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Kayla Lockmiller
Grand Valley State University

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Presence and Distribution of Polycyclic Aromatic Hydrocarbons in Sediment Contaminated with Tar Sands Crude Oil

Kayla Lockmiller, Dr. Tara Kneeshaw

Abstract.

Contamination of sediment with polycyclic aromatic hydrocarbons (PAHs) derived from heavy crude oils (ex. tar sands oil) pose significant threats to human health as well as to the natural ecosystem. These compounds may persist in the environment for long periods of time following a crude oil spill. As such, this study sought to evaluate the persistence of PAHs in sediment and possible correlation between PAH distribution and grain size. This was accomplished through the collection of sediment samples from a portion of river bank along the Kalamazoo River near Ceresco, MI. Five years previously, a pipeline break spilled an estimated 843,000 gallons of diluted bitumen being transported from Alberta, Canada's Athabasca oil field. Samples were collected from two areas: 1) an area of the river bank that was reworked following the spill and 2) an area in the floodplain thought to have been inundated with oil at the time of the spill but has since remained relatively undisturbed. The samples were analyzed using gas chromatography-flame ionization detection (GC-FID) for 17 PAHs known to have potentially harmful human and ecosystem health effects. Results indicate the presence of PAHs in all samples, including individual compounds which can be used as biomarkers for the Athabasca oil field. In addition, a detailed analysis of grain size was carried out on each sediment sample. There is some variability in the presence of specific PAHs between sample location and sediment grain size fraction, though identifying a clear correlation is complex. Since production and transportation of tar sands oil is projected to increase in the coming years, understanding the fate of PAHs in the environment is crucial to remediation preparedness. By relating the persistence of PAH compounds to grain size in a dynamic natural environment, it may be possible to better predict areas where PAHs may concentrate in future spills of tar sands oil, thus better informing future remediation efforts in similar environments.

Introduction.

A recent spill of Athabasca tar sands oil in south western Michigan has raised concerns about the fate of persistent, heavy, and potentially dangerous compounds known as poly-aromatic hydrocarbons (PAHs). This is a preliminary study which seeks to identify whether or not PAHs still persist in this location, or if remediation efforts were sufficient in removing the compounds. Future studies hope to explore various remediation methods in order to prepare for forthcoming spills in other locations to better repair the environment and protect human health.

Dwindling sources of conventional oil have forced a shift in the economic and geologic approach to fuel. Unconventional oil sources, which include tar sands, oil shales, and shale gas are rapidly

becoming a more common source of energy (Bjorlykke 2010). They are complex, heavy compounds that are confined within rock strata or in pores between sediments (Gordon 2012). Because these resources are trapped within the earth, unconventional hydrocarbons require more energy to produce than conventional oil. Large amounts of water and natural gas are used to create the steam required to extract these hydrocarbons from the earth, as well as for dilution and transport of the viscous oils (Selley, R. C., 1998). One of the least studied forms of unconventional oil are tar sands. Tar sands, or bitumen, are so viscous that they will not typically flow at surface temperatures, and thus are commonly diluted with a solvent to facilitate transportation (Wennekers, N., 1981). This high viscosity can be attributed to the complex PAH compounds which are composed of two or more benzene rings arranged in various configurations (Cerniglia 1992).

PAHs also occur naturally, from forest fires and volcanism, and are released from other anthropogenic sources such as vehicle exhaust or burning fossil fuels (ATSDR, 2008). PAH's are typically not very soluble in water, and therefore tend to cling to soil particles or fine particulate matter in the atmosphere, depending on the weight of the compound (ATSDR, 2008). Polycyclic aromatic hydrocarbons that are typically associated with tar sands oil include volatiles (i.e. benzene, toluene, and xylene), and heavier, more persistent compounds such as naphthalenes, phenanthrenes, and chrysenes (NRDC, 2014, Jiayu,N., and Jianyi,H., 1999). Each source of tar sands oil has its own combination of PAHs that act as its finger print; these are called biomarkers. Biomarkers for the raw Athabasca tar sands oil field in Alberta, Canada, for example, include acenaphthene, flouranthene, and pyrene (Yang et al., 2011). Biomarkers for the solvents used to transport Athabasca crude consist of acenaphthylene and anthracene (Yang et al., 2011). All of these compounds are known to bioaccumulate and persist in the environment for long periods of time (Jiayu,N., and Jianyi,H., 1999). Additionally, many PAHs from tar sands oil are known carcinogens and have other human health risks beyond their environmental concerns (NRDC, 2014).

Enbridge Inc. is a company that owns and operates numerous gas and oil pipelines that span internationally across Canada and the United States, many sourcing from the Athabasca tar sands in Alberta. The Athabasca tar sands oil field is the largest of its kind in the world (Palmer, 2011). In its expansive area and overwhelming volume of hydrocarbon reserves, the Athabasca oil field is four times the size of the giant conventional oil fields in Ghawar, Saudi Arabia (Demaison, G.J., 1977). These large numbers are staggering considering how little is known about the fate of tar sands oil post-extraction. Transportation of diluted bitumen, or dilbit, by pipeline, tanker, and rail provide an enormous risk for spills across North America (NRDC 2014).

