RESIDUAL DIESEL RANGE ORGANICS AND SELECTED FROTHERS IN PROCESS WATERS FROM FINE COAL FLOTATION

Joshua Powell Morris

Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Master of Science
In
Mining and Minerals Engineering

Emily Sarver, Committee Chair

Gerald Luttrell
John Novak

May 8, 2013
Blacksburg, VA

Keywords: Processing Reagents, Coal Preparation, Flotation, Water Management, Diesel Range Organics, DRO, Polyaromatic Hydrocarbons, PAHs, Gas Chromatography

RESIDUAL DIESEL RANGE ORGANICS AND SELECTED FROTHERS IN PROCESS WATERS FROM FINE COAL FLOTATION

Joshua Powell Morris

ABSTRACT

The purpose of this thesis is to examine some of the potential fates of processing reagents in a coal preparation plant. The focus is specifically on petro-diesel (termed "diesel" in this paper), which is used as a collector in the flotation of fine coal. Diesel range organics (DRO) and polyaromatic hydrocarbons (PAHs) are measured in aqueous samples using gas chromatography equipped with either a flame ionization detector (GC-FID) or a mass spectrometer (GC-MS). Samples are subjected to a variety of test conditions in order to understand the behavior of diesel compounds in coal processing streams.

Results show that frother and collector reagents are not likely to partition completely to a single fraction of the process slurry. Further test work has shown that sub-ppm levels of DRO dominated by the water soluble fraction of diesel are expected to be present in process waters; however, PAHs and insoluble DRO may be removed via volatilization and/or degradation. DRO and PAHs are also expected to be desorbed from coal particles when contacted with fresh water. Flotation tests have revealed that low levels of DRO are found in both the concentrate and tailings processing streams with slightly higher concentrations being found in the concentrate stream. From the tests performed in this thesis, it appears as though there is no apparent environmental concern when coal preparation plants are operating under normal conditions.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 LITERATURE REVIEW

1. Introduction

Coal preparation is often required in order to produce clean, efficient "thermal" coal for steam generation, or to produce high quality "metallurgical" coal suitable for coking (Pitt and Millward 1979; Lu et al. 2012). In order to complete this requirement, ash minerals (e.g., sulfur and ash) must be removed. Unwanted minerals are separated from coal particles through a range of processes depending on the particle size. Coarse and intermediate sized particles are separated based on gravity and do not require reagents whereas fine and ultra-fine sized particles are separated via froth flotation which does require the addition of chemical reagents, as described below. Following flotation, or other wet processing, excess moisture can be removed from coal product via dewatering mechanisms such as screens, centrifuges, filters, and thickeners, and thermal dryers (Bratton and Luttrell).

Since water is used as a continuous phase for particulate processes within the preparation plant (Adel 2012), it may concentrate residual reagents from various preparation circuits, including flotation. Flotation feed slurries usually consists of around 5% solids, meaning that for every ton of feed entering the flotation circuit, roughly 17,000 liters of water is required. Water is recycled within a preparation facility as much as possible. It can be either recycled within the plant itself, or re-circulated back from a tailings impoundment after being pumped there with fine refuse material; ideally, the fine particles settle in the impoundment and the water being pumped back to the plant is "clear." While in the impoundment, water, and any chemicals contained within it, could interact appreciably with the environment (e.g., via release into surface waters, seepage into underlying soil or vaporization to the atmosphere).

1.1 Environmental Context

Federal water contaminant levels for petro-diesel (i.e., total diesel range organics or DRO) do not currently exist in the US (EPA 2003); however, some states have specified contamination levels of DRO for drinking water standards (DEP 2002). As stated above, environmental concerns with low-level petro-diesel (termed "diesel" in this paper) concentrations in water are primarily associated with potential PAH release. The US EPA has

developed a list of 16 priority PAHs, one of which (i.e., benzo-[a]-pyrene) does have a maximum contaminant level (EPA 2011). Benzo-[a]-pyrene was not found in the diesel used in this paper and only trace levels of six PAHs were detected. No PAHs were detected in the biodiesel used as well as an obtained sample of pine oil. Unlike diesel, ideally biodiesel does not contain any aromatics as well (Demirbas 2007). PAHs have been found in the liquid phase of coal waste slurry; however, it is difficult to determine the origin of these compounds (i.e., naturally or from pollutants).

Diesel is currently restricted in coal processing under certain conditions, such as when coal waste slurry is planned to be disposed by underground injection. This ban exists on any substance that is or contains what is classified as a hazardous waste by toxicity under the Resource Conservation and Recovery Act (RCRA). In these instances, collectors such as biodiesel and pine oil represent potential alternatives. Studies have shown that DRO can be measured in waste slurry, and the source of the DRO is from coal preparation (WV-DEP 2009). Although diesel is banned from being used where underground injection takes place in West Virginia, there are no criteria for diesel under the West Virginia water quality criteria for warm water fishery nor is it subject to a drinking water standard (Ducatman et al. 2010).

1.2 Performance Characteristics

Diesel is commonly used as a collector in fine coal flotation due to its wide-spread availability, low cost, and well-established performance. Recent laboratory and full-scale results have shown that alternative collectors, made of renewable and biodegradable materials, can outperform diesel regarding yield and product ash even at lower dosage levels. A higher yield corresponds to a lower cost for water clarification as well as a reduction in material heading to the impoundment. The flotation kinetics of these alternative collectors was also better than diesel, which would allow for higher throughput (Eraydin et al. 2012). Other studies have shown that waste vegetable oils can be used to agglomerate coal cleaning fines wastes; however, these studies used a large amount of oil – 5% by weight (Valdes and Garcia 2005). Alternative collectors have also been developed from the pulping of trees. The resulting crude tall oil, a byproduct of pine trees in making paper and tissue, has shown improvements in plant performance regarding an increase in combustible recovery (Hines et al. 2011). Patents have

recently been placed on the use of fatty acids, the main component of biodiesel, and rosin acids, regarded as pine oil, as well as a combination of the two (Hines et al. 2009).

2. Research Questions Addressed in this Thesis

Chapter 1: Literature Review

- What components of diesel are currently regulated?
- Are there any restrictions on when diesel can be used in coal processing?
- How does the performance of alternative collectors compare to diesel?
- What makes up diesel?
- How are trace levels of DRO measured in water samples?

Chapter 2: Reagents In Coal Preparation: Where Do They Go?

- What are the potential fates of reagents used in coal processing?
- Do frother and collector reagents partition completely to either the solid or liquid fraction of coal slurry?
- Does any frother sorb to the coal surface or does it completely remain in the water?
- Does any diesel remain in the water after it is contacted with coal?
- Do residual DRO results differ depending on the dewatering technique (i.e., filtration vs. centrifuge)?
- Are results reproducible for measuring low level DRO?
- What is the effect of percent solids on residual DRO?
- What is the effect of ash on residual DRO?

Chapter 3: Diesel Range Organics In Coal Preparation

- Are PAHs measured in process water after coal has been contacted with diesel?
- Are PAHs concentrated relative to total DRO in process water samples?
- What is the persistence of residual DRO and PAHs once it is in process water?
- What is the desorption of DRO and PAHs from coal surfaces after being exposed to fresh water?

Chapter 4: Flotation Tests

- Is DRO measured in process water after flotation?
- Does the amount of DRO measured in process water vary between the concentrate and tailings?
- Are naphthalenes measured in process water after flotation?
- Does flotation concentrate the naphthalenes found in the process water after flotation?
- How does flotation performance compare with residual DRO?

Chapter 5: Conclusions: Challenges And Lessons Learned

- What sample size should be used for measuring residual DRO?
- What is the preferred technique for concentrating samples?
- What internal standard should be used when measuring residual DRO?

3. Literature Review

3.1 Use of Reagents in Coal Preparation

Chemical reagents are used in coal preparation for particle separation and water clarification. The primary use of reagents in coal preparation is for froth flotation, a technique that enhances the hydrophobicity of coal such that the coal will attach to air bubbles and rise to form a stable froth and be removed while the unwanted minerals sink. Two of the main types of reagents used in flotation are collectors and frothers. The insoluble collectors coat the surface of the coal particles, which helps to enhance their hydrophobic behavior, allowing them to float more easily. The frothers are water-soluble surfactants used to create a stable froth on top of the flotation cell or column, which collects the floated particles and acts as a mode of transport to remove them to the concentrate stream. Three of the main groups of frothers include aliphatic alcohols, polyglycols, and hydroxylated polyethers. The two frothers used in this thesis are methyl isobutyl carbinol (MIBC), an aliphatic alcohol, and polypropylene glycol (PPG), a polyglycol (Laskowski 2001). Although frothers are briefly mentioned, diesel collectors are the focus of this thesis.

3.2 Petro-Diesel as a Collector

Over 40 years ago, collectors were coke-oven by-products; but these collectors have been largely discontinued since they contain an abundance of potentially toxic aromatic hydrocarbons. Most collectors are now derived from crude oil, a more environmentally friendly alternative to the coke-oven by-products (Laskowski 2001); however, they still contains a small amount of aromatics (Morris et al. 2013). Common collectors for coal preparation include petroleum products like petro-diesel (termed "diesel" here), kerosene and fuel oil. Diesel, developed from the fractional distillation of crude oil, is currently the most commonly used collector for coal flotation. Diesel is produced all over the world from highly variable crude feed stocks and, as a result, is subject to significant variability (AMMA).

Diesel is a complex mixture of compounds spanning a range of roughly C_{10} to C_{19} hydrocarbons, and varying not only with the crude oil source, but also with the refining process(es) (ATSDR 1999). Because of the complexity and variability of diesel, characterization is difficult; however, broad categories are typically assigned to the diesel range organics (DRO) (ATSDR 1995). Saturated hydrocarbons (e.g., alkanes, cycloalkenes) usually make up 90% of diesel by weight, whereas aromatics (e.g., naphthalenes, acenaphthenes, acenaphthylenes) make up about 10% (Wang et al. 2003). Waxes and resins are typically not quantified since they account for a very small amount of the diesel. In small volumes or concentrations, saturated hydrocarbons are not typically considered significant environmental concerns, because they tend to break down easily and are relatively non-toxic. However the aromatics, specifically polycyclic aromatic hydrocarbons (PAHs), may be harmful even in small volumes or concentrations and have received a great deal of attention by the research and regulatory communities over the past several decades.

The US EPA has developed a list of 16 priority PAHs, which are considered hazardous due to their potential toxicity, including carcinogenicity, mutagenicity, and teratogenicity. Low molecular weight PAHs (i.e., 2 or 3 aromatic rings) have a relatively lower toxicity than high molecular weight PAHs (i.e., five or six aromatic rings) due to their structure (ATSDR 2009). Of the 16 priority PAHs, 7 are classified as being probably carcinogenic while the remaining 9 are not classifiable, meaning that the carcinogenic levels are significantly lower. Studies on mice show that the 7 probable carcinogenic PAHs have toxicity equivalency factors, or relative toxicities, that are 100 to 1000 times higher than the other 9 non-classifiable PAHs (Lee and Vu

2010). In addition to being potentially toxic, PAHs are also known to be relatively difficult and/or slow to degrade. Degradation rates vary from a few hours to days in air to several months to years in soil (SCF 2002). Diesel is known to contain mostly lightweight PAHs (e.g., naphthalenes, fluorenes, phenanthrenes) that are typically more volatile and soluble, as well as easier to degrade, than the higher molecular weight PAHs (Wick et al. 2011).

While ideal (or "parent") PAHs do exist in diesel and other petroleum products, it is important to note that modified (e.g., alkylated) PAHs are also present, and generally at much higher concentrations. These modified PAHs are essentially variations on parent PAHs, whereby various functional groups have been added (Irwin et al. 1997). The range of possible modifications is immense, particularly as the number of potential functional group sites increases with increasing aromatic ring number, which leads to a high degree of variability in terms of quantity and diversity of individual compounds in any petroleum product. For example, there are 22 individual compounds in just the class of methylated naphthalenes, which is the simplest class of alkylated PAHs (i.e., only two aromatic rings, and only methyl group additions). In diesel, di- and tri-methylated naphthalene compounds may be present at about three times the concentration of pure naphthalene; whereas mono- and tetra-methylated compounds may be present at similar concentrations to pure naphthalene (Abraham et al. 2005).

Since naphthalene is the most prevalent PAH in diesel, it provides an illustrative example of the challenges that arise when attempting to characterize specific components of the variable product. Naphthalene is typically classified based on the number of methyl groups, ranging from C0-C4 with C-0 being the parent compound (i.e., pure naphthalene) and C1-C4 being alkylated naphthalenes. It is important to note that since these alkylated naphthalenes are so complex, making them difficult to quantify, they are often not measured. When they are, naphthalene is sometimes reported as "total naphthalenes", which is the sum of the C0-C4 compounds (Irwin 1997).

Studies have shown that the alkylated compounds in diesel account for 93% of total PAHs. The focus for the work described in this thesis regarding PAHs is on naphthalene because total naphthalenes make up 80% of total PAHs, with alkylated naphthalenes making up 77% of total PAHs (Wang et al. 2003). By measuring the aniline point, an inverse relation to the amount of aromatics, studies have shown that mono-alkylated naphthalene compounds tend to have a higher aromatic content than the poly-alkylated naphthalene compounds (Hessell 2003; Hourani

6

2007). It is expected that the lighter compounds would be more aromatic, and so it is important to understand the behavior and characteristics of the alkylated compounds since they may behave slightly different. Since aromatic hydrocarbons are more water soluble than aliphatics (Schein et al. 2008), it is likely that the mono-alkylated naphthalenes are more water soluble than the poly-alkylated naphthalenes.

3.3 Biodiesel as a Collector

Biodiesel may represent a potentially "greener" alternative to petro-diesel as a coal collector. Biodiesel is generally marketed as a renewable energy source made from recycled vegetable oil or from agricultural co-products and by-products such as soybean oil. It is a fuel consisting of long-chain mono alkyl esters, also known as fatty acids, designated by the requirements of ASTM D 6751 (NBB 2013). Biodiesel is made by a process called trans-esterification, where oil or fat is reacted with a short-chain alcohol such as methanol with a catalyst, typically sodium hydroxide or potassium hydroxide. The result of reacting 100 pounds of oil or fat with 10 pounds of alcohol is approximately 100 pounds of biodiesel and 10 pounds of glycerin (DOE 2013).Typically, when biodiesel is produced for fuel, quality is standardized by limiting free glycerol and total glycerol where the values must be less than 0.02 and 0.24% by weight, respectively (Gerpen et al. 2004). However, it is not clear if such standards are necessarily in force in the context of coal preparation, since quality control measures could be different depending on the intended use of the biodiesel product.

Environmentally, the main benefits of biodiesel are generally regarded to be its biodegradability, non-toxicity, and renewability as energy source, making it "carbon neutral" (RyeBiofuels 2013). Other advantages include lower sulfur content and – particularly interesting for its use as an alternative coal collector – theoretically no aromatic content (Demirbas 2007). One of the drawbacks to using biodiesel is its incompatibility with rubber – it will eventually dissolve the rubber – which presents fouling issues in coal preparation facilities where rubber components (e.g., tubing or reactor liners) are common. Another mechanical issue with biodiesel is that it has the tendency to gel at low temperatures, especially biodiesel derived from animal fat (TriangleBiofuelsIndustries 2007). These mechanical issues mean that physical changes to the processing circuit may need to be made to switch from diesel to biodiesel, such as replacing rubber tubing or installing heaters near biodiesel storage tanks.

Since operating conditions will most likely be different when using biodiesel than it is using diesel, coal operators that have used diesel for many years may be resistant or unwilling to accept this new change. Another drawback of biodiesel, similar to that of diesel, is variability. The composition of biodiesel not only varies based on the refining process, but also on the type of oil or fat that is used (Gerpen et al. 2004). Biodiesel production also has very large water and land use requirements. A study in China showed that the land footprint of biofuel ranges from 2-28 m^2 of land per liter of fuel produced and the water footprint ranges from 1.5-15 m^3 of water per liter of fuel produced (Yang et al. 2009).

Other alternative collectors are available in addition to biodiesel such as pine-based products. Regarding production, the benefit of pine oil is that it is a byproduct of paper and tissue making (Hines et al. 2011). Information regarding production and performance of pine oil in the context of coal flotation is very limited; however, like diesel and biodiesel, variability in composition is presumably high, and performance is likely linked quite closely to operating parameters.

3.4 Analytical Methods

Measuring residual reagents in process water from coal preparation is a difficult undertaking given the range of potential compounds and relatively low concentrations that may be present. Thus, it is important to understand the processes by which these reagents are measured so that the results can be viewed with a better understanding of the challenges leading up to those results. Gas chromatography is a technique used to separate volatile substances from one another. In gas-liquid chromatography (referred to as "GC" here), the sample is injected into the chromatography column with a carrier gas, and the non-volatile solvent-coated column selectively partitions the sample components; the result is that elution of each component from the column occurs at a different time. By reference to known, characteristic elution times of compounds of interest, inference can be made regarding the compounds present in the sample.

To quantify compound proportions in the sample, gas "chromatographs" are utilized. As the sample elutes from the column, a detector then records the time at which components leave the column and the result is a chromatograph showing millivolts as a function of time. Ideally, each unique compound is represented by an individual peak, where the millivolt reading begins at zero, spikes, and then returns back to zero, granted there is adequate separation between peaks.

The separation between each peak is dictated by the retention time (i.e., the time corresponding to the substance's adherence to the column) and is a function of temperature, linear velocity of the carrier gas, and column type. The area under each peak is proportional to the concentration of that compound. Internal standards are used to help quantify compounds of interest by comparing the peak area of the internal standard to the peak area of the compound of interest. Gas chromatography is one of the most effective techniques of separating and quantifying compounds in an unknown gas or liquid (McNair and Bonelli 1968). There are multiple detectors that can be used with a GC, depending on the intended purpose.

3.5 Detection with Flame Ionization

For analysis of diesel and other alternative coal collectors like biodiesel, a flame ionization detector (FID) and a mass spectrometer (MS) are common. The FID functions with a hydrogen flame that burns the sample within the column, creating an electronic current from the ionic fragments and free electrons. The current is proportional to the concentration of sample because a sample with a higher carbon concentration contains more carbon to burn, which corresponds to a larger current (Ridgeon 2012). The FID is also reliable and has a high sensitivity; however, the chemistry of the compound only has a slight impact on the response (Haddad and MacMurphey 2006). FID is commonly used for quantification of ranges of organic compounds present in diesel (i.e., DRO).

Preliminary work for this thesis included screening the suitability for GC-FID to quantify residual alternative collector concentrations in flotation process waters; Appendix A shows an example of promising results for a high-purity biodiesel sample. Testing of several pine oil-derived collectors indicated that much more work in methods development would be needed to perform similar analyses for these collectors as that presented in this thesis for DRO.

3.6 Detection with Mass Spectrometry

The MS response on the other hand, is affected by the quantity and chemistry of the compound, making this a superior technique in determining the concentration of specific compounds. Because the response is affected by the chemistry of the compound, internal standards are typically used for each compound of interest to avoid quantification errors. For this reason the MS is better suited for quantification of compounds whereas the FID is better suited

for quantification of mixtures. With this being said, studies performed showed that for certain mixtures (i.e., TPH in soil samples), results appear similar between the MS and FID detectors (Haddad and MacMurphey 2006).

Two different modes can be used on a MS detector: Full Scan and selective ion monitoring (SIM). Full Scan mode is used to detect unknown compounds by comparing their mass to charge ratio over a given time duration (i.e., mass spectra) to that contained in a computer library. SIM mode can then be used to enhance the sensitivity by 10 to 100 times by only searching for specific compounds of interest. This is accomplished by searching for two to four ions per compound and the ratios of these ions represent a unique compound. Used in conjunction with one another, GC-MS Full Scan and SIM modes are highly effective tools for identification and quantification of trace compounds (ALS 2008).

3.7 Sample Preparation

Before a sample can be run on a GC-FID or GC-MS it must be concentrated and prepared in an acceptable solvent (e.g., hexane, but not water). This can be accomplished using a variety of techniques such as solid-phase micro extraction (SPME), solid-phase extraction (SPE), and liquid-liquid extraction (LLE) (Koning et al. 2008). The work described in this thesis deals primarily with SPE; however, LLE is also used. LLE selectively partitions the component of interest from the rest of the sample using two phases, or solvents. Sometimes multiple steps are required to increase recovery as well as using an additional solvent(s), which can be costly as well as time-consuming. The solvent is then evaporated to concentrate the analyte, but the large sample volume will increase the time required for this step (McDonald 2001). Along with these problems, LLE also requires the use of breakable glassware. For these reasons, particularly focusing on the amount of solvent and time required, SPE is the preferred method of separation (SigmaAldrich 1998).

Solid-phase extraction deals with the separation of a component of interest via two phases: a solid phase and a liquid, emulsion, gas, or supercritical fluid phase. The work described in this thesis deals with extraction between a solid and liquid phase. The partitioning between the two phases occurs when the analyte adsorbs to the solid phase or remains in the liquid phase. If the analyte adsorbs to the solid phase, a separate solvent is then used to elute the sample which is then concentrated by evaporation of the solvent. The principle of SPE is similar

to LLE, with the solid phase replacing one of the liquid phases. Problems can arise with SPE when the sample capacity of the cartridge is exceeded or liquid remains trapped in the solid phase (McDonald 2001). Flow rate can also impact the separation efficiency by not allowing the analyte sufficient interaction with the cartridge which can result in a low recovery (Waters 2009).

Different modes of extraction exist for SPE such as reversed phase and normal phase. Each of these modes utilizes the chemistry of the sample matrix and the analyte of interest. Reversed phase involves a polar sample matrix, a nonpolar stationary phase, and a nonpolar analyte whereas normal phase involves a nonpolar matrix, a polar stationary phase, and a polar analyte. The procedure used in this paper is reversed phase since the samples are in water, a polar phase, and the analytes, collectors comprised of hydrocarbons, are nonpolar. The recommended solvent used with this method for extraction is hexane, due to its non-polarity (SigmaAldrich 1998). The C18 cartridge was used in this paper for this separation mode because it contains a strongly hydrophobic phase and is recommended for measuring trace organics in environmental water samples (McDonald 2001).

The steps associated with SPE vary in terminology; however, the process is similar regardless of the cartridge manufacturer. For the work presented in this thesis, the first step is to wash the cartridge (i.e., run methanol through the cartridge, followed by hexane.) This process rids the cartridge of any potential contaminants. The next step is to condition the cartridge with methanol and then water. This process is to essentially wet the entire surface area of the cartridge, and without it, results would not be reproducible. The next step is to extract the sample by running the sample through the cartridge. The sample must be acidified prior to extraction; this is said to be done in order to prevent microbiological activity (Hach 2009) as well as to increase the capacity of the cartridge, which will help to avoid sample breakthrough. Most reversed-phase cartridges have a sample capacity of up to 100 mg, much larger than the sub-ppm levels observed in this testing (McDonald 2001). Finally, the last step in SPE is to elute the sample with hexane and concentrate by evaporation.

Sample size is one of the more difficult decisions for sample preparation by SPE. Based on experience gained through the research reported here, it is recommended that a sample size of 200 mL be used for future work, particularly for flotation test samples. A larger sample size results in better detection and quantification of analytes; however, the tradeoff is the time it takes

to prepare these samples. Fine particles may be able to pass through filter paper during dewatering, but the particles can become trapped in the cartridge used for SPE which makes it more difficult for liquid to pass. The pump pressure can be increased, but the rate at which liquid passes through the cartridge becomes increasingly difficult to maintain between cartridges. For these reasons, 200 mL samples have been determined to be a proper balance between tradeoffs.

At least one blank should always be extracted during SPE, but two blanks are recommended. Along with extracting a blank, it is advised that a standard solution (i.e., known concentration of diesel) be extracted as well in order to determine the extraction efficiency. In some tests reported here, a surrogate was also used with the intent of determining the extraction efficiency. However, it was determined that this method was not desirable for two reasons: 1) the surrogate chromatogram results interfered with the DRO results, and 2) without further testing, it is unclear whether or not the surrogate extraction efficiency corresponds to the DRO extraction efficiency.

When analyzing samples by GC, it is important to run hexane between each set of samples to ensure that the GC is clean and there is no carryover between samples; the hexane essentially purges the column of contaminants and resulting chromatograms can be utilized to confirm that compounds which may interfere with sample analysis are not present. If there are multiple GC users, and particularly if a variety of sample types are being analyzed on the same column, it is advised that the hexane purge be performed twice at the beginning of a sample run. It is also important to add an internal standard to each sample prior to analysis on the GC.

While sample area can be used to compare results to one another from the same GC run, it is also advisable to consider the internal standard since it can also be used to compare results from one sample run to another. If any variation of the equipment exists, the sample area relative to the internal standard area should remain consistent. For the work in this thesis, 20 μl of phenol-d6 was used as the internal standard. If an internal standard is not available the sample area can still be analyzed; however, this can reduce confidence in results, particularly when comparing one set of samples to another in cases where any conditions might change within the GC between runs.

3.8 Data Analysis and Challenges

Data analysis is probably the most difficult aspect of gas chromatography. It is important to achieve adequate separation efficiency between compounds if individual compounds are to be measured. Separation efficiency is dependent upon the column type, length, and temperature, and carrier gas and airflow rate (UMass ; UniversityofWashington). The sample size and injection time can also affect the results of the chromatograph, creating taller and wider peaks for larger samples and longer injection times, respectively (McNair and Bonelli 1968). A 30 m x 0.25 mm ID x 0.25 um film thickness Rxi-5sil MS with 5% diphenyl and 95% dimethyl polysiloxane column was used for the work described in this thesis. The FID uses hydrogen at 45 mL/min, air at 450 ml/min, and nitrogen as the make flow at 30 ml/min, while the carrier gas has a flow rate of 1 ml/min. The injector temperature is 250 ^{o}C and the GC begins timing at 40 ^{o}C and after three minutes increases by 10 ^{o}C per minute until reaching a final temperature of 300 ^{o}C after 29 min. The GC maintains this temperature for another six minutes and then the program ends.

