Molecular Evidence of Heavy-Oil Weathering Following the M/V *Cosco Busan* Spill: Insights from Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Lemkau, K.L. (MIT/WHOI); McKenna, A.M.; Podgorski, D.C.; Rodgers, R.P. (NHMFL, Chemistry); C.M. Reddy (WHOI)

Results and Discussion

Recent studies have highlighted a critical need to investigate oil weathering beyond the analytical window afforded by conventional gas chromatography (GC). In particular, techniques capable of detecting polar and higher molecular weight (HMW; > 400 Da) components abundant in crude and heavy fuel oils (HFOs) as well as transformation products. Here, we used atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry (APPI FT-ICR MS) to identify molecular transformations in oil-residue samples from the 2007 M/V Cosco Busan HFO spill (San Francisco, CA). Over 617 days, the abundance and diversity of oxygen-containing compounds increased relative to the parent HFO, likely from bio- and photodegradation. HMW, highly aromatic, alkylated compounds decreased in relative abundance concurrent with increased relative abundance of less alkylated stable aromatic structures. Combining these results with GC-based data yielded a more comprehensive understanding of oil spill weathering. For example, dealkylation trends and the overall loss of HMW species observed by FT-ICR MS has not previously been documented and is counterintuitive given losses of lower molecular weight species observed by GC. These results suggest a region of relative stability at the interface of these techniques, which provides new indicators for studying long-term weathering and identifying sources.

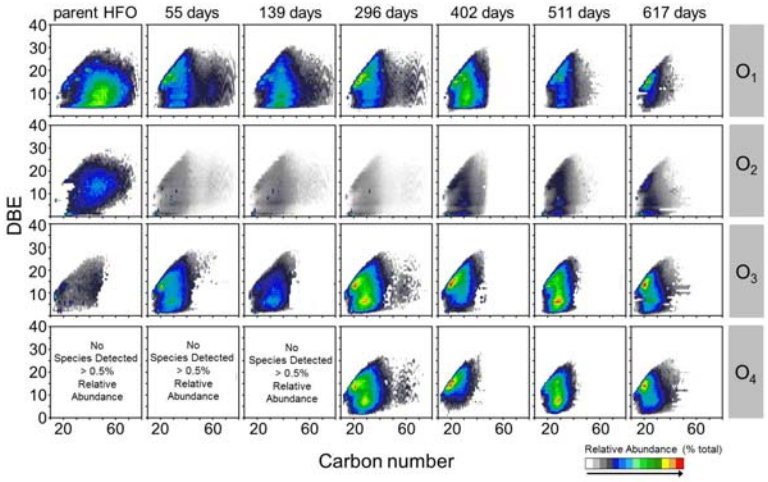

Figure 1. Isoabundance-contoured plots of double bond equivalents (DBE) versus carbon number for the O_1 – O_4 heteroatom classes (shown on right) for the parent HFO and field samples collected from 55 to 617 days postspill. Each compositional image is normalized to the most abundant species within that heteroatom class for that sample. Compounds that contain one oxygen atom (O_1) showed no overall shift in average DBE (14 in both the parent and HFO and after 617 days) but carbon number decreased by an average of 19 carbons per molecule. A bimodal distribution was observed in the O_2 class with compounds with 2 DBE corresponding to naphthenic acids (naturally occurring alkyl-substituted saturated cyclic and noncyclic carboxylic acids). The decrease in average carbon number is less prominent in the O_3 and O_4 classes than in other classes, with average carbon number decreasing only by 5 for the O_3 class. These newly formed, highly oxygenated compounds are relatively resistant to degradation, comprised of mixed phenol, ketone and carboxylic acid species, and likely correspond to compounds formed through the biotic and abiotic oxidation of native HFO compounds.

Acknowledgements

This work was supported by WHOI academic program funds, the Coastal Ocean Institute, the Richard and Rhoda Goldman Fund, the Ocean Ventures Fund and NSF grants EAR-0950670 and OCE-0960841. National High Magnetic Field Laboratory work was supported by NSF Division of Materials Research through DMR-06-54118, NSF CHE-10-49753 (RAPID), and the State of Florida, BP/Gulf of Mexico Research Initiation through the Deep-C Consortium.

References [1] Lemkau, K.L., *et al*., Environ. Sci. Tech., **48**, 3760-3767 (2014)