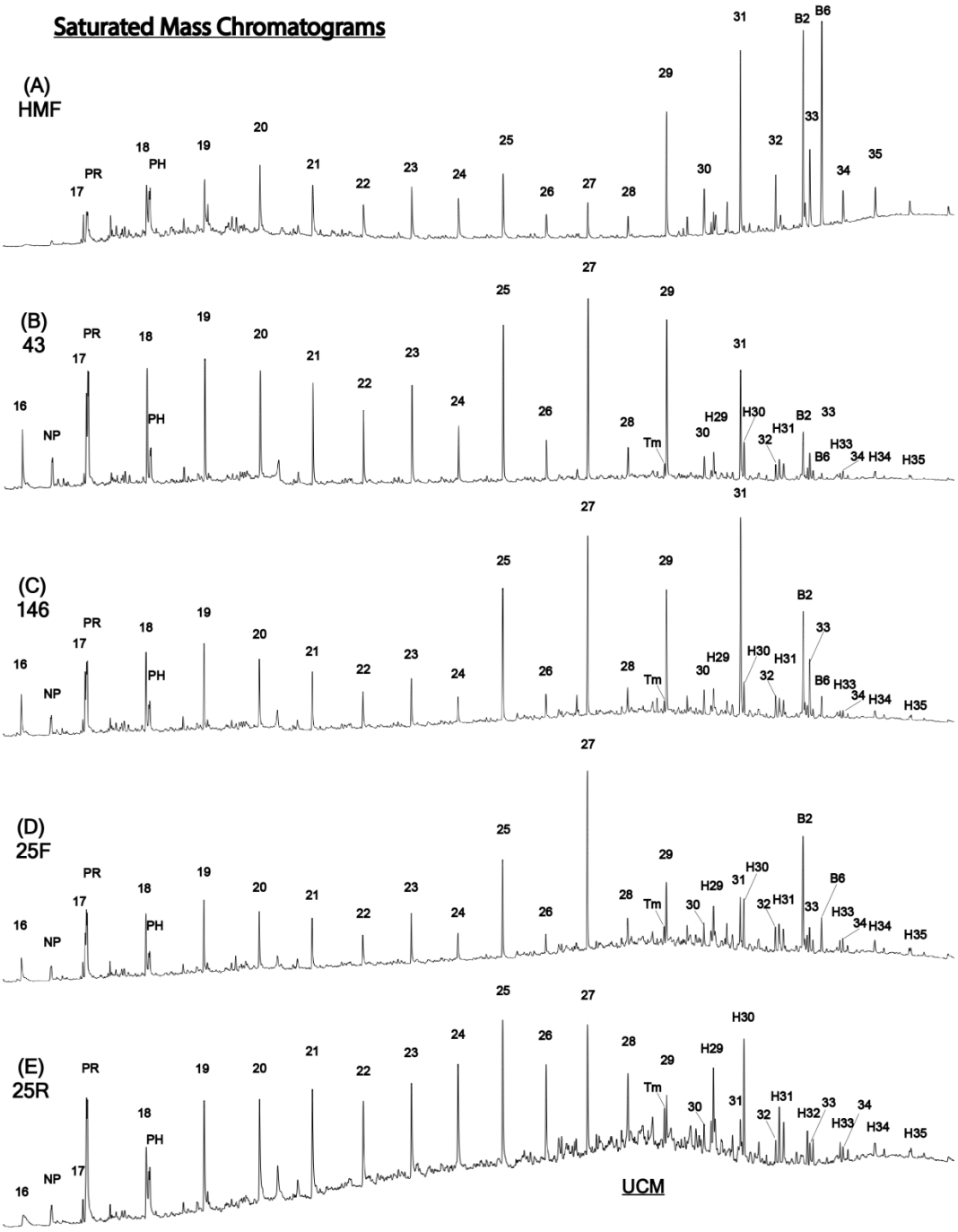

Fig. 13: Distribution of saturated hydrocarbons in the analyzed LSP and reference site soils. GC-MS total ion current (See Table 2 for peak identification).

Abbreviation	Compound
Pr	Pristane
Ph	Phytane
Hx	Hopane (x is the carbon number)
Sx*	Sterane (x is the carbon number; * is A/B for and *R/S*)
Ts	18α(H)-22,29,30-trisnorhopane
Tm	17α(H)-22,29,30-trisnorhopane
TRx	tricyclic terpane (x is the carbon number)
Dx*	Diasterane (x is the carbon number, * is for *R/S*)
B2	Diploptene (also called hopene or A'-Neogammacer-22(29)-ene)
B6	Amyrin derivative
ND	Nor-drimane
FR	Farmesane
EU	4α(H)-eudesmane
DR	8 (H)-drimane
HF	Homofarnesane
HD	8 (H)-homodrimane

Table 2: Abbreviations for chemical compounds.

4.2 *n*-Alkanes and isoprenoid alkanes

In this Figure (Fig. 14), all the *n*-alkanes were shown in each site. There are four major phenomena that were more prevalent in this Figure (Fig. 14), which were the odd-even predominance (OEP), Pr/C17 ratio, Ph/C18 ratio, and the Pr/Ph ratio. OEP or odd-even predominance is the odd/even carbon numbered *n*-alkanes alternating in intensities in the chromatographs due to degradation rates. The biodegradation deals with higher plant matter, and the more degraded the soils, more of the even carbon numbered *n*-

alkanes get broken down first. Minor OEP are all across the HMF, 43, 146, and 25F chromatographs (Fig. 14A-D), but they are most apparent in the *n*-alkanes greater than C_{25}. In HMF (Fig. 14A), the OEP is most seen in C_{29}-C_{33} and because the higher plant matter is fresher and either has not been degraded for a long time or minimal plant matter has fallen to the pedosphere. Site 43 (Fig. 14B) has evidence of more plant degradation by the widening of its OEP to C_{23}-C_{33}. In 146 and 25F (Fig. 14C-D), all the *n*-alkanes intensities are lowered. This would be due to the sites having the maximum plant degradation. Even though the intensities are lowered the odd carbon numbered *n*-alkanes still have the same magnitude of intensity as HMF and 43 (Fig. 14A-B). The OEP for 146 (Fig. 14C) is similar to 43 (Fig. 14B). This would likely indicate that they are both around the same local region spatially. In 25F (Fig. 14D), the OEP decreased its most prominent range to only C_{25}-C_{27}. By the time one sees 25R (Fig. 14E), only a little trace of the OEP remains because the site's terrain is mostly barren with no higher plant matter to degrade. This chromatograph's *n*-alkane signal intensities suddenly increased beyond all the other sites. The reason is: site 25R has the highest measurable amount of fossil fuel contamination (Hagmann et al., submitted). The next three phenomena that are seen are all ratios: Pr/C_{17}, Ph/C_{18}, and Pr/Ph. Both Pr/C_{17} or pristane over *n*-alkane C_{17} and Ph/C_{18} or phytane over *n*-alkane C_{18} are also indicators of biodegradation, along with thermal maturity of kerogen type (Peters et al., 2005). In biodegradation, the compounds C_{17} and C_{18} are broken down before pristane and phytane are broken down by the anaerobic bacteria in the soils (Peters et al., 2005). This is due to the differences in the compounds' configurations, with C_{17} and C_{18} being linear while pristane and phytane being branched. One would conclude that the more biodegrading a particular soil is, the

more pristane and phytane peak intensities one should find in their chromatographs compared to C17 and C18. This is actually the case seen in Fig. 14, but the relative magnitudes between sites are not showing a pattern; therefore, another aspect to the ratios is thermal maturity. Thermal maturity is the primary indicator used for these two ratios. As the kerogen is more matured the ratios decrease (Peters et al., 2005).