The area under each peak is calculated by the computer based on the user defined baseline. Either a baseline can be drawn for each individual peak as shown in Figure 1.1 or one baseline can be drawn as shown in Figure 1.2. The challenge with drawing one baseline as shown in Figure 1.2 is that sometimes the peaks do not return to one baseline, so this can create user variability. To quantify the example shown, the total area calculated in Figure 1.1 is 5.75 mV•min whereas the total area calculated in Figure 1.2 is 11.15 mV•min. The advantage of drawing a baseline for each peak is that the variability is removed; however, this increases time. A method can be set up on the GC to draw the baseline for each peak, which removes the variability and ultimately decreases time required if many samples are going to be analyzed. The method parameters for this paper inhibit integration from occurring until after 10 minutes, and then the minimum area to be considered is 0.01 mV•min. The purpose for not integrating until after 10 minutes is so that neither hexane nor methylene chloride are calculated in the total area and results show that under the GC operating conditions, DRO do not elute from the column until after 10 minutes. The purpose for not considering areas less than 0.01 mV•min is to eliminate noise. The data in Chapters 2 and 3 were calculated using the user drawn baseline, but then after learning about the program method technique; this was used for calculating the data in Chapter 4.
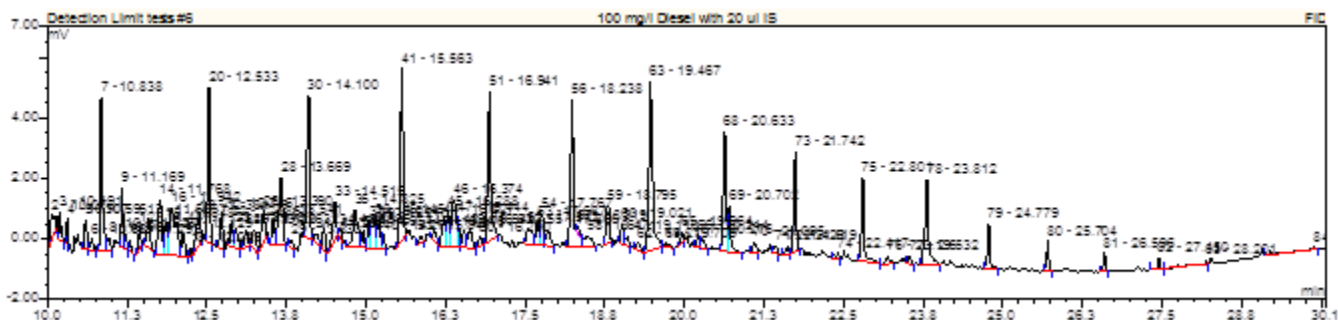
Figure 1.1: Diesel sample chromatogram using a baseline for each individual peak
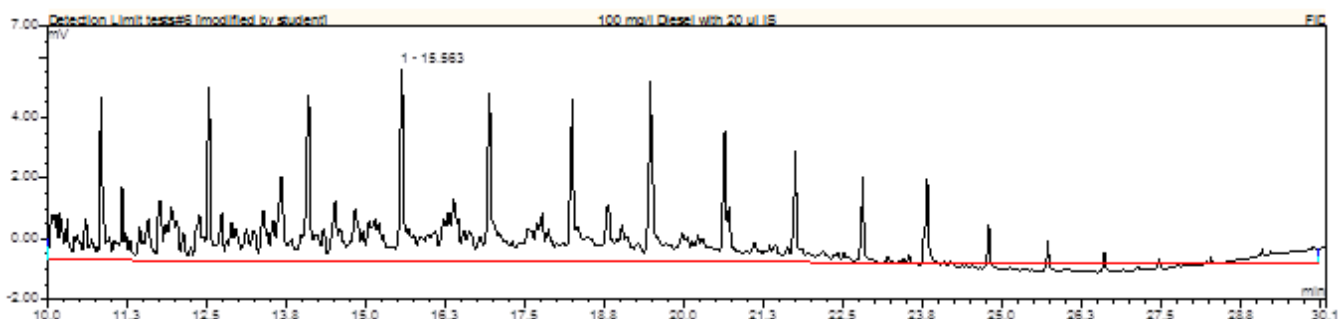
Figure 1.2: Diesel sample chromatogram using one baseline for all peaks

The unknown concentration of a sample is calculated based on its peak area relative to the peak area of a known concentration, typically that of a standard. Realistic detection limits are in the order of 0.01 mg/L for water samples containing dissolved organics (Senn and Johnson 1987). Detection limits for PAHs are more in the order of 0.1 µg/L for water samples. The challenge of accurately measuring small volumes of liquid makes quantitative analysis for gas chromatography difficult. Nonetheless, an internal standard should be used; one that is not present in the original sample and has a unique peak – one that is not interfered by other compounds (Jeffery et al. 1989). The internal standard used in this paper is phenol-d6 mixed with methylene chloride. Figure 1.3 shows a chromatograph of the internal standard along with diesel.
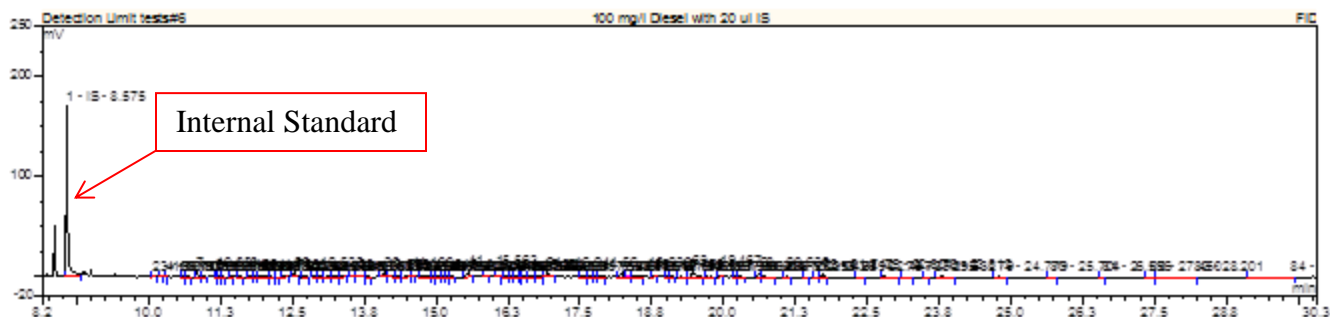
Figure 1.3: Chromatogram showing the internal standard and diesel

Chromatographs are qualitatively analyzed based on retention times, since each compound has a unique retention time. Typically a library is used to match compounds with the MS spectra. The best way to quantitatively measure a mixture of compounds is to first develop a calibration curve based on the ratio of the peak areas of the known concentration mixture to that of the internal standard. Then when a mixture's concentration is unknown its ratio of peak area to internal standard is compared to the calibration curve to determine a measured concentration (Jeffery et al. 1989). If an internal standard is not present, the peak area of the unknown mixture can simply be compared to the calibration curve based on the peak areas for mixtures of known concentrations. This is not the preferred method since the internal standard is used to help alleviate any changes that may exist within the GC between runs.

4. Conclusions

Water quality is an issue of increasing concern for the coal mining industry. Although processing reagents have not previously been scrutinized for environmental transport and fate, it is an important topic requiring further research for reasons previously stated, particularly regarding PAHs. While external research is underway regarding the performance of renewable and biodegradable collectors, the tests described in this thesis for diesel as a collector can be used as a guideline for future test work using these new, alternative collectors. The analytical techniques described in this chapter can also be adapted to test for other organic processing reagents in water samples.

5. References

Abraham, M., Autenrieth, R. and Dimitriou-Christidis, P. (2005). "The estimation of physicochemical properties of methyl and other alkyl naphthalenes." The Royal Society of Chemistry 2005(7): 5.

Adel, G. (2012). Particulate Process Modeling. 2.1.1 Examples of Particulate Processes, Department of Mining and Minerals Engineering.

ALS. (2008). "GC/MS-Full Scan vs GC/MS-SIM." 2012, from http://www.caslab.com/News/gcms-full-scan-vs-cgms-sim.html.

AMMA. "Diesel Fuel." Retrieved January 16, 2013, 2013, from http://www.miningoilgasjobs.com.au/Oil-Gas-Energy/Hydrocarbons-and-Energy/Hydrocarbons/Oil-and-Gas/Downstream/Diesel-Fuel.aspx.

ATSDR (1995) "Fuel Oils - Chemical and Physical Information." 105-109.

ATSDR (1999). Total Petroleum Hydrocarbons - Identity and Analysis of Total Petroleum Hydrocarbons. Atlanta, Georgia, Agency for Toxic Substances and Disease Registry: 315.

ATSDR. (2009). 2012.

ATSDR (2009). Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs): 68.

Bratton, R. and Luttrell, G. H. Environmental Practices for Coal Preparation Plants.

Coffey, A. and Lambert, N. (2008). Development of an Online Residual Frothing Propensity Detector. 12th Australian Coal Preparation Society Conference. Sydney, Australia.

Demirbas, A. (2007). "Importance of biodiesel as transportation fuel." Energy Policy 35(2007): 10.

DEP (2002). Historical Oil Contamination Travel Distances in Ground Water at Sensitive Geological Sites in Maine, Bureau of Remediation & Waste Management: 7.

DEP, M. (2002). Rules for Underground Oil Storage Facilities. 691. United States, Maine DEP.

DOE. (2013). "Biodiesel Production and Distribution." 2013, from http://www.afdc.energy.gov/fuels/biodiesel_production.html.

Ducatman, A., Ziemkiewicz, P., Quaranta, J., Vandivort, T., Mack, B. and VanAken, B. (2010). Coal Slurry Waste Underground Injection Assessment. Final Report: Phase II. Morgantown, WV, West Virginia University: 261.

EPA (2003) "Nonhalogenated Organics using GC/FID." 1-37.

EPA (2011). 2011 Edition of the Drinking Water Standards and Health Advisories. Washington, DC, Office of Water: 18.

Eraydin, M., Zhang, J. and Blubaugh, S. (2012). Separation Technologies for Minerals, Coal, and Earth Resources, SME.

Gerpen, J., Shanks, B., Pruszko, R., Clements, D. and Knothe, G. (2004). Biodiesel Analytical Methods. Golden, Colorado, Midwest Research Institute: 100.

Hach. (2009). "Product - Xenosep - FAQ." 2013, from http://www.hach.com/xenosepguide-faq.

Haddad, R. and MacMurphey, J. (2006). TPH Measurements. The Advantage of Using GC/MS, ENTRIX, Inc.

ZymaX envirotechnology, inc: 5.

Hessell, E., Abramshe, R. (2003). "Alkylated Naphthalenes as High-Performance Synthetic Fluids." Journal of Synthetic Lubrication 20: 14.

Hines, J., Dopico, P. and Kennedy, D. (2011). Novel Coal Collector Derived from Pine Tree Pulping. SME Annual Meeting. Denver, CO, SME: 3.

Hines, J., Kennedy, D. and Hurd, P. (2009). Method for the Beneficiation of Coal. U. S. P. a. T. Office. United States, Georgia-Pacific Chemicals, LLC: 8.

Hines, J., Kennedy, D. and Hurd, P. (2009). Method for the Froth Flotation of Coal. U. S. P. a. T. Office. United States, Georgia-Pacific Chemicals LLC.

Hourani, M., Hessell, E., Abramshe, R., Liang, J. (2007). "Alkylated Naphthalenes as High-Performance Synthetic Lubricating Fluids." Tribology Transactions 50: 6.

Howard, P. H. (1993). Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Chelsea, MI, Lewis Publishers.

Irwin, R., VanMouwerik, M., Stevens, L., Seese, M. and Basham, W. (1997) "Environmental Contaminants Encyclopedia Entry on Alkyl PAHs (Alkyl Homologs of PAHs)." 18.

Irwin, R., VanMouwerik, M., Stevens, L., Seese, M., Basham, W. (1997) "Environmental Contaminants Encyclopedia C4-Naphthalene Entry." 26.

Jeffery, G., Bassett, J., Mendham, J. and Denney, R. (1989). Vogel's Textbook of Quantitative Chemical Analysis. New York, John Wiley & Sons, Inc.

Knapp, J. M. S. (1990). A Study of Flotation Froth Behavior. Master of Science, Virginia Polytechnic Institute and State University.

Koning, S., Janssen, H. and Brinkman, U. (2008). "Modern Methods of Sample Preparation for GC Analysis." Chromatographia 2009(69): 46.

Lahey, A. and Clarkson, C. (1999). Development of Automatic Control Techniques for New Flotation Technologies. C Clarkson & Associates Pty Ltd.

Laskowski, J. (2001). Developments in Mineral Processing. Amsterdam, The Netherlands, Elsevier Science B.V.

Lee, B. and Vu, V. (2010). Sources, Distribution and Toxicity of Polyaromatic Hydrocarbons (PAHS) in Particulate Matter, InTech.

Liu, G. J., Niu, Z. Y., Niekerk, D. V., Xue, J. and Zheng, L. (2008). "Polycyclic aromatic hydrocarbons (PAHs) from coal combustion: emissions, analysis and toxicology." Reviews of Environmental Contamination and Toxicology(192): 1-28.

Lu, T., Eng, P. and Laman, G. (2012). A Preliminary Comparison of Coal Classification and Processing between Canada and China. 44th Annual Meeting of the Canadian Mineral Processors. Ottawa, Canada, Canadian Institute of Mining, Metallurgy, and Petroleum (CIM): 13.

McDonald, P. (2001). A Sample Preparation Primer and Guide to Solid Phase Extraction Methods Development. P. McDonald and E. Bouvier, Waters Corporation: 83.

McIntyre, D. G. F. (1974). Mineral Processing Chemicals Operational Mechanisms and Environmental Effects. AIME Meeting. Dallas, Texas: 20.

McNair, H. and Bonelli, E. (1968). Basic Gas Chromatography, Varian.

Morris, J., Sarver, E. and Luttrell, G. (2013). Diesel Range Organics In Coal Preparation. Environmental Considerations in Energy Production. J. Craynon. Charleston, WV, SME: 11.

MSHA. (2009). 2012.

Nave, R. "Surface Tension."   Retrieved 03/22/2012, 2012.

NBB. (2013). "Biodiesel Basics." 2013, from http://www.biodiesel.org/what-is-biodiesel/biodiesel-basics.

Pitt, G. J. and Millward, G. R. (1979). Coal and Modern Coal Processing: An Introduction. New York, New York, Academic Press Inc.

Pugh, R. J. (1996). "Foaming, foam films, antifoaming and defoaming." Advances in Colloid and Interface Science 64: 76.

Ridgeon, P. (2012). "How Does Gas Chromatography Work?" Retrieved March 11, 2013, 2013, from http://www.anatune.co.uk/about/how-does-gas-chromatography-work.

RyeBiofuels. (2013). "BioDiesel FAQs." 2013, from http://www.ryebiofuels.co.uk/bio-diesel-faq/.

SCF (2002). Polycyclic Aromatic Hydrocarbons - Occurrence in foods, dietary exposure and health effects. Brussels, Belgium, European Commission.

Scheepers, P. and Bos, R. (1992). "Combustion of diesel fuel from a toxicological perspective. II. Toxicity." Int Arch Occup Environ Health 64(3): 163-177.

Schein, A., Scott, J., Mos, L. and Hodson, P. (2008). "Oil Dispersion Increases the Apparent Bioavailability and Toxicity of Diesel to Rainbow Trout (Oncorhynchus Mykiss)." Environmental Toxicology and Chemistry 28(3): 8.

Scott, J. H. (1976). Coagulation Study of a Bound Water Bulked Sludge. Master of Science, Virginia Polytechnic Institute and State University.

Senn, R. and Johnson, M. (1987). "Interpretation of Gas Chromatography Data as a Tool in Subsurface Hydrocarbon Investigations." Groundwater Monitoring & Remediation 7(1): 6.

SigmaAldrich (1998). Guide to Solid Phase Extraction, Sigma Aldrich: 12.

Sweet, C., Hoogstraten, J. V., Harris, M. and Laskowski, J. S. (1997). The Effect of Frother on Bubble Size and Frothability of Aqueous Solutions, Processing of Complex Ores. The 2nd UBC-McGill Int. Symposium, Montreal, Canada, Metallurgical Society of CIM.

Szwilski, T. (1986). Mining, Our Own Business: Small Underground Coal Operations. SME Annual Meeting. New Orleans, LA: 3.

TriangleBiofuelsIndustries. (2007). "Am I Ready for Biodiesel?", 2013, from http://www.trianglebiofuels.com/faq.php.

UMass. "Factors Affecting the Separation in the GC." 2013, from http://www.chem.umass.edu/~samal/269/lecture/cyc/cyc10.pdf.

UniversityofWashington GC Columns: Factors affecting retention and separation, University of Washington: 1.

USEPA. (1999). 2012.

Valdes, A. and Garcia, A. (2005). "On the utilization of waste vegetable oils (WVO) as agglomerants to recover coal from coal fines cleaning wastes (CFCW)." Fuel 85(2006): 8.

Wang, Z., Hollebone, B., Fingas, M., Fieldhouse, B., Sigouin, L., Landriault, M., Smith, P., Noonan, J. and Thouin, G. (2003). Characteristics of Spilled Oils, Fuels, and Petroleum Products: 1. Composition and Properties of Selected Oils.

Waters (2009). Care and Use Manual. Milford, MA, Waters Corporation: 6.

Watts, R. J. (1998). Hazardous Wastes: Sources, Pathways, Receptors. New York, NY, John Wiley and Sons.

Wick, A., Haus, N., Sukkariyah, B., Haering, K. and Daniels, W. (2011). Remediation of PAH-Contaminated Soils and Sediments: A Literature Review. Blacksburg, VA, Virginia Polytechnic Institute and State University: 102.

Wills, B. (2006). Wills' Mineral Processing Technology. Burlington, MA, Elsevier Ltd.

WV-DEP (2009). An Evaluation of the Underground Injection of Coal Slurry in West Virginia. Phase I: Environmental Investigation.

Yang, H., Zhou, Y. and Liu, J. (2009). "Land and water requirements of biofuel and implications for food supply and the environment in China." Energy Policy 37(2009): 10.

2   REAGENTS IN COAL PREPARATION: WHERE DO THEY GO?

Josh Morris, Emily Sarver, Gerald Luttrell, John Novak

1. Abstract

A variety of reagents are utilized in coal preparation, but aside from performing their desired function relatively little is known about the behavior of these reagents within the processing circuits. Where exactly do reagents go once dosed? In this paper, we present preliminary results of partitioning studies on frother (i.e., MIBC) and collector (i.e., petro-diesel) chemicals commonly used in coal flotation, and examine implications for water management (e.g., in closed-loop systems). Additionally, we discuss the usefulness of such data in predicting environmental transport and fate of chemicals − which is currently a top priority for industry.

2. Introduction

The purpose of coal preparation is to upgrade mined coal into more valuable products. Since coal is primarily used as a fuel source for electricity generation, product specifications are typically contracted to minimize unwanted constituents that detract from the overall heat value (e.g., ash and moisture) or that add to environmental pollution or other problems like corrosion at a power plant (e.g., sulfur) (Pitt and Millward 1979). Failure to meet specifications results in a financial penalty for the coal producer (Szwilski 1986), and thus preparation processes have evolved to simultaneously optimize recovery of valuable "clean" coal with rejection of mineral matter and moisture. In addition to advancements in equipment and circuitry, development and application of various chemical reagents has dramatically improved the performance of coal preparation processes.

Contemporary preparation plants typically include multiple circuits that can be categorized by the size of particles they process: coarse, intermediate, and fine/ultra-fine (Figure

2.1). Coarse and intermediate circuits generally rely on size classification and gravity separations (e.g., dense-media cyclones), and do not require significant chemical reagents. However, fine and ultra-fine circuits often use froth flotation to separate coal from impurities, which requires chemical additives (Table 2.1). The primary additives include collectors, which coat the surface of the coal particles to render them (more) hydrophobic and thus more likely to attach to air bubbles and float; and frothers, which aid in the formation and stability of the froth that will accumulate the floated coal particles. Modifiers are also commonly added to flotation circuits to regulate pH in instances where coal or impurity characteristics may change water chemistries (Laskowski 2001). Following flotation, coagulants and flocculants are often utilized in solid-liquid separations (i.e., dewatering or clarification) for coal products, and for tailings slurries prior to their disposal in impoundments. Coagulants function via double-layer compression[1] to bring colloidal particles together, while flocculants promote bridging between the grouped colloids – and the combined result is enhanced sedimentation (Wills 2006). Defoaming or anti-foaming agents may also be required to avoid fouling of dewatering operations.

---

[1] Double-layer compression refers to the action of added ionic species on the electrical double layer surrounding a colloid or fine particle. In the case of negatively charged coal, the addition of a cationic coagulant effectively reduces the (repulsive) electrostatic forces between particles such that Van Der Waals' forces may attract the particles together Scott, J. H. (1976). Coagulation Study of a Bound Water Bulked Sludge. Master of Science, Virginia Polytechnic Institute and State University..
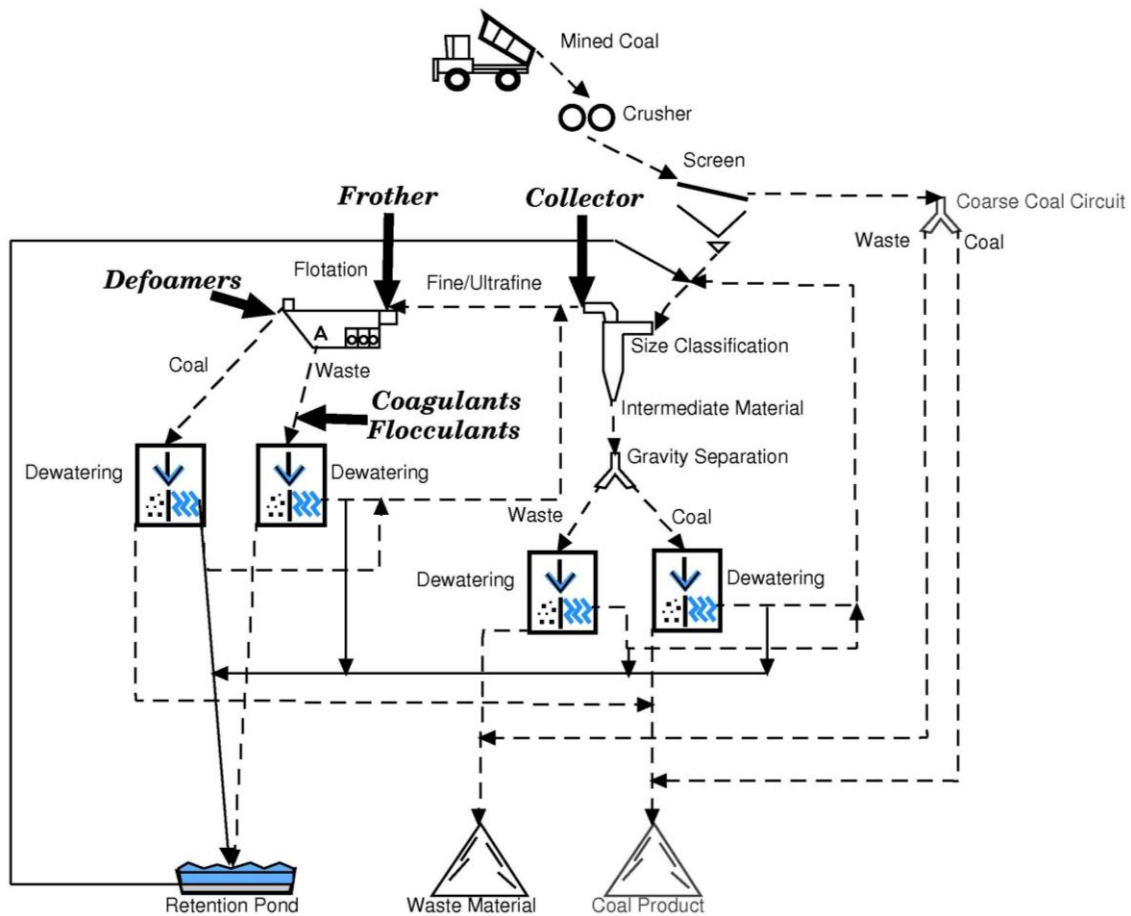
Figure 2.1: Simple processing circuit with typical reagent addition points

Conventional development and application of coal processing chemicals have been predominantly driven by economic motivations (e.g., to meet contract specifications, to reduce reagent costs, etc.). However, growing trends in corporate environmental and social responsibility provide a basis for more holistic approaches. In addition to understanding the effects of reagents on coal recoveries and yields, it is becoming increasingly important to understand potential effects on environments and communities. To do so, a number of important questions must be addressed: What transport mechanisms may introduce reagents into environmental media? What are the potential fates of these reagents? Do they pose risks to human or ecosystem health? Furthermore, with increased efforts to minimize net environmental impacts, a new challenge for the coal industry is to operate completely closed water loops. Given current circuit designs, will reagents have any effects on preparation plant efficiency?

The goal of this paper is to begin answering these questions. The following sections review the potential fates and impacts of coal preparation reagents, and present preliminary data regarding the partitioning of frothers and collectors between coal and process water.

Table 2.1: Common reagents in coal preparation (McIntyre 1974; Knapp 1990; Pugh 1996; Laskowski 2001)

Type	Group	Reagent
Collectors	Hydrocarbons	Fuel Oil No. 1 - Kerosene
		Fuel Oil No. 2 - Diesel
		Fuel Oil No. 6
Frothers	Aliphatic Alcohols	Methyl Isobutyl Carbinol (MIBC)
	Polyglycols	DF 250
	Hydroxylated Polyethers	Dowfroth M150
		Nalco 8836
		Polyoxyl Sorbitan Monolaurate (PSM)
Modifiers	Promoters	NaCl
		$CaCl_2$
		Na_2SO_4
	pH Regulators	H_2SO_4
		CaO
Dewatering/Clarification Reagents	Coagulants (cationic)	Organic Starches
		Inorganic Salts
		Polyamines
	Flocculants (non-ionic)	Organic Starches
		Polyacrylamide
	Flocculants (anionic)	Organic Starches
		Acrylamide/Acrylate Copolymers
		Polyacrylates
Defoaming Reagents	Defoamers	Tributyl Phosphate (TBP)
		Polydimethylsiloxane (PDMS)

3. Reagent Fates and Implications

Determining the fate of coal processing reagents necessitates tracking those reagents from their addition points in a preparation plant (e.g., Table 2.1) to some ultimate destination. Based on a simple materials balance approach, only a fixed number of possibilities exist for reagents leaving the plant: they may end up with the clean coal products, with the tailings by-products, or with recycled water, or they may be lost (e.g., via volatilization or spills).

3.1 Environmental Fate and Transport

The environmental fate and transport of processing reagents has been scarcely examined. It is generally expected that collectors (e.g., petro-diesel) substantially partition to coal products because their chemistry promotes sorption to the coal particles (Watts 1998). Any collector that does not sorb may remain with water, either floating on the water surface, as an emulsion, or as a dissolved species – although water solubility is likely low. Frothers, on the other hand, are not expected to significantly sorb to coal (or other solids), and thus should follow water streams. Alcohol-based frothers like MIBC tend to have relatively low water solubility and low to moderate volatility (Howard 1993), which indicate that they may remain at the water-air interface; whereas glycol-based frothers like Dowfroth M150 are much more soluble in water and are relatively non-volatile. Coagulant and flocculant reagents are of course expected to partition to fine coal or tailings particulates, at least in the short-term. These chemicals may well remain with dewatered coal products; but in the case of reagents associated with tailings solids, it is difficult to predict how they might react or mobilize under disposal facility conditions.

Reagents that partition to coal products are likely to be combusted with the coal – unless they volatilize during handling and transport. The combustion by-products of the reagents may enter the atmosphere as either gaseous or particulate emissions, which may then be returned to the earth via either wet or dry deposition. In the case of petro-diesel collector (termed "diesel" in this paper), for example, it is expected that much of the alkane fraction[2] will be completely combusted and converted to carbon dioxide and water; however, PAHs that occur naturally in the diesel or that form as a result of incomplete combustion might also be released.[3] In addition to atmospheric emissions, reagents or combustion by-products of reagents might become part of the solid fly ash (i.e., waste from coal combustion) and eventually disposed (e.g., in landfills), either because the reagents were associated with the mineral fraction (i.e., noncombustible) of the coal or because their aerosols were scrubbed from flue gases. In the example of diesel

---

[2] Diesel is not a specific compound, but rather a range of compounds collected from fractional distillation of petroleum (i.e., between 200-400 °C). Its general composition includes primarily moderate weight alkanes (i.e., C_{15}-C_{25}), and also cycloalkenes and polyaromatic hydrocarbons (PAHs) Watts, R. J. (1998). Hazardous Wastes: Sources, Pathways, Receptors. New York, NY, John Wiley and Sons..

[3] PAHs are an environmental concern because they pose human and ecological health risks ATSDR. (2009). 2012.. However, the bioavailability of PAHs derived from diesel combustion is not well understood Scheepers, P. and Bos, R. (1992). "Combustion of diesel fuel from a toxicological perspective. II. Toxicity." Int Arch Occup Environ Health 64(3): 163-177..

collector that partitions to coal products, this is another likely scenario for some PAHs (Liu et al. 2008). Following atmospheric deposition or disposal of fly ash, coal processing reagents or their by-products could move through terrestrial and aquatic ecosystems via hydraulic or biologic transport processes.

For reagents that partition to either the water or solid fractions of coal tailings, environmental fate and transport is heavily dependent on the tailings disposal conditions. If tailings are disposed via underground injection, reagent fate will be governed by chemical conditions of the storage cavity (i.e., atmosphere, water chemistry, and wall rock mineralogy); and reagent transport will depend on the degree to which groundwater interacts with the cavity. More often, tailings are disposed above ground in impoundments or ponds, where the water fraction is expected to clarify as the solid particles slowly settle. Some of the water is generally recycled back to the preparation plant and used as make-up water, but a portion of it is released to the environment via evaporation, engineered discharges (i.e., through decant structures or spillways) (MSHA 2009), or percolation to the subsurface since impoundments for coal refuse are rarely lined (USEPA 1999). If reagents or reagent by-products are present in impoundments, water releases could possibly mobilize them. Other possibilities include photo- or bio-degradation within the impoundment (e.g., MIBC), or sorption to soils beneath the impoundment (e.g., diesel).

