# Geochemical Tools for Monitoring Petroleum Hydrocarbon Sources and Remediation in the Environment

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## Summary

Assessment and differentiation of the sources and fates of petroleum hydrocarbons and their residues in environmental systems is critical to effective site management and remediation efforts. However, such assessment can face a number of challenges. In many systems multiple sources may be contributing to petroleum compounds observed at a site and there is a need to differentiate the relative contributions of each source. And while the majority of potential sources are anthropogenic in some cases anthropogenic impacts must be differentiated from naturally occurring sources that may also contribute the same compounds present in petroleum. Assessing the occurrence and extent of biodegradation of petroleum hydrocarbons can also be challenging. Biodegradation of petroleum compounds by environmental microbial communities is known to occur in many systems. But demonstrating the effectiveness of this process in site remediation can be challenged by highly heterogeneous compound distributions, complex mixtures of thousands of petroleum hydrocarbons and/or slow reaction rates. Further, in many cases, it is only a subset of petroleum derived compounds present in a complex mixture that pose a risk to human health or the environment. There is thus a need to develop approaches that can resolve specific petroleum hydrocarbon compounds within complex mixtures and assess their fate within environmental systems.

This presentation will provide an overview of some of the new approaches my group has developed to address these issues. Our work has developed the application of compound specific radiocarbon analysis (CSRA) as a tool to differentiate petroleum hydrocarbons from naturally occurring compounds, and to directly demonstrate biodegradation/bioremediation of petroleum hydrocarbons within environmental systems. In addition, we are developing comprehensive gas chromatography mass spectrometry (GCxGC) techniques that generate a molecular fingerprint of petroleum hydrocarbons in order to allow assessment of the relative contributions of potential sources and/or the extent of degradation of petroleum hydrocarbons in the Alberta Oil Sands Region.

## Theory / Method / Workflow

Compound specific isotope analysis (CSIA) has been recognized as a powerful tool in the environmental industry for some time. Compound specific radiocarbon analysis (CSRA) builds on this technique by expanding to analysis of the radiocarbon content of individual organic compounds or compound classes as a tool to differentiate their sources. In the context of petroleum hydrocarbon sources and remediation, this approach relies on the fact that

petroleum carbon is millions of years old and thus contains no significant $^{14}C$ ($\Delta^{14}C$ = -1000 ‰) while recently fixed natural organic matter in the environment contains modern levels of $^{14}C$ ($\Delta^{14}C$ = ~50 ‰). This difference provides a natural abundance tracer that can be used to resolve mixing of as little as 4% of petroleum carbon with natural organic matter.    By separating and collecting individual petroleum compounds, or compound classes, the contribution of petroleum hydrocarbons can be assessed based on isotopic mass balance.

Comprehensive two-dimensional gas chromatography (GC×GC) provides greater chromatographic resolution of petroleum hydrocarbons present as unresolved complex mixtures in environmental samples. In this system, two columns with different stationary phases are connected sequentially in a GC oven and a modulator is used to fractionate effluent from the primary ($^1$D) to the secondary ($^2$D) column throughout the run in regular occurring intervals (frequency of modulation for a typical GC×GC method is typically between 2 to 5 seconds). GC×GC-based approaches significantly increase the number of resolvable features in a chromatogram and can allow for the identification of a greater array of petroleum compounds. As a result, this approach can also separate, identify and quantify isomers of individual compounds.  Molecular fingerprints based on compound and/or isomer distributions can then be used to differentiate sources or identify the occurrence of biodegradation.

## Results, Observations, Conclusions

Previously our group has applied the Compound Specific Radiocarbon Analysis approach to differentiate background PAH deposition resulting from forest fires from PAH deposition derived from combustion of fossil fuel sources in the sediments of Siskiwit Lake, on Isle Royale in Northern Ontario.  As well as to differentiate alkanes present in estuary sediments derived from terrestrial sources from those derived from industrial activities. We have also applied this approach to directly demonstrate the role of microbial biodegradation in remediation of petroleum hydrocarbons.  Analysis of sediments from Barataria Bay, LA, impacted by the Deepwater Horizon oil spill identified temporal trends in petroleum hydrocarbon mass loading and demonstrated the role of biodegradation in mass losses of petroleum hydrocarbons.  In this and previous work we have observed microbial biomarkers where carbon derived from petroleum comprised of more than 80% of membrane lipids, directly demonstrating microbial degradation as a mechanism of mass loss.

Our group is also applying GC×GC-TOFMS approaches to investigate the sources and potential processing of petroleum hydrocarbons in Base Mine Lake, the first pit lake commissioned in the Alberta Oil Sands Region.  We have identified more than one hundred petroleum hydrocarbon and naphthenic acid compounds in water samples from the site.  By comparing the molecular fingerprints based on these suites of compounds we have been able to identify distinct differences between naphthenic acids fingerprints in the water column of BML and those in the underlying tailings. This distinction has important implications to understanding the sources and processing of naphthenic acids within this system.  Our ongoing investigations are working to determine the extent to which this distinction is driven by differences in

naphthenic acids sources between the tailings and water column, or due to biological processing of the naphthenic acids within the water column. Our work to date has shown that, at least in some cases, differences in concentrations of naphthenic acid species were driven by differences in only one or two isomers of a given isomer series. Understanding the potential for distinct behavior of specific isomers can have important implications to understanding the potential contributions of different sources or the extent of microbial biodegradation. In addition, if only some isomers are bioactive, the ability to differentiate isomers may contribute to a greater ability to assess potential toxicological effects.

## Novel/Additive Information

The geochemical approaches we are developing provide new ways to assess the sources and/or processing of petroleum hydrocarbons in environmental systems. In the case of CSRA this approach is particularly powerful in differentiating the contributions of anthropogenic compounds from naturally occurring compounds. This includes directly tracing petroleum hydrocarbon derived carbon into micro-organisms, and thus directly demonstrating the occurrence of biodegradation. Comprehensive gas chromatography (GC×GC) provides a means to develop molecular fingerprints of potential petroleum hydrocarbon and naphthenic acids sources. Using isomeric fingerprints we can elucidate the contributions of potential sources to a system, such as the Base Mine Lake water column. The insights this work develops can then inform management decisions during reclamation activities and will provide tools to apply in future situations.

## Acknowledgements