On July 25, 2010, a gash in the Enbridge pipeline that stretches from the Athabasca tar sands in Alberta, Canada, through Wisconsin and Lake Michigan, and finally exits in Portland, Maine resulted in an estimated 843,000-gallon spill of diluted bitumen (Enbridge 2015). The spill originated in a tributary of the Kalamazoo River in southern Michigan and affected a thirty-five-mile stretch of this river (EPA 2014). Now, over five years later, the company's obligations for remediation are complete. In addition to capture and removal of the spilled bitumen, major reworking of river bank sediment and planting of new vegetation has been done since the spill. However, the heavier PAH components of the bitumen may still linger in sediments on the river's edge. As such, this research aims to identify PAH's in the area associated with the 2010 spill, and to determine if the PAHs are concentrated within any one particular grain size fraction (ex. sand, silt, or clay) within the affected sediments.

Methods.

Study Site

Sample collection was conducted during summer 2015 on the banks of the Kalamazoo River in Ceresco, Michigan from a portion of river affected by the 2010 spill. Pore water samples were collected at two locations: one in the river (OC1), roughly three feet from the south river bank, and one

approximately 7.5 feet landward from the river's edge (OC 4) (**Figure 1**). Sediment samples were taken at five locations. Samples OC1 through OC4 were taken along a transect on the south river bank (**Figure 1**). Sample DC1 was taken from a dry creek bed to the south east of the other sample locations (**Figure 1**). This area was not re-worked post-spill and is thought to have been inundated with water at the time of the spill, as the river was in flood stage.

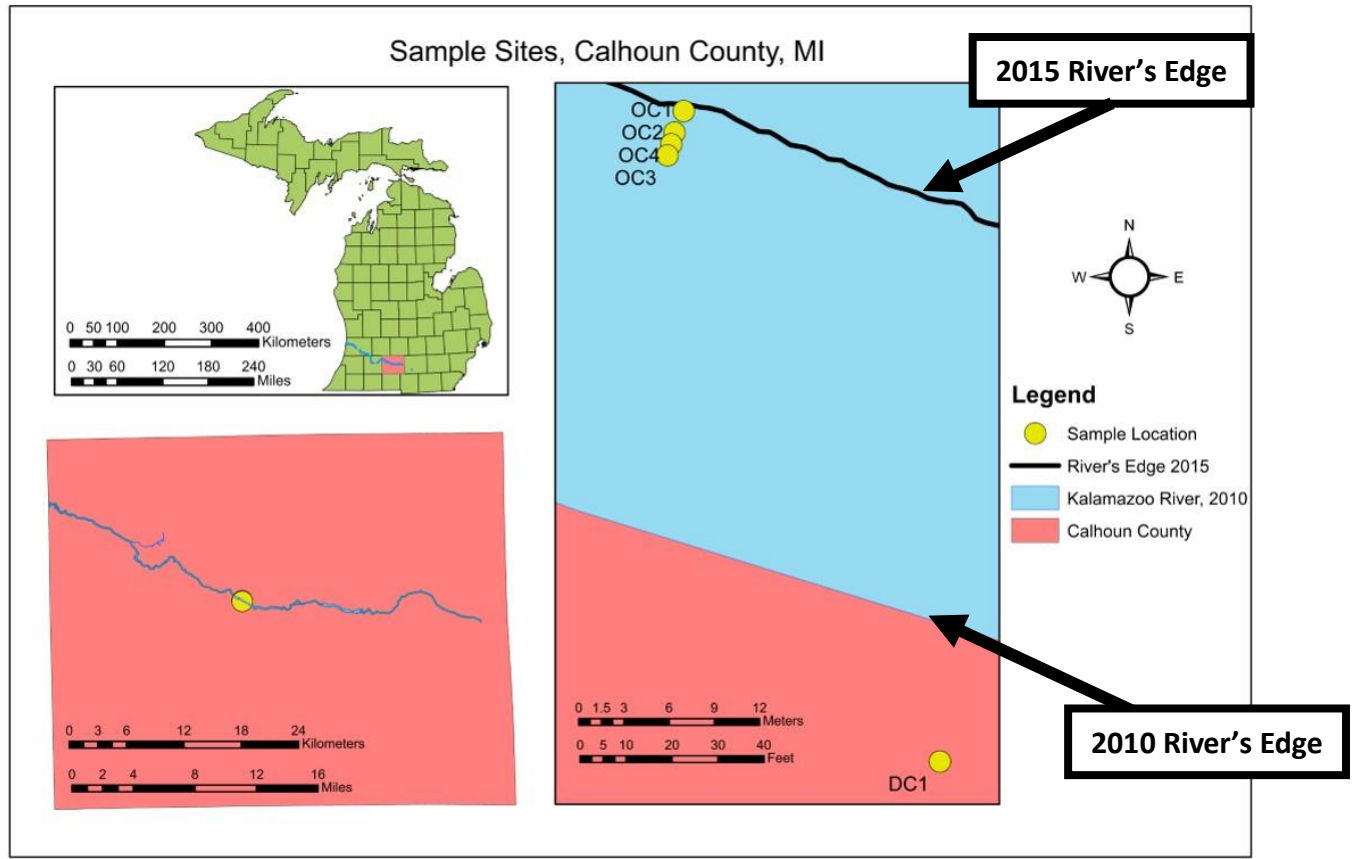


Figure 1. Sample collection locations along the Kalamazoo River, Ceresco, Michigan. At the time of the 2010 tar sands oil spill, the locations of all samples were inundated with water, as the river was in flood stage.