In the context of environmental fate and transport, it is also important to note that coal processing reagents are seldom pure products with constant composition. For instance, diesel can vary with the properties of the petroleum feedstock used to produce it, and some frother reagents are actually acquired as by-products from the manufacture of other products (e.g., brake fluids). While variability in reagent quality will not be discussed in detail here, it is a topic that deserves further attention.

3.2 Residuals in Operations

In addition to tracking processing reagents to better understand environmental implications, it is becoming increasingly important to understand implications for preparation plants that utilize large volumes of recycled water. Use of closed water systems (i.e., zero discharge from site) is growing in response to calls for both water efficiency and water resource protection. For coal preparation facilities, such systems generally combine the plant and tailings

water circuits, such that "clear" water from an impoundment is recycled back to the plant as makeup water. Water may also be recycled within the plant (e.g., from the coal product thickener back to cyclone or flotation circuits).

To the extent that processing reagents (or their by-products) remain in the recycled water, chemical concentration may have significant impacts on plant operation. While residual chemicals could potentially reduce the rate of new chemical addition in some cases, it is also possible that reduced efficiency or fouling of some unit processes may occur. For example, residual frothers may impact processes that cause significant agitation (e.g., dense media cyclone separations) (Lahey and Clarkson 1999), or where water chemistry promotes foaming (e.g., where recycling has caused increased salt concentrations). Even at sites where only a portion of water is recycled throughout the plant, it is already well established that such problems lead to preventative under-dosing of frother in flotation circuits, which in turn sacrifices recovery of fine coal (Coffey and Lambert 2008). For closed water systems, the implications may be far more significant, and additional water treatment efforts might be required to maintain efficient operations.

In light of the environmental and operational implications of processing reagent fates, it is important to understand how they partition between solid and liquid fractions in preparation plants.

4. Experimental Methods

Partitioning studies were carried out to obtain preliminary data on the potential fates of common frother and collector reagents for fine coal flotation[4]. The frothers were MIBC, polyoxyl sorbitan monolaurate (PSM), Dowfroth M150, and Nalco 8836, and the collector was diesel. Raw coal samples were ground using a laboratory hammer mill, and sized by wet screening for the desired test conditions (Tables 2.2 to 2.4). Full proximate analysis was not conducted on any of the raw coal samples, however approximate ash contents were determined (see below). For each test, a slurry sample was prepared by adding the required weight of sized raw coal to distilled water, followed by the required volume of reagent. Slurries were mixed for a

---

[4] The frother partitioning tests were partially reported in an MS thesis (Knapp, 1991), but have not been published elsewhere.

specified contact time, and then the coal particles were separated from the water by either centrifuging or filtration. Finally, the water was then analyzed for residual reagent.

It should be noted that range of test conditions (i.e., frother and collector dosages, and coal slurry solid to liquid ratios) included in this work is much wider than that which may be encountered in practice. This is because as a major objective here was to determine under what conditions the processing reagents would sorb to coal versus remain in water, and vice versa. For the purpose of making relative comparisons, a froth flotation circuit in a typical coal preparation plant might operate with coal slurries of 1-10% solids (by weight), which require 4-20 µL/L frother (usually specified in mg/L; ~5-25 mg/L) and 1.5-150 µL/L (usually specified in lb/ton of coal; ~0.5-5 lb/ton).

4.1 Frother Partitioning

For the frother partitioning tests, coal samples were obtained from the Elkhorn #3 and the Cedar Grove seams (both <5% ash), and were sized to -100 mesh prior to testing. Slurries were mixed for five minutes by rapid stirring in open beakers, and then centrifuged for three minutes. To analyze the relative amount of frother left in the clear water fraction of the slurry, surface tension measurements were conducted using a Fisher surface tensiometer. The tensiometer utilizes a platinum-iridium ring, and measures the force required to detach this ring from the liquid surface. The ring was thoroughly cleaned between tests by immersing it in benzene, then acetone, and finally passing it through a flame to remove of any surface contaminants. Glassware was also thoroughly cleaned between tests by washing with chromic acid solution and distilled water.

4.2 Collector Partitioning

For the collector partitioning tests, two separate raw coal samples were obtained: one from the Hagy Seam (~ 35% ash), and one from Pocahontas Seam (~ 16% ash). The former sample was sized to -100 mesh for the first set of tests, and then a subsample of that material was screened to 100 x 150 mesh for the second set of tests. The later sample was only used in the second set of tests, and was also screened to obtain 100 x 150 mesh particles. For the first set of tests, slurries were mixed in a kitchen blender for four minutes and then centrifuged until the water was clear; however, it should be noted that a large amount of colloidal matter in these

28

samples prevented removal of all color from the water. In the second set of tests, the slurries were mixed in open flasks on a shaking table for four minutes, and then filtered (through 25 μm paper) using a vacuum pump. The residual diesel in the clear water fraction from each test was analyzed using an Agilent 5890 gas chromatograph equipped with a flame ionization detector (GC-FID), by following EPA Method 3150 for quantifying diesel range organics (DRO) in water samples.

Table 2.2: Experimental conditions for frother tests

Test	Coal Seam	Coal Dosage (wt. % solids)	Frother Type	Frother Dosage (μL/L)
1-18	Elkhorn #3	0, 0.1, 0.5, 0.7	M150	0.4[a], 4, 40, 400, 4000
19-34	Elkhorn #3	0, 0.1, 0.5, 0.7	PSM	4, 40, 400, 4000
35-48	Elkhorn #3	0, 0.1, 0.5, 0.7	Nalco 8836	4, 40[b], 400, 4000
49-60	Elkhorn #3	0, 0.1, 0.5, 0.7	MIBC	10, 100, 1000
61-64	Cedar Grove	0.5	M150	4, 40, 400, 4000
65-68	Cedar Grove	0.5	PSM	4, 40, 400, 4000
69-72	Cedar Grove	0.5	Nalco 8836	4, 40, 400, 4000
73-75	Cedar Grove	0.5	MIBC	10, 100, 1000

[a] Only for 0 and 0.1% solids
[b] Only for 0 and 0.5% solids

Table 2.3: Experimental conditions for first set of collector tests

Test	Coal Seam	Coal Dosage (wt. % solids)	Diesel dosage (lb/ton coal)	Diesel dosage (mg/L)	Solid/Liquid Separation	Residual DRO (mg/L)
1	Hagy	0	N/A	500	Centrifuge	425.1
2	Hagy	1	0	0	Centrifuge	<0.05
3	Hagy	1	1	4.9	Centrifuge	0.39
4	Hagy	1	1	4.9	Centrifuge, then filtration	0.42
5	Hagy	1	1	4.9	Filtration	0.46
6	Hagy	1	10	50	Centrifuge	0.68
7	Hagy	5	0.25	6.3	Centrifuge	0.50
8	Hagy	5	1	25	Centrifuge	0.53
9	Hagy	5	10	250	Centrifuge	0.95

Table 2.4: Experimental conditions for second set of collector tests

Test	Coal Seam	Coal Dosage (wt. % solids)	Diesel dosage (lb/ton coal)	Diesel dosage (mg/L)	Solid/Liquid Separation	Residual DRO (mg/L)
10	Pocahontas	0	N/A	0.85	N/A	1.35
11	Pocahontas	0	N/A	0.425	N/A	0.63
12	Pocahontas	1	0.17	0.85	Filtration	0.42
13	Pocahontas	10	0.017	0.85	Filtration	0.31
14	Pocahontas	5	10	250	Filtration	0.47
15	Pocahontas	5	10	250	Filtration	0.40
16	Pocahontas	5	10	250	Filtration	0.50
17	Pocahontas	5	10	250	Filtration	0.51
18	Pocahontas	5	10	250	Filtration	0.47
19	Pocahontas	5	10	250	Filtration	0.42
20	Pocahontas	1	50	250	Filtration	0.79
21	Pocahontas	5	50	1250	Filtration	1.02
22	Pocahontas	10	50	2500	Filtration	1.92
23	Pocahontas	5	1	25	Filtration	0.49
24	Hagy	5	10	250	Filtration	0.88
25	Hagy	5	50	1250	Filtration	2.67

5. Results and Discussion

Results of the partitioning tests confirmed that, in general, frother and collector reagents do not partition completely to either the solid or liquid fraction of a coal slurry − and therefore it is possible that, to some extent, these reagents may end up in coal products, tailings impoundments and in recycled water.

5.1 Frother Adsorption

The surface tension results for varying frother dosages and varying coal slurries are shown in Figure 2.2. The dashed horizontal line at 72.8 dyne/cm represents the theoretical surface tension of pure water (Nave); the bold line shows the measured surface tension for frother only (no coal added). For all frothers, it appears that the reagent tends to sorb somewhat to the coal surface. This can be seen most clearly at moderate test dosages (i.e., 40-400 μL/L),

where a significant difference was observed in surface tension between tests with frother only and tests with frother and coal. As expected, more frother generally tended to sorb to coal when more coal was present (i.e., 0.7% vs. 0.1% solids).

At very high dosages (i.e., 1000-4000 µL/L), the effect of the coal becomes less significant for MIBC and Dowfroth M150, and nearly insignificant for PSM and Nalco 8836. This indicates that sorption sites on the coal surface may be completely filled, and thus most of the frother remains in the water. At very low test dosages (i.e., 4 µL/L), the PSM exhibits seemingly complete sorption to the coal particles, as the surface tension when coal is present is effectively that of pure water, as compared to substantially less with frother only. The Dowfroth M150 also exhibits significant sorption to the coal at very low dosages, although the surface tension is slightly less than that of pure water (for the 0.5 and 0.7% coal tests), which suggests that some frother did not sorb. At very low dosages of MIBC and Nalco 8836 (i.e., 10 and 4 µL/L, respectively), it is uncertain to what extent the coal particles were able to sorb frother because the frother did not depress the surface tension of the water. This highlights a major shortcoming of the use of surface tension measurements to study frother reagents, which has been previously noted by other researchers (Sweet et al. 1997).

Coal properties were found to play a role in the sorption behavior of PSM and MIBC. As evident in Figure 2.2, at equal levels of slurry solids (i.e., 0.5% coal), the Cedar Grove coal did not appear to significantly sorb these frothers, whereas the Elkhorn #3 coal did. However, the sorption behavior of the Dowfroth M150 and Nalco 8836 was observed to be quite similar between the two coals. Since proximate analysis was not performed on the coal samples, it is difficult to speculate on specific explanations for these results; but coal properties (other than particle size) do seem to be important in terms of frother sorption capacities.

In the context of a coal preparation plant, the results from these tests indicate a significant degree of frother sorption to coal surfaces can be anticipated. While practical conditions include only the low to very low ranges of frother dosages tested here, they typically have higher slurry solids contents, and thus higher coal surface areas – which suggests that perhaps a relatively large fraction of frother reagents may associate with the coal. Given that frothers are well known to cause problems via entrainment in recycled water, there may be several plausible explanations for the findings presented here: 1) frother sorption to coal may only be temporary, and desorption may occur downstream of flotation processes (e.g., during dewatering); 2) the presence of other

reagents, particularly collectors, may substantially interfere with frother sorption to coal; and 3) the experimental conditions (e.g., mixing, effective contact time) used here may not be representative of plant conditions. Considering these, the sorption mechanisms of frothers to coal and tailings particles is deserving of further study. If, for example, frothers are identified which sorb strongly to coal through flotation and dewatering, this may have significant implications for reducing fouling of process circuits in closed water systems, as well as reducing environmental releases through tailings impoundments. For frothers that do not sorb to and remain with coal, novel water treatment strategies may be devised to remove these reagents from water prior to recycling or environmental discharges.
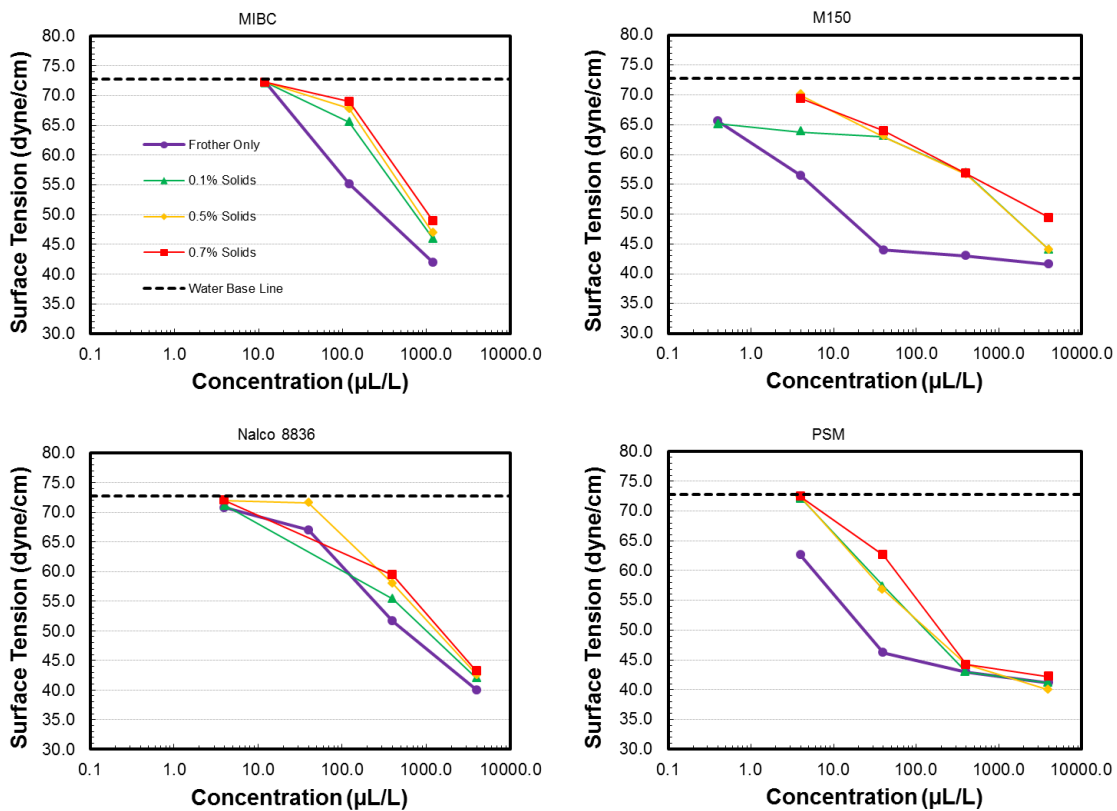
Figure 2.2: Surface tension versus varying dosage levels of frother and coal

5.2 Collector Adsorption

DRO results (i.e., the residual DRO in the clear water fractions of tested coal slurries) are presented in Tables 2.3 and 2.4 for all test conditions. The most striking observation is that there is some low level of DRO in every test, despite the addition of even large amounts of coal (i.e.,

10% solids). For instance, tests 12 and 13 clearly show that at relatively high solids content (i.e., 1 and 10%, respectively) and very low dosages of diesel (i.e., <1 mg/L; or 0.17 and 0.017 lb/ton, respectively), about 0.3-0.4 mg/L DRO remains in the water fraction of the slurry. Moreover, the level of DRO does not change dramatically between tests, considering the extreme changes in diesel and coal dosages. In test 20, for example, which had the same amount of coal but nearly 300x more diesel added than test 12, the DRO concentration was only about 2x higher than that of test 12 (i.e., 0.79 vs. 0.42 mg/L, respectively). And in test 22, which had the same amount of coal but nearly 3000x more diesel added than in test 13, the DRO concentration was only increased by about 6x (i.e., 1.92 vs. 0.31 mg/L, respectively). These results seem to indicate that a small amount of diesel (~0.3 mg/L or less) is always soluble in the water, but that the coal particles have a *very* high adsorption capacity for the diesel that is not dissolved. Another factor that may have been at play here is the possible presence of colloidal matter in the water fraction of the slurries; if diesel sticks to the colloids, it would likely be measured as DRO. However, it is important to note that, no matter what the reason, these tests indicate that a small amount of diesel will effectively partition with water in a flotation circuit.

Figure 2.3 highlights other specific observations in the collector partitioning tests. In the far left plot, the effect of solid-liquid separation technique on the results is shown. The three tests (#s 3-5) were conducted using identical slurries (i.e., % coal solids and diesel dosage), but one was centrifuged, one was filtered, and the other was centrifuged and then filtered. DRO concentrations in the clear water fraction from each of these tests were all within about 15% of each other − a reasonable range for preliminary tests − and it was concluded that the solid-liquid separation methods did not substantially impact partitioning results (e.g., by sorption of diesel to the filter paper).
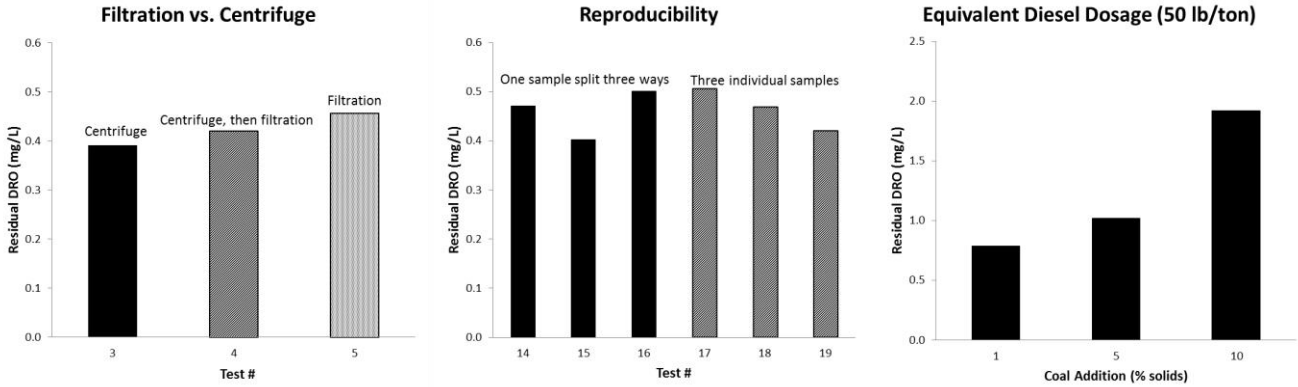
Figure 2.3: Diesel sorption test results

The middle plot of Figure 2.3 shows the results from six tests to determine the reproducibility of the test and analytical methods used here. Tests 14-16 show DRO measured three separate times (i.e., in triplicate) from a single sample. The results for these tests are within about 20% of each other and suggest that the analytical method is fairly reproducible. Likewise, tests 17-19 show DRO measured from samples from three separate, but identical tests. In this case, the results are within about 18% of each other and indicate that the test method is also reproducible.

In the right plot of Figure 2.4 are the results from three tests conducted to determine the effect of proportionally similar coal and diesel additions (i.e., tests at 1, 5 and 10% solids, each with a diesel dosage of 50 lb/ton coal). Since the diesel was dosed on the basis of coal weight, it seems intuitive that DRO concentrations should have been similar between these tests; instead, with increasing additions of coal, less diesel actually sorbed. One possible explanation for this phenomenon may be that with more coal in the slurry, particles are sticking to each other or being bridged together by diesel such that there are effectively fewer sorption sites available. For tests where coal content remained constant (e.g., tests 7-9) but diesel dosage was varied, measured DRO in the water did increase with a substantial increase in diesel dosage – although not proportionally. For instance, in tests with 5% Hagy Seam coal (-100 mesh), DRO was roughly equal for diesel dosages of 0.25 and 1.0 lb/ton (i.e., 0.50 and 0.53 mg/L), but essentially doubled when the diesel dosage was raised to 10 lb/ton (i.e., to 0.95 mg/L).

It was further observed that the ash content of coal appears to affect diesel sorption. At equal slurry contents and diesel dosages (i.e., 5% solids, and diesel dosages of 10 or 50 lb/ton), the Pocahontas Seam coal (~16% ash) sorbed about 2-2.5x as much diesel as the Hagy Seam

34

coal (~35% ash) (see Table 2.4). This is likely because coal has a higher affinity for diesel than ash does. It is difficult to assess whether or not the sized Hagy Seam coal (100 x 150 mesh) behaved differently than that which was only ground (-100 mesh), since just one test condition was repeated between the first and second set of tests (i.e., tests 9 and 24; 5% coal and diesel dosage of 10 lb/ton); however, the DRO results for these tests were practically very similar.

In terms of real preparation plants, the results of the collector partitioning tests presented here indicate that, as expected, most diesel should partition with the coal. However, some (presumably soluble) diesel may well remain in the process water – eventually being sent to tailings impoundments or being recycled back through the plant. While no Federal water quality standards currently exist for DRO, some states have set levels of concern at 0.05 mg/L (e.g., through reporting levels for diesel spills or contamination from underground storage tanks) (DEP 2002). The topic of soluble DRO, including the relative solubility of specific diesel compounds and potential remediation strategies, is deserving of additional research.

6. Conclusions

Processing reagents used in coal preparation have a wide range of potential environmental fates, as well as implications for preparation circuits that are designed or revised to utilize closed water systems. The preliminary test work presented in this paper confirms that common frother and collector reagents are not likely to partition completely to a single fraction of the process slurry. Instead, the partitioning phenomena are complex, and appear to depend on many operating variables including coal and reagent characteristics and dosages.

To gain a better understanding of the ultimate fates of these reagents and related impacts, further work should focus on determining the mechanisms by which various reagents may associate with solid and liquid fractions of coal slurries. Moreover, work is needed to elucidate strategies for controlling/optimizing reagent partitioning, or treatment of affected process streams.

7. Acknowledgments

expressed in this paper are solely those of the authors and do not imply any endorsement by DOE or ARIES.

8. References

ATSDR. (2009), 2012

Coffey, A., & Lambert, N. (2008). *Development of an Online Residual Frothing Propensity Detector*. Paper presented at the 12th Australian Coal Preparation Society Conference, Sydney, Australia.

Rules for Underground Oil Storage Facilities, Maine DEP (2002).

Howard, P. H. (1993). *Handbook of Environmental Fate and Exposure Data for Organic Chemicals* (Vol. 4). Chelsea, MI: Lewis Publishers.

Knapp, J. M. S. (1990). *A Study of Flotation Froth Behavior.* Master of Science, Virginia Polytechnic Institute and State University, Blacksburg, VA. Available from Virginia Tech ETD database.

Lahey, A., & Clarkson, C. (1999). Development of Automatic Control Techniques for New Flotation Technologies. C Clarkson & Associates Pty Ltd.

Laskowski, J. S. (2001). *Developments in Mineral Processing* (First ed. Vol. 14). Amsterdam, The Netherlands: Elsevier Science B.V.

Liu, G. J., Niu, Z. Y., Niekerk, D. V., Xue, J., & Zheng, L. (2008). Polycyclic aromatic hydrocarbons (PAHs) from coal combustion: emissions, analysis and toxicology. *Reviews of Environmental Contamination and Toxicology*(192), 1-28.

McIntyre, D. G. F. (1974). *Mineral Processing Chemicals Operational Mechanisms and Environmental Effects*. Paper presented at the AIME Meeting, Dallas, Texas.

MSHA. (2009), 2012

Nave, R. Surface Tension Retrieved 03/22/2012, 2012

Pitt, G. J., & Millward, G. R. (1979). *Coal and Modern Coal Processing: An Introduction*. New York, New York: Academic Press Inc.

Pugh, R. J. (1996). Foaming, foam films, antifoaming and defoaming. *Advances in Colloid and Interface Science, 64*, 76.

Scheepers, P., & Bos, R. (1992). Combustion of diesel fuel from a toxicological perspective. II. Toxicity. *Int Arch Occup Environ Health, 64*(3), 163-177.

Scott, J. H. (1976). *Coagulation Study of a Bound Water Bulked Sludge.* Master of Science, Virginia Polytechnic Institute and State University, Blacksburg, VA. Available from Virginia Tech ETD database.

Sweet, C., Hoogstraten, J. V., Harris, M., & Laskowski, J. S. (1997). *The Effect of Frother on Bubble Size and Frothability of Aqueous Solutions, Processing of Complex Ores.* Paper presented at the The 2nd UBC-McGill Int. Symposium, Montreal, Canada.

Szwilski, T. (1986). *Mining, Our Own Business: Small Underground Coal Operations*. Paper presented at the SME Annual Meeting, New Orleans, LA.

USEPA. (1999), 2012

Watts, R. J. (1998). *Hazardous Wastes: Sources, Pathways, Receptors*. New York, NY: John Wiley and Sons.

Wills, B. A. (2006). *Wills' Mineral Processing Technology* (Seventh ed.). Burlington, MA: Elsevier Ltd.

3   DIESEL RANGE ORGANICS IN COAL PREPARATION

Josh Morris, Emily Sarver, Gerald Luttrell

1. Abstract

Recent laboratory testing has suggested that partitioning of petro-diesel collector reagents in coal flotation circuits is not perfectly ideal. In this paper, we investigate the persistence of diesel range organic (DRO) compound residuals in process waters under a number of physio-chemical conditions. Additionally, we investigate desorption of DRO from coal surfaces exposed to fresh water. In both cases, we also examine the behavior of individual PAH compounds. Results are discussed in the context of potential environmental transport and fate of DRO compounds in water from coal preparation plants. While our results indicate that DRO concentrations in process waters are expected to be at sub-ppm levels under normal operating conditions, we note that "green" collectors are available for coal flotation.

2. Introduction

The primary function of coal preparation is removal of mineral matter (i.e., ash), which detracts from the coal value. Preparation plants typically have multiple circuits for processing materials of different particle sizes. In the fine circuits (i.e., -100 mesh particles), froth flotation is often used to separate coal from ash. In 2012, about 30% of the coal preparation plants in the US (i.e., 82 of 289) were reported to operate fine coal flotation circuits, and virtually all of these (i.e., 80 of 82) are located in the Central Appalachian basin (Fiscor 2012). For reference, this basin also accounted for about 85% of the total preparation plants (i.e., 248 of 289).

Froth flotation of coal works on the basic principle that coal particles are relatively hydrophobic and lightweight, such that they easily float to the top of the flotation columns or cells and can be recovered from a froth that forms there; while ash mineral particles are relatively

hydrophilic and dense, such that they sink and are rejected to the tailings stream. Coal particles are naturally hydrophobic to some degree, depending on their specific chemical properties (e.g., surface oxidation, liberation from mineral matter), but "collector" reagents that increase their hydrophobicity are often used to aid the flotation process (Wills 2006). Globally, petro-diesel (termed "diesel" in this paper) is the most commonly used collector given its relatively low cost and proven performance (Laskowski 2001). However, collector dosages are quite variable (e.g., diesel may be dosed in the range of 0-5 lb/ton) due to flotation circuit parameters and feed quality; dosage at a single plant may be adjusted frequently.

While collectors work by sorbing to the coal surface (Kondrat'ev 2009), recent studies have indicated that the partitioning of diesel between coal and process water is not perfectly ideal (Morris et al. 2012). In bench-scale experiments, under a variety of test conditions mixing water, coal and diesel, low-level diesel range organic (DRO) compound residuals were consistently measured in process water. Results suggested that the DRO residuals may primarily consist of the water soluble fraction (WSF) of the diesel, which exists at sub-ppm levels. At present, DRO is not monitored in impoundments or discharges, however, given increasing concerns over diesel contamination of water resources by leaking underground storage tanks, highway and blacktop runoff, and events such as the recent Deepwater Horizon oil spill in the Gulf of Mexico (Sementelli and Simons 1997; Lloyd and Cackette 2011; Osofsky et al. 2011), it is important to understand the potential transport mechanisms and fate of DRO from coal processing. It should be noted that alternative "green" collector reagents such as bio-diesel and pine oil products are already being utilized for fine coal flotation in some instances. These collectors are significantly more expensive than diesel but may be required in special circumstances, such as safeguarding groundwater resources when coal waste slurry is intended to be disposed via underground injection (WV-DEP 2009).

