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Detection of hydrocarbon contaminants in groundwater systems

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Detection of hydrocarbons in groundwater systems

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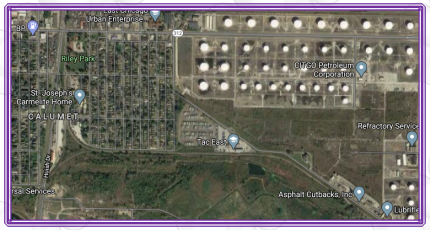
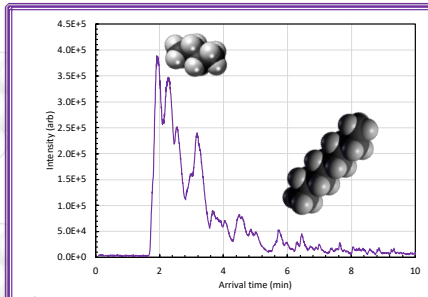
Abstract

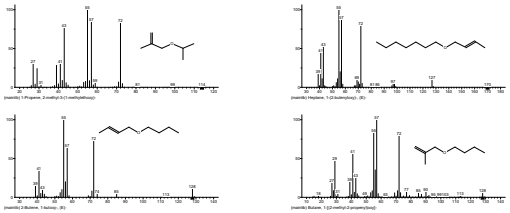
We present a study of groundwater contaminants from infiltration of heavy hydrocarbon pollution sources. This study primarily focuses on the volatile and non-volatile components of crude and processed oils. Many storage terminals and buried pipelines have experienced historical failures and present industrialized Northwest Indiana with a source of legacy pollution. We examine the aqueous phase and gas phase components of crude and diesel oils for identification of groundwater matrix markers from hydrocarbon emulsions. Using gas phase phase chromatography predominantly light (< C_8) hydrocarbons were found to be present in heavily emulsified aqueous solutions.





Of concern are hydrocarbons found in both crude and light processed oils from terminal lines and/or above ground storage tanks. These terminal tanks have been in use for approximately a century. Early forms of the tanks were created with wood bottoms leaving the oils exposed to the water table. Groundwaters are typically raised to around a foot of depth near Lake Michigan.

These data were taken from crude oil sampled near the Harding County Red River Formation. Crude oil contains many volatiles shown in this gas chromatogram which are typically seen to vary from butane up to higher order C_8 - C_{12} compounds. Predominantly the light compounds are found via mass spectrometric analysis, due to signal ambiguity specific molecular identification remains an unknown.

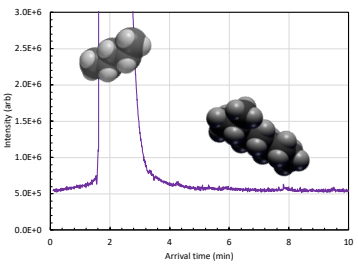


Mass spectrometry is often used in conjunction with chromatographic techniques to quantitatively identify compounds and their molecular structure. This is often done by library searches of mass fragmentation patterns typical for compounds broken through electron impact ion sources.

Unfortunately as displayed above the mass fragmentation patterns for *n*-pentane display compounds of similar hydrocarbon structure that are nearly indistinguishable. This presents a significant problem when analyzing crude oil or other combustible fuel sources and requires unique mass spectrometers, with very high mass resolution, such as time of flight (TOF) or ion cyclotron resonance (ICR) instruments which are both prohibitively expensive to acquire and operate. As such our chromatographic identification remains qualitative at best.

Experimental

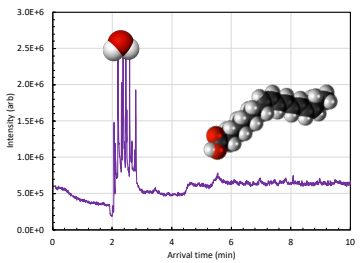
- Two hydrocarbon fuel sample types were investigated: crude oil and diesel fuel
- Samples were prepared by multiple techniques which included headspace sampling of raw sample aliquot, solvent (pentane and water) dissolution injection, and pentane extraction from aqueous mixture
- Chromatographic separation was completed using an Agilent 7890A gas chromatograph with compounds detected by an Agilent 5975C quadrupole mass spectrometer
- Individual samples were run in triplicate interspaced by cleaning solution and chloroform injections to clear column residues
- Analysis of individual peaks were compared through the NIST 2011 mass spectral library
- High pressure liquid chromatography aliquots were not analyzed for the current study, but remain a future endeavor



The left figure shows chromatographic analysis of crude oil in pentane (large peak) demonstrating a 1:1000 dilution of the fingerprint region (> 4 min) indicating unknown larger hydrocarbons in the diluted mixture.

In the right figure a 1:100 crude oil in water dilution indicates a somewhat larger intensity of fingerprint peaks likely due to the decreased dilution factor. These peaks were not seen in all samples and may be representative of selected oil droplets picked up during injection.

As of the latest analysis it is unknown if small peaks after 4 min represent the same compounds or a different selection. We hypothesize that based on intermolecular forces it is likely these are NOT the same structures but further results are necessary to confirm the molecular differences if any.

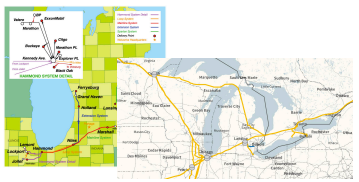


Discussion

- Numerous compounds are present in crude and diesel oils both as low and high molecular weight hydrocarbons, which are particularly difficult to analyze with mass spectrometry
- Low molecular weight hydrocarbons were found in varying abundance through headspace analysis, ultimately the distribution of light compounds decreased over time as the gas phase components were depleted
- Results of the dilutions for both crude and diesel in water were dependent on the emulsification of the sample and rest time between analytical runs
- Difficulties were encountered for the aqueous sample integrity through multiple injections, often samples did not present the same peak profiles indicating the aqueous samples were not homogeneous
- Further testing is needed, but currently the affinity of the smaller (< C_8) hydrocarbons to the gas chromatographic technique will require specific column selection or different carrier gasses to lower background for field samples

Future work

Future analysis will be augmented with high pressure liquid chromatography to search for additional hydrocarbon elements likely larger than C_8. A more specific method will be required to identify contaminated field samples. We anticipate using enhanced chromatographic analysis of the compounds with a more specific hydrocarbon column with helium carrier gas. Additionally we plan to analyze a standard solution of normal hydrocarbons, which should alleviate the need for exact mass spectrometric determination of the compounds.



Hydrocarbon pollution remains a major issue for industrialized Northwest Indiana and the Great Lakes region. Currently expansion efforts are underway at the British Petroleum Whiting refinery. Additional terminal lines only increase the risk of leaks.

The authors, all scholar athletes from the Great Lakes region, would like to acknowledge the efforts and invaluable assistance of the Department of Chemistry at Valparaiso University. Without their dedication and efforts in the classroom and laboratory, none of this work would have been possible.