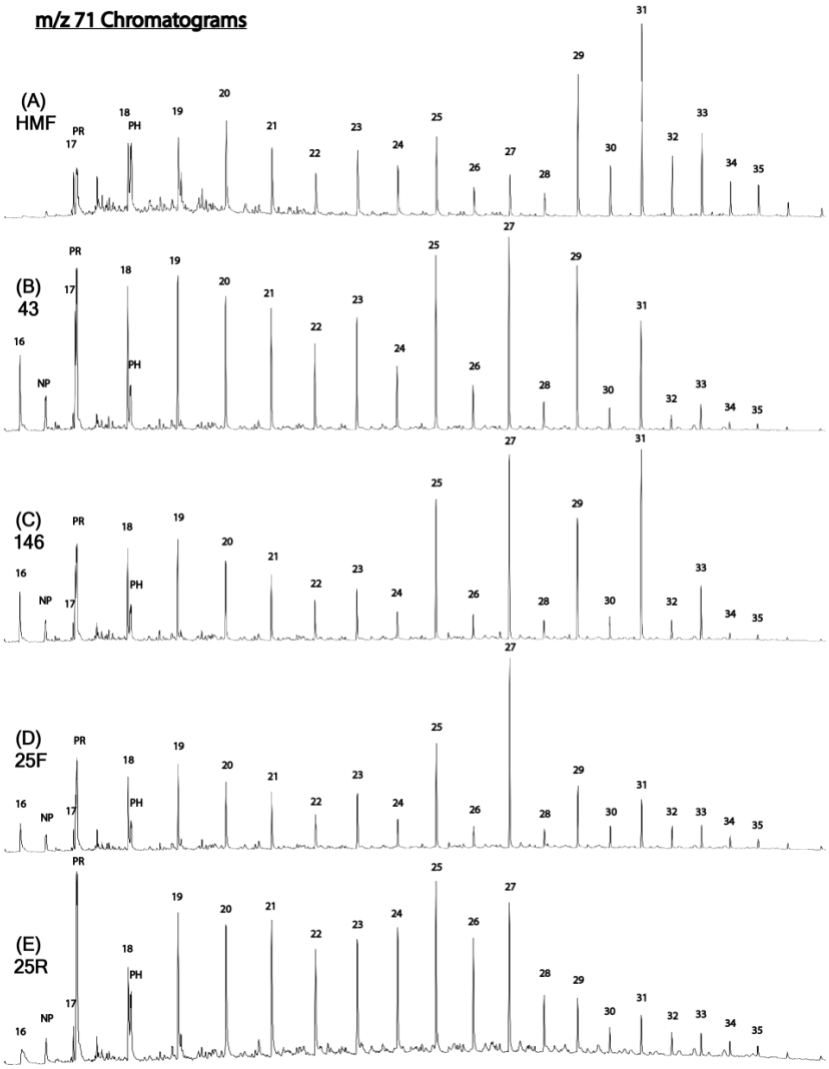

Fig. 14: Mass chromatograms (m/z 71) showing the distribution of normal and isoprenoid alkanes in the five soil extracts. There are three phenomena happening: C17/PR, C18/PH, and OEP. Numerals indicate *n*-alkane carbon number; for other symbols see Table 2.

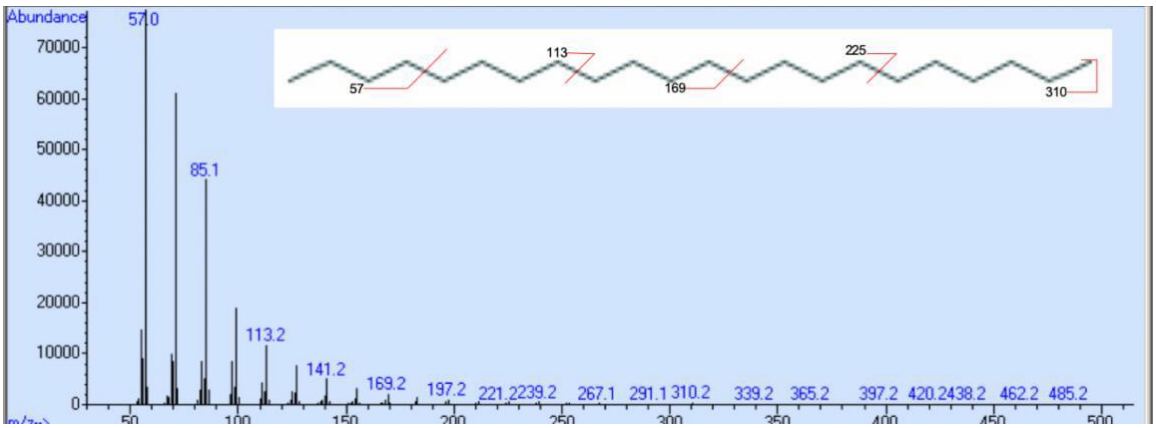

Fig. 15: Representative *n*-alkane mass spectrum (*n*-docosane, $C_{22}H_{46}$) and its molecular structure showing mass spectral fragmentation points.

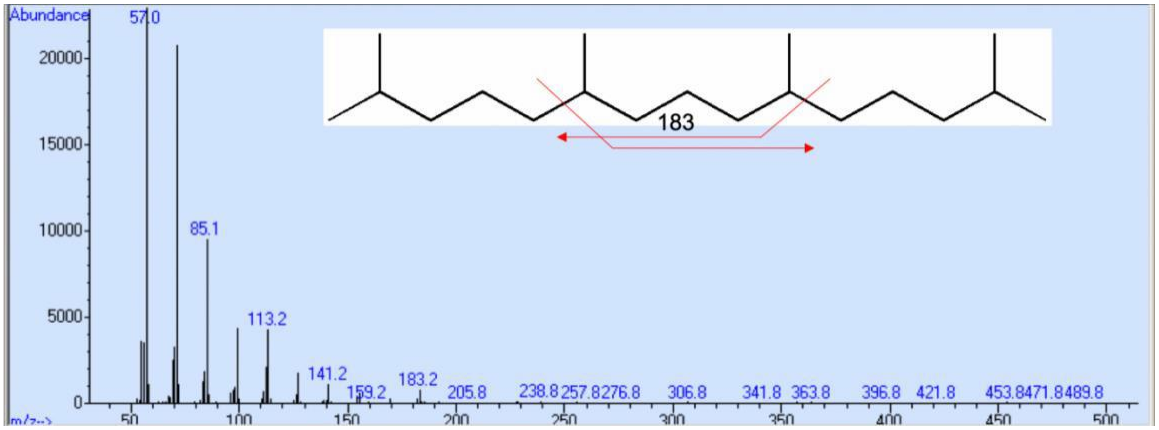

Fig. 16: Representative isoprenoid alkane mass spectrum (pristane, $C_{19}H_{38}$) and its molecular structure showing mass spectral fragmentation points.