2.1 Environmental Fate and Transport of Diesel Compounds in Water

Diesel has a mixed composition of roughly C_{10} to C_{19} hydrocarbons, which, like for many petroleum products, varies based on the crude oil source and refining process(es) (ATSDR 1999). This variability makes it difficult to uniquely classify the chemical and environmental characteristics of diesel, and also to accurately measure individual components (ATSDR 1995). Instead, diesel is usually described in terms of major compound categories: total saturated

hydrocarbons (e.g., alkanes, cycloalkenes) and total aromatic hydrocarbons (e.g., naphthalenes, acenaphthenes, acenaphthylenes). Saturated hydrocarbons typically account for about 90% (by weight) of total diesel, while aromatics account for about 10% (Wang et al. 2003). Any remaining components (e.g., waxes and resins) usually make up a very small fraction of the total diesel and are not often quantified.

In addition to broad categorical classification, the nature of diesel and other petroleum products is sometimes characterized by measuring a series of ideal (i.e., n-alkanes) and/or priority compounds (i.e., specific aromatics). Typical analytical techniques include GC-FID, GC-MS and fluorometry (Wang et al. 2003). It is important to note that while specific compounds may be targeted by these techniques, the large number of individual compounds present in diesel (e.g., branched alkanes, functionalized aromatics) makes it impossible to quantify each and every one (ATSDR 1995). Moreover, the diesel composition may change dramatically in the environment as it weathers (e.g., via volatilization, bio- or photo-degradation). Such complexities make predicting environmental implications of diesel releases quite challenging, but offer unique opportunities for source tracking in some cases (Wang et al. 1996).

A basic understanding of environmental transport mechanisms and fate of diesel can be gleaned from properties of the compounds in the broad categories mentioned above. Generally speaking, the saturated hydrocarbons are relatively volatile (Fingas 1994; Fingas 1995), insoluble in water, and photo- and bio-degradable (Olson et al. 1999; Marquez-Rocha et al. 2001; Cohen et al. 2002; Kakkar et al. 2011). Thus, at relatively low levels, this group of compounds does not present major concerns for water resources. Aromatics in the diesel range are also typically volatile and insoluble in water, but are much more persistent in the environment because they resist degradation (Olson et al. 1999). Further, some monocyclic and polycyclic aromatic hydrocarbons (MAHs and PAHs) have been classified as possible or probable human carcinogens (ATSDR 2009), and have been linked to acute or chronic toxicity in aquatic organisms (Schein et al. 2008). Thus, if significant concentrations and exposure pathways exist, these compounds may present ecological and human health hazards. Indeed, the US EPA has developed a list of 16 priority PAHs, although only one compound (i.e., benzo-[a]-pyrene) is regulated by a maximum contaminant level in drinking water (EPA 2011). Total DRO is not federally regulated (EPA 2003).

PAHs exist naturally in fossil fuels and their derivatives, and can also be formed via incomplete combustion of these and other sources of organic carbon (e.g., wood and other plant matter) (SCF 2002). Common contributors to DRO and PAHs in water include oil spills and leaks (e.g., from underground storage tanks), urban run-off, and municipal and industrial effluents. PAHs in the atmosphere, which originate from sources such as volcanic eruptions, forest fires, combustion of fossil fuels, waste incineration, coke and asphalt production, oil refining, and aluminum production, can also deposit into surface waters (Manoli and Samara 1999). In diesel, the most prevalent PAH groups are typically those with the lowest molecular weights (e.g., naphthalenes, fluorenes, phenanthrenes) as shown in Table B.1 in Appendix B; these PAHs have weights in the same range as saturate compounds in diesel (e.g., C_{10}-C_{19} alkanes) The fate of individual PAHs is dependent on their physicochemical properties (e.g., molecular weight, structure, water solubility, and vapor pressure) (Manoli and Samara 1999; Wick et al. 2011), but it can be generally stated that light-weight PAHs tend to be more soluble and volatile than their heavier counterparts. As molecular weight increases, water solubility and vapor pressure decrease and the compound becomes more difficult to degrade (Wick et al. 2011).

With regard to diesel reagents used in fine coal processing, it is important reiterate that under normal operating conditions, nearly all but the soluble DRO are expected to be effectively sorbed to the coal surface based on prior work (Morris et al. 2012). Thus, only those compounds that do not sorb, desorb or that are soluble can potentially move with process water. While the sum of EPA-listed PAHs (and their simple alkylates) do not generally make up a significant fraction of total diesel (i.e., less than a few percent) (EPA 1990), the current attention on this broad category of compounds warrants investigation to ensure that coal preparation activities do not present cause for concern. Here, our objective was to gain a better fundamental understanding of potential fates and transport mechanisms of diesel, including PAH compounds, from fine coal processing.

3. Experimental Methods

Partitioning studies were carried out to obtain preliminary data on the likely fate of residual DRO, including PAH compounds from fine coal flotation. In one set of tests, the potential for diesel removal from process water by heating, stirring, and aeration was analyzed; in another test, desorption of diesel from coal surfaces was investigated. A sample of raw coal

was obtained from the Hernshaw coal seam in Kanawha, West Virginia which was determined to be 44.6% ash. The coal was prepared for testing only by sizing. It was crushed using a laboratory jaw crusher followed by a roll crusher, and then screened to obtain material in the range of 74-149 microns (i.e., 100 x 200 mesh). A sample of diesel was purchased from a local fuel station, and stored in an amber, airtight glass jar. Basic characterization of the diesel via GC-FID (as described in EPA, 2003) showed that it consisted of 87.4% saturates and 11.5% aromatics. Appendix B shows the details for how the percent saturates and percent aromatics were determined.

For each test, a slurry sample (5 % solids by weight) was prepared by adding the dry, sized coal to deionized water (DI); then diesel was added to achieve an effective dosage of 10 lb diesel/ton coal (Figure 3.1). Slurries were mixed using a hand blender for two minutes, and then the coal particles were separated from the water by filtration (through 25 µm paper) using a vacuum pump.
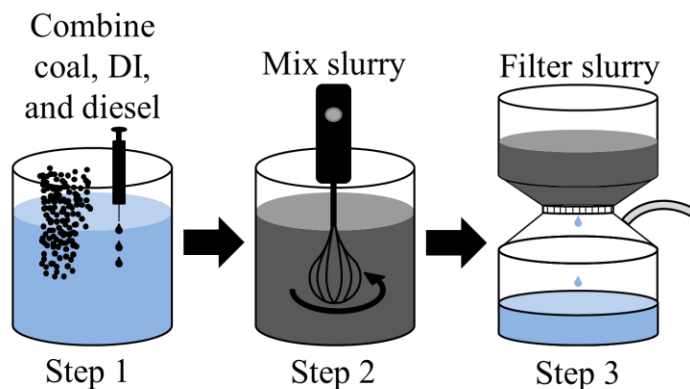
Figure 3.1: Sample preparation for DRO tests

3.1 DRO Removal

For the diesel removal tests, a total of 2 L of filtrate was prepared, with 150 mL of this being immediately stored in an airtight amber jar for analysis (i.e., t = 0). The rest of the filtrate was split into 8 equal subsamples for individual test conditions (Figure 3.2). The test conditions were: stagnant (open jar in ambient room temperature and pressure), gentle stirring, gentle aeration and heating ($40^{o}C$); and for each, one sample was conditioned for 2 hours and another

was condition for 4 hours. At the end of those time increments, the subsamples were stored for analysis.
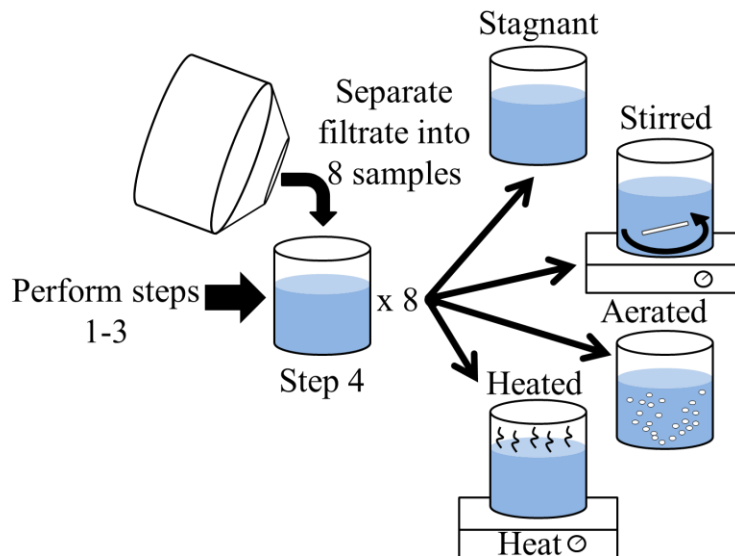
Figure 3.2: DRO removal – experimental methods

3.2 Diesel Desorption

For the diesel desorption tests, slurry was also prepared and filtered. Following collection and storage of the initial filtrate, coal particles remaining on the filter paper were carefully removed (Figure 3.3) and mixed into a new volume of deionized water (again at 5% solids) – this time without the addition of diesel. The slurry was then filtered, and the filtrate was again collected for analysis. This process was repeated multiple times to investigate the trend in DRO and PAH concentrations for successive rinses. In the first test (Test A) a total of four rinse cycles were completed, one immediately after the next. In the next test (Test B), a total of six rinse cycles were completed; however, for the last two cycles, the coal particles were allowed to air dry for 24 hours.
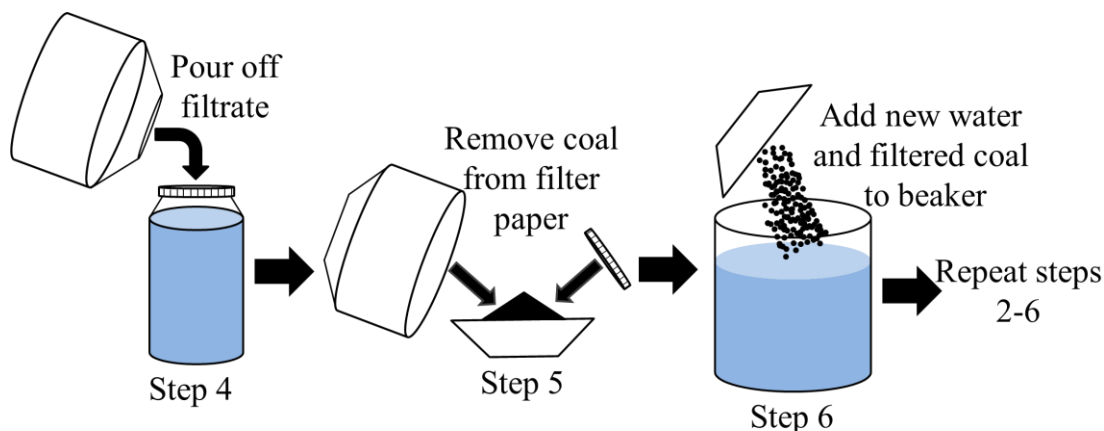
Figure 3.3: DRO desorption – experimental methods

3.3 Analytical Methods

Residual diesel in each sample was analyzed using an Agilent 5890 gas chromatograph equipped with a flame ionization detector (GC-FID); we followed EPA Method 3150 for quantifying diesel range organics (DRO) in water samples. Samples were also analyzed for a group of target PAHs using a Thermo Trace GC equipped with a Thermo DSQ II mass spectrometer (GC-MS); we followed EPA Method 3535A: Solid-Phase Extraction (SPE). The target PAHs were: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, acenaphthene, acenaphthylene, anthracene, benzo(ghi)perylene, fluoranthene, fluorine, naphthalene, phenanthrene, and pyrene.

4. Results

Results of all tests confirmed that a small fraction of diesel tends to partition to the process water – and this is typically limited to the soluble fraction. The converse side of this observation is therefore that the coal particles have a very high capacity for sorption of insoluble diesel.

4.1 Potential for Diesel Removal from Process Water

Table 3.1 presents results for DRO and PAH residuals in the tests designed to investigate potential for diesel removal from process water. Figure 3.4 also graphically displays the results for DRO and naphthalene. The rate of DRO removal was significantly higher for the stirred and

aerated conditions than for the heated and stagnant conditions, with DRO concentrations leveling off just below 0.3 ppm. This concentration corresponds to the solubility limit of diesel in water at ambient temperature and pressure. For the heated and stagnant conditions, DRO actually increased after 2 hours (more significantly for the stagnant sample), and then began decreasing after 4 hours. Over the test period, the heated sample did lose significant volume due to evaporation, and it is also possible that the observed increase in DRO in this sample is related to the time required for equilibration (i.e., as water evaporates, DRO does not immediately come out of solution and vaporize.) This would also explain the slower DRO removal in the stagnant condition, wherein there was no additional driving force to quickly remove all insoluble diesel from the water (vs. the stirred and aerated conditions.) In an additional experiment to test this hypothesis, the stagnant and aerated conditions were repeated and samples were collected and measured after 24 hours; results confirmed that the total DRO was similar for both conditions. After 48 hours, total DRO was again similar between the two conditions.

PAH removal trends appeared to be similar to those of the total DRO for all tests, in that 1) the concentrations decreased over time, 2) the rate of decrease was fastest for the stirred and aerated conditions and slowest for the stagnant and heated conditions. However, it should be noted that the PAHs tended to be removed from the process water much more quickly overall than the total DRO. This is illustrated in Figure 3.4 by comparing DRO to naphthalene, which had the highest measured concentrations of all target PAHs, followed by acenapthene and fluorene. For the stirred and aerated conditions, while the DRO does decline (to about 70% of its initial concentration), the naphthalene is removed down to sub-ppb levels (to about 1% of its initial concentration). The other PAHs behaved similarly as shown in Figure C.1 in Appendix C. Thus, it appears that the relative abundance of PAHs in the WSF of diesel may be much smaller than in the total diesel.

Table 3.1: DRO and PAH removal results

Test Condition	Time (hr)	PAHs (ppb)						DRO (ppm)
		Naphthalene	Acenaphthene	Fluorene	Anthracene	Fluoranthene	Pyrene	
Initial	0	60	6.5	6.8	2.7	0.14	0.18	0.43
Stagnant	2	56	7.1	7.6	2.8	NF	0.27	0.59
	4	34	5.1	5.6	NF	NF	0.25	0.53
Stirring	2	2.5	0.99	1.6	1.5	NF	0.16	0.30
	4	0.51	0.15	0.37	0.81	NF	NF	0.27
Aeration	2	0.98	0.10	NF	NF	NF	NF	0.27
	4	0.69	0.41	NF	NF	NF	NF	0.29
Heating	2	17	2.9	3.5	2.0	NF	0.13	0.48
	4	12	2.0	2.7	1.6	NF	0.12	0.38

NF indicates the compound was not found.
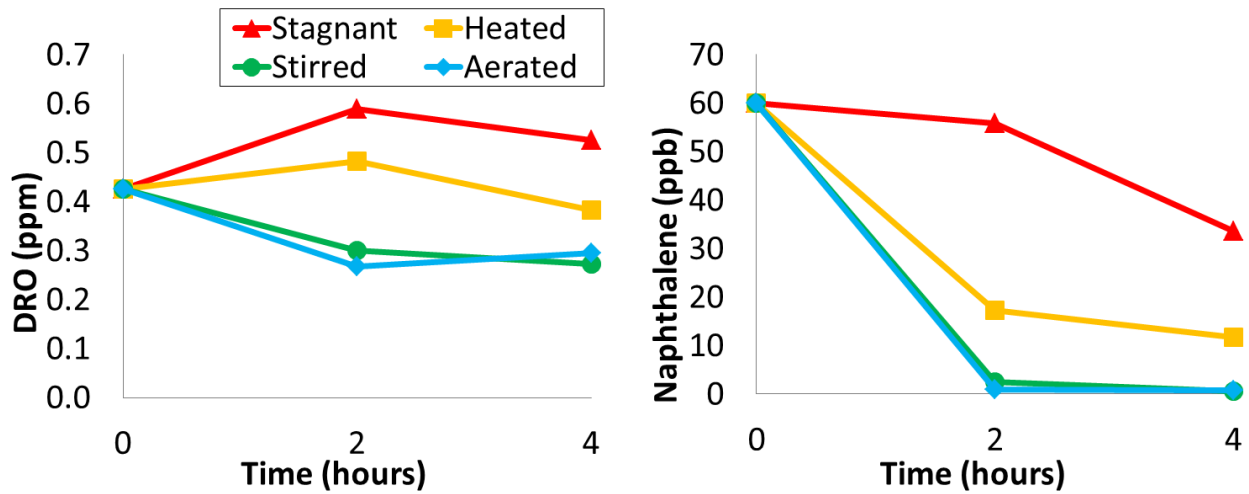
Figure 3.4: DRO and naphthalene removal results

4.2 DRO Desorption

Previous work has demonstrated that the sorption capacity of raw coal for diesel is very high (e.g., all but the soluble portion of diesel sorbs to the coal) – even beyond practical operating conditions for fine coal flotation (Monsalve 2010; Morris et al. 2012). The goal of the present testing was to determine if the sorbed diesel might be easily removed again from the coal, for example during dewatering or other instances where the coal product is contacted with

water, or in instances where ultrafine coal with sorbed diesel reports to tailings impoundments. Figure 3.5 shows the total DRO concentrations measured in filtrate samples following successive rinsing of diesel-contacted coal for two separate tests (i.e., A and B). The declining trends indicate that, initially, the clean water is likely rinsing free diesel from the coal surfaces (i.e., diesel that was not actually sorbed to the coal, but rather caught between particles); however, with subsequent rinses, diesel is desorbing from the coal. With more rinsing cycles, it is expected that the diesel would eventually desorb from the coal to satisfy the solubility limit in the fresh water.

For test B, the target PAHs were also measured (Figure 3.6). It should be noted that the initial naphthalene concentration measured in this test was much lower than that in the tests presented in Table 3.1 (by nearly an order of magnitude). An explanation for this is not clear. However, the significant decline in naphthalene shown in Figure 3.6 following the first rinse cycle is consistent with the DRO observations and the idea that naphthalene is not very abundant in the WSF of diesel. Acenaphthene, fluorene and anthracene also exhibit similar behaviors, although these compounds require more rinse cycles before significant decline is observed. Pyrene and acenaphthylene are present in only very small concentrations and remain relatively constant. Table C.1 in Appendix C shows the data values for the PAH desorption results.
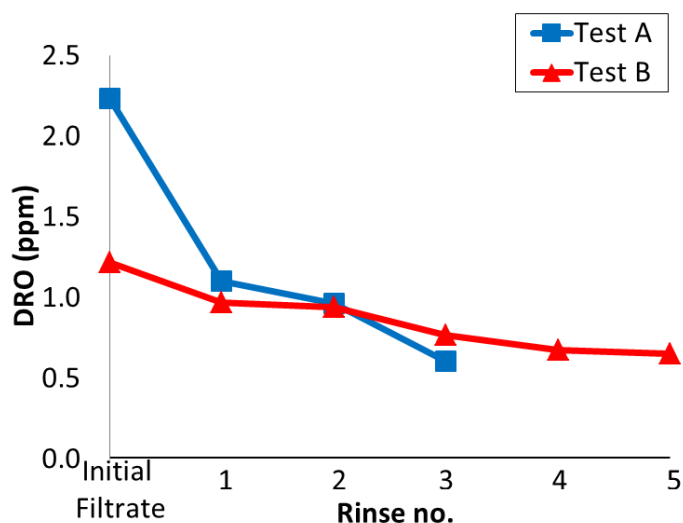
Figure 3.5: DRO desorption results
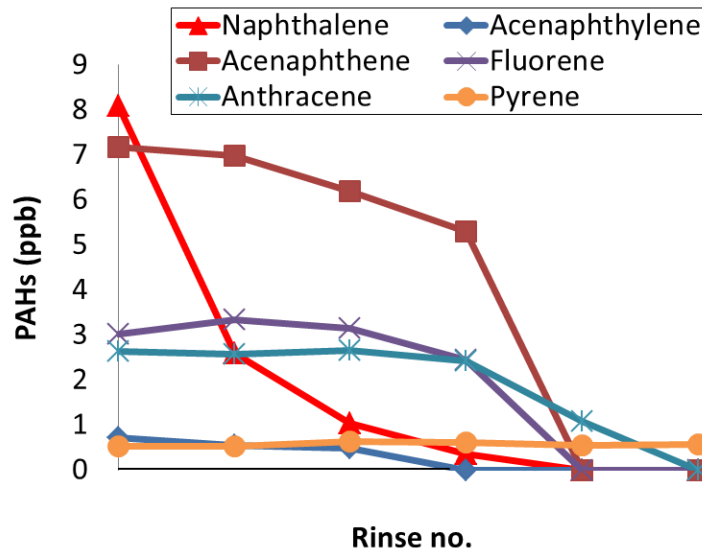
Figure 3.6: PAH desorption results

5. Discussion

The results presented here provide some fundamental insights to the probable behavior of diesel compounds in fine coal flotation circuits. It is clear that some low-level diesel will likely report with process water to tailings impoundments or other waste repositories. In open-air systems, insoluble DRO may be gradually removed from process water, and removal may be accelerated in systems that promote aeration, mixing or heating; and these conditions which are commonly encountered in both impoundments (or slurry cells) and preparation plants where recycled flotation-process water may be utilized. Under normal operating conditions, a system is expected to continuously equilibrate such that only the WSF of diesel persists to any appreciable degree, and thus high concentrations of DRO are not expected accumulate. In a typical impoundment, the WSF will likely also be subject to photo- and bio-degradation.

We have also shown that diesel-contacted coal may release diesel to fresh water. In terms of environmental fate, this may be most important for clean coal stocks that are wetted, or in the instance of ultrafine coal that ends up in an impoundment. In the latter case, it is expected that diesel will desorb from the coal particles only until equilibrium with respect to diesel solubility in the impoundment is reached.

In regards to behavior of PAHs, it has been demonstrated here that some of these compounds may be expected to quickly leave an impoundment via volatilization, which may be encouraging – at least for water quality. Naphthalene was the most abundant of any of the PAHs

48

targeted in this work, and at even the highest measured concentration of approximately 60 ppb, this is still lower than EPA lifetime advisory limits of 100 ppb for drinking water (EPA 2006).

It should be noted that the PAH contents measured in process waters in this study do appear to suggest some concentration effects (vs. the pure diesel), meaning that all components of the diesel do not remain in constant proportions. For instance, naphthalene in the pure diesel was measured to be approximately 0.1%, while in the initial filtrate sample used in the diesel removal tests the naphthalene was calculated to be about 13% (i.e., 60.1 ppb naphthalene in 0.43 ppm total DRO). This may suggest that coal selectively sorbs saturate compounds over aromatics. However, according to the observed behavior of PAHs under conditions of stirring, aeration, stagnation and heating, this concentration effect might be quickly reduced or even reversed.

Another important point of discussion in regards to PAHs in diesel is that of the relative abundance of target vs. actual compounds. While ideal PAHs (i.e., simple aromatics of fused benzene rings without functional groups) do exist in diesel, it is well established that alkylated PAHs are typically present at much higher concentrations (Irwin et al. 1997). The simplest alkylated PAHs are formed when the parent PAH compound is functionalized by addition of one or more methyl groups, which may occur during the digenesis of fossil fuels from organic sediments. Naphthalene can accommodate up to four methyl groups, and there are 22 individual compounds in the class of methylated naphthalenes (Abraham et al. 2005). Since quantification of specific compounds is highly complex, oftentimes only the parent compound (i.e., the EPA priory compound) such as naphthalene is measured to characterize fuel products or environmental samples. Additional testing of the diesel used in this work has revealed that di-and tri-methylated naphthalene compounds are present at about 3x the concentration of pure naphthalene; while mono- and tetra- compounds are present at more similar concentrations as the pure naphthalene. Considering this, it may be prudent to target the more abundant compounds in future testing – although, if the behavior of the alkylated compounds are similar to that of their parent, environmental implications may not differ significantly.

6. Conclusions

Diesel is a common collector reagent in fine coal flotation circuits in both the US and abroad. Despite coal's very high sorption capacity for this reagent, sub-ppm levels of DRO

dominated by the WSF of diesel are expected to be present in process waters. In a typical tailings impoundment or open-air portions of the flotation circuit, DRO may be removed relatively quickly via volatilization and/or degradation. The most prevalent PAHs may also volatilize quickly, particularly where mixing, aeration or heating of the water occurs. DRO may desorb from diesel-contacted coal; however, in the context of settled ultrafine coal in an impoundment, this process should be limited diesel solubility in the impoundment water. Relative concentrations of both total DRO and PAHs targeted in this study do not appear to present significant concerns for water quality under normal operating conditions – but variances from such conditions should clearly be avoided. "Green" reagents such as bio-diesel and pine oil products, both of which should not contain PAHs, are being considered as alternative collectors for fine coal flotation; however, these have not yet gained widespread use throughout the industry.

7. Acknowledgments

8. References

Abraham, M., Autenrieth, R. and Dimitriou-Christidis, P. (2005). "The estimation of physicochemical properties of methyl and other alkyl naphthalenes." The Royal Society of Chemistry 2005(7): 5.

Adel, G. (2012). Particulate Process Modeling. 2.1.1 Examples of Particulate Processes, Department of Mining and Minerals Engineering.

ALS. (2008). "GC/MS-Full Scan vs GC/MS-SIM." 2012, from http://www.caslab.com/News/gcms-full-scan-vs-cgms-sim.html.

AMMA. "Diesel Fuel." Retrieved January 16, 2013, 2013, from http://www.miningoilgasjobs.com.au/Oil-Gas-Energy/Hydrocarbons-and-Energy/Hydrocarbons/Oil-and-Gas/Downstream/Diesel-Fuel.aspx.

ATSDR (1995) "Fuel Oils - Chemical and Physical Information." 105-109.

ATSDR (1999). Total Petroleum Hydrocarbons - Identity and Analysis of Total Petroleum Hydrocarbons. Atlanta, Georgia, Agency for Toxic Substances and Disease Registry: 315.

ATSDR. (2009). 2012.

ATSDR (2009). Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs): 68.

Bratton, R. and Luttrell, G. H. Environmental Practices for Coal Preparation Plants.

Coffey, A. and Lambert, N. (2008). Development of an Online Residual Frothing Propensity Detector. 12th Australian Coal Preparation Society Conference. Sydney, Australia.

Cohen, M., Williams, J. and Yamasaki, H. (2002). "Biodegradation of Diesel Fuel by an Azolla-Derived Bacterial Consortium." Environmental Science and Health A37(9): 14.

Demirbas, A. (2007). "Importance of biodiesel as transportation fuel." Energy Policy 35(2007): 10.

DEP (2002). Historical Oil Contamination Travel Distances in Ground Water at Sensitive Geological Sites in Maine, Bureau of Remediation & Waste Management: 7.

DEP, M. (2002). Rules for Underground Oil Storage Facilities. 691. United States, Maine DEP.

DOE. (2013). "Biodiesel Production and Distribution." 2013, from http://www.afdc.energy.gov/fuels/biodiesel_production.html.

Ducatman, A., Ziemkiewicz, P., Quaranta, J., Vandivort, T., Mack, B. and VanAken, B. (2010). Coal Slurry Waste Underground Injection Assessment. Final Report: Phase II. Morgantown, WV, West Virginia University: 261.

EPA (1990). Documentation of 7-PAH and 16-PAH National Emission Estimates.

EPA (2003) "Nonhalogenated Organics using GC/FID." 1-37.

EPA. (2006). "Drinking Water Health Advisories 2006 Edition." from http://water.epa.gov/action/advisories/drinking/dwstandards.cfm.

EPA (2011). 2011 Edition of the Drinking Water Standards and Health Advisories. Washington, DC, Office of Water: 18.

Eraydin, M., Zhang, J. and Blubaugh, S. (2012). Separation Technologies for Minerals, Coal, and Earth Resources, SME.

Fingas, M. (1994). "Evaporation of Oil Spills." ASCE: 8.

Fingas, M. (1995). "A literature review of the physics and predictive modelling of oil spill evaporation." <u>Hazardous Materials</u> 42(1995): 19.

Fiscor, S. (2012). "U.S. Prep Plant Census 2012." <u>Coal Age</u> 117(10): 14.