Sample Collection

Pore water was collected at sites OC1 and OC4 (**Figure 1**) using a drive point well and a 60 mL syringe. Volumes of 94 mL and 30 mL were purged from OC1 and OC4 respectively. Samples were then collected into a 10 mL syringe and filtered through a 0.45-micron filter directly into EPA certified HDPE

sample vials. Sulfide samples were preserved with zinc acetate and anion samples were preserved with formaldehyde. Samples were maintained at 4° C until analyzed.

Sediment samples were collected from OC1, OC2, OC3, OC4, and DC1 (**Figure 1**) using a hand driven split spoon sampler. Twelve-inch sediment cores were split into top and bottom halves (six inches each), placed in sterilized glass jars and stored at 4 °C.

Pore water Geochemistry

Samples OC1, OC4, and SW were analyzed upon collection for temperature, pH, conductivity, oxidation/ reduction potential, and total dissolved solids. Alkalinity of these samples were analyzed via titration with 0.02 N H₂SO₄. Microliter additions of were added to 1 mL of samples OC1, OC4, and SW until pH dropped below 4.5 (**Table 1**). Alkalinity as mg/L CaCO₃ was determined using the GRAN titration function. Sulfide concentrations of samples OC1, OC4, and SW were determined using a Spec200 (Thermo Scientific) and a colorimetric reaction. The colorimetric determination consisted of an amine-sulfuric/ ferric chloride reaction. A wavelength of 670 nanometers was maintained for all samples. Absorbance readings were replicated three times and an average was recorded (**Table 1**). Samples OC1, OC4, and SW were analyzed for concentrations of major anions (F⁻, Cl⁻, Br⁻, SO₄²⁻, NO₂⁻, N (NO₃⁻), and PO₄³⁻) using an ion chromatograph (Dionex, Thermo Scientific). A colorimeter was used to analyze samples OC1, OC4, and SW for total iron, nitrate, chloride, and sulfate concentrations (**Table 1**).

Grain Size and Soil Moisture.

Analyses of homogenized sediment samples OC1, OC2, OC3, and DC1 were conducted following the American Society for Testing and Materials (1970) and Folk (1974). Approximately 30 grams of sediment were dried in an aluminum tin for 24 hours at 105° C. Samples were then disaggregated.

Exactly 30 grams of dried sample were measured out and used for analyses. Dried samples were placed on the top of a stack of six sieves underlain by a collection pan. Sieves were stacked coarsest to finest and included United States Standard Sieve (USSS) numbers: 10 (2.38 – 2.00 mm), 18 (1.19 -1.00 mm), 35 (0.59- 0.0 mm), 60 (0.297- 0.250 mm), 120 (0.149- 0.125 mm), and 230 (0.074- 0.062 mm). Each sample was sorted into size fractions by shaking for 10 minutes. The weights of sample remaining in each sieve were recorded (**Table 1**). Statistical analyses for all grain size fractions were conducted using the GRADISTAT program with Microsoft Excel.

In addition, soil moisture analyses were carried out to determine the ratio of total volume of sample to total volume of water following Black (1965). Approximately 10 grams of moist sediment were added to pre-weighed, aluminum tins. Samples were dried for 24 hours at 105° C. Weights of dry samples were measured, and samples were dried another 12 hours to ensure all moisture was removed. A second dry weight was recorded. Percent soil moisture was determined by subtracting dry sediment weight from initial weight, and multiplying by 100.

Polycyclic Aromatic Hydrocarbon Analyses

Gas chromatography-flame ionization detection (GC-FID) was used to look for 17 PAHs. A liquid/liquid extraction method following a modification of EPA method 3510 was used (EPA ,1996). Sediment samples were freeze dried and dry weights (approx. 3 g) were recorded. Two grams of sodium sulfate were added to the sediment in a 50 mL amber vial. 10 mL of hexane and acetone, as well as 10 µL of PCB 142 – 10 ppm surrogate standard were added to the vial. Samples were then shaken, sonicated, and placed in a centrifuge at 3000 RPM for two minutes at each stage. The top layer of sample was then extracted into a turbo tube. This extraction was repeated using an additional 10 mL of hexane, and the top layer was again removed. The extracts were then cleaned by passing them through a column of 5g 2% deactivated Florosil, overlain with 1.5g of anhydrous sodium sulfate. Turbo tubes

were washed continuously with hexane until approximately 30 mL of eluent collected in a clean amber vial. The contents were then transferred into a turbo tube, and the vial was washed with hexane. Eluent was concentrated down to 1 to 2 mL using a nitrogen gas stream. 1.0 mL of isooctane was added into a small amber vial. Eluate was then pipetted into the vial, and hexane was evaporated using a N₂ stream. The turbo tube was washed with approximately 2 mL of hexane and pipetted into the small vial. Eluate was again concentrated to mL using N₂ stream, and the vial was capped. 10 µL of internal standard (PCB 204 – 10 ppm) was added to each sample. Analysis was then carried out via GC-FID using the following conditions: injector temperature: 280°C, detector temperature: 300°C, initial GC oven temperature: 45°C held for 3 min and then increased at 12°C/min to 275°C and then held at 275°C for 12 min, split injection, flow rate: 2mL/min, total run time: 35 min.

Results.