4.3 Hopanes (Triterpenoids)

These identified compounds could be separated into two groups, tricyclic terpanes and hopanes (pentacyclic terpanes). For this Figure (Fig. 17), the key attribute to point out is the correlation between fossil fuel contamination, triterpenoid distribution, and the

biotic biomarkers. HMF (Fig. 17A) has minimal fossil fuel contamination and minimal traces of any triterpenoids but has an overabundance of two particular compounds called diploptene (peak B2) and an amyrin derivative (B6). Diploptene or hopene is similar to the hopane molecule, but it contains a double bond at the end, on one of the methyl group in the isopropyl constituent (Fig. 19). These two molecules are both anaerobic microbial biomarkers and can easily be formed to one another by a chemical reaction (Fig. 20; Simoneit, 2005). The second biomarker is uncertain, but it is known by most of this compound's chromatograph to be amyrin-like or an amyrin derivative. These groups of compounds are found in higher plant cells, but instead of the usual organelles or material found inside of a plant's cell, these compounds are a storing place for latex (Simoneit, 2005; Peters et al., 2005). Similar to diploptene, these molecules have their own group of chemical reactions (Fig. 21; Simoneit, 2005). It makes sense that one would find the compounds more in a biotically productive, less contaminated environment, since one is microbial (diploptene) and the other is from higher plants (amyrin). The trend for all the chromatographs (Fig. 17) is that the biomarker diploptene is always more than two magnitudes higher than the amyrin derivative. As soon as you scan through the LSP sites (Fig. 16B-E), there are immediately higher triterpenoid compounds and the previous two biomarkers are lowered. The general shape that these four chromatographs (Fig. 17B-E) follow is a bell-curve, with the triterpanes to the left being a flat line and the hump being towards the common C_{30}-hopane (H30). It is also seen that the amyrin derivative dramatically drops to a miniscule amount, almost as high as the triterpenoid heights. Surprisingly, in the chromatographs of sites 146 and 25F (Fig. 17C-D) the diploptene biomarkers are higher than H30 even though those sites are in LSP. This reflects the

actual site's terrain since these two sites have the most vegetation out of all the analyzed LSP sites. In the final chromatograph of 25R (Fig. 17E) we see negligible amounts of both biomarkers and only has the triterpenoid compound series is present. This makes sense because in the actual site's terrain there is minimal plant growth and only pollution from fossil fuels (Fig. 7b).

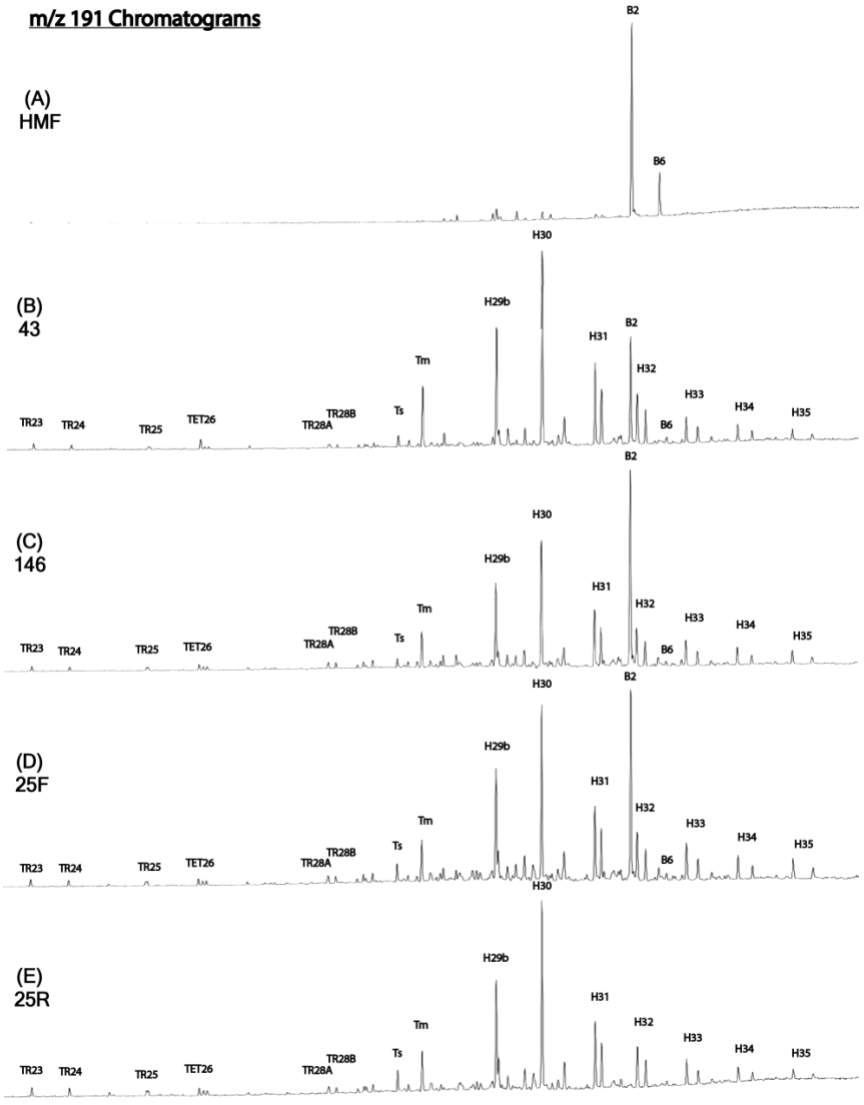

Fig. 17: Mass chromatograms (m/z 191) showing the distribution of triterpenoid compounds in the five soil extracts. For peak identification see Table 2.

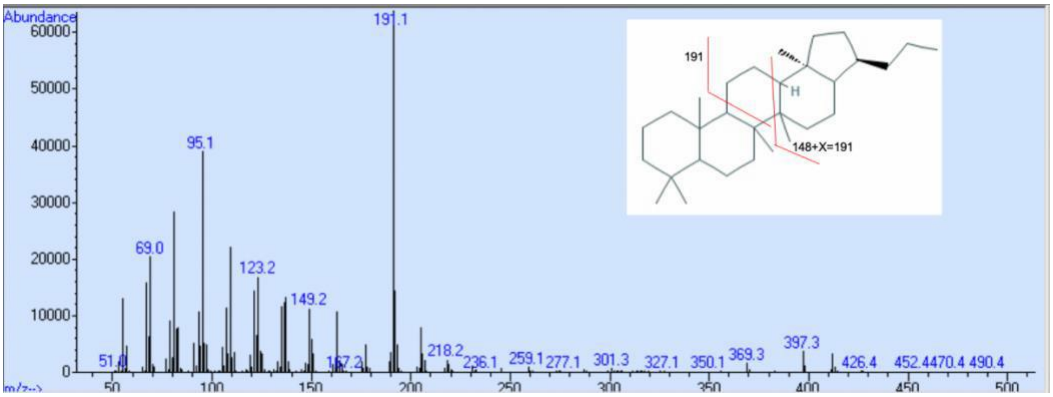

Fig. 18: Mass spectrum of 17α(H),21β(H) hopane ($C_{30}H_{52}$) and its molecular structure showing mass spectral fragmentation points.

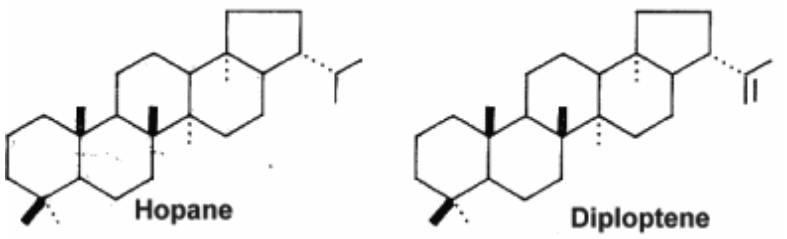

Fig. 19: Structural difference between hopane and diploptene (Google search).