Gerpen, J., Shanks, B., Pruszko, R., Clements, D. and Knothe, G. (2004). Biodiesel Analytical Methods. Golden, Colorado, Midwest Research Institute: 100.

Hach. (2009). "Product - Xenosep - FAQ." 2013, from http://www.hach.com/xenosepguide-faq.

Haddad, R. and MacMurphey, J. (2006). TPH Measurements. <u>The Advantage of Using GC/MS</u>, ENTRIX, Inc.

ZymaX envirotechnology, inc: 5.

Hessell, E., Abramshe, R. (2003). "Alkylated Naphthalenes as High-Performance Synthetic Fluids." <u>Journal of Synthetic Lubrication</u> 20: 14.

Hines, J., Dopico, P. and Kennedy, D. (2011). Novel Coal Collector Derived from Pine Tree Pulping. <u>SME Annual Meeting</u>. Denver, CO, SME: 3.

Hines, J., Kennedy, D. and Hurd, P. (2009). Method for the Beneficiation of Coal. U. S. P. a. T. Office. United States, Georgia-Pacific Chemicals, LLC: 8.

Hines, J., Kennedy, D. and Hurd, P. (2009). Method for the Froth Flotation of Coal. U. S. P. a. T. Office. United States, Georgia-Pacific Chemicals LLC.

Hourani, M., Hessell, E., Abramshe, R., Liang, J. (2007). "Alkylated Naphthalenes as High-Performance Synthetic Lubricating Fluids." <u>Tribology Transactions</u> 50: 6.

Howard, P. H. (1993). <u>Handbook of Environmental Fate and Exposure Data for Organic Chemicals</u>. Chelsea, MI, Lewis Publishers.

Irwin, R., VanMouwerik, M., Stevens, L., Seese, M. and Basham, W. (1997) "Environmental Contaminants Encyclopedia Entry on Alkyl PAHs (Alkyl Homologs of PAHs)." 18.

Irwin, R., VanMouwerik, M., Stevens, L., Seese, M., Basham, W. (1997) "Environmental Contaminants Encyclopedia C4-Naphthalene Entry." 26.

Jeffery, G., Bassett, J., Mendham, J. and Denney, R. (1989). <u>Vogel's Textbook of Quantitative Chemical Analysis</u>. New York, John Wiley & Sons, Inc.

Kakkar, P., Saxena, R., Rathee, N. and Joshi, M. (2011). "Water soluble fraction of diesel fuel induced histopathological alterations in the liver of Channa punctatus." <u>Toxicology International</u> 18(1): 3.

Knapp, J. M. S. (1990). A Study of Flotation Froth Behavior. Master of Science, Virginia Polytechnic Institute and State University.

Kondrat'ev, S. (2009). "Physically Sorbed Collectors in Froth Flotation and their Activity. Part II." Journal of Mining Science 45(2): 9.

Koning, S., Janssen, H. and Brinkman, U. (2008). "Modern Methods of Sample Preparation for GC Analysis." Chromatographia 2009(69): 46.

Lahey, A. and Clarkson, C. (1999). Development of Automatic Control Techniques for New Flotation Technologies. C Clarkson & Associates Pty Ltd.

Laskowski, J. (2001). Developments in Mineral Processing. Amsterdam, The Netherlands, Elsevier Science B.V.

Lee, B. and Vu, V. (2010). Sources, Distribution and Toxicity of Polyaromatic Hydrocarbons (PAHS) in Particulate Matter, InTech.

Liu, G. J., Niu, Z. Y., Niekerk, D. V., Xue, J. and Zheng, L. (2008). "Polycyclic aromatic hydrocarbons (PAHs) from coal combustion: emissions, analysis and toxicology." Reviews of Environmental Contamination and Toxicology(192): 1-28.

Lloyd, A. and Cackette, T. (2011). "Diesel Engines: Environmental Impact and Control." Journal of the Air and Waste Management Association 51(6): 38.

Lu, T., Eng, P. and Laman, G. (2012). A Preliminary Comparison of Coal Classification and Processing between Canada and China. 44th Annual Meeting of the Canadian Mineral Processors. Ottawa, Canada, Canadian Institute of Mining, Metallurgy, and Petroleum (CIM): 13.

Manoli, E. and Samara, C. (1999). "Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis." Trends in Analytical Chemistry 18(6): 12.

Marquez-Rocha, F., Hernandez-Rodri, V. and Ma, L. (2001). "Biodegradation of Diesel Oil in Soil by a Microbial Consortium." Water, Air, & Soil Pollution 128(3-4): 8.

McDonald, P. (2001). A Sample Preparation Primer and Guide to Solid Phase Extraction Methods Development. P. McDonald and E. Bouvier, Waters Corporation: 83.

McIntyre, D. G. F. (1974). Mineral Processing Chemicals Operational Mechanisms and Environmental Effects. AIME Meeting. Dallas, Texas: 20.

McNair, H. and Bonelli, E. (1968). Basic Gas Chromatography, Varian.

Monsalve, C. (2010). Process for the Containment of Oil Spills. United States Patent Office. P. A. Publication. United States. US 2011/0203996 A1: 8.

Morris, J., Sarver, E. and Luttrell, G. (2013). Diesel Range Organics In Coal Preparation. Environmental Considerations in Energy Production. J. Craynon. Charleston, WV, SME: 11.

Morris, J., Sarver, E., Luttrell, G. and Novak, J. (2012). Reagents in Coal Preparation: Where do they go? Annual Conference of Metallurgists 2012. Niagara Falls, Canadian Institute of Mining, Metallurgy and Petroleum (CIM): 12.

MSHA. (2009). 2012.

Nave, R. "Surface Tension." Retrieved 03/22/2012, 2012.

NBB. (2013). "Biodiesel Basics." 2013, from http://www.biodiesel.org/what-is-biodiesel/biodiesel-basics.

Olson, J., Mills, G., Herbert, B. and Morris, P. (1999). "Biodegradation Rates of Separated Diesel Components." Environmental Toxicology and Chemistry 18(11): 6.

Osofsky, H., Baxter-Kauf, K., Hammer, B., Mailander, A., Mares, B., Pikovsky, A., Whitney, A. and Wilson, L. (2011). "Environmental Justice and the BP Deepwater Horizon Oil Spill." New York University Environmental Law Journal 20(1): 81.

Pitt, G. J. and Millward, G. R. (1979). Coal and Modern Coal Processing: An Introduction. New York, New York, Academic Press Inc.

Pugh, R. J. (1996). "Foaming, foam films, antifoaming and defoaming." Advances in Colloid and Interface Science 64: 76.

Ridgeon, P. (2012). "How Does Gas Chromatography Work?" Retrieved March 11, 2013, 2013, from http://www.anatune.co.uk/about/how-does-gas-chromatography-work.

RyeBiofuels. (2013). "BioDiesel FAQs." 2013, from http://www.ryebiofuels.co.uk/bio-diesel-faq/.

SCF (2002). Polycyclic Aromatic Hydrocarbons - Occurrence in foods, dietary exposure and health effects. Brussels, Belgium, European Commission.

Scheepers, P. and Bos, R. (1992). "Combustion of diesel fuel from a toxicological perspective. II. Toxicity." Int Arch Occup Environ Health 64(3): 163-177.

Schein, A., Scott, J., Mos, L. and Hodson, P. (2008). "Oil Dispersion Increases the Apparent Bioavailability and Toxicity of Diesel to Rainbow Trout (Oncorhynchus Mykiss)." Environmental Toxicology and Chemistry 28(3): 8.

Scott, J. H. (1976). Coagulation Study of a Bound Water Bulked Sludge. Master of Science, Virginia Polytechnic Institute and State University.

Sementelli, A. and Simons, R. (1997). "Regulation of Leaking Underground Storage Tanks: Policy Enforcement and Unintended Consequences." Economic Development Quarterly 11(3): 13.

Senn, R. and Johnson, M. (1987). "Interpretation of Gas Chromatography Data as a Tool in Subsurface Hydrocarbon Investigations." Groundwater Monitoring & Remediation 7(1): 6.

SigmaAldrich (1998). Guide to Solid Phase Extraction, Sigma Aldrich: 12.

Sweet, C., Hoogstraten, J. V., Harris, M. and Laskowski, J. S. (1997). The Effect of Frother on Bubble Size and Frothability of Aqueous Solutions, Processing of Complex Ores. The 2nd UBC-McGill Int. Symposium, Montreal, Canada, Metallurgical Society of CIM.

Szwilski, T. (1986). Mining, Our Own Business: Small Underground Coal Operations. SME Annual Meeting. New Orleans, LA: 3.

TriangleBiofuelsIndustries. (2007). "Am I Ready for Biodiesel?", 2013, from http://www.trianglebiofuels.com/faq.php.

UMass. "Factors Affecting the Separation in the GC." 2013, from http://www.chem.umass.edu/~samal/269/lecture/cyc/cyc10.pdf.

UniversityofWashington GC Columns: Factors affecting retention and separation, University of Washington: 1.

USEPA. (1999). 2012.

Valdes, A. and Garcia, A. (2005). "On the utilization of waste vegetable oils (WVO) as agglomerants to recover coal from coal fines cleaning wastes (CFCW)." Fuel 85(2006): 8.

Wang, Z., Hollebone, B., Fingas, M., Fieldhouse, B., Sigouin, L., Landriault, M., Smith, P., Noonan, J. and Thouin, G. (2003). Characteristics of Spilled Oils, Fuels, and Petroleum Products: 1. Composition and Properties of Selected Oils.

Wang, Z., Hollebone, B., Fingas, M., Landriault, M., Sigouin, L. and Feng, Y. (1996). <u>Using Systematic and Comparative GC/MS and GC/FID Data to Identify the Source on Contaminated Birds</u>. Nineteeth Arctic Marine Oilspill Program, Ottawa, Canada.

Waters (2009). Care and Use Manual. Milford, MA, Waters Corporation: 6.

Watts, R. J. (1998). <u>Hazardous Wastes: Sources, Pathways, Receptors</u>. New York, NY, John Wiley and Sons.

Wick, A., Haus, N., Sukkariyah, B., Haering, K. and Daniels, W. (2011). Remediation of PAH-Contaminated Soils and Sediments: A Literature Review. Blacksburg, VA, Virginia Polytechnic Institute and State University: 102.

Wills, B. (2006). <u>Wills' Mineral Processing Technology</u>. Burlington, MA, Elsevier Ltd.

WV-DEP (2009). An Evaluation of the Underground Injection of Coal Slurry in West Virginia. <u>Phase I: Environmental Investigation</u>.

Yang, H., Zhou, Y. and Liu, J. (2009). "Land and water requirements of biofuel and implications for food supply and the environment in China." <u>Energy Policy</u> 37(2009): 10.

4   FLOTATION TESTS

1. Introduction

The previous chapters in this thesis discuss the potential presence of diesel range organics (DRO) in processing streams based on the results from laboratory tests where reagents are aggressively agitated with fine coal and water, and then filtered. This chapter builds upon that fundamental work by investigating the partitioning of petro-diesel (termed "diesel" in this paper) in actual froth flotation experiments. The purpose of these experiments was to more closely simulate real coal preparation operations and determine residual DRO and PAHs of interest in the process waters associated with the concentrate and tailings.

The flotation tests differ from previous tests by attempting to separate the coal from the ash and measuring the process water from both of these products. Based on prior results, it is expected that DRO may be limited to the WSF. Based on the results from *Chapter 3*, it is expected that the concentrate water will have higher DRO than the tails since the diesel sticks to the coal but then may come off with the water during dewatering.

2. Experimental Methods

Flotation studies were carried out to understand DRO partitioning, including PAH-compound partitioning, between concentrate and tailings process waters. The flotation tests investigated a range of diesel dosages (as described below) on three coal types, which differed by source and ash content. Coals 1, 2 and 3 had ash contents of 10.8, 10.6, and 45.7%, respectively. Coal types 1 and 2 were collected as flotation feed from a coal preparation plant, while coal type 3 was collected as raw feed prior to entering the plant. The coal was prepared for testing only by sizing. Coal type 3 was crushed using a laboratory jaw crusher followed by a roll crusher, and then wet screened to obtain material in the range of 44-149 microns (100 x 325 mesh). Coal types 1 and 2 were wet screened at +44 microns (+325 mesh).

Figures 4.1-4.3 show the particle size distribution for the three coal types. For each coal type, the distribution was determined from 5 samples and the error bars in these figures represent one standard deviation from the mean. Coal types 1 and 2 contain coarser material than coal type 3. Most of the material for coal type 3 is within the 100 x 325 mesh range as it should be.

Coal type 2 contains material that is slightly coarser than coal type 1; however, both coal types have material that is similarly sized.
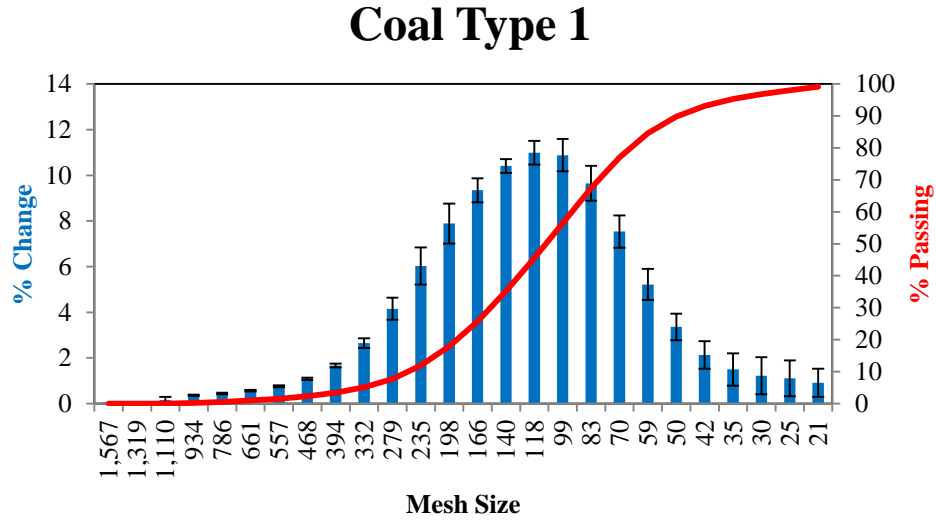
Coal Type 1

Figure 4.1: Particle size distribution of coal type 1
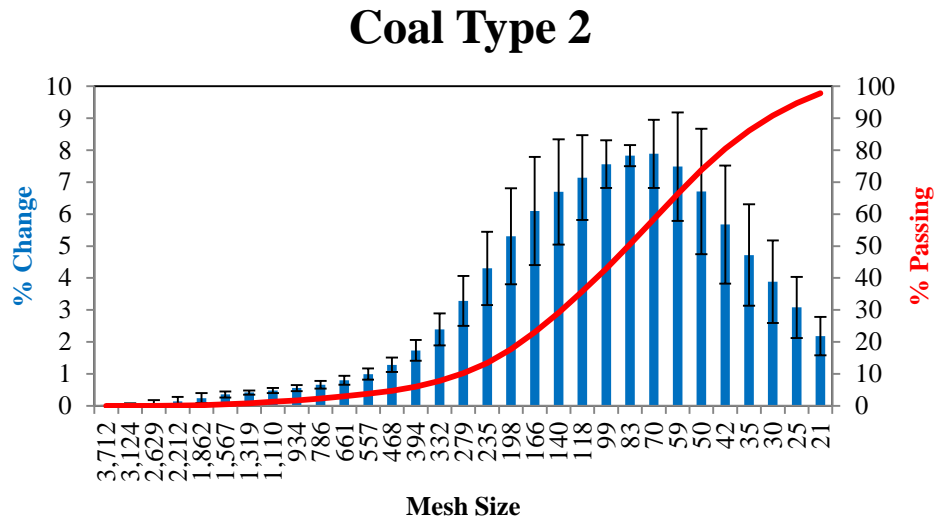
Coal Type 2

Figure 4.2: Particle size distribution of coal type 2

Coal Type 3
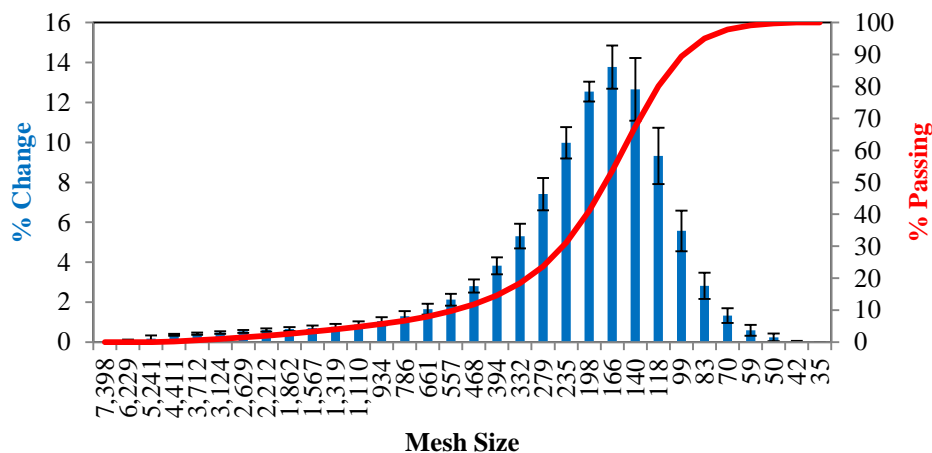
Figure 4.3: Particle size distribution of coal type 3

The diesel used in these tests was purchased from a local fuel station, and stored in an amber, airtight glass jar. A sample of 99+% methyl isobutyl carbinol (MIBC), the frother used in these tests, was purchased from Fisher Scientific. The MIBC dosage was kept constant at 10 ppm, while diesel dosage was varied at 0.1, 0.5, 1, and 2 lb/ton. Slurry percent solids was kept constant at 5% (by weight) and the flotation tests were performed in a Denver cell with 2 L of deionized water (DI). Mixing velocity was held constant at 1300 rpm, with the air valve completely open during flotation. The flotation time was fixed at 2 minutes for all tests. Prior to flotation, there was a fixed mixing time of the slurry for two minutes, and an additional fixed conditioning time of two minutes after adding the diesel to the cell. The concentrate and tailings products were then dewatered by filtration (through 5 μm paper using a vacuum pump), and the filtrate was collected for DRO and PAH analysis. The dewatering equipment including the vessel and tubing were thoroughly cleaned between each sample by rinsing with deionized water and methanol.

Identical to analytical procedures outlined in *Chapter 3*, DRO was determined using an Agilent 5890 gas chromatograph equipped with a flame ionization detector (GC-FID), following EPA Method 3150. Samples were also analyzed for a group of target PAHs (i.e., phenanthrene and naphthalenes) using a Thermo Trace GC equipped with a Thermo DSQ II mass spectrometer (GC-MS), following EPA Method 3535A: Solid-Phase Extraction (SPE).

Following dewatering of the concentrate and tailings, the solid materials for each sample (i.e., cake on filter paper) was placed in an oven to dry until no incremental weight change was measured (i.e., all moisture was removed). Ash content was analyzed in each solid sample using a LECO model 601-400-600 ash analyzer, and the yield and combustible material recovery for each flotation test was then determined (Equations 4.1 and 4.2). Y represents the yield, FA represents the ash content measured in the feed, TA represents the ash content measured in the tailings, FA represents the ash content measured in the feed, and R represents the recovery.

$$Y = \frac{FA - TA}{CA - TA} \; x \; 100 \qquad\qquad\qquad \text{Equation 4.1}$$

$$R = \frac{100 - CA}{100 - FA} \; x \; Y \qquad\qquad\qquad \text{Equation 4.2}$$

3. Results and Discussion

Similar to findings of fundamental laboratory tests described in *Chapters 2* and *3*, results of the flotation tests consistently indicate that a small fraction of diesel partitions to the process waters associated with both the tailings and concentrate; and again the amount of DRO appears to be limited to the soluble portion. Table 4.1 summarizes the tests and shows that residual DRO in both the concentrate and tailings process waters tend to increase with increasing diesel dosage. Figures 4.4-4.7 show the concentrate and tailings residual DRO content for the three coal types. Tests were repeated for coal type 2 and are displayed as "Test 1" and "Test 2" for coal type 2. For all three coal types, residual DRO in the concentrate process water samples was significantly higher than that in the tailings process water, usually by a factor of two or more. Moreover, for all three coal types, residual DRO in the process water tended to increase with increasing diesel dosage.

Table 4.1: Flotation test results

Test Name	Yield (%)	Recovery (%)	Ash Rejected (%)	DRO (mg/L)	Processing Stream
Coal Type 1 0 lb/ton	92.7	99.2	61.1	N/A	Concentrate
				N/A	Tailings
Coal Type 1 0.1 lb/ton	93.0	99.2	58.0	0.12	Concentrate
				0.01	Tailings
Coal Type 1 0.5 lb/ton	93.6	99.5	55.2	0.23	Concentrate
				0.07	Tailings
Coal Type 1 1 lb/ton	93.8	99.5	53.1	0.51	Concentrate
				0.14	Tailings
Coal Type 1 2 lb/ton	93.6	99.4	54.6	0.60	Concentrate
				0.43	Tailings
Coal Type 2 0 lb/ton	93.1	99.0	56.5	N/A	Concentrate
				N/A	Tailings
Coal Type 2 Test 1 0.1 lb/ton	92.1	98.8	56.5	0.21	Concentrate
				0.01	Tailings
Coal Type 2 Test 1 0.5 lb/ton	92.9	99.0	51.0	0.32	Concentrate
				0.04	Tailings
Coal Type 2 Test 1 1 lb/ton	95.6	99.3	31.4	0.30	Concentrate
				0.07	Tailings
Coal Type 2 Test 1 2 lb/ton	89.2	95.9	59.6	0.45	Concentrate
				0.28	Tailings
Coal Type 2 Test 2 0.1 lb/ton	94.6	99.3	44.2	0.12	Concentrate
				0.00	Tailings
Coal Type 2 Test 2 0.5 lb/ton	93.9	99.1	50.3	0.07	Concentrate
				0.00	Tailings
Coal Type 2 Test 2 1 lb/ton	93.1	98.9	55.6	0.11	Concentrate
				0.02	Tailings
Coal Type 2 Test 2 2 lb/ton	92.5	97.5	50.0	0.55	Concentrate
				0.23	Tailings
Coal Type 3 0 lb/ton	55.8	87.9	82.4	N/A	Concentrate
				N/A	Tailings
Coal Type 3 0.1 lb/ton	63.1	93.5	73.1	0.14	Concentrate
				0.01	Tailings
Coal Type 3 0.5 lb/ton	62.0	93.1	74.9	0.01	Concentrate
				0.00	Tailings
Coal Type 3 1 lb/ton	67.1	94.3	65.3	0.12	Concentrate
				0.02	Tailings
Coal Type 3 2 lb/ton	71.2	94.8	57.0	0.20	Concentrate
				0.03	Tailings
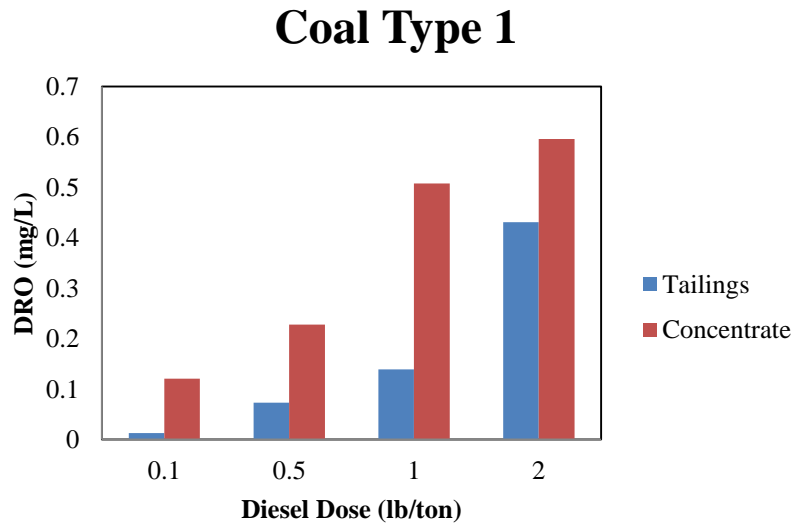
Coal Type 1

Figure 4.4: Residual DRO – concentrate and tailings for coal type 1
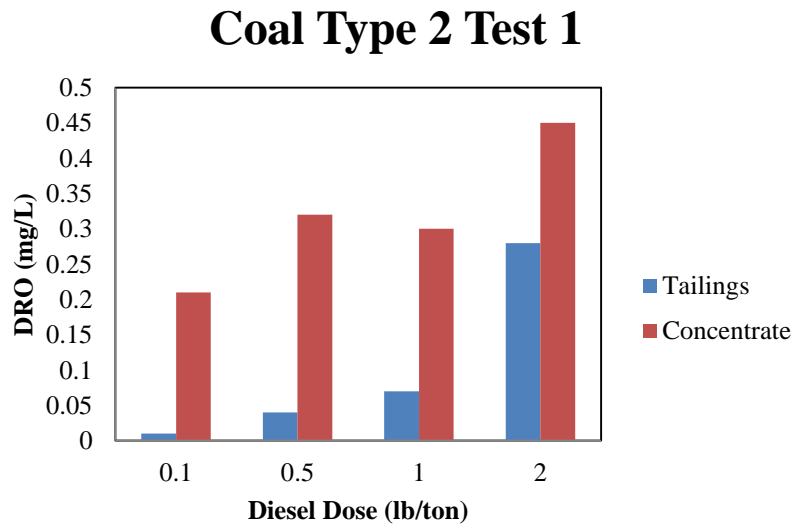
Coal Type 2 Test 1

Figure 4.5: Residual DRO – concentrate and tailings for coal type 2, test 1

Coal Type 2 Test 2
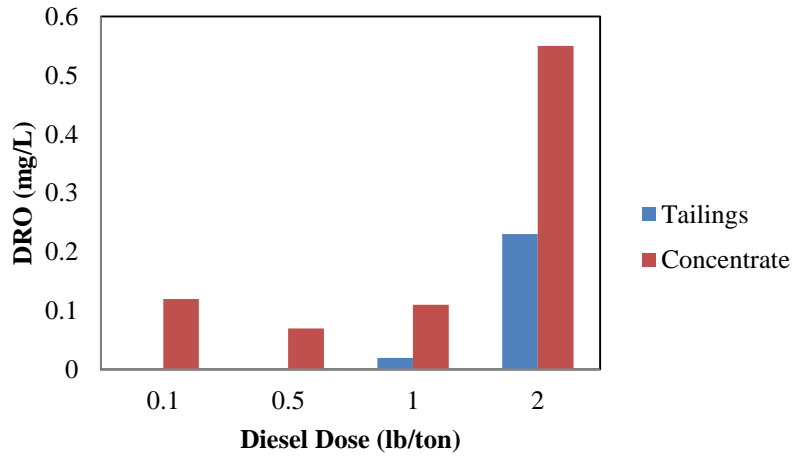
Figure 4.6: Residual DRO – concentrate and tailings for coal type 2, test 2

Coal Type 3
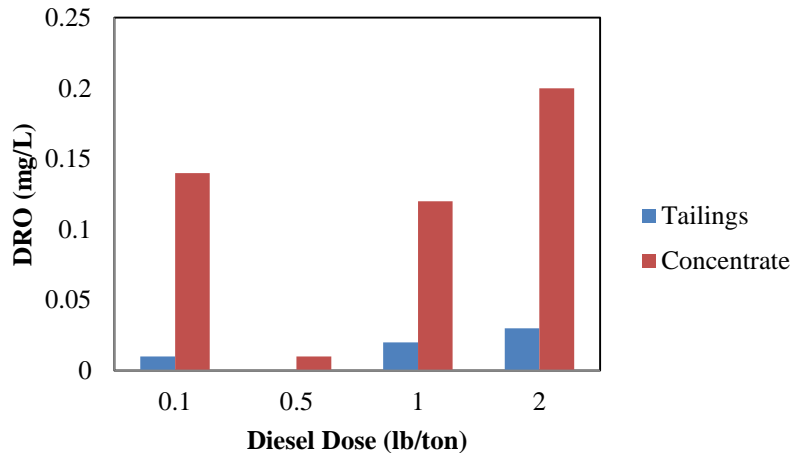
Figure 4.7: Residual DRO – concentrate and tailings for coal type 3