Pore water Geochemistry

Results showed neutral pH in pore water and slightly acidic surface water (**Table 1**). Conductivity and total dissolved solids were observed in higher concentrations in pore water samples compared to surface water (**Table 1**). Alkalinity in pore water was greater than that of surface water (**Table 1**). Surface water contained nearly three times the amount of nitrate than did pore water samples (**Table 1**). Chloride and iron concentrations were highest in OC4 and OC1, respectively. Concentrations of sulfate were highest in surface water, however, concentrations within pore water samples varied greatly (**Table 1**). All samples collected showed very similar, low concentrations of sulfide (**Table 1, Figure 2**).

Table 1. Field site and laboratory readings for pore water and surface water samples.

Parameter	OC1	OC4	SW
Temperature (°C)	18.4	21.0	22.1
pH	6.97	6.87	7.94
Conductivity (µS)	743.3	880.5	543.3
Oxidation-Reduction Potential (mV)	NA	-134	13
Total Dissolved Solids (ppm)	479.0	569.9	333.6
Alkalinity (mg/ L CaCO ₃)	4270	5429	2989
Nitrate (ppm)	0.26	0.28	1.41
Chloride (ppm)	13.5	9.2	5.7
Sulfate (ppm)	40	8.0	44.0
Ferrous Iron (ppm)	5.8	10.4	0
Total Iron (ppm)	6.0	20.4	0.1
Sulfide (ppm)	BDL	BDL	BDL

NA = not analyzed

BDL = below detection limit

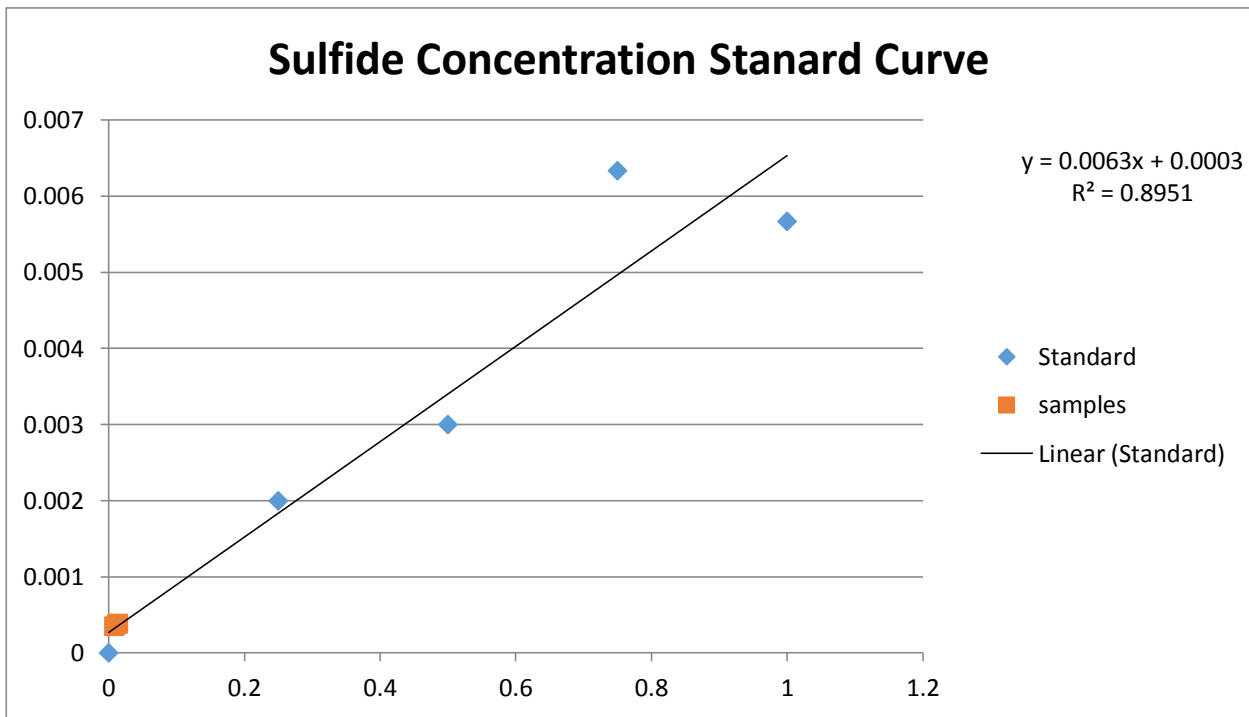


Figure 2 Graph showing sulfide standards plotted with samples OC1, OC4, and SW, shown as orange squares. All three samples had concentrations at or below the detection limit for the method.

Sediment Analyses

OC1 contained the least amount of moisture, while the other three samples had higher moisture contents (**Table 2**). All samples were composed of primarily sand-sized grains, but were all classified as at least poorly sorted (**Table 2**). OC1 and OC2 had much of the same composition, however OC3, which was collected in sequence with the former, had more fine grains present (**Table 2, Figure 3, Figure 4**). DC1 had the finest grains, but was also the most variable in size range (**Table 2, Figure 3, Figure 4**).