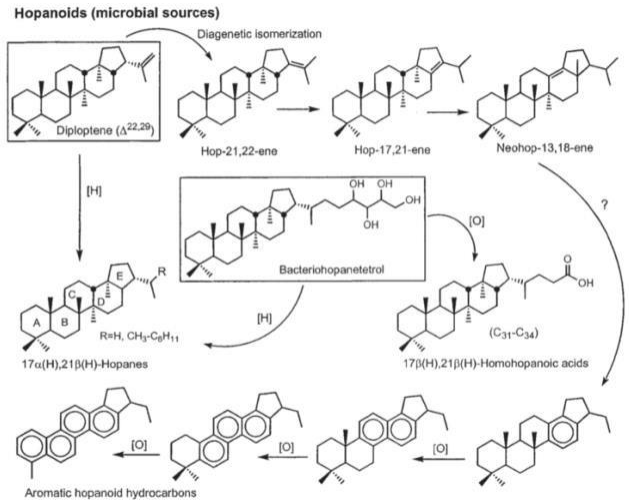

Fig. 20: Diploptene's chemical reactions during biodegradation (Simoneit 2005).

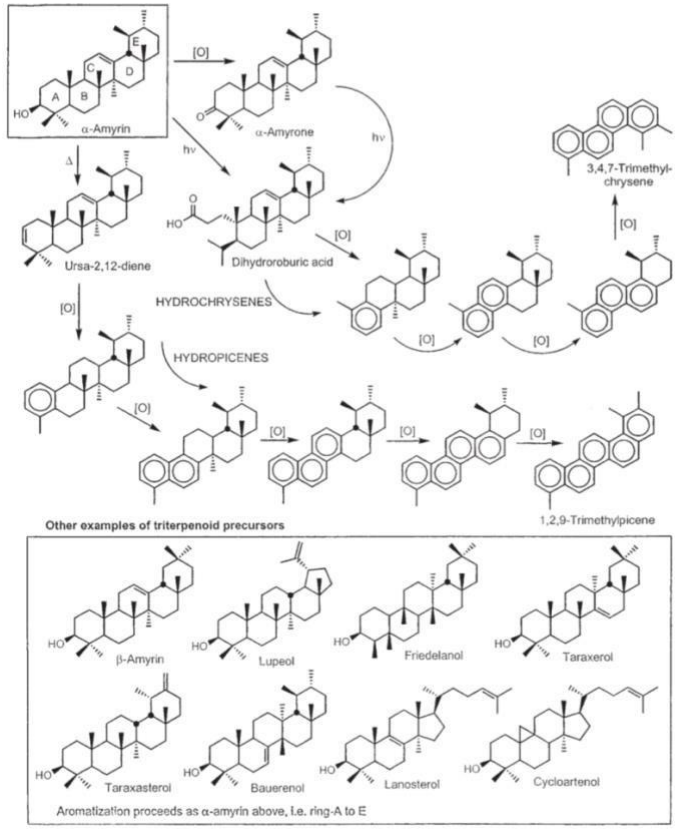

Fig. 21: Alteration pathways for α-amyrin (Simoneit 2005).

4.4 Sesquiterpanes

The compounds show in Fig. 22 are bicyclic sesquiterpanes. Their origins are suggested to be from higher plants and prokaryotic algae/bacteria, but this has not been fully explored (Peters et al., 2005, Nytoft et al., 2009, Wang et al., 2005). There are other studies that say these compounds can be used to detect lighter-distillate oil in crude oil that was dumped in an area (Yang et al., 2009, Song et al., 2016). There are other studies that state they were formed from other chemical processes, such as broken/separated off from regular terpanes, cyclization and degradation of squalene or higher aliphatics, or degradation of oleanoids (Nytoft et al., 2009, Gordadze et al., 2010). Whatever their

origins are, they are still another biomarker of terrestrial plants. The interesting thing with that idea is that HMF (Fig. 22A) has an undetectable amount while all the sites in LSP (Fig. 22A-E) have them. Another surprise is that sites 43 and 146 (Fig. 22B-C) have the highest amount of all identifiable sesquiterpanes out of all of the LSP sites. This could be due to an intermediate environment where it is not too forested like HMF or too contaminated like 25F and 25R. It could also be some unique plant species that were only found in sites 43 and 146 but not the others. Speculations aside, this could more readily explained as evidence for coal in site's 43 and 146 because sesquiterpenoids are one of the compound types that is generated by ancient higher plants/coal (Fig. 6a; Peters et al., 1993).

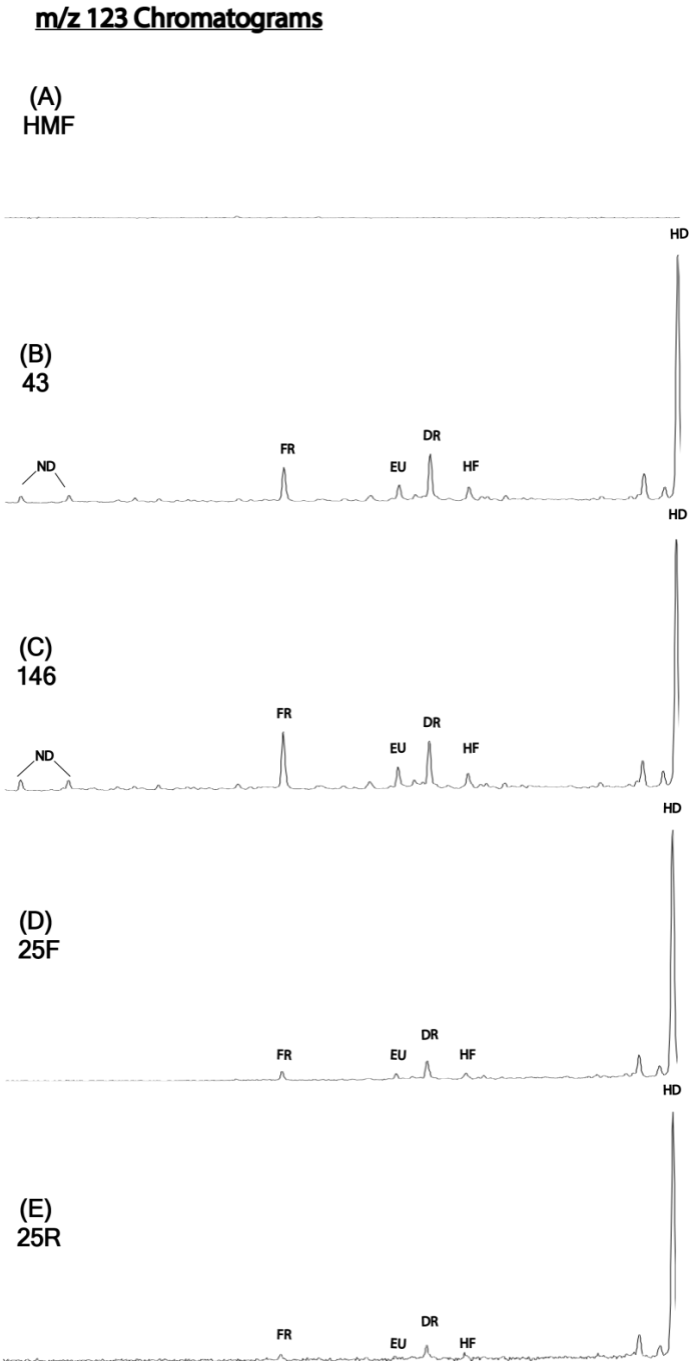

Fig. 22: Mass chromatograms (m/z 123) showing the distribution of sesquiterpanes in five soil extracts. See Table 2 for peak identifications.