Figure 4.8 shows ash rejected versus combustible recovery for coal type 1. The ash rejected, AR, is simply the ash in the tailings relative to that in the feed (Equation 4.3). The graph shows that the combustible recovery is almost unchanged when more diesel is dosed (i.e., 1 and 2 lb/ton); however, the ash rejection improves significantly when less diesel is dosed (i.e., 0.1 and 0.5 lb/ton). This effect might be explained by a tendency for un-liberated ash particles

(i.e., ash-coal matrix particles) to float when sufficient diesel is present. Figure 4.9 shows ash rejection vs. combustible recovery for coal type 3 and Figures 4.10 and 4.11 show ash rejection vs. combustible recovery for coal type 2 - tests 1 and 2. The graph for coal type 3 is quite similar to that of coal type 1, with the highest ash rejection resulting from the lowest diesel dosages. For coal type 2, ash rejections are relatively low for all diesel dosages – perhaps due to a relatively higher proportion of un-liberated ash particles in this coal sample vs. coal types 1 and 3 – but a substantial decrease in recovery is seen at the highest diesel dosage. This may be related to a negative effect on frothing with too much diesel present. To put the observed flotation performance in perspective for all four sets of tests, Figure 4.12 shows the ash rejected vs. combustible recovery.

$$AR = \frac{TA}{FA} \, x \, (100 - Y) \qquad\qquad \text{Equation 4.3}$$
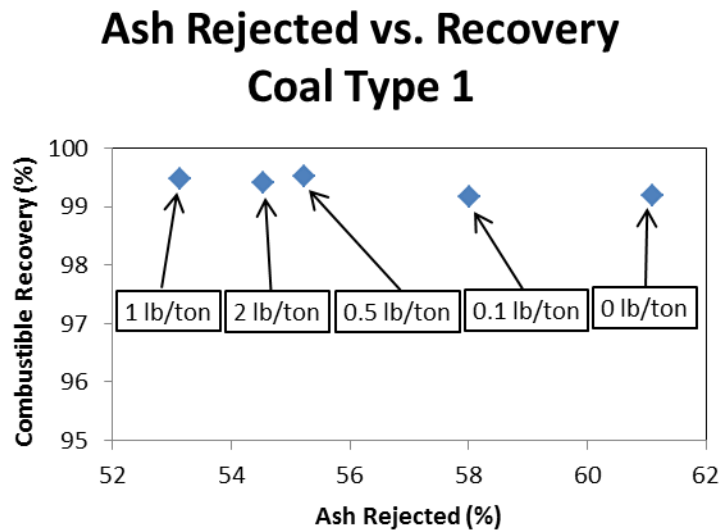
Figure 4.8: Ash rejected vs. combustible recovery for coal type 1
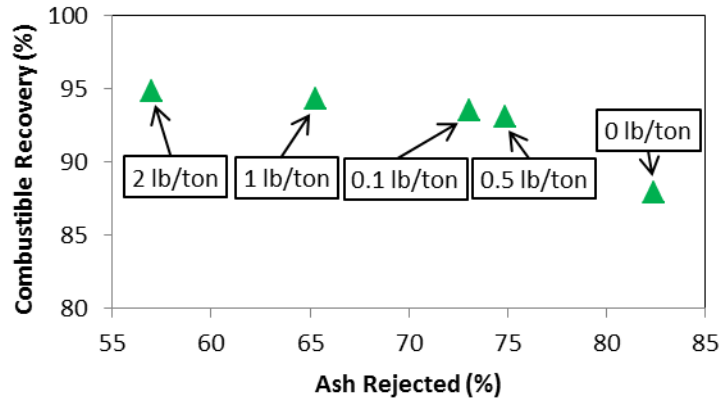
Figure 4.9: Ash rejected vs. combustible recovery for coal type 3
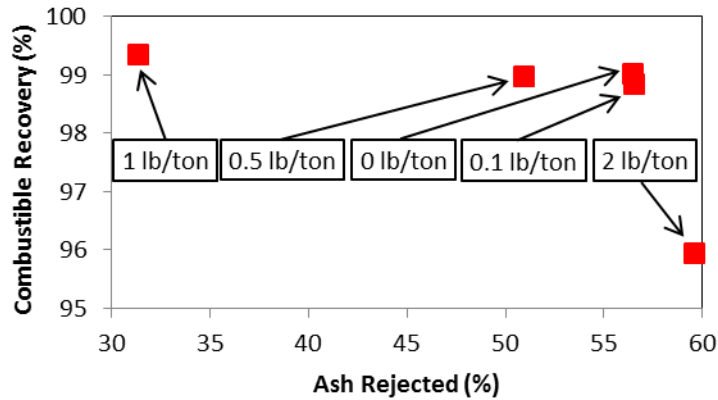
Figure 4.10: Ash rejected vs. combustible recovery for coal type 2, test 1
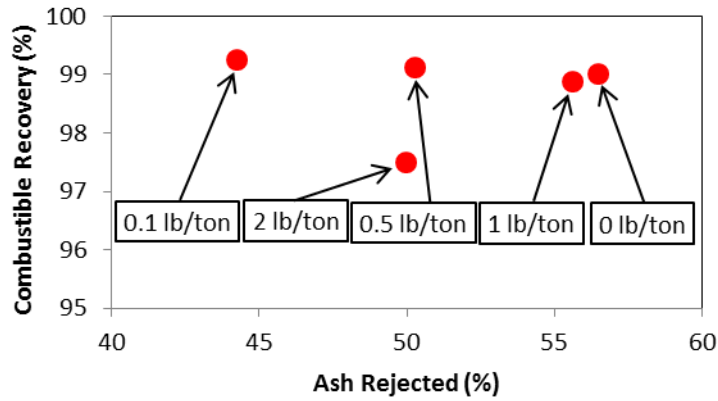
Figure 4.11: Ash rejected vs. combustible recovery for coal type 2, test 2
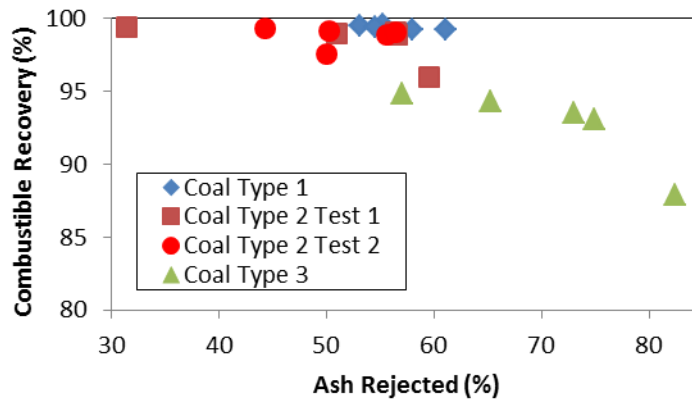
Figure 4.12: Ash rejected vs. combustible recovery for all four sets of tests

Because the test work presented in *Chapter 3* showed that napthalenes account for the highest PAH concentrations in the test diesel (see Table B.1 in Appendix B) and are also expected to be present in relatively higher concentrations than other PAH in the flotation process waters, GC-MS was used to screen for naphthalene and 22 of its methylated compounds in all flotation process water samples. Phenanthrene was also present in the test diesel, but previously

66

did not show up in process water samples (see *Chapter 3*). This compound was additionally investigated by GC-MS in all flotation process water samples.

Like in results reported in *Chapter 3*, no residual phenanthrene could be detected in the flotation water samples. In total, six naphthalene compounds were detected: (naphthalene, 2-methylnaphthalene, naphthalene C2a, naphthalene C3a, naphthalene C3c, naphthalene C4a). Results are shown for naphthalene (Figure 4.13) and 2-methylnaphthalene (Figure 4.14) since most of the samples contained at least a trace amount of these compounds, whereas the other three compounds that were detected were only found in a few samples and at levels of 10 to 100 times lower (see Appendix D, Table D.1). Results are displayed based on the relative response factor (RRF), the sample area divided by the internal standard area, rather than as a calculated concentration because all the results are significantly lower (i.e., 10 to 500 times) than the lowest PAH standard analyzed (1 mg/L containing multiple PAHs). Thus, reporting the RRF illustrates the relative differences in results between samples, but does not attempt to quantify the PAH concentrations. In general, the PAHs appear to be present at higher concentrations in the concentrate samples as compared to the tailings samples. For some samples, naphthalene was below the detection limit. Equation 4.4 shows how the RRF is calculated using the sample area, SA, and the internal standard area, ISA.

$$RRF = \frac{SA}{ISA}$$

Equation 4.4
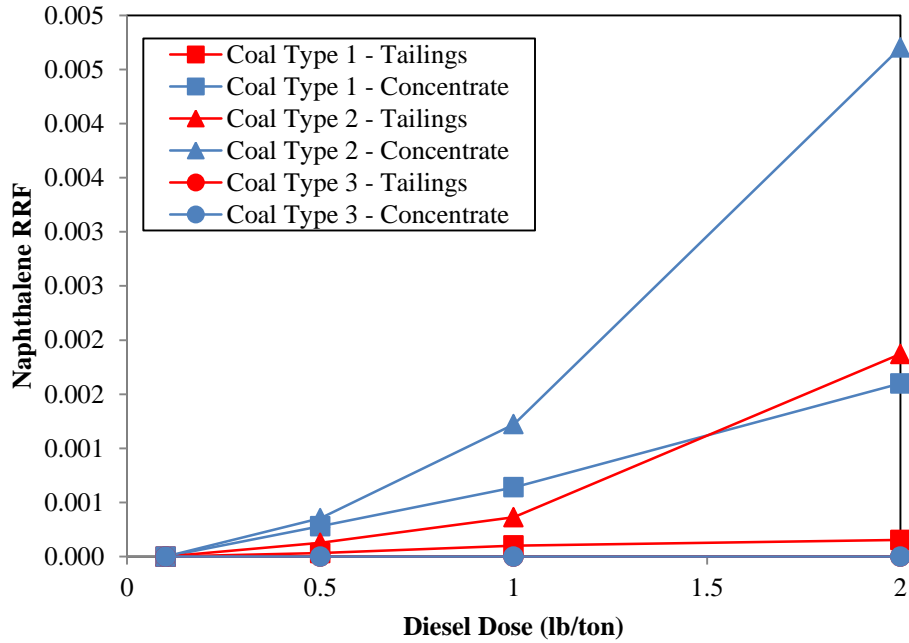
Figure 4.13: Naphthalene in flotation samples
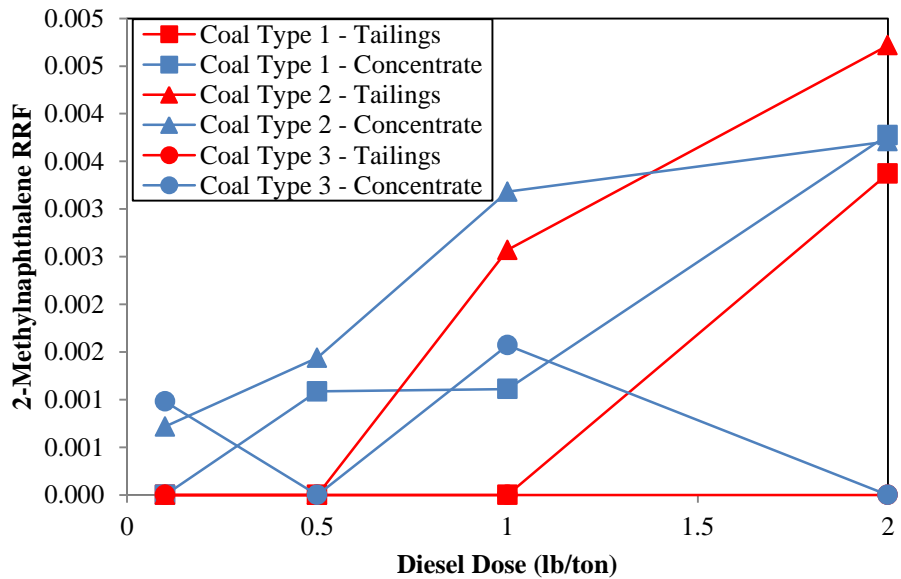
Figure 4.14: 2-Methylnaphthalene in flotation samples

The previous results suggest that the fate of DRO is similar to what was previously hypothesized: DRO may be limited to the WSF and the concentrate water will have higher DRO

than the tails since the diesel sticks to the coal but then may come off with the water during dewatering. Given that DRO also tended to be higher in the concentrate samples, this is consistent with prior results that indicated PAHs tended to partition proportionately with total DRO (see *Chapter 2*). Moreover, the residual PAHs also tended to be higher in samples where diesel dosage was higher – which also suggests that these compounds partition proportionally with total DRO.

Collectors like diesel are used in flotation to enhance the performance of the process. For all types of coal, there is likely a diesel dosage that will maximize the flotation performance in terms of particle separation by optimizing coal recovery and ash rejection simultaneously; however, this dosage may vary substantially between coal types. For the experiments reported here, only a limited range of diesel dosages has been explored for a limited selection of coal types and within limited particle size distributions. Clearly, all three coals used here required relatively low levels of diesel for favorable flotation performance.

4. Conclusions

As a result of these findings, there appears to be a potential correlation between residual DRO and flotation performance. It appears as though operating performance and residual DRO may go hand in hand. This means that under normal operating conditions, residual DRO does not seem to be an issue; however, during abnormal conditions, such as when conditions exist where diesel is effectively overdosed significantly (e.g., in cases where the flotation coal feed is reduced or halted, while diesel continues to be fed into the flotation system), DRO in process water may be a potential issue. In order to account for the chance of abnormal conditions occurring such as when the feed may stop entering the circuit, an automatic switch should be connected so that when the feed stops, reagent dosing stops as well. Likewise, it would be environmentally wise to develop a programmable logic controller that determines the amount of material being fed into the flotation circuit and based on this amount, adjusts the reagent dosage being fed into the circuit.

5   CONCLUSIONS: CHALLENGES AND LESSONS LEARNED

1. Introduction

Measuring low-level organic reagents in coal preparation process waters is a difficult task, and this chapter is designed as an aid for future work. The intent is to highlight several challenges that were encountered in this work, and outline a structured methodology for researchers investigating diesel range organic (DRO) compounds in aqueous samples from coal processing. Sample preparation, GC analysis, and results interpretation are all specifically discussed.

2. Challenges And Lessons Learned

2.1 Sample Preparation

Variability of test materials (i.e., coal) and reagents (e.g., petro-diesel) may easily affect results of DRO partitioning tests and should be considered in the design of future experiments. Here, petro-diesel (termed "diesel" in this paper) was simply collected from local a fuel station, and care was taken to use the same diesel across all experiments where results were directly compared to one another (e.g., in tests where PAHs were measured). Several coal samples were used over the course of the project, including   raw coal that was crushed and sized in the laboratory, and flotation feed slurries that only required dewatering and screening to the desired size range. All coals tested differed noticeably by ash content, which likely had some relative effect on DRO partitioning per *Chapter 2* findings. Additionally, it is expected that other properties (e.g., rank, porosity, etc.) also differed between the coals studied; however no testing was done to quantify these properties. All else being equal, it is recommended that flotation feed slurry be used for future work since, simply put, this allows testing of coal samples representative of a real preparation plant.

While many experiments described here only included strong agitation of coal, water and reagents prior to analysis of process water, actual flotation experiments provide a more practical understanding of field conditions. Typically during laboratory flotation tests water is added to the cell to remove material that adheres to the cell wall as well as to replace water that has been removed from the cell while paddling the concentrate out of the cell. The concern with this regarding measuring the amount of DRO in process streams is that adding water changes the

concentration of the DRO. It is difficult to determine how much of the water added will end up in the concentrate stream and how much will remain in the cell. What was done for the flotation tests in this thesis and is recommended is to not add any additional water to the cell. It can be assumed that the material adhering to the cell wall above the water line is concentrate since this material floated to reach that point on the cell wall. Paddle strokes can be adjusted to account for the loss in water.

Another note to make regarding sample preparation deals with dewatering. Tests showed that there was no difference in results for samples that were filtered vs. centrifuged. It is highly recommended that samples should be filtered instead of centrifuged based on time requirements as well as typical capacities of laboratory equipment.

The final sample preparation note concerns the sample container. While it is known that diesel contains volatile components, no testing was performed to determine if samples that had headspace in their holding jars would differ from those where no headspace was present. Instead, it is advised that samples shall be stored without headspace. If for some reason samples need to be stored for more than a day, it is also advised that they be stored in a refrigerator.

2.2 Analysis of Results

The first challenge of data analysis, as discussed in *Chapter 1* is calculating the area underneath each peak. It is advised to use a program that will calculate the total area instead of using a baseline drawn by the user for reasons such as user variability as well as time required. The total area is the area underneath each peak, between the peak and the baseline, as previously described in *Chapter 1*. Another challenge was discovered with the GC-FID results from the flotation tests showing large peaks within the diesel range, but presumably not associated with the diesel (Figure 5.1). These samples were run on the GC-MS and these peaks were determined to be phthalates, a compound commonly found in plastics (Figure 5.2) (Jobling et al. 1995). The laboratory source of the phthalates is unknown; however, the phthalates only appear in samples that were from the flotation tests. The amount of phthalates found in the flotation samples is shown in Table D.2 in Appendix D. It is hypothesized that the source may be plastic tubing used for dewatering. Regardless of the source, the chromatogram results need to be adjusted accordingly. The two main options are to remove the time frame at which the phthalates elute from the column (i.e., around 25 minutes) or to remove each peak individually.

71
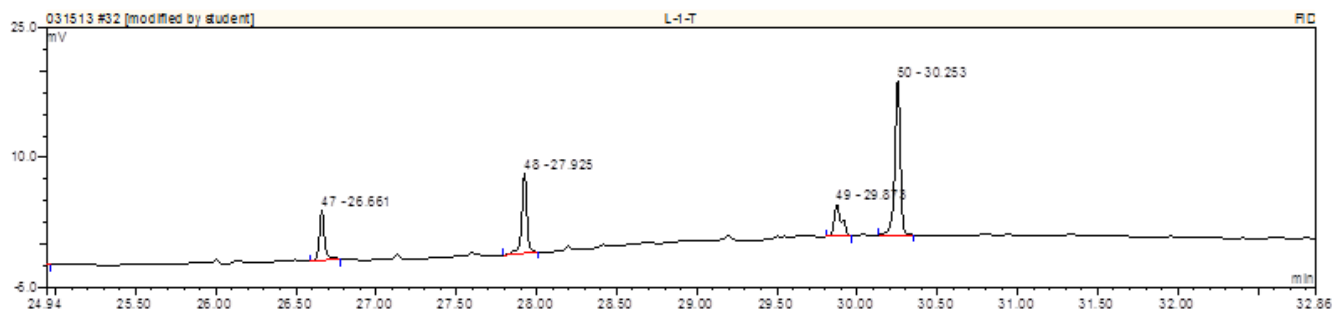
Figure 5.1: GC-FID chromatogram showing phthalates
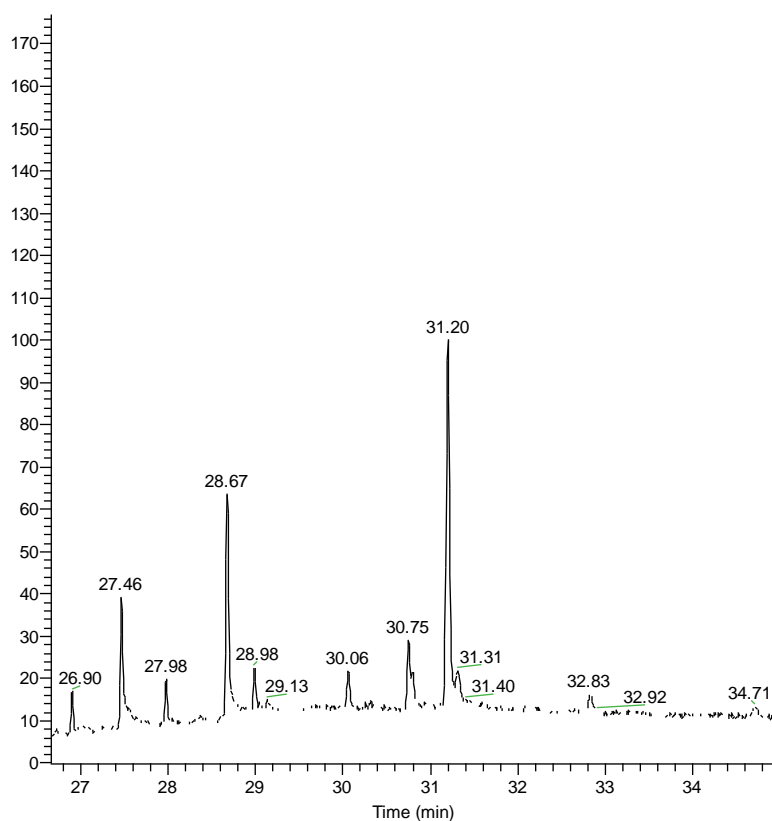
Figure 5.2: GC-MS chromatogram showing phthalates

Removing the time frame is much easier and less time consuming since the program can be adjusted to stop calculating the sample area after 25 minutes; however, a small amount of the diesel is still present after 25 minutes (Figure 5.3). While this change will solve the problem associated with the phthalates, it introduces a systematic error. If the amount of DRO eluting from the column after 25 minutes is proportional to that eluting before 25 minutes for all samples

then this is the simple solution; however, if it is not proportional then this technique may not be the best option to account for the phthalates. The problem with individually removing the phthalates peaks besides increased time is that this introduces the potential for user error.
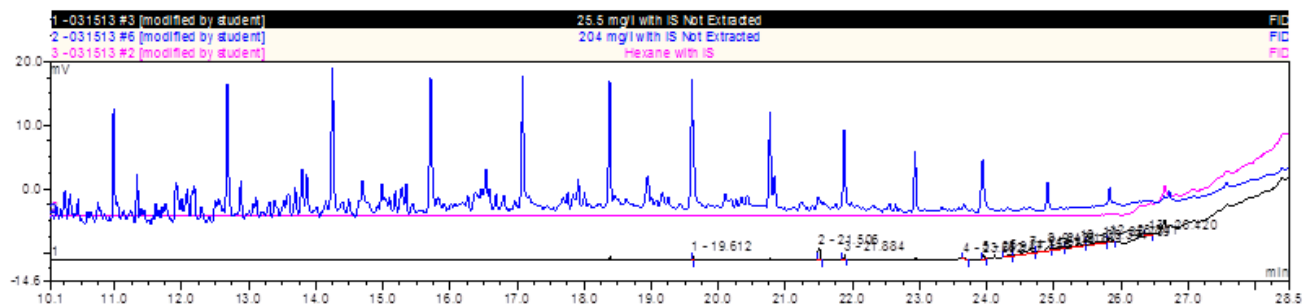
Figure 5.3: Diesel standard showing DRO past 25 minutes

Figure 5.3 shows the 204 mg/L standard (i.e., 204 mg diesel per L of hexane) in blue, the 25.5 mg/L standard in black, and Hexane in pink. The blue line shows that some of the DRO is removed after 25 minutes; however, the amount removed relative to the peaks before 25 minutes is quite small. The pink line shows that excess noise is detected after 26 minutes. The black line shows that the area underneath the peaks after 25 minutes is quite significant relative to the area underneath the peaks before 25 minutes; however, most of it may be due to noise instead of DRO compounds. Figure 5.4 shows enlarged graph of the 25.5 mg/L standard, shown in black, and hexane, shown in blue, that was shown in Figure 5.3. The graph indicates that after 25 minutes, most of the peaks are due to noise as can be seen in the hexane sample. As a result, it was determined that adjusting the program to only include peak area prior to 25 minutes is a justifiable solution for dealing with the phthalates issue. It was also determined that the 25.5 mg/L standard is below the detection limit and should not be used in the calibration curve since most of the DRO peaks are not detected and area is more likely to be affected by noise.
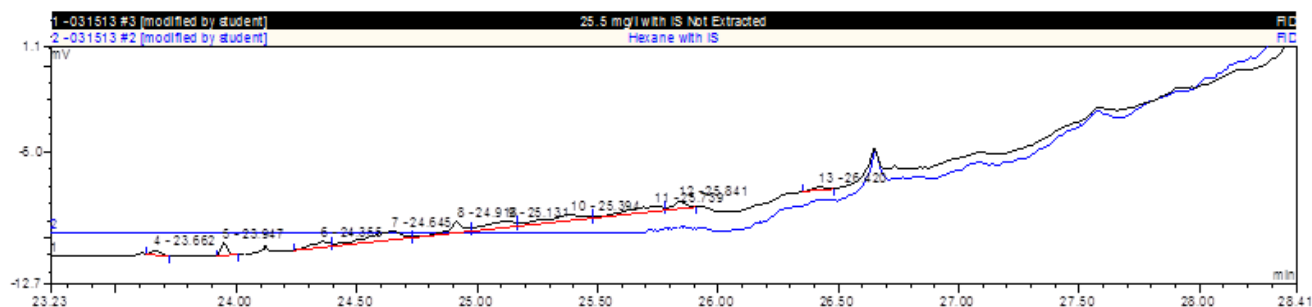
Figure 5.4: Low level diesel standard and hexane past 25 minutes

Interpretation of chromatogram results is another common challenge of using GC to quantify analytes. A calibration curve must be created by analyzing standards, which contain known amounts of the analyte (i.e., diesel). For this work, once the diesel concentration range anticipated in the samples was determined, a calibration curve was developed accordingly. Since most samples typically appeared to contain between 0.3 to 1 mg/L with a concentration factor of 100 or 200, calibration points of 50, 100, and 200 mg/L were used. The internal standard was then added to the standards and they were run on the GC-FID with the experimental samples.

The relative response factor (RRF) was calculated by dividing the sample area, SA, by the internal standard area, ISA (Equation 5.1). The RRF was then plotted against the known concentration to develop a calibration curve (Figure 5.5). The calibration curve was then used to calculate the extracted sample concentrations. These concentrations were subsequently adjusted for the concentration factor. For example, in the flotation tests, a total of 200 mL of concentrate or tailings water sample was concentrated to just 1 mL, thus giving a concentration factor of 200x. Additionally, an extraction efficiency factor was applied to all adjusted sample concentrations. To determine the extraction efficiency, EE, the adjusted sample concentration of the *extracted standards, SC,* was divided by the known concentration, KC (Equation 5.2). The average extraction efficiency could then be applied to all extracted experimental samples. Finally, the average measured concentration in the extracted blanks was subtracted from the samples to account for noise.

$$RRF = \frac{SA}{ISA} \qquad\qquad \text{Equation 5.1}$$

74

$$EE = \frac{SC}{KC} \qquad\qquad\qquad \text{Equation 5.2}$$

This is the recommended technique for analysis of results based on the experience gained throughout this work. Not only is DRO difficult to measure, but because there are many steps required and the amount measured is so low, quantification can be quite difficult. When attempting to quantify results, keep in mind the degree of precision that is desired. It is recommended to place more focus on sample trends rather than the quantification itself.