Sample ID	OC1	OC2	OC3	DC1
Textural Group	Sandy Gravel	Sandy Gravel	Gravelly Muddy Sand	Gravelly Muddy Sand
Sediment Name	Sandy Very Fine Gravel	Sandy Very Fine Gravel	Fine Gravelly Medium Silty Medium Sand	Very Fine Gravelly Very Coarse Silty Very Fine Sand
Mean Grain Size	Coarse Sand	Coarse Sand	Medium Sand	Fine Sand
Sorting	Poorly Sorted	Poorly Sorted	Very Poorly Sorted	Very Poorly Sorted
Percent Soil Moisture	34.4%	88.5%	88.5%	88.3%

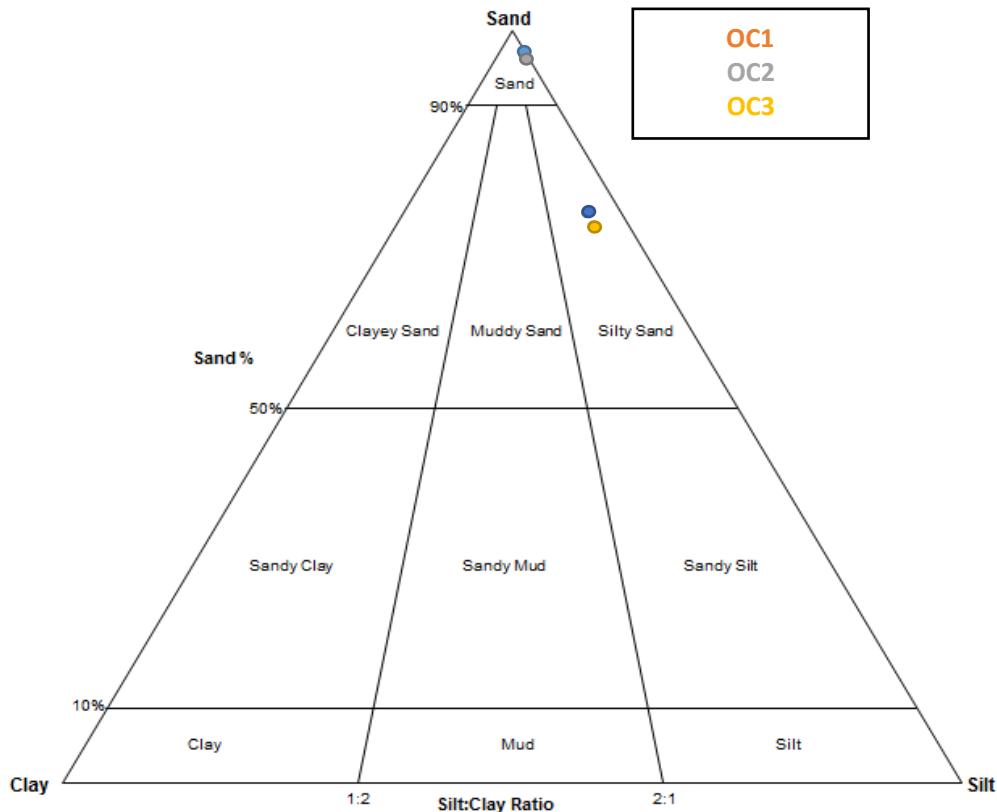


Figure 3. Textural diagram showing percentages of silt, sand, and clay. All samples were predominantly sand sized, however, samples OC3 and DC 1 plot within the Silty Sand category.