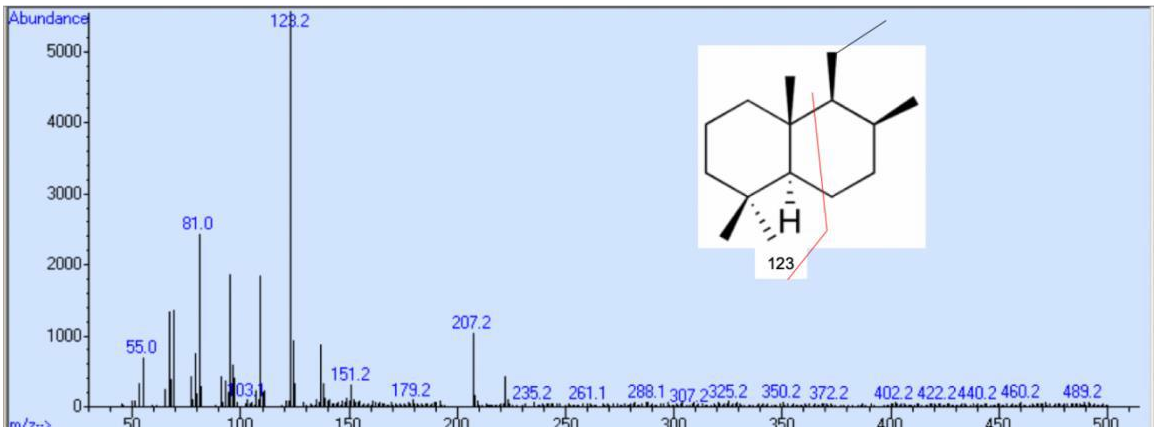

Fig. 23: Mass spectrum of the bicyclic sesquiterpane, homodrimane ($C_{16}H_{30}$) and its molecular structure showing mass spectral fragmentation points.

4.5 Steranes

In order to show all the chemical compounds in the sterane series in the same proportion the m/x 217 was used, but one can emphasize the regular steranes (m/z 218) and the diasteranes (m/z 259) to look at them individually with greater clarity. As with all the chromatograph Figures before this HMF is always the least interesting in terms of the number of compounds it has. Fig. 24A mostly has noise because the sterane series is already after the hopane series, getting near the completion of the chemical analysis so it starts to heat up and detect the compounds in the lining inside the capillary tube. Besides that, there are a mix of identifiable compounds and unidentifiable compounds. The overall outline for Fig. 24B-E is two consecutive concave depressions and then a gradual decrease. The first peak is on a C_{27} diasterane (peak D27S), the middle peak is a mixture of a C_{29} diasterane and a C_{27} regular sterane (D29+S27BR), and the last peak is a C_{29} regular sterane (S29AS). Most of these compounds are not different as in carbon number except they are different in their isomerization, which is the configurations of the atoms

in the molecule itself. The main three carbon numbers are C_{27}, C_{28}, and C_{29} and because of that, a ternary diagram can be created to see from what historic period or what original ecosystem the sterane precursors came from (Fig. 26). One of the differences is in the coelution peak of D29+S27BR becoming more distinct and separate, as you go from site 43 (Fig. 24B) to site 25R (Fig. 24E). Another difference is that all the compounds increased in site 25F (Fig. 24D). That is interesting because right away in site 25R (Fig. 24E) most of the compounds decreased in abundance. Site 25R (Fig. 21E) should of stayed around the same intensity as site 25F (Fig. 24D) because they are both in excess in organic contamination. This could mean that sterane is not as much of a petroleum indicator as it is a biological indicator. As I talk about it in the next section, steranes are the most complex and more biotically versatile than a more complex compound like hopane. Going back to the ternary diagram (Fig. 26), one sees that all the four sites (146, 43, 25F, and 25R) that has most identified steranes are close to the C_{29} corner. C_{29} steranes or 24-ethylcholestanes comes from a land-plant source (Peters et al., 2005). Land or vascular plants make coal most likely through Type III diagenesis (Killops and Killops 2005). This conclusion is also supported by the fact that the coal that was historically brought there was from Pennsylvania and of Late Carboniferous age (about 320 million years ago) (Böcker et al., 2012). As for the other corners of C_{27} and C_{28} there are many detailed interpretations, but in general C_{27} represents planktonic species and C_{28} represent lacustrine-algae species (Adegoke et al., 2014; Togunwa and Abdullah 2017; Saeed and Mohialdeen 2016). The names commonly associated with C_{27} is cholestane, C_{28} is ergostane, and C_{29} is stigmastane. Overall, this indicates the origins of fossil fuel was

coal from the Carboniferous period that was transported to from Pennsylvania to CNJ railyard.

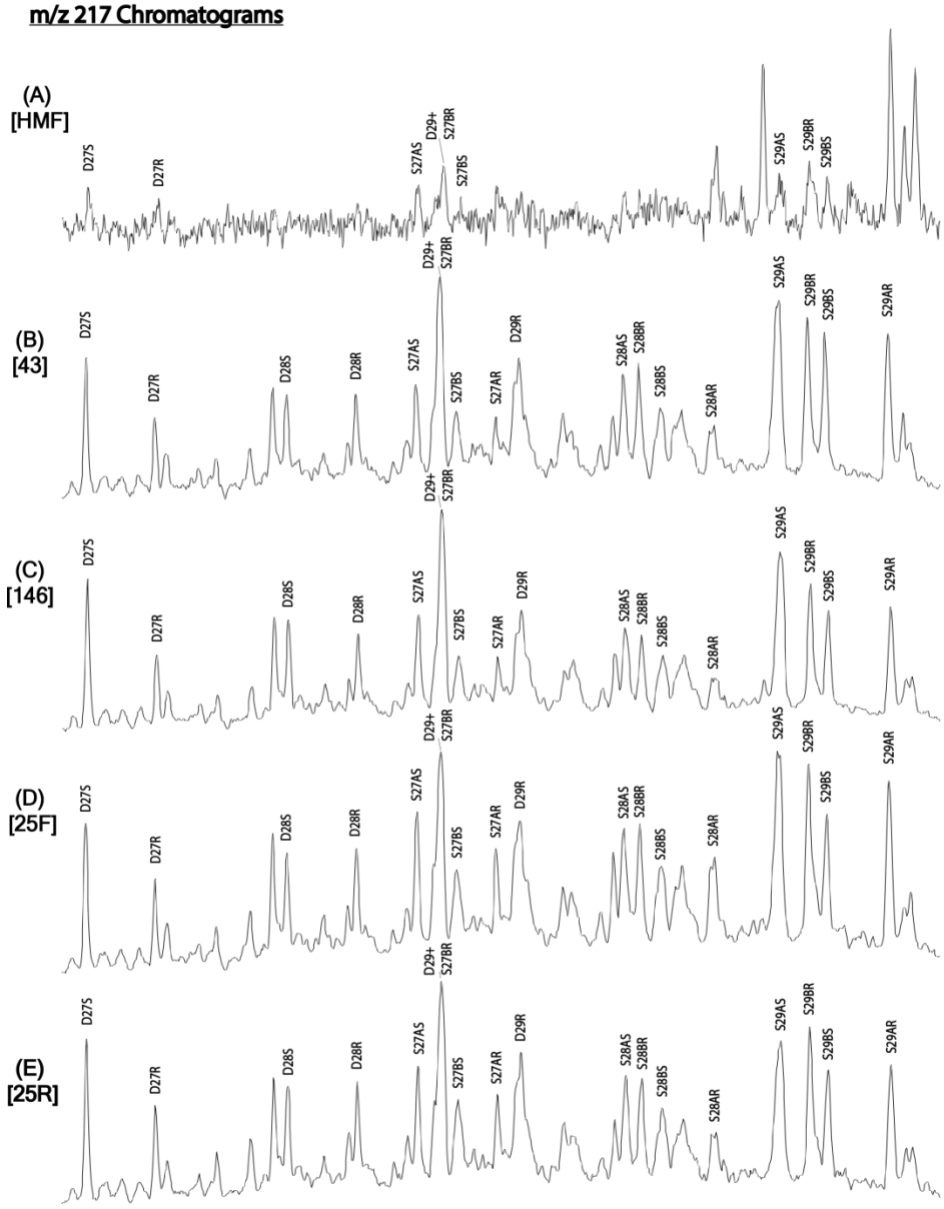

Fig. 24: Mass chromatogram (m/z 217) showing the distribution of steranes in the five soil extracts. See Table 2 for explanation of peak labels.