Calibration Curve

y = 0.0196x - 0.272
R^2 = 0.9797
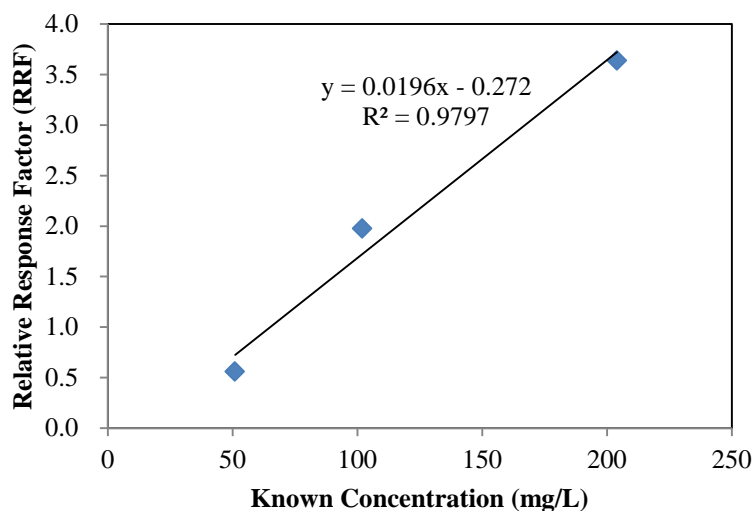
Figure 5.5: DRO calibration curve

3. Conclusions

This thesis answers a number of preliminary questions regarding the potential fate of reagents, particularly diesel collector, from coal processing. *Chapter 1: Literature Review* outlines these questions and provides background information necessary to frame the potential problem and design relevant experiments. *Chapter 2: Reagents in Coal Preparation: Where Do They Go?* discusses preliminary test work regarding conditions such as dewatering techniques and reproducibility of results, along with work associated with measuring frother. This chapter illustrates that reagents are not likely to partition completely to a single fraction of the process slurry. Importantly, data presented in this chapter also indicates that some frothers may behave

quite differently than others depending on dosage *and* slurry percent coal solids – which may have implications for the preparation circuit performance when water is recycled from the flotation units to other unit operations. Figure 2.2 illustrates that for M150 and PSM frothers the water surface tension is highly sensitive to frother dosage and coal percent solids. Only at very low dosages and higher percent solids does most of the frother appear to sorb to the coal. In a plant setting, this suggests that residual frother may quickly accumulate in the process water; and based on independent practical observations, these frothers are indeed known to have a tendency to foul processing circuits where water is recycled, often causing problems with pumping and foaming in tanks. On the other hand, results for MIBC and Nalco 8836 show that the water surface tension does not change significantly at relatively low frother dosages (i.e., practical dosages) across all coal percent solids values. Likewise, these frothers are practically known to cause fewer foaming problems in preparation plants.

Chapter 3: Diesel Range Organics In Coal Preparation discusses the ability to remove DRO from water, the desorption capacity of DRO from coal, as well as the investigation of PAHs in these tests. These tests show that insoluble diesel and most PAHs may be removed via normal plant operating conditions; however, soluble diesel may remain. While most heavier, PAHs (i.e., those with a great number of rings) were not detected, pyrene, a PAH with four rings, was consistently measured at low concentrations. Although pyrene is not highly soluble in water, it is possible that in the case of DRO residuals in water, co-solvency may occur by which pyrene is dissolved in other diesel compounds, which are themselves dissolved in the water. By means of co-solvency, some PAHs like pyrene may be able to remain dissolved in water to some small extent so long as their direct solvent is present. Finally, *Chapter 4: Flotation Tests* discusses DRO results from flotation test work. These tests show that in terms of environment and performance, it pays to operate efficiently. The tests in this thesis are all geared towards investigating the potential fates of reagents in a preparation plant. While it appears as though these reagents do not impose significant concern under normal operating conditions, further work may certainly be warranted to understand partitioning behavior under conditions outside of the norm.

Future Work

The main points regarding future work are as follows:

1. Obtaining field data to confirm the results shown here
2. Determining what happens when operating conditions are outside of normal
3. Developing operating systems to help avoid abnormal conditions and thus DRO transport to the environment
4. Understanding other reagents that may be potential environmental concerns

This future work is aimed towards the application of fundamental knowledge gained from the test work shown here.

References

Jobling, S., Reynolds, T., White, R., Parker, M. and Sumpter, J. (1995). "A Variety of Environmentally Persistent Chemicals, Including Some Phthalate Plasticizers, Are Weakly Estrogenic." Environmental Health Perspectives **103**(6): 6.

Appendix A: Biodiesel characteristics

Biodiesel Calibration Curve

y = 3.0348x - 8.9394
R² = 0.9996

(y-axis: Biodiesel (mg/L), x-axis: Area)
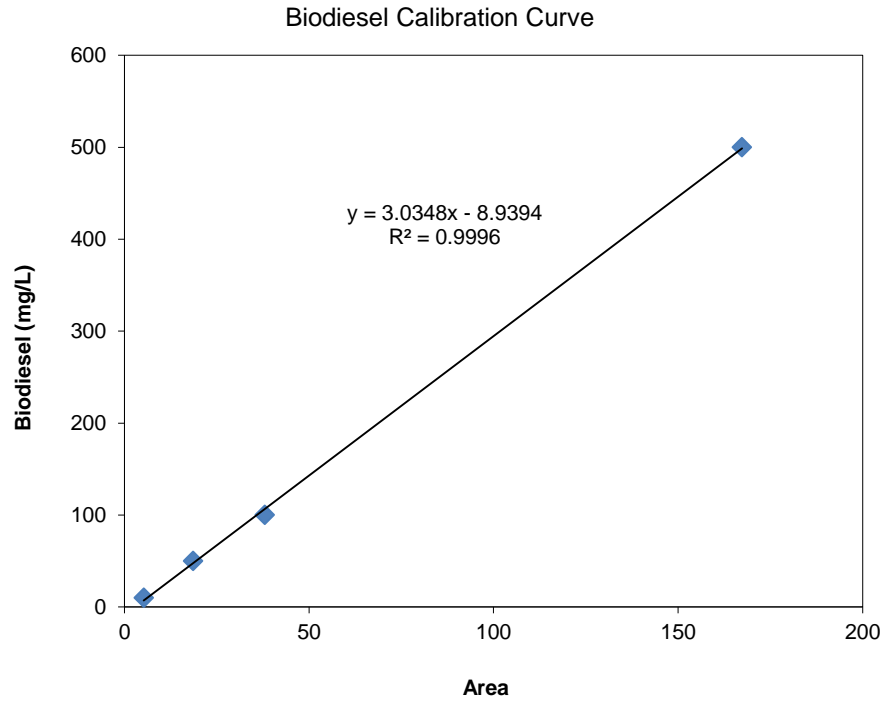
Figure A.1: Biodiesel calibration curve

Table A.1: Biodiesel calibration curve data

(mg/L)	Average RRF	Calculated mg/L
10	5.2	7.0
50	18.6	47.6
100	38.1	106.5
500	167.3	498.9

Appendix B: Diesel characteristics

Table B.1: PAHs found in test diesel and after contact with coal

PAH	Amount in test diesel (ppm)	Amount in water after contacted with coal (ppm)[a]
benz(a)anthracene	Not Found	Not Found
benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene	Not Found	Not Found
dibenz(a,h)anthracene	Not Found	Not Found
idenol(1,2,3-c,d)pyrene	Not Found	Not Found
Naphthalene	249.3	0.0601
Acenaphthene	34.1	0.0065
Fluorene	94.5	0.0068
Anthracene	Not Found	0.0027
Phenanthrene	61.5	Not Found
Pyrene	72.8	0.0002

[a] Water sample from a control test where diesel at 10 lb/ton was mixed with water and coal at 5% solids per the experimental procedure outlined in *Chapter 3*.

Table B.2: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C9

C9 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.77	19.82	0.24	8.64	
25 mg/l IS	11.10	20.21	0.55	23.62	
50 mg/l IS	23.63	20.19	1.17	53.75	
75 mg/l IS	33.49	19.90	1.68	78.64	
100 mg/l IS	43.12	21.27	2.03	95.35	
F1 (11/15) 20X Dil w/IS	12.53	17.09	0.73	32.56	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-3.04	0.170
F3 (11/15) 20X Dil w/IS	5.93	15.20	0.39	15.91	0.170
F1-STD (11/15) 5X Dil w/IS	34.13	19.51	1.75	81.86	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	18.13	20.61	0.88	39.66	

Figure B.1: C9 calibration curve

Table B.3: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C10

C10 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	5.01	19.82	0.25	8.54	
25 mg/l IS	11.44	20.21	0.57	23.55	
50 mg/l IS	24.24	20.19	1.20	53.96	
75 mg/l IS	34.50	19.90	1.73	79.54	
100 mg/l IS	43.48	21.27	2.04	94.40	
F1 (11/15) 20X Dil w/IS	20.60	17.09	1.21	54.20	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-3.58	0.170
F3 (11/15) 20X Dil w/IS	9.70	15.20	0.64	27.02	
F1-STD (11/15) 5X Dil w/IS	34.01	19.51	1.74	81.56	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	18.30	20.61	0.89	40.06	

C10 Calibration Curve

$y = 47.932x - 3.5761$
$R^2 = 0.9865$

X-axis: Area
Y-axis: C10 Conc.(mg/L)

Figure B.2: C10 calibration curve

Table B.4: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C11

C11-used C10 Calibration Curve for calculations. C11 was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	5.01	19.82	0.25	8.54	
25 mg/l IS	11.44	20.21	0.57	23.55	
50 mg/l IS	24.24	20.19	1.20	53.96	
75 mg/l IS	34.50	19.90	1.73	79.54	
100 mg/l IS	43.48	21.27	2.04	94.40	
F1 (11/15) 20X Dil w/IS	38.86	17.09	2.27	105.40	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-3.58	0.170
F3 (11/15) 20X Dil w/IS	17.80	15.20	1.17	52.55	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.5: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C12

C12

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	5.07	19.82	0.26	7.76	
25 mg/l IS	13.40	20.21	0.66	24.80	
50 mg/l IS	27.62	20.19	1.37	54.28	
75 mg/l IS	37.85	19.90	1.90	76.61	
100 mg/l IS	50.60	21.27	2.38	96.55	
F1 (11/15) 20X Dil w/IS	39.38	17.09	2.30	93.41	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-2.93	0.170
F3 (11/15) 20X Dil w/IS	17.90	15.20	1.18	46.31	
F1-STD (11/15) 5X Dil w/IS	34.20	19.51	1.75	82.03	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.73	20.61	0.86	38.71	
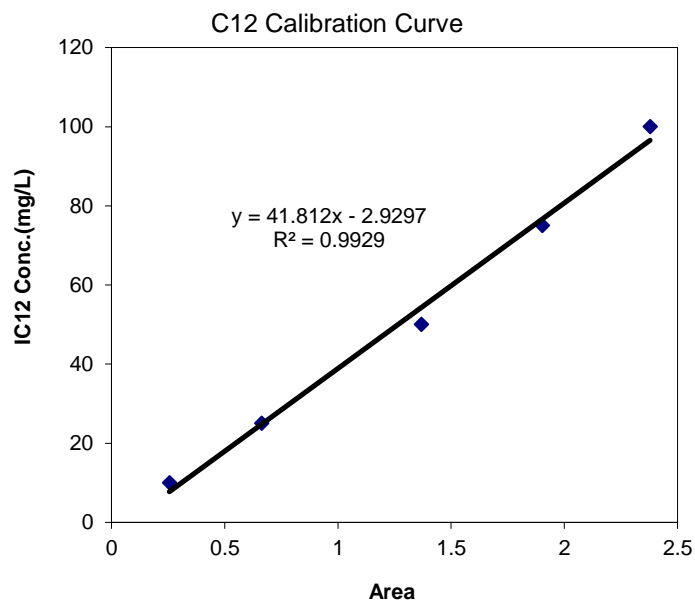
Figure B.3: C12 calibration curve

Table B.6: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C13

C13-used C12 Calibration Curve for calculations. C13 was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	5.07	19.82	0.26	7.76	
25 mg/l IS	13.40	20.21	0.66	24.80	
50 mg/l IS	27.62	20.19	1.37	54.28	
75 mg/l IS	37.85	19.90	1.90	76.61	
100 mg/l IS	50.60	21.27	2.38	96.55	
F1 (11/15) 20X Dil w/IS	45.18	17.09	2.64	107.60	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-2.93	0.170
F3 (11/15) 20X Dil w/IS	20.49	15.20	1.35	53.43	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.7: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C14

C14 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.55	19.82	0.23	9.58	
25 mg/l IS	11.08	20.21	0.55	23.71	
50 mg/l IS	24.02	20.19	1.19	52.14	
75 mg/l IS	34.67	19.90	1.74	76.63	
100 mg/l IS	47.29	21.27	2.22	97.94	
F1 (11/15) 20X Dil w/IS	43.19	17.09	2.53	111.41	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.59	0.170
F3 (11/15) 20X Dil w/IS	19.04	15.20	1.25	54.92	
F1-STD (11/15) 5X Dil w/IS	34.41	19.51	1.76	82.55	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.21	20.61	0.84	37.49	
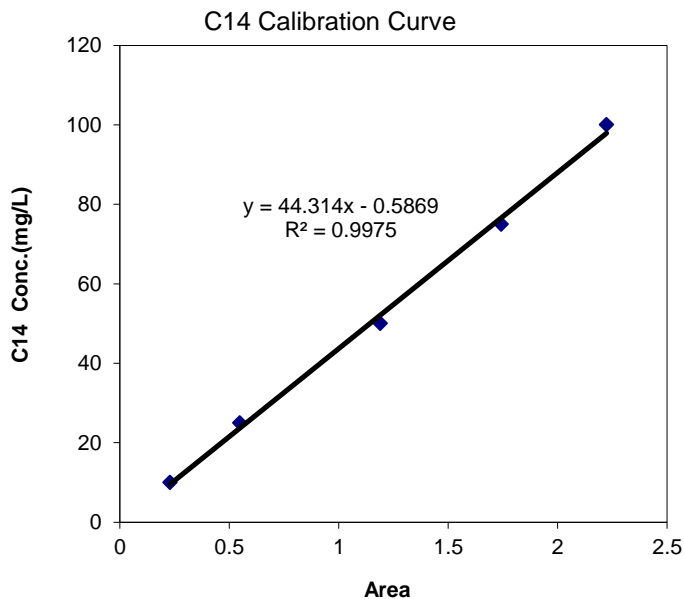
Figure B.4: C14 calibration curve

Table B.8: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C15

C15-used C14 Calibration Curve for calculations. C15 was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.55	19.82	0.23	9.58	
25 mg/l IS	11.08	20.21	0.55	23.71	
50 mg/l IS	24.02	20.19	1.19	52.14	
75 mg/l IS	34.67	19.90	1.74	76.63	
100 mg/l IS	47.29	21.27	2.22	97.94	
F1 (11/15) 20X Dil w/IS	39.39	17.09	2.30	101.56	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.59	0.170
F3 (11/15) 20X Dil w/IS	17.60	15.20	1.16	50.73	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.9: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C16

C16 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.85	19.82	0.24	9.46	
25 mg/l IS	11.29	20.21	0.56	23.89	
50 mg/l IS	23.69	20.19	1.17	52.13	
75 mg/l IS	33.90	19.90	1.70	76.48	
100 mg/l IS	46.21	21.27	2.17	98.03	
F1 (11/15) 20X Dil w/IS	38.76	17.09	2.27	102.42	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-1.78	0.170
F3 (11/15) 20X Dil w/IS	18.96	15.20	1.25	55.50	
F1-STD (11/15) 5X Dil w/IS	34.01	19.51	1.74	81.56	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.01	20.61	0.83	37.02	

C16 Calibration Curve

$y = 45.945x - 1.7827$
$R^2 = 0.9977$
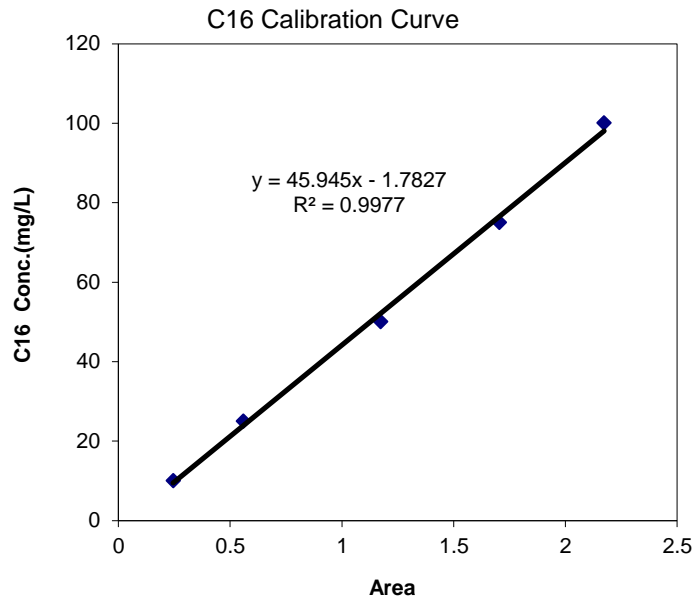
Figure B.5: C16 calibration curve

Table B.10: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C17

C17-used C16 Calibration Curve for calculations. C17 was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.85	19.82	0.24	9.46	
25 mg/l IS	11.29	20.21	0.56	23.89	
50 mg/l IS	23.69	20.19	1.17	52.13	
75 mg/l IS	33.90	19.90	1.70	76.48	
100 mg/l IS	46.21	21.27	2.17	98.03	
F1 (11/15) 20X Dil w/IS	26.95	17.09	1.58	70.67	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-1.78	0.170
F3 (11/15) 20X Dil w/IS	12.31	15.20	0.81	35.41	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.11: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – Pristane

Pristane-used C18 Calibration Curve for calculations. Pristane was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.76	19.82	0.24	9.24	
25 mg/l IS	11.84	20.21	0.59	24.21	
50 mg/l IS	25.07	20.19	1.24	52.59	
75 mg/l IS	35.17	19.90	1.77	75.34	
100 mg/l IS	49.04	21.27	2.31	98.62	
F1 (11/15) 20X Dil w/IS	12.53	17.09	0.73	30.57	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-1.15	0.170
F3 (11/15) 20X Dil w/IS	5.90	15.20	0.39	15.65	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.12: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C18

C18 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.76	19.82	0.24	9.24	
25 mg/l IS	11.84	20.21	0.59	24.21	
50 mg/l IS	25.07	20.19	1.24	52.59	
75 mg/l IS	35.17	19.90	1.77	75.34	
100 mg/l IS	49.04	21.27	2.31	98.62	
F1 (11/15) 20X Dil w/IS	24.53	17.09	1.44	60.96	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-1.15	0.170
F3 (11/15) 20X Dil w/IS	10.90	15.20	0.72	29.88	
F1-STD (11/15) 5X Dil w/IS	34.20	19.51	1.75	82.03	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.20	20.61	0.83	37.47	

C18 Calibration Curve

y = 43.273x - 1.1486
R² = 0.9981
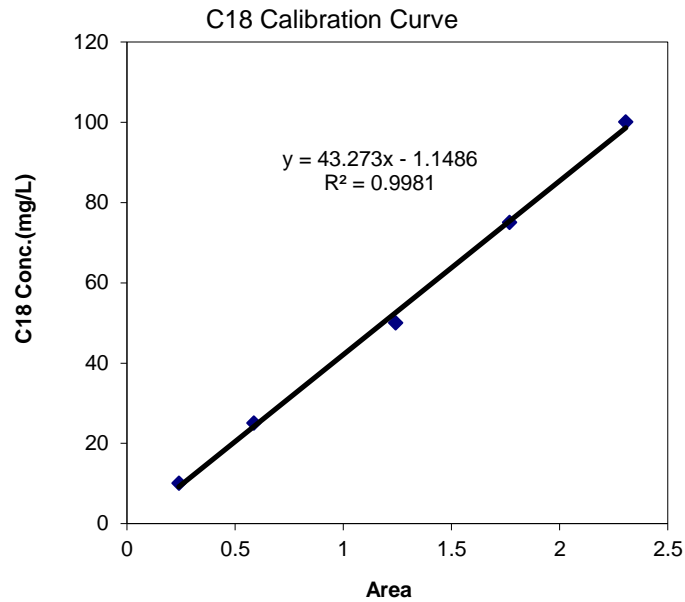
Figure B.6: C18 calibration curve

Table B.13: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – Phytane

Phytane-used C18 Calibration Curve for calculations. Phytane was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.76	19.82	0.24	9.24	
25 mg/l IS	11.84	20.21	0.59	24.21	
50 mg/l IS	25.07	20.19	1.24	52.59	
75 mg/l IS	35.17	19.90	1.77	75.34	
100 mg/l IS	49.04	21.27	2.31	98.62	
F1 (11/15) 20X Dil w/IS	8.09	17.09	0.47	19.33	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-1.15	0.170
F3 (11/15) 20X Dil w/IS	3.79	15.20	0.25	9.65	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.14: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C19

C19-used C18 Calibration Curve for calculations. C19 was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.76	19.82	0.24	9.24	
25 mg/l IS	11.84	20.21	0.59	24.21	
50 mg/l IS	25.07	20.19	1.24	52.59	
75 mg/l IS	35.17	19.90	1.77	75.34	
100 mg/l IS	49.04	21.27	2.31	98.62	
F1 (11/15) 20X Dil w/IS	17.59	17.09	1.03	43.39	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-1.15	0.170
F3 (11/15) 20X Dil w/IS	7.90	15.20	0.52	21.34	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.15: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C20

C20 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.47	19.82	0.23	9.63	
25 mg/l IS	11.23	20.21	0.56	24.00	
50 mg/l IS	24.12	20.19	1.19	51.80	
75 mg/l IS	34.84	19.90	1.75	76.00	
100 mg/l IS	48.27	21.27	2.27	98.56	
F1 (11/15) 20X Dil w/IS	10.05	17.09	0.59	25.40	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.17	0.170
F3 (11/15) 20X Dil w/IS	4.47	15.20	0.29	12.62	
F1-STD (11/15) 5X Dil w/IS	33.98	19.51	1.74	81.48	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.21	20.61	0.84	37.49	
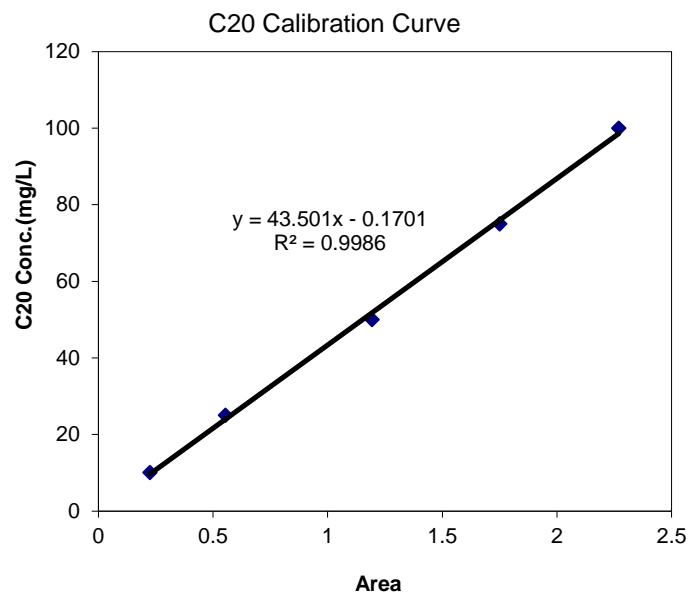
Figure B.7: C20 calibration curve

Table B.16: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – C21

C21 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.70	19.82	0.24	9.93	
25 mg/l IS	11.10	20.21	0.55	23.70	
50 mg/l IS	23.88	20.19	1.18	51.65	
75 mg/l IS	34.59	19.90	1.74	76.16	
100 mg/l IS	47.77	21.27	2.25	98.56	
F1 (11/15) 20X Dil w/IS	10.05	17.09	0.59	25.41	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.53	0.170
F3 (11/15) 20X Dil w/IS	4.50	15.20	0.30	12.54	
F1-STD (11/15) 5X Dil w/IS	33.78	19.51	1.73	80.99	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.43	20.61	0.85	38.00	
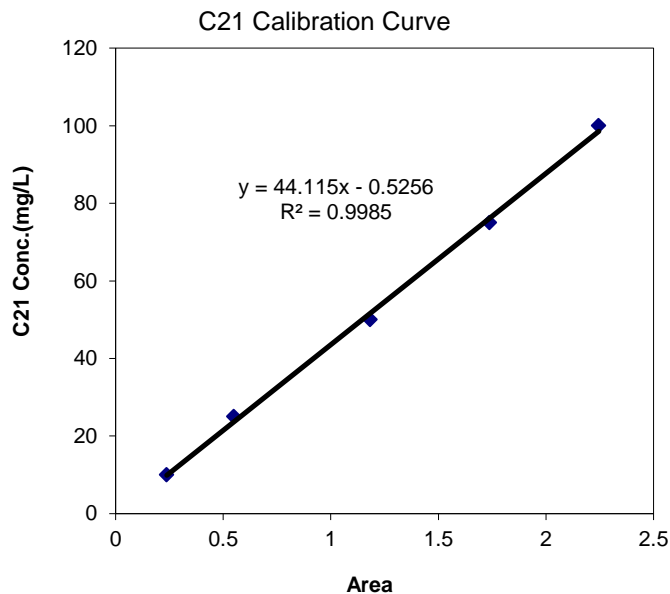
Figure B.8: C21 calibration curve

Table B.17: Determination of percent saturates and aromatics in diesel used for
***Chapter 3* and *4* experiments – C22**

| C22 | | | | conc (mg/l) | Diesel |
Description	Area	IS Area	RRF	using IS	Extraction (g)
10 mg/l IS	4.54	19.82	0.23	9.76	
25 mg/l IS	10.91	20.21	0.54	23.71	
50 mg/l IS	23.79	20.19	1.18	52.35	
75 mg/l IS	33.68	19.90	1.69	75.41	
100 mg/l IS	47.08	21.27	2.21	98.78	
F1 (11/15) 20X Dil w/IS	4.97	17.09	0.29	12.53	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.52	0.170
F3 (11/15) 20X Dil w/IS	2.29	15.20	0.15	6.24	0.170
F1-STD (11/15) 5X Dil w/IS	32.03	19.51	1.64	76.63	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	16.50	20.61	0.80	35.81	
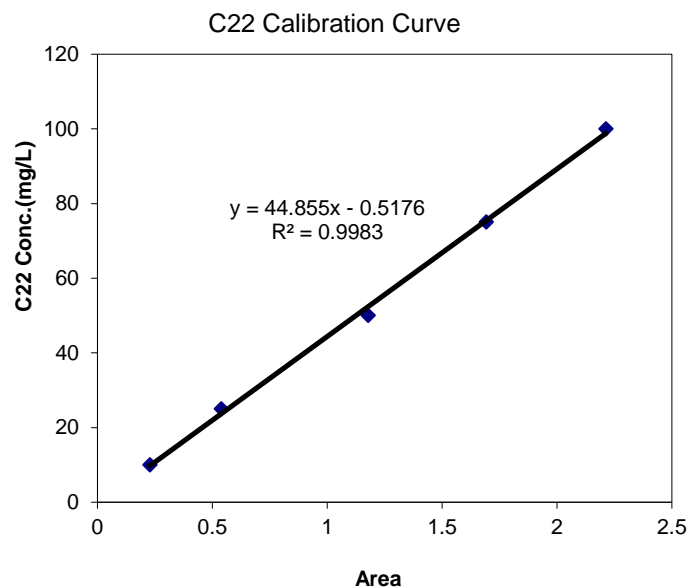
Figure B.9: C22 calibration curve

Table B.18: Determination of percent saturates and aromatics in diesel used for
Chapter 3 **and** *4* **experiments – C23**

C23-used C22 Calibration Curve for calculations. C23 was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.54	19.82	0.23	9.76	
25 mg/l IS	10.91	20.21	0.54	23.71	
50 mg/l IS	23.79	20.19	1.18	52.35	
75 mg/l IS	33.68	19.90	1.69	75.41	
100 mg/l IS	47.08	21.27	2.21	98.78	
F1 (11/15) 20X Dil w/IS	2.31	17.09	0.14	5.55	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.52	0.170
F3 (11/15) 20X Dil w/IS	1.07	15.20	0.07	2.64	0.170
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-3.04	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-3.04	

Table B.19: Determination of percent saturates and aromatics in diesel used for
***Chapter 3* and *4* experiments – C24**

C24 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.58	19.82	0.23	9.94	
25 mg/l IS	10.61	20.21	0.52	23.59	
50 mg/l IS	22.85	20.19	1.13	51.75	
75 mg/l IS	33.05	19.90	1.66	76.32	
100 mg/l IS	45.44	21.27	2.14	98.40	
F1 (11/15) 20X Dil w/IS	2.04	17.09	0.12	4.75	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.78	0.170
F3 (11/15) 20X Dil w/IS	0.94	15.20	0.06	2.08	
F1-STD (11/15) 5X Dil w/IS	32.91	19.51	1.69	77.53	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-0.78	
F3-STD (11/15) 5X Dil w/IS	17.53	20.61	0.85	38.70	