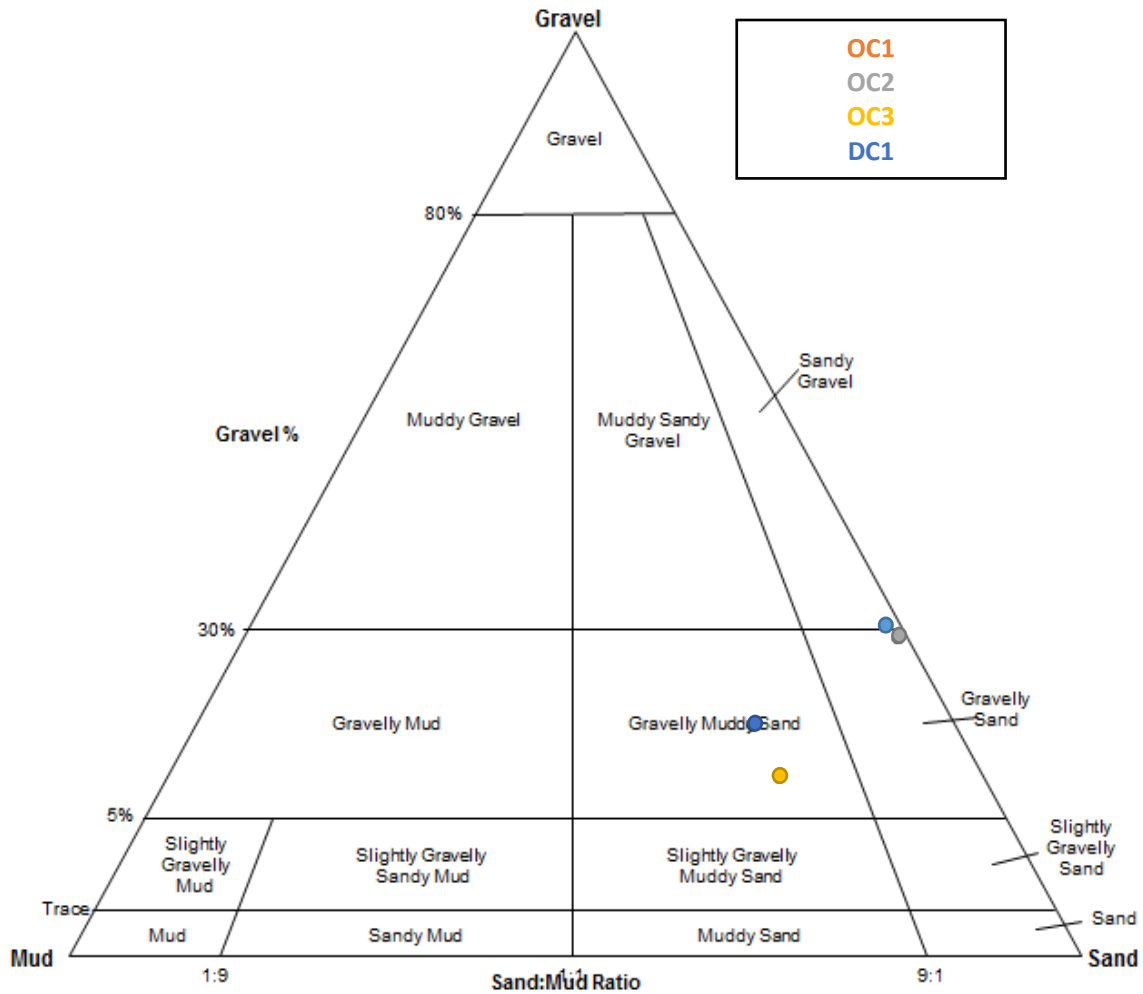


Figure 4. Textural diagram showing percentages of sand, mud, and gravel. All samples are composed of at least 70% sand sized grains. Samples OC1 and OC2 contained more large grains and are classified here as a gravelly sand. Samples OC3 and DC1 contained more mud, therefore they are plotted as a gravelly muddy sand.

Polycyclic aromatic hydrocarbon analyses:

A PAH mixed standard (Z-014G-R from AccuStandard) was used to determine presence and concentration of 17 compounds (**Table 3**). Fifteen of these analytes are frequently monitored by the US Environmental Protection Agency as they are known carcinogens and/ or mutagens (Al-Isawi, 2016). Naphthalenes, anthrenes, flourene, and anthracene were found in all samples tested (**Table 3**). Pyrenes were found in all samples with the exception of DC1 BAG, likely because it wasn't stored in the proper glass container. The highest concentration observed in the PAHs detected in all samples was for naphthalene (**Figure 5**), which contained nearly double the OSHA recommended exposure limit in OC4:

Clay and DC1 (OSHA, 2006). Concentrations of the other PAHs were variable amongst samples. Flourene was found in notably high concentrations in OC2: Top and DC1, but was considerably lower in all other samples analyzed. Acenaphthylene and anthracene were present in the lowest concentrations across all samples (**Figure 5**). In addition to PAH compounds, several terpenes were found in each of the samples. These are organic compounds, which are derived from plants and some insects. Most notably was the presence of eucalyptol, cadina, and trifluoracetyl.

Table 3. Analytes from mixed PAH standard present and absent in sediment samples

PAHs Present (in all samples)	PAHs Absent
<ol style="list-style-type: none"> 1. Naphthalene 2. Acenaphthylene 3. Acenaphthene 4. Flourene 5. Phenanthrene 6. Anthracene 7. Flouranthrene/ Pyrene 	<ul style="list-style-type: none"> • Benz(a)anthracene • Benzo(a)pyrene • Benzo(b)flouranthene • Benzo(g,h,i)perylene • Benzo(k)flouranthene • Crysene • Dibenz (a,h)anthracene • Indenol (1,2,3-cd) pyrene • Carbazole