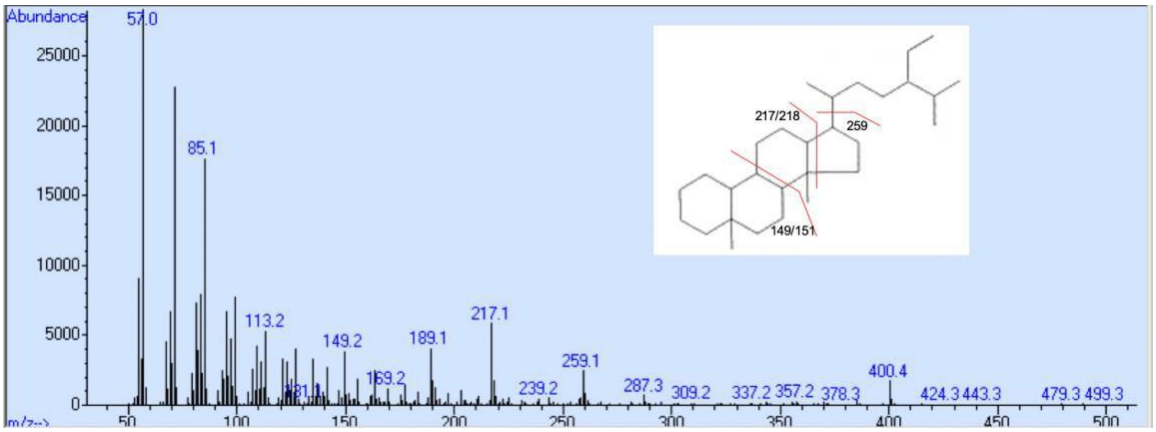

Fig. 25: Mass spectrum of the rearranged sterane 13α (H),17β(H) 20R diastigmastane (C29H52) and its molecular structure showing mass spectral fragmentation points.

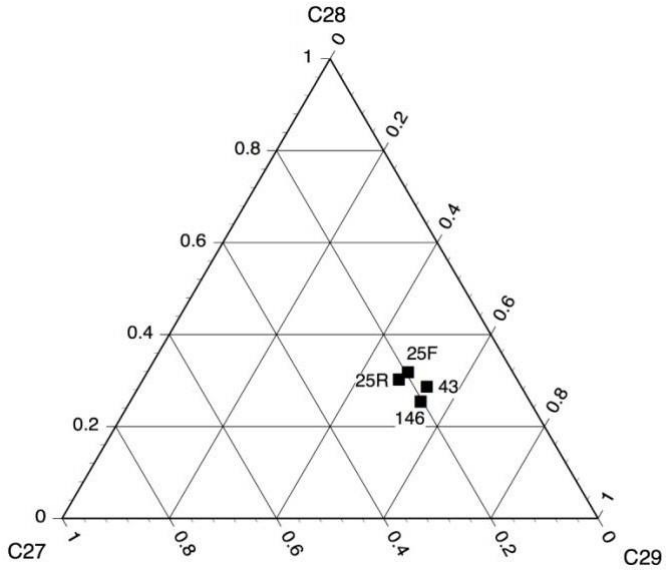

Fig. 26a: Ternary diagram of the sterane carbon number distribution in the four LSP soil extracts (146, 43, 25F, and 25R). (Add reference)

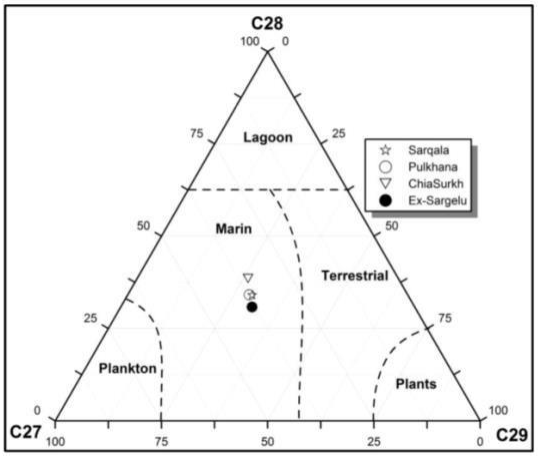

Fig. 26b: Example of a sterane ternary diagram as used to infer environments of deposition for the fossil fuel precursors (Saeed and Mohialdeen 2016)

5. Environmental Toxicology/Impacts

Since this is a strictly organics analysis study, the findings for this section is only going to deal with organic contaminants and not inorganic even though there is that problem. In the case of human health and prolonged exposure as did the people working on the railyard, studies have shown that they developed numerous life-threatening diseases. One would think the health effects would mostly come from coal, but the majority of the articles that was founded focuses more on diesel exposure. One study found out of 523 workers that died, the majority of them either had cancers (n=129) or circulatory diseases (n=252) (Schenker et al., 1984). The cancers of that study included esophagus, stomach, rectum, respiratory, lung, bladder, kidney, brain, thyroid, lymphatic, and leukemia (Schenker et al., 1984). In the 1900s, cigarette smoking was very popular even a portion of railroad workers would smoke. People in the 21st century would know that smoking is bad for you and that you are inhaling nicotine combustion particles, but combine that with working on railroads would increase that exposure by four times (Woskie et al., 1988). This is one of the major pathways that the gases either from coal, oil, diesel, and asbestos can cause harm to an organism. One of the most direct outcomes of prolonged inhalation of those gases would be lung cancer, which most of the studies back then focused on. The papers that analyze that categorize the workers based on the Interstate Commerce Commission codes/job titles like shop workers, engineers and fireman, brakeman/conductors/hostlers, clerical workers, and signalmen (Garshick et al., 1988). As technology gets better at seeing smaller and smaller pieces of matter such as air/dust particles in the 21st century, the scientific community researching on railroad/construction health started shifting away from analyzing participant's data and

analyzing the particles that produced those pollutants in those areas instead, even to a nanoscale like Saikia et al., 2017. This could be helpful information in deciding whether or not the contaminated soil in the LSP plot should be removed or not. In recently years, there is less of a concern for coal pollution, one because the CNJ railyard has been abandoned for around five decades and second because the use of coal as an energy source is more archaic and moved on to oil, natural gas, and renewables. The only organic contaminant that seems to be in effect now and still likely to pose health risks is from the petroleum. A new way to analyze these health effects would be to go to the molecular level and to investigate each category chemical group. Since the chemical groups that was analyzed in this paper was saturates, the saturates are going to be looked at. First, the *n*-alkanes, this group would be considered the easiest to breakdown and therefore not pose any major health concerns (Fig. 27, Varjani 2017). These compounds are the basic straight chain connections for any macromolecule, even in human blood (Mochalski 2012). They wouldn't cause the most minimal harm out of all the saturated compounds because either they would be broken down to smaller units (smallest unit analyzed is C_{16}) or they need other chemical reactions in order to place various double bonds or elemental constituents on them in order to mimic or function as another biological molecule. The second group of saturates that is higher in complexity is the isoprenoids. Isoprenoids would be the most concerning because the they are constructed out of terpenes and could be intermediate molecules for complex ringed structures, like triterpenoids or hopanes. These functions would only be possible if the isoprenoids have double bonds where there are branches occurring in the carbon atom. Once they are double bonded, they are helpful to biological processes with attachments of different

