Characterization of the BP petroleum residuals in the sediment of the Salt Marshes in the Northern Gulf of Mexico by Fourier Transform Ion Cyclotron Resonance mass spectrometry

Authors: Huan Chen[1], Nabanita Bhattacharyya[2], Rui Zhang[2], Aixin Hou[2], Ryan Rodgers[1, 3] and Amy M. McKenna[1]

[1]National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Dr., Tallahassee, FL 32310-4005

[2]Department of Environmental Sciences, Louisiana State University, Baton Rouge, LA 70803

[3]Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306

Introduction

Of the estimated 5 million barrels of crude oil released into the Gulf of Mexico from the BP Deepwater Horizon event, a fraction heavily oiled Louisiana's coastal salt marshes (Fig.1).

Figure 1. An oil-impacted area of marshland in Bay Jimmy near the Louisiana coast Oct. 29, 2010. Photo courtesy: Patrick Semansky.

Oil inputs may significantly alter the abundance, structure and diversity of the microbial communities inhabited in the sediments, and subsequently affect essential microbial services.

In this study, detailed analysis was conducted to investigate the possible impact of petroleum residuals on soil microbial communities of salt marsh in northern Barataria Bay of the Gulf of Mexico after the oil spill.

Methods

Sediment samples from heavily oil sites were collected after 9 months, 18 months, 24 months, 31months 36 months and 41 months of the spill (Fig. 2).

Samples from sites representative of unoiled (reference) and moderately oiled conditions were also included in the analysis.

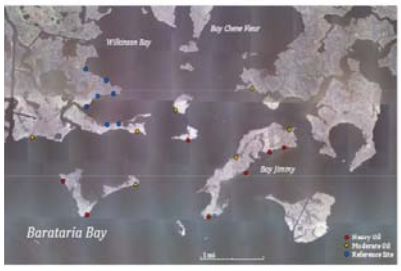

Figure 2. Study area and sampling stations

The petrogentic material was extracted with methylene chloride followed by ultrahigh resolving power Fourier Transform Ion Cyclotron Resonance mass spectrometry (FT-ICR MS) to address the compositional complexity of high molecular weight, nonvolatile petroleum fractions of the oil containments that are not readily degraded by the indigenous microbial community.

Results and Discussion:

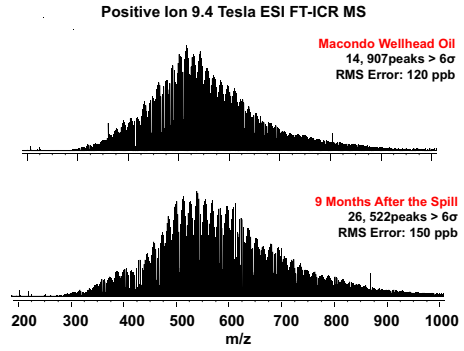

Figure 3. Positive ion electrospray ionization (ESI) FT-ICR MS of Macondo wellhead crude oil and a sample from heavily oiled site. ESI broadband FT-ICR MS identifies thousands of basic polar species in the oil samples. The broadband FT-ICR mass spectra for the macondo oil and weathered seep (9 months) span nearly identical molecular weight range. However, the weathered sample shows a much higher isobaric compositional complexity than the un-weathered Macondo oil. .

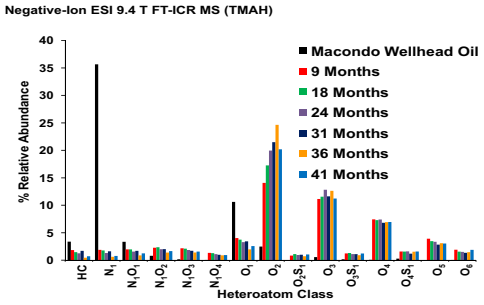

Figure 4. Heteroatom class distributions from samples derived from negative ESI 9.4 T FT-ICR mass spectra. The heteroatom classes differ dramatically between the marsh samples and the Macondo wellhead oil . The Macondo oil has higher content of classes containing pyrrolic (5-membered ring) nitrogen (N_1) but lower acidic oxygenated class levels. The O_2 species (presumably carboxylic acids) are dominant in weathered marsh samples. High abundance of carboxylate acids has previously been reported as an indicator of extensive biodegradation.