C24 Calibration Curve

$y = 46.428x - 0.7827$
$R^2 = 0.9982$
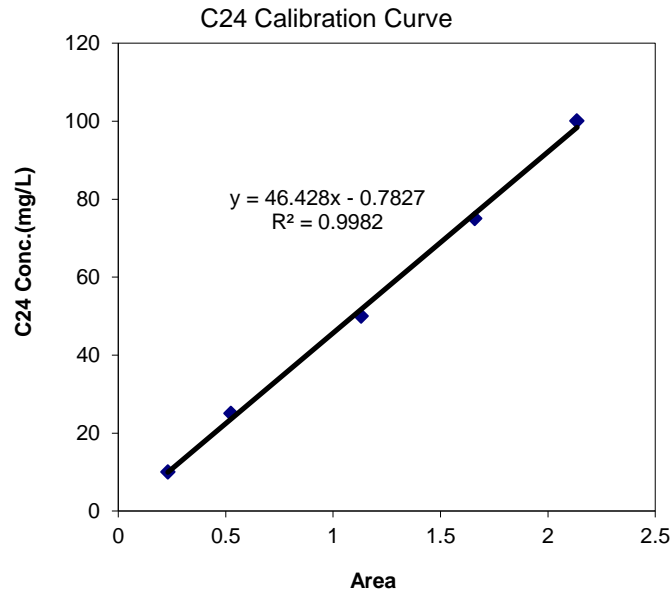
Figure B.10: C24 calibration curve

Table B.20: Determination of percent saturates and aromatics in diesel used for
Chapter 3 and _4_ experiments – C25

C25-used C24 Calibration Curve for calculations. C25 was not in the mixed standard

Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.58	19.82	0.23	9.94	
25 mg/l IS	10.61	20.21	0.52	23.59	
50 mg/l IS	22.85	20.19	1.13	51.75	
75 mg/l IS	33.05	19.90	1.66	76.32	
100 mg/l IS	45.44	21.27	2.14	98.40	
F1 (11/15) 20X Dil w/IS	0.78	17.09	0.05	1.34	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.78	0.170
F3 (11/15) 20X Dil w/IS	0.48	15.20	0.03	0.68	
F1-STD (11/15) 5X Dil w/IS	0.00	19.51	0.00	-0.78	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-0.78	
F3-STD (11/15) 5X Dil w/IS	0.00	20.61	0.00	-0.78	

Table B.21: Determination of percent saturates and aromatics in diesel used for
Chapter 3 and _4_ experiments – C26

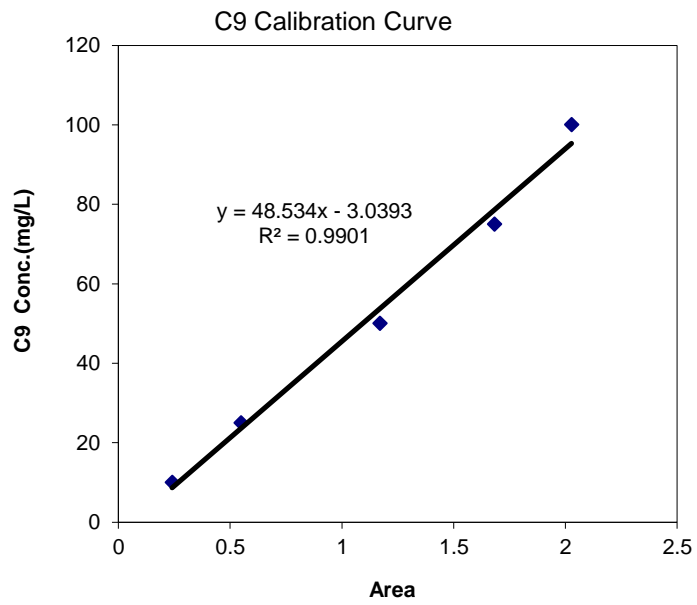| C26 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.27	19.82	0.22	8.67	
25 mg/l IS	10.08	20.21	0.50	23.90	
50 mg/l IS	21.24	20.19	1.05	53.59	
75 mg/l IS	29.67	19.90	1.49	77.16	
100 mg/l IS	39.44	21.27	1.85	96.67	
F1 (11/15) 20X Dil w/IS	1.04	17.09	0.06	0.39	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-2.89	0.170
F3 (11/15) 20X Dil w/IS	0.87	15.20	0.06	0.18	
F1-STD (11/15) 5X Dil w/IS	32.10	19.51	1.65	76.81	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.01	20.61	0.83	37.02	
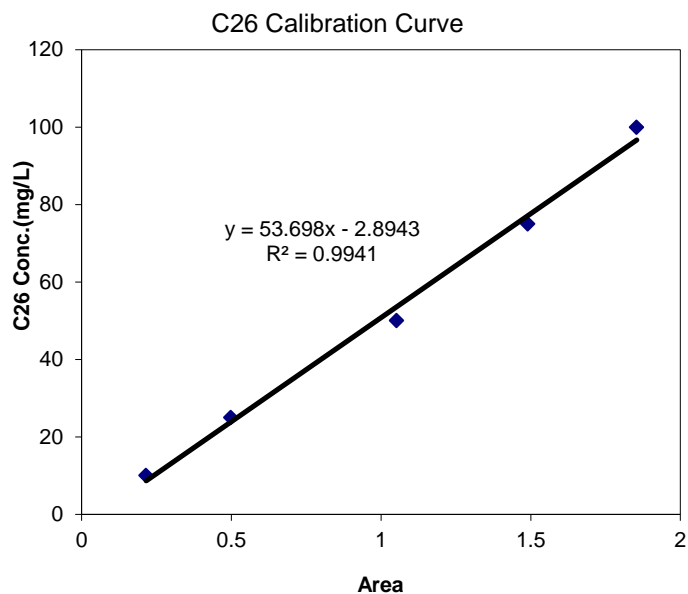
Figure B.11: C26 calibration curve

Table B.22: Determination of percent saturates and aromatics in diesel used for
Chapter 3 **and** *4* **experiments – C28**

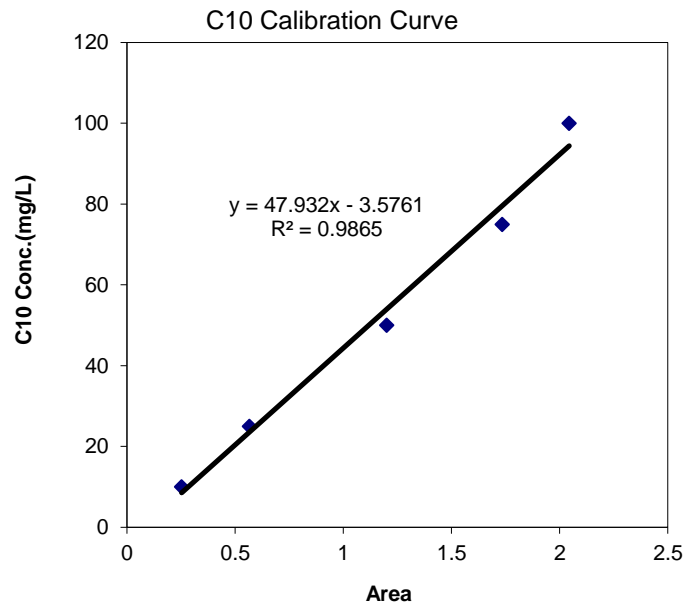| C28 Description	Area	IS Area	RRF	conc (mg/l) using IS	Diesel Extraction (g)
10 mg/l IS	4.55	19.82	0.23	9.58	
25 mg/l IS	11.08	20.21	0.55	23.71	
50 mg/l IS	24.02	20.19	1.19	52.14	
75 mg/l IS	34.67	19.90	1.74	76.63	
100 mg/l IS	47.29	21.27	2.22	97.94	
F1 (11/15) 20X Dil w/IS	0.00	17.09	0.00	-0.59	0.170
F2 (11/15) 1X Dil w/IS	0.00	19.42	0.00	-0.59	0.170
F3 (11/15) 20X Dil w/IS	0.00	15.20	0.00	-0.59	
F1-STD (11/15) 5X Dil w/IS	32.12	19.51	1.65	76.86	
F2-STD (11/15) 5X Dil w/IS	0.00	19.32	0.00	-3.04	
F3-STD (11/15) 5X Dil w/IS	17.21	20.61	0.84	37.49	
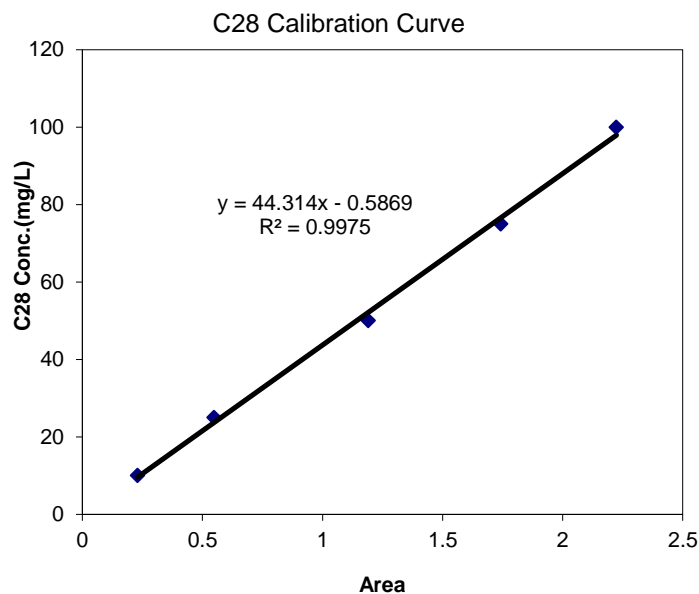
Figure B.12: C28 calibration curve

Table B.23: Determination of percent saturates and aromatics in diesel used for *Chapter 3* and *4* experiments – TPH Summary

TPH Description	Area	IS Area	Average RRFs	conc (mg/l) using IS	Corrected for Dilution (mg/l)	mg of TPH in 170mg of Diesel
10 mg/l IS			0.24			
25 mg/l IS			0.56			
50 mg/l IS			1.19			
75 mg/l IS			1.72			
100 mg/l IS			2.17			
F1 (11/15) 20X Dil w/IS	2610.00	18.66	139.89	7509.13	150182.539	150.183
F2 (11/15) 20X Dil w/IS	667.24	18.12	36.82	1974.10	19740.982	19.741
F3 (11/15) 40X Dil w/IS	1459.75	18.24	80.05	4295.73	171829.141	171.829

Table B.24: TPH Summary

% Composition of Diesel based on separation
Fractions F1, F2 and F3

Saturates (F1)	87.4%
Aromatic (F2)	11.5%

Appendix C: *Chapter 3* **supplemental data**
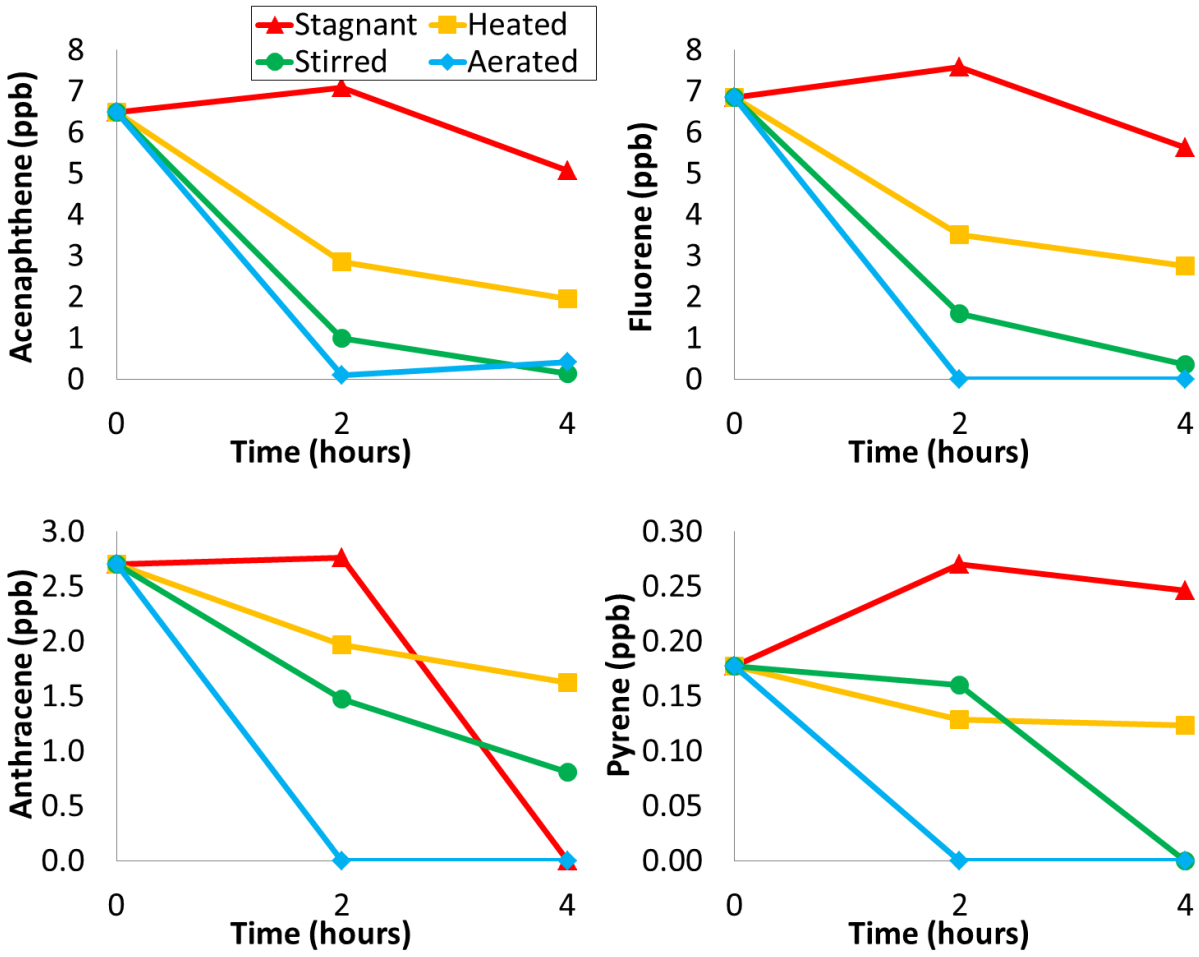
Figure C.1: PAH removal results

Table C. 1: Data for diesel desorption

Sample Name	Naphthalene		Acenaphthylene		Acenaphthene		Fluorene		Anthracene		Pyrene	
	ppb	% of total DRO	ppb	% of total DRO	ppb	% of total DRO	ppb	% of total DRO	ppb	% of total DRO	ppb	% of total DRO
DD1	8.10	0.67	0.72	0.06	7.16	0.59	3.02	0.25	2.63	0.22	0.53	0.04
DD2	2.58	0.27	0.54	0.06	6.99	0.72	3.33	0.34	2.57	0.26	0.52	0.05
DD3	1.04	0.11	0.47	0.05	6.19	0.66	3.15	0.33	2.64	0.28	0.62	0.07
DD4	0.36	0.05	0.00	0.00	5.31	0.69	2.45	0.32	2.41	0.31	0.60	0.08
DD5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.09	0.16	0.54	0.08
DD6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.56	0.09

Appendix D: *Chapter 4* supplemental data

Table D.1: Naphthalenes in flotation samples

Description	Internal Standard Area	Naphthalene RRF	Nap C1a RRF	Nap C1b RRF	2-Methylnapthalene RRF	Nap C2a RRF	Nap C2b RRF	Nap C2c RRF	Nap C2d RRF	Nap C2e RRF	Nap C3a RRF	Nap C3b RRF	Nap C3c RRF	Nap C3d RRF	Nap C3e RRF	Nap C3f RRF	Nap C3g RRF	Nap C4a RRF	Nap C4b RRF	Nap C4c RRF	Nap C4d RRF	Nap C4e RRF	Nap C4f RRF	Nap C4g RRF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hex w/IS	134804293	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
25.5 mg/l Not Extr	132187078	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
51 mg/l Not Extr	134048216	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	0.0000	NF	NF	NF	NF	NF	NF
102 mg/l Not Extr	144768418	0.0009	NF	NF	0.0004	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
204 mg/l Not Extr	149046670	0.0017	NF	NF	0.0010	0.0003	NF	NF	NF	NF	0.0002	NF	0.0007	NF	NF	NF	NF	0.0002	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 5	152973298	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 6	163934049	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 7	163499176	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 5	153455746	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 7	174633779	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 5	150871004	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 7	168703982	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Std 0.51 mg/l Extr	174279786	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Std 1.02 mg/l Extr	176043281	0.0005	NF	NF	0.0004	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
Std 2.04 mg/l Extr	159922685	0.0011	NF	NF	0.0012	0.0002	NF	NF	NF	NF	0.0002	NF	NF	NF	NF	NF	NF	0.0002	NF	NF	NF	NF	NF	NF
Std 0.51 mg/l Extr	199790106	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Std 1.02 mg/l Extr	212660384	0.0003	NF	NF	0.0001	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
Std 2.04 mg/l Extr	207755707	0.0008	NF	NF	0.0008	0.0001	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
Std 0.51 mg/l Extr	184753352	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Std 1.02 mg/l Extr	188714876	0.0003	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
Std 2.04 mg/l Extr	202005879	0.0005	NF	NF	0.0002	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
W.R. 1/2	165544418	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
W.R. 2/2	141135713	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
M.R. 1/2	175712012	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-0.1-T	219819412	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-0.1-C	208652959	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-0.5-T	201984899	0.0000	NF	NF	NF	NF	NF	NF	NF	NF	0.0000	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-0.5-C	239393765	0.0003	NF	NF	0.0011	NF	NF	NF	NF	NF	0.0000	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-1-T	154318074	0.0001	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-1-C	170817773	0.0006	NF	NF	0.0011	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-2-T	176712662	0.0002	NF	NF	0.0034	0.0001	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
L-2-C	175961888	0.0016	NF	NF	0.0038	0.0002	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
102 mg/l Not Extr	149068197	0.0006	NF	NF	0.0003	NF	NF	NF	NF	NF	0.0002	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane with IS	59868263	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
25.5 mg/l NE	58184757	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
51 mg/l NE	88237045	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
102 mg/l NE	132600832	0.0003	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
204 mg/l NE	55237101	0.0022	NF	NF	0.0013	0.0003	NF	NF	NF	NF	0.0003	NF	NF	NF	NF	NF	NF	0.0005	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 5	80884921	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 7	92084500	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
std 1.02	95917535	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-0.1-T	64998803	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-0.1-C	83325142	NF	NF	NF	0.0007	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-0.5-T	70997006	0.0001	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-0.5-C	70948222	0.0004	NF	NF	0.0014	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-1-T	63841252	0.0004	NF	NF	0.0026	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-1-C	53050053	0.0012	NF	NF	0.0032	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 5	31961791	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 7	29512122	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
std 1.02	33528528	0.0014	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	0.0002	NF	NF	NF	NF	NF	NF
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-2-T	24738845	0.0019	NF	NF	0.0047	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-2-C	32903999	0.0047	NF	NF	0.0037	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-0.1-T	38198674	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-0.1-C	21486165	NF	NF	NF	0.0010	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-0.5-T	42896280	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-0.5-C	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
PAH 1mg/l w/IS	13648795	0.0643	NF	NF	0.0306	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
PAH 5mg/l w/IS	14235687	0.3166	NF	NF	0.1816	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
PAH 10mg/l w/IS	13160967	0.6449	NF	NF	0.3858	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane w/IS	10535127	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
25.5 NE	15754981	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
51 NE	17231571	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
102 NE	21054022	0.0005	NF	NF	0.0011	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
204 NE	5351712	0.0019	NF	NF	0.0022	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	0.0003	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 5	10063386	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 7	13003569	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
std 1.02	12060094	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-1T	8800267	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-1C	17734438	NF	NF	NF	0.0016	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-2T	18360372	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-2C	17711073	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF
W/O F.P.	12797086	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
M.R.-2/2	13048110	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane w/IS New	11039506	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
25.5 New	12998919	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
51 New	14523118	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
102 New	21347344	0.0009	NF	NF	0.0009	NF	NF	NF	NF	NF	0.0001	NF	NF	NF	NF	NF	NF	0.0003	NF	NF	NF	NF	NF	NF
204 New	17519971	0.0017	NF	NF	0.0020	0.0005	NF	NF	NF	NF	0.0003	NF	NF	NF	NF	NF	NF	0.0006	NF	NF	NF	NF	NF	NF

NF = No peak was found

Table D.2: Phthalates in flotation samples

Description	IS Intensity	Hexanedoic Acid Intensity	Hexanedoic Acid RRF	Phthalate 1 Intensity	Phthalate 1 RRF	Phthalate 2 Intensity	Phthalate 2 RRF	Phthalate 3 Intensity	Phthalate 3 RRF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hex w/IS	134804293	NF	NF	NF	NF	NF	NF	NF	NF
25.5 mg/l Not Extr	132187078	NF	NF	NF	NF	NF	NF	NF	NF
51 mg/l Not Extr	134048216	NF	NF	NF	NF	NF	NF	NF	NF
102 mg/l Not Extr	144768418	NF	NF	NF	NF	NF	NF	NF	NF
204 mg/l Not Extr	149046670	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 5	152973298	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 6	163934049	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 7	163499176	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 5	153455746	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 7	174633779	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 5	150871004	NF	NF	NF	NF	NF	NF	NF	NF
Blk pos 7	168703982	NF	NF	NF	NF	NF	NF	NF	NF
Std 0.51 mg/l Extr	174279786	NF	NF	NF	NF	NF	NF	NF	NF
Std 1.02 mg/l Extr	176043281	NF	NF	NF	NF	NF	NF	NF	NF
Std 2.04 mg/l Extr	159922685	NF	NF	NF	NF	NF	NF	NF	NF
Std 0.51 mg/l Extr	199790106	NF	NF	NF	NF	NF	NF	NF	NF
Std 1.02 mg/l Extr	212660384	NF	NF	NF	NF	NF	NF	NF	NF
Std 2.04 mg/l Extr	207755707	NF	NF	NF	NF	NF	NF	NF	NF
Std 0.51 mg/l Extr	184753352	NF	NF	NF	NF	NF	NF	NF	NF
Std 1.02 mg/l Extr	188714876	NF	NF	NF	NF	NF	NF	NF	NF
Std 2.04 mg/l Extr	202005879	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
W.R. 1/2	165544418	1740063	0.0105	3642620	0.0220	3459044	0.0209	17879649	0.1080
W.R. 2/2	141135713	727778	0.0052	2209036	0.0157	3278652	0.0232	16634207	0.1179
M.R. 1/2	175712012	257251	0.0015	5059865	0.0288	276980	0.0016	1204830	0.0069
L-0.1-T	219819412	424683	0.0019	1898115	0.0086	243040	0.0011	956733	0.0044
L-0.1-C	208652959	1593248	0.0076	6916988	0.0332	910430	0.0044	4493843	0.0215
L-0.5-T	201984899	671032	0.0033	6237680	0.0309	641012	0.0032	2738032	0.0136
L-0.5-C	239393765	3160224	0.0132	9163947	0.0383	1869138	0.0078	9624837	0.0402
L-1-T	154318074	1600777	0.0104	2927093	0.0190	1038311	0.0067	5363637	0.0348
L-1-C	170817773	7708141	0.0451	9569016	0.0560	3229799	0.0189	16841698	0.0986
L-2-T	176712662	941245	0.0053	2281749	0.0129	570708	0.0032	2462687	0.0139
L-2-C	175961888	3341693	0.0190	4126795	0.0235	903868	0.0051	4413052	0.0251
102 mg/l Not Extr	149068197	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
Hexane with IS	59868263	NF	NF	NF	NF	NF	NF	NF	NF
25.5 mg/l NE	58184757	NF	NF	NF	NF	NF	NF	NF	NF
51 mg/l NE	68237045	NF	NF	NF	NF	NF	NF	NF	NF
102 mg/l NE	132600832	NF	NF	NF	NF	NF	NF	NF	NF
204 mg/l NE	55237101	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 5	80884921	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 7	92084500	NF	NF	NF	NF	NF	NF	NF	NF
std 1.02	95917535	NF	NF	NF	NF	NF	NF	NF	NF
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-0.1-T	64998803	157824	0.0024	933189	0.0144	201719	0.0031	827625	0.0127
K-0.1-C	83325142	143833	0.0017	884365	0.0106	150605	0.0018	621352	0.0075
K-0.5-T	70997006	160804	0.0023	267612	0.0038	75632	0.0011	210120	0.0030
K-0.5-C	70948222	24891	0.0004	305885	0.0043	112003	0.0016	397833	0.0056
K-1-T	63841252	NF	NF	72178	0.0011	13071	0.0002	44887	0.0007
K-1-C	53050053	226485	0.0043	841349	0.0159	157400	0.0030	650404	0.0123
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 5	31961791	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 7	29512122	NF	NF	NF	NF	NF	NF	NF	NF
std 1.02	33528528	NF	NF	NF	NF	NF	NF	NF	NF
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
K-2-T	24738845	NF	NF	98966	0.0040	50033	0.0020	NF	NF
K-2-C	32903999	208113	0.0063	374205	0.0114	160720	0.0049	554077	0.0168
O.C.-0.1-T	38198674	23225	0.0006	91774	0.0024	43677	0.0011	199784	0.0052
O.C.-0.1-C	21486165	191761	0.0089	697874	0.0325	79375	0.0037	330507	0.0154
O.C.-0.5-T	42896280	NF	NF	21142	0.0005	NF	NF	19504	0.0005
O.C.-0.5-C	39624681	NF	NF	NF	NF	NF	NF	NF	NF
hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
Alkanes 1mg/l w/IS	34256148	NF	NF	NF	NF	NF	NF	NF	NF
Alkanes 5mg/l w/IS	36213541	NF	NF	NF	NF	NF	NF	NF	NF
Alkanes 10mg/l w/IS	38240012	NF	NF	NF	NF	NF	NF	NF	NF
Hexane w/IS	10535127	NF	NF	NF	NF	NF	NF	NF	NF
25.5 NE	15754981	NF	NF	NF	NF	NF	NF	NF	NF
51 NE	17231571	NF	NF	NF	NF	NF	NF	NF	NF
102 NE	21054022	NF	NF	NF	NF	NF	NF	NF	NF
204 NE	5351712	NF	NF	NF	NF	NF	NF	NF	NF
Hexane	NF	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 5	10063386	NF	NF	NF	NF	NF	NF	NF	NF
blk pos 7	13003569	NF	NF	NF	NF	NF	NF	NF	NF
std 1.02	12060094	NF	NF	NF	NF	NF	NF	NF	NF
O.C.-1T	8800267	NF	NF	30989	0.0035	27485	0.0031	120135	0.0137
O.C.-1C	17734438	33356	0.0019	153498	0.0087	152010	0.0086	689659	0.0389
O.C.-2T	18360372	50576	0.0028	102393	0.0056	84016	0.0046	333859	0.0182
O.C.-2C	17711073	80009	0.0045	101785	0.0057	38810	0.0022	187298	0.0106
W/O F.P.	12797086	NF	NF	NF	NF	NF	NF	NF	NF
M.R.-2/2	13048110	NF	NF	NF	NF	NF	NF	NF	NF
CHK STD 102	17635609	NF	NF	NF	NF	NF	NF	NF	NF
Hexane w/IS New	11039506	NF	NF	NF	NF	NF	NF	NF	NF
25.5 New	12998919	NF	NF	NF	NF	NF	NF	NF	NF
51 New	14523118	NF	NF	NF	NF	NF	NF	NF	NF
102 New	21347344	NF	NF	NF	NF	NF	NF	NF	NF
204 New	17519971	NF	NF	NF	NF	NF	NF	NF	NF

NF = No peak was found