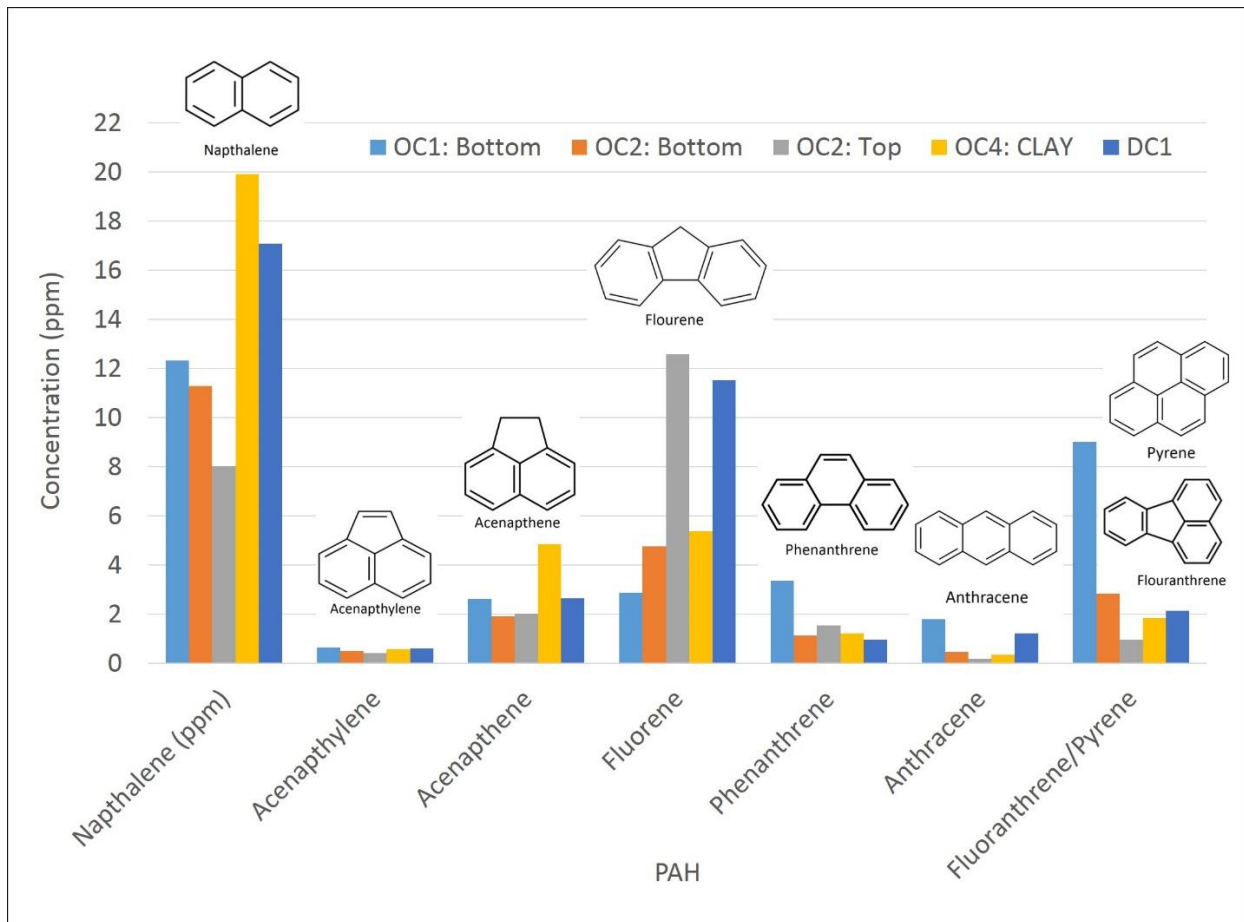


Figure 5. 2015 Concentrations of PAH Compounds found in Kalamazoo River Sediments

Discussion.

Expected conductivity for freshwater streams ranges from 2 to 100 μS (Sanders, 1998). Sample SW (surface water) was measured at a value of 543.3 μS , which is over five times the typical range (**Table 1**). This may indicate an unhealthy stream system (Behar, 1997). High levels of nitrate and sulfate in SW can likely be attributed to agricultural run-off and not to the oil spill (**Table 1**). Groundwater conductivity typically ranges from 50 to 50,000 μS , and pore water samples OC1 and OC4 fell within this range (**Table 1**) (Sanders, 1998). Additionally, the surface water sample had an oxidation/ reduction potential (13 mV, **Table 1**) which is much lower than the anticipated values of +300 to +500 mV for a healthy freshwater stream (Sanders, 1998). This could be because samples were collected close to the river banks where

groundwater is likely contributing to the stream. Surface water is, therefore, not completely oxygenated due to this mixing effect. Standard oxidation/ reduction potential for groundwater ranges from -200 to +100 mV (Sanders, 1998); pore water sample OC4 fell within this range (**Table 1**). Results for pH and total dissolved solids in surface and pore water fall within expected ranges for a healthy stream environment (Sanders, 1998).

A previous study analyzed for the presence of PAHs in the same location (Al-Isawi, 2016). Al-Isawi (2016) did not report any naphthalene, acenaphthylene, or flourene in sediment samples, however all of these compounds were found in all samples in this study. This discrepancy can likely be attributed to variation in drying methods as Al-Isawi (2016) used a conventional oven-drying method that may have caused some PAH in those samples to volatilize, while samples in this study were freeze dried in order to minimize total PAH loss. Al-Isawi's loss of acenaphthylene is crucial, as this compound has been found in Athabasca oil (Yang et. al, 2011).

All sediment samples that were analyzed for PAH contained seven of the 17 compounds present in the mixed PAH standard (**Table 3**). Of the PAHs detected, acenaphthene, flouranthene, and pyrene can be directly attributed to raw Athabasca tar sands oil (Yang et. al, 2011). These PAHs can be used as biomarkers for the Athabasca oil field, and directly link the compounds in this study to the 2010 spill. Pyrene is seen in moderate concentrations in this study and in very high concentrations in previous studies at this site and with Athabasca tar sands (Al-Isawi, 2016, Yang et. al, 2011). However, pyrene is also seen upstream and downstream of the spill site, indicating its presence isn't entirely due to the spill. This compound occurs commonly in motor vehicle exhaust, which is a likely source for its existence in the control areas analyzed by Al-isawi (2016, **Figure 6**) (Grimmer, 1977). Since pyrene likely already existed in the environment before the spill, its presence throughout the spill site is likely due to the addition of Athabasca pyrene to preexisting pyrene.