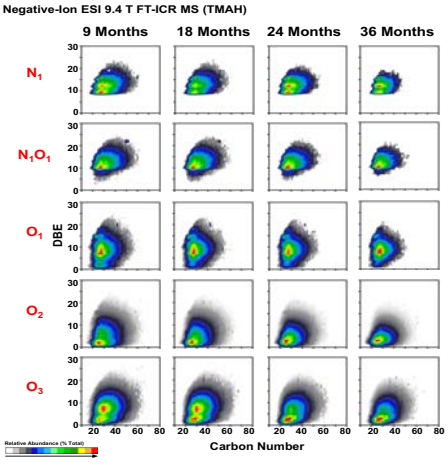

Figure 5. Negative ESI-derived isoabundance color-contoured plots of double bond equivalents (DBE= rings plus double bonds to carbon) vs. carbon number for N, NO_1, and O_{1-3} containing classes of the samples from heavily oiled site. The classes of marsh samples 9 months, 18 months, and 24 months span similar compositional spaces. The heteroatom classes from the 36 months, the most weathered sample, exhibit lower carbon numbers and less aromaticity than the other 3 samples.

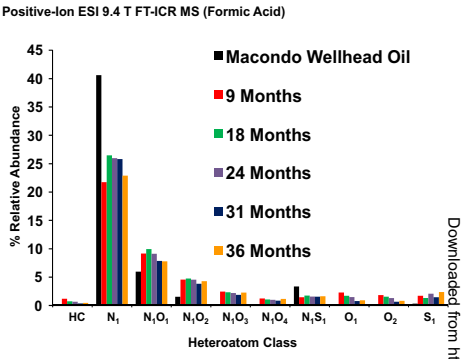

Figure 6. Heteroatom class distributions for positive-ion electrosprayed salt marsh samples. The heteroatom compositions of basic polar species in the seep samples are similar regardless of weathering degrees or sample location and are dominated by pyridinic (6-membered ring nitrogen) N_1, N_1O_{1-4}, N_1S_1 and O_{1-2}. In contrast to previous report on Deepwater Horizon (DWH) oil spill contaminants, for which the oxyhydrocarbons increase upon weathering, the salt marsh samples are less oxygenated and the oxygen content decrease with weathering. Basic Ox classes (i.e., ketones) are detected in all marsh sediment samples.

Conclusions

Mass spectrometry analysis of these samples display a 1.5 to 2.5 fold increase in the molecular complexity, particularly oxygen compounds relative to the original Macondo well oil and ketone species were abundantly present in the oiled sediment extracts.

Detailed compositional characterization of weathered oil collected from different sites and exposure reveals unique compositional trends. The polar species remain stable in the contaminated samples from 9 months to 41 months after the rig explosion.

The comprehensive analysis on the petroleum residues will help us better understand the fate of oil released into the environment and the long-term impact of BP oil spill.

Acknowledgments

Work performed was supported by NSF Division of Materials Research through DMR-11-57490, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, and the State of Florida.

References

1. Kaiser, N. K.; Quinn, J. P.; Blackney, G. T.; Hendrickson, C. L.; Marshall, A. G., A novel 9.4 Tesla FTI-CR Mass Spectrometer with Improved Sensitivity, Mass Resolution and Mass Range. J. Am. Soc. Mass. Spectrom. 2011, 22 (1343-1351).

2. McKenna, A. M.; Rodgers, R. P.; Nelson, R. K.; Reddy, C. M.; Savory, J. J.; Kaiser, N. K.; Fitzsimmons, J. E.; Marshall, A. G., Expansion of the Analytical Window for Oil Spill Characterization by Ultrahigh Resolution Mass Spectrometry: Beyond Gas Chromatography. Environ. Sci. Technol. 2013.

3. Mapolelo, M. M.; Rodgers, R. P.; Blakney, G. T.; Yen, A. T.; Asomaning, S.; Marshall, A. G., Characterization of naphthenic acids in crude oils and naphthenates by electrospray ionization FT-ICR mass spectrometry. Int. J. Mass spectrom. 2011, 300 (2), 149-157.

4. Aeppli, C.; Carmichael, C. A.; Nelson, R. K.; Lemkau, K. L.; Graham, W. M.; Redmond, M. C.; Valentine, D. L.; Reddy, C. M., Oil weathering after the Deepwater Horizon disaster led to the formation of oxygenated residues. Environ. Sci. Technol. 2012, 46 (16), 8799-8807.