functional groups such as: alcohols, carboxylic acids, aromatic rings, phosphates, or proteins. The isoprenoids that are attached to alcohols are associated with lipids (Ward et al., 2009, Savidov et al., 2018). The isoprenoid lipids that are found in Savidov et al., 2018 are ones that are formed into rings, this would mean that it would be hard for the contaminated straight-chained isoprenoid to form into these cyclic-ringed isoprenoids and that it would be a minimal chance of mimicry causing toxicity. Those kinds of lipids are only found in fungus or fungi endophytes, which are not known to be found in the entire LSP soil plot. Another form of the lipid, which is straight-chained, could be more easily replicated in the contaminated isoprenoids. One study examined dolichol and dolichoic acid (isoprenoid derivatives) connects with the releasing of neuromelanin which is one of the causes of Parkinson's disease (Ward et al., 2009). Another constituent group that isoprenoids will attach onto would be the aromatic rings and therefore would become a macromolecule, meaning different categories of naming them. What is meant by aromatic rings does not mean the cyclic carbon molecule has full pi bonds to delocalize its electrons all around, it just means there are double bonds spread out with some rings to make the molecule rigid and less likely to break apart. These macromolecules are called carotenoids, tocopherols, and chlorophylls (Stinco et al., 2018). All three are important for characteristic biological functions such as pigment color, nutrients, and pregnancy. If isoprenoids try to replicate these compounds it would take isoprenoids a long time and through high temperatures because of the size and different constituent groups in the macromolecule itself. The last category of functional groups that is likely to attach to isoprenoids is phosphates. These can actually be replicated by the contaminated isoprenoids because they only come in straight-chained form (Hooff et al., 2010, Osborn-

Heaford et al., 2015, Mo et al., 2012, Cole and Vassar 2005). The papers that were searched linked isoprenoids that are attacked to either phosphates or other proteins with crucial functions in human diseases like alzheimer's, osteoclastogenesis/osteoblastogenesis, and fibrosis. The next level of saturated molecules is sesquiterpanes, which is either novel in its research or easily go to a sterically stable state of more (triterpenoid) or less (isoprenoid) complex. The only groups of biologically studied sesquiterpenes that have frequently came in papers is known as "sesquiterpene lactones" (Fig. 28). Despite that the molecules are minimal in quantity and as of now unknown on how other free-floating compounds could replicate the lactones (Adekenov 2017). The next two compound categories, steranes and triterpenoids, could sometimes automatically mimic/replicate the natural compounds that are in human bodies because most of their chemical backbone is already assembled. Steranes are very alike to their natural derivatives sterols, that it only needs an alcohol functional group and alkene/isoprene side chains (Fig. 29, Kunz and Matysik 2019, Vanmierlo et al., 2015). Since these mimicked compounds can serve the same bodily functions, they are not necessarily toxic, but they can cause unforeseen consequences. One example is that sterols play crucial role in ensuring fluidity in the plasma membrane of a cell by preventing the lipids in forming a gel phase (Menon 2018). The plasma membrane gets their sterols from the endoplasmic reticulum–plasma membrane (ER-PM) sterol concentration gradient through sterol transport proteins (STPs) (Menon 2018). This gets into the most popular animal (and human) sterol which is cholesterol. These sterols could also form other isomers affecting other organisms or induce other reactions (Fig. 30). The last category of chemicals are the triterpenoids, which include the hopanes. They

have similar effects to organisms like the steranes do. The main difference is structurally steranes have more alkanes to their side chains, and the triterpenoids have a fifth ring attached to the base (Fig. 19).

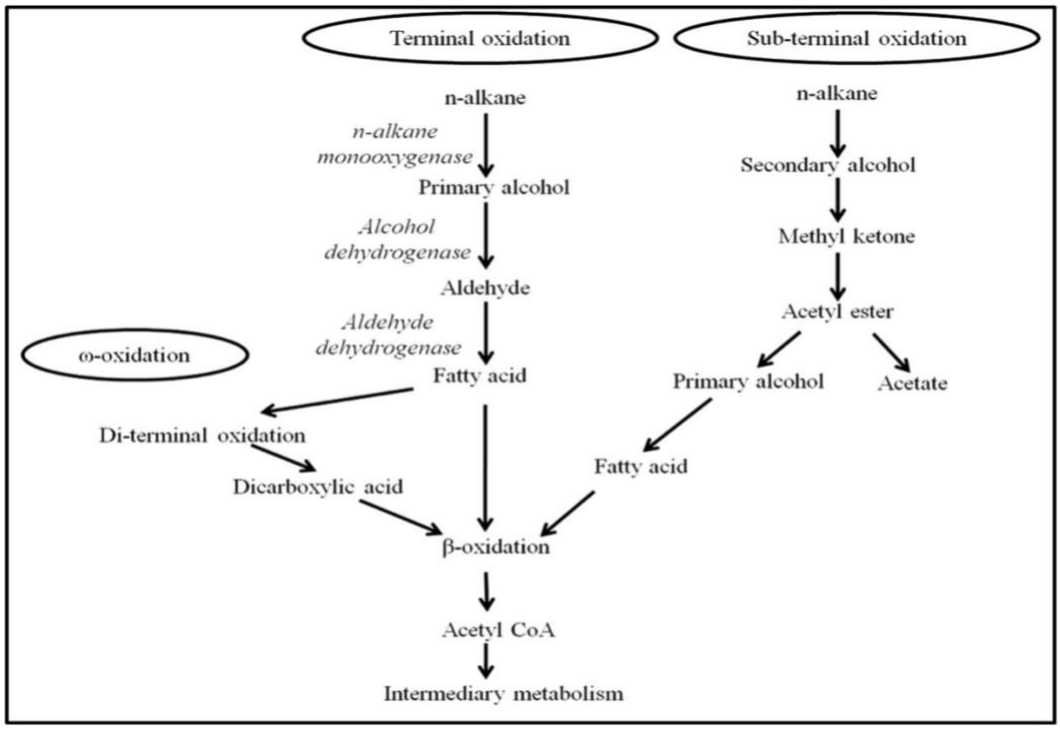

Fig. 27: Microbial alternation pathways for *n*-alkanes (Varjani 2017)

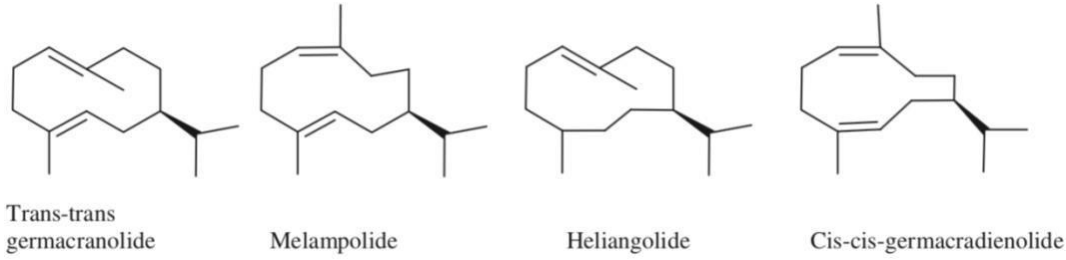

Fig. 28: Examples of sesquiterpene lactones (Adekenov 2017)