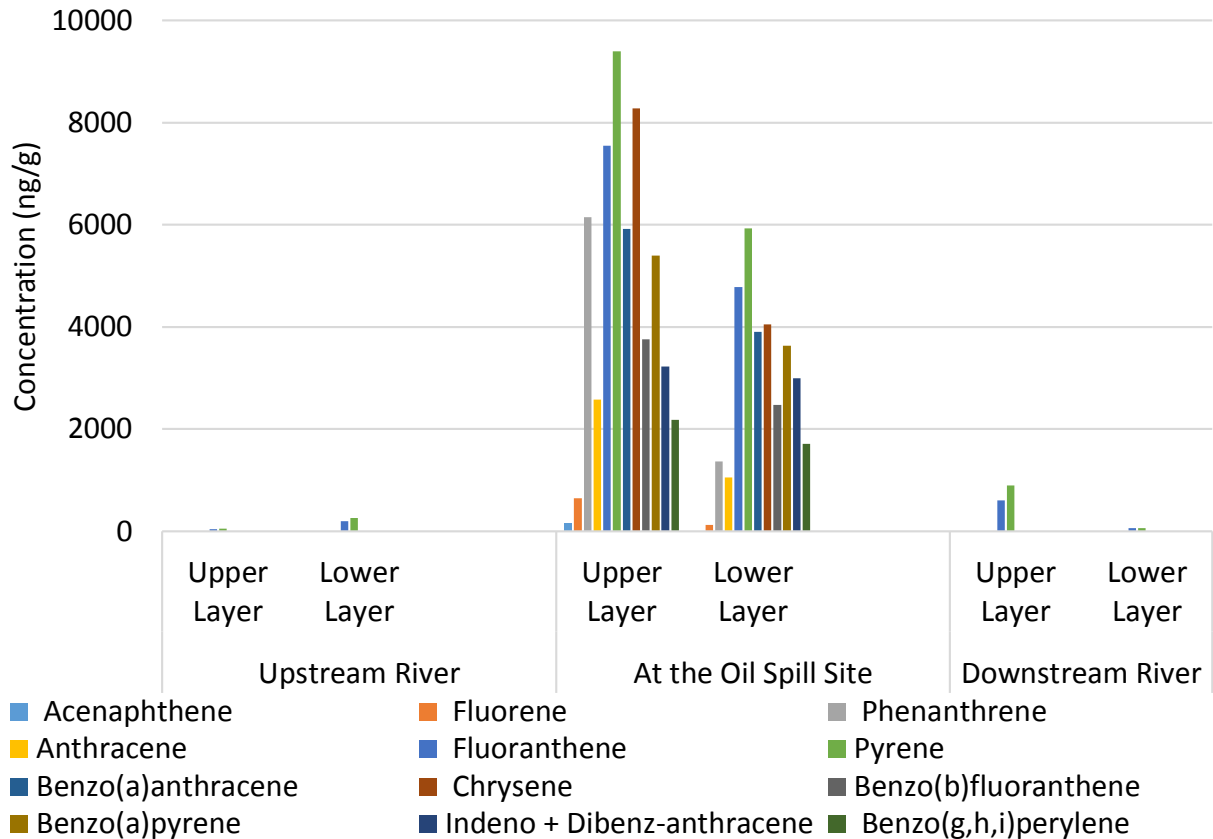


Figure 6. From Al-Isawi, 2016. Graph showing the presence and concentrations of PAHs at the spill site. The presence of pyrene/ fluoranthene up and downstream of the site is likely due to their presence in motor vehicle exhaust.

Naphthalene is observed in the highest concentrations of all PAHs detected in this study. This is thought to be a result of heavier, more complex compounds degrading into naphthalene's simple two-ring structure (Zhang et al., 2006). As microorganisms degrade PAHs through numerous metabolic pathways, entire rings of hydrocarbons are cleaved off. Anthracene, for example is a straight, three-ring structure (**Figure 5**). One of these rings could be removed by bacterium such as *Sphingomonas* and *Pseudomonas*, leaving the chemical structure with two benzene rings, as seen in naphthalene (Zhang et al., 2006).

Acenaphthylene and anthracene are not found in the unprocessed tar sands oil, however, they are found in diluted bitumen that is produced in the Athabasca oil field (Yang et. Al, 2011). These compounds must therefore be added to the product as part of the dilution process, which allows the bitumen to be transported via pipeline. These biomarkers were found in all samples from this study, and in previous studies concerning this spill (Yang et. Al, 2011, Al-Isawi, 2016) (**Table 3**). Control samples from upstream of the spill site in Al-Isawi (2016) indicate that these compounds are not native to the area (**Figure 6**). Therefore, it can be argued that PAHs still present in this region are a result of the 2010 spill.

Further, it is likely the terpenes identified in the samples are also associated with the spill, as terpenes may have been used as bio-based solvents to dilute the oil or in the clean-up process (Rapp, 2010). There are no other known natural sources of the terpenes identified (ex. eucalyptol) to this region. The presence of these terpenes may therefore be another mode of fingerprinting the PAHs found to the 2010 spill.

Conclusions.

After 5 years of continuous remediation, measurable concentrations of PAHs remain in Kalamazoo River Sediments within the spill area. The PAHs identified are consistent with those expected from Athabasca tar sands oil as evidenced by biomarkers from the raw product and associated dilbit. Concentrations of some PAHs (e.g. naphthalene) are above a safe level for human and ecosystem health, and therefore place inhabitants of this area at risk of cancers and other mutagenic effects. Identifying a correlation between PAH concentration and sediment grain size is unclear, but finer sediments do seem to be associated with higher PAH concentrations. Future work will include investigation of degradation rates and pathways of persistent PAHs to improve future remediation efforts.

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