Diesel Range Organics In Coal Preparation

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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 physiochemical conditions. Additionally, we investigate desorption of DROs 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.

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; ash mineral particles, on the other hand, 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, petrodiesel (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, DROs are not monitored in impoundments or discharges. However, given increasing concerns over diesel contamination of water resources by leaking underground storage tanks, highway and blackjack runoff, and events such as the recent Deepwater Horizon oil spill in the Gulf of Mexico (Sementelli and Simons 1997; Lloyd and Cockett 2011; Osofsky et al. 2011), it is important to understand the potential transport mechanisms and fate of DROs 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).

Environmental Fate and Transport of Diesel Compounds in Water

Diesel has a mixed composition of roughly C_{10} to C_{19} hydrocarbons, which, as for many petroleum products, varies based on the crude oil source and refining processes (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 and cycloalkanes) and total aromatic hydrocarbons (e.g., naphthalenes, acenaphthenes, and 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 and 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 the 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; Kalkkar 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 soluble 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, and phenanthrenes); these PAHs have weights in the same range as saturated 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 to reiterate that under normal operating conditions, nearly all but the soluble DROs 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 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.

**EXPERIMENTAL METHODS**

Partitioning studies were carried out to obtain preliminary data on the likely fate of residual DROs, 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 roller 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. 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 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.
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 2). The test conditions were: stagnant (open jar in ambient room temperature and pressure), gentle stirring, gentle aeration and heating (40°C); and for each, one sample was conditioned for 2 hours and another was conditioned for 4 hours. At the end of those time increments, the subsamples were stored for analysis.

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) 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.

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 5335A: 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(g,h,i)perylene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene.

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.

Table 1. DRO and PAH removal results

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Time (hr)</th>
<th>Naphthalene (ppb)</th>
<th>Acenaphthene (ppb)</th>
<th>Fluorene (ppb)</th>
<th>Anthracene (ppb)</th>
<th>Fluoranthene (ppb)</th>
<th>Pyrene (ppb)</th>
<th>DRO (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0</td>
<td>60</td>
<td>6.5</td>
<td>6.8</td>
<td>2.7</td>
<td>0.14</td>
<td>0.18</td>
<td>0.43</td>
</tr>
<tr>
<td>Stagnant</td>
<td>2</td>
<td>56</td>
<td>7.1</td>
<td>7.6</td>
<td>2.8</td>
<td>NF</td>
<td>0.27</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>34</td>
<td>5.1</td>
<td>5.6</td>
<td>5.6</td>
<td>NF</td>
<td>0.25</td>
<td>0.53</td>
</tr>
<tr>
<td>Stirring</td>
<td>2</td>
<td>2.5</td>
<td>0.99</td>
<td>1.6</td>
<td>1.5</td>
<td>NF</td>
<td>0.36</td>
<td>0.30</td>
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<tr>
<td></td>
<td>4</td>
<td>0.51</td>
<td>0.15</td>
<td>0.37</td>
<td>0.81</td>
<td>NF</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Aeration</td>
<td>2</td>
<td>0.98</td>
<td>0.10</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.69</td>
<td>0.41</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
<td>0.13</td>
<td>0.48</td>
</tr>
<tr>
<td>Heating</td>
<td>2</td>
<td>17</td>
<td>2.9</td>
<td>3.5</td>
<td>2.0</td>
<td>NF</td>
<td>0.12</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>12</td>
<td>2.0</td>
<td>2.7</td>
<td>1.6</td>
<td>NF</td>
<td>0.12</td>
<td>0.38</td>
</tr>
</tbody>
</table>

NF indicates the compound was not found.

Potential for Diesel Removal from Process Water
Table 1 presents results for DRO and PAH residuals in the tests designed to investigate potential for diesel removal from process water. Figure 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 two hours (more significantly for the stagnant sample), and then began decreasing after four 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 4 by comparing DRO to naphthalene, which had the highest measured concentrations of all target PAHs, followed by acenaphthene 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. Thus, it appears that the relative abundance of PAHs in the WSP of diesel may be much smaller than in the total diesel.

**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 contacts water, or in instances where ultrafine coal with sorbed diesel reports to tailings impoundments. Figure 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 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 1 (by nearly an order of magnitude). An explanation for this is not clear. However, the significant decline in naphthalene shown in Figure 6 following the first rinse cycle is consistent with the DRO observations and the idea that naphthalene is not very abundant in the WSP 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.

**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 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 WSP of diesel persists to any appreciable degree, and thus high concentrations of DROs are not expected accumulate. In a typical impoundment, the WSP 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 ultrathin 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 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 saturated 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 benzenic 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 priority 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.

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 DROs dominated by the WSF of diesel are expected to be present in process water in a typical tailings impoundment or open-air portions of the flotation circuit. DROs 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. DROs 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.

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