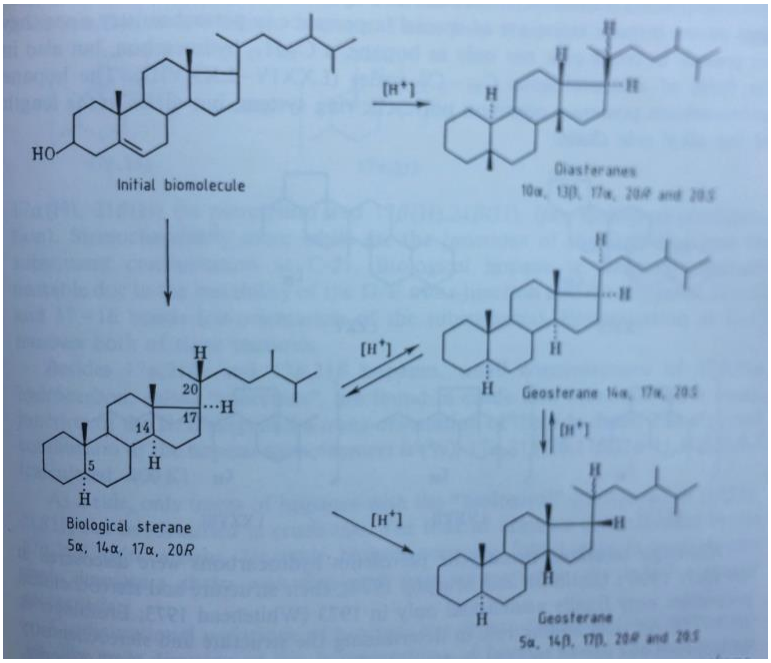

Fig. 29: Sterol (precursor biomolecule) alternation pathways (Petrov 1987)

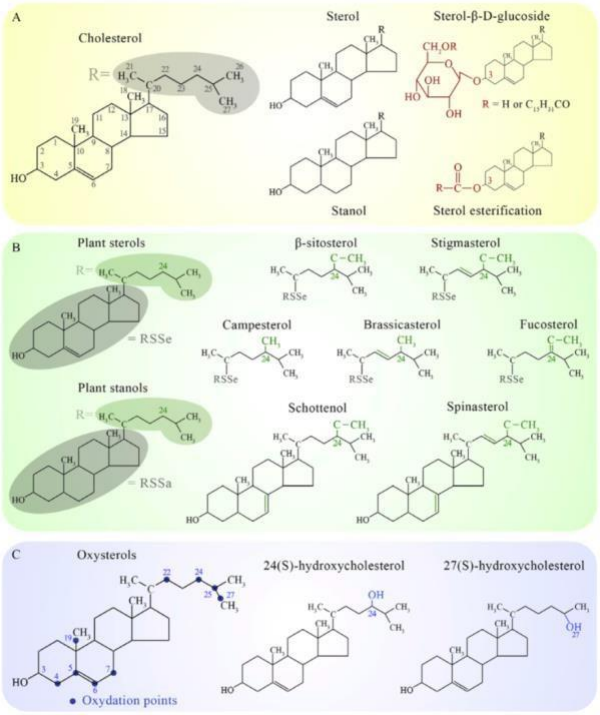

Fig. 30: Major sterols found in animals (A), plants (B), and example of their oxidative products (C) (Vanmierlo et al., 2015).

6. Conclusion

This is an assessment of all the data that was collected so far and an attempt to connect it back to the overall environments of HMF and LSP. The assessment analyzes each type of hydrocarbon one by one. First, for the *n*-alkanes and isoprenoids in Figure 14, the C17/PR and C18/PH ratios are indicators of biodegradation of organic contaminants. The ratios tell one that by showing in what proportions the soil microbes break down these hydrocarbons. Soil microbes would likely breakdown the normal alkanes first such as C17 and C18. The reason is because it's easier to metabolize and react with straight chain compounds than branched, in which case it takes more time to metabolize into the enzymes' organelles. By having HMF (Fig, 14A) showing the proportions of C17/PR and C18/PH being very similar, it proves that the actual environment stayed consistent over time and with minimal to no organic contamination. The other extreme of 25R (Fig. 14E) has a drastic disproportion between its ratios. This must mean that the site's environment has experienced much organic contamination and then over time the soil microbes degrade the most soluble compound out of the two (*n*-alkanes and isoprenoids), which are the *n*-alkanes. This forms a gradient that, in between (Fig. 14B-D), have not as much organic contaminants or are in the newly to mid degradation stage. This gradient can translate over to the various phenomena that will be discussed here further. A second phenomena that is in Figure 14 is the OEP or odd-even predominance. OEP shows turnover of plants or their degradation in the soil. It could indicate if there are any plants in the sites and how abundant the plants are. In this case, there is not so much a gradient as there is extremes and intermediates. HMF and LSP (Fig, 14A and E) have a narrow range for their OEP, but both environments could not be

more opposite in terms of their plant productivity. HMF is a preserved forest for many years, while 25R is a barren site that was a result of its location during the Central Railroad of New Jersey (CNJ) years in business (Fig. 28). The OEP for 25F (Fig. 14D) is just like 25R (Fig. 14E), which is interesting because the site's environment has plant productivity, but not as much as site 43 or 146. Site 43 (Fig. 14B) and 146 (Fig. 14C) OEPs are the intermediates with the widest ranges. It could be that in addition to having the most plant productivity out of LSP, they also are contaminated with organics. This could explain the reason why even though HMF is a forest, both of the LSP sites (43 and 146) have a wider OEP. The second compound type to look at is the hopanes or triterpenoids. At one extreme there are two biomarkers signifying biological organisms of HMF (Fig. 17A). This mean the site's environment is as natural as possible. At the other extreme is a close to perfect distribution of all triterpenoids and hopanes in 25R (Fig. 17E). All the sites in between (Fig. 17B-D) are a combination of the compound distribution and the two biomarkers. This reflects their environments because even though they have contamination, they still have plants in them. The third category type are sesquiterpanes. The two compounds to keep in mind are eudesmane and drimane. Eudesmane is mostly linked to higher plants while drimane is linked to bacteria (Philp 1985). The compounds farnesane and homofarnesane technically belong to the isoprenoids so they do not really count in the sesquiterpane assessment. Figure 22 shows that 43 and 146 (Fig. 22B and C) have the most abundant compound peaks out of all the sites. This would suggest that the two sites have high amounts of plants and bacteria. At first it makes sense because the other two LSP sites, 25F and 25R (Fig. 22D and E) have a lower compound abundance and reflect the lower biotic activity in those two sites.

Then, one looks at HMF (Fig. 22A) and sees there are no signals in the chromatograph or it is too low compared to the other sites. This make sense because HMF would mostly have compounds from living organisms, which have double bonds except of the single bonds found in this study. The compound abundances in LSP proves that most of the organic compounds comes from fossilized organisms and not living ones. This would suggest that even though the two compounds are biotic in origin, they need organic contaminants to activate them. The final compound type to assess are steranes. The main importance of these molecules is that they are linked to the original environment of the contaminant, which in turn can Figure out what organic contaminant is prominent. HMF (Fig. 24A) does not have many identifiable compounds, probably because the site has minimal organic contamination. From the ternary diagram (Fig. 26a) we can see all of the LSP sites are placed around the C_{29} corner, which indicates a terrestrial environment with higher plants that turned out to be coal. On closer inspection, site 146 and 43 lean more towards C_{29} and site 25F and 25R toward C_{28}. This would make sense when compared to the map of Figure 6a/b. It shows the sites 146 and 43 are near rail lines that shipped coal, while site 25R and 25F were almost at the opposite side of the railyard (Fig. 6a/b.

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