Targeted Petroleomics: Analytical Investigation of Macondo Well Oil Oxidation Products from Pensacola Beach

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Results and Discussion

Of the estimated 5 million barrels of crude oil released into the Gulf of Mexico from the Deepwater Horizon oil spill, a fraction washed ashore onto sandy beaches from Louisiana to the Florida panhandle. Here, we compare the detailed molecular analysis of hydrocarbons in oiled sands from Pensacola Beach to the Macondo wellhead oil (MWO) by electrospray (ESI) and atmospheric pressure photoionization (APPI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to identify major environmental transformation products of polar, high molecular weight (C>25) "heavy ends" (high-boiling species) inaccessible by gas chromatography. The petrogenic material isolated from the Pensacola Beach sand displays greater than 2-fold higher molecular complexity than the MWO constituents, most notably in oxygenated species absent in the parent MWO. Surprisingly, the diverse oxygenated hydrocarbons in the Pensacola Beach sediment extracts were dominant in all ionization modes investigated, (±) ESI and (±) APPI. Thus, the molecular-level information highlighted oxygenated species for subsequent "targeted" analyses. First, time-of-flight mass spectrometry analysis of model compounds attributes the unusually large oxygen signal magnitude from positive electrospray to ketone transformation products (O1–O8 classes). Next, negative electrospray mass spectrometry reveals carboxylic acid transformation products. Two-dimensional gas chromatography with mass spectrometry analysis of anion-exchange chromatographic fractions unequivocally verifies the presence of abundant alkyl ketone fragments in sand extracts, and FT-ICR MS analysis reveals the distribution of high-boiling ketone, carboxylic, and higher numbered (3+) oxygen-containing transformation products too polar to be analyzed by gas chromatography. The results expand compositional coverage of oxygen-containing functionalities beyond the classic naphthenic acid type species to complex/mixed ketone, hydroxyl, and carboxylic acid classes of molecules that have been recently identified in produced water, emulsions, and petroleum production deposits.

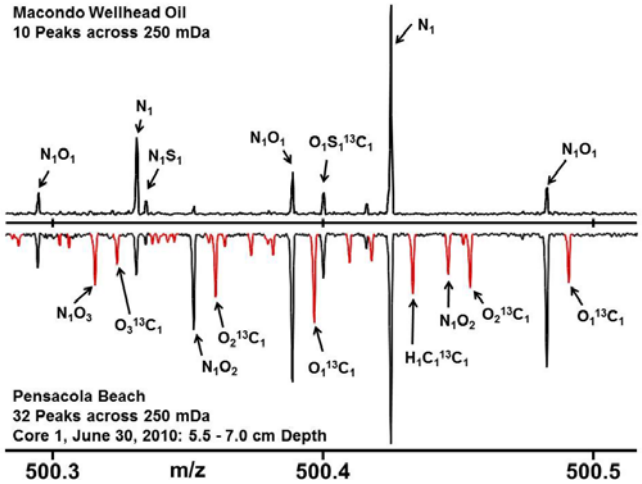

Figure 1. Positive ESI 9.4 T FT-ICR mass scale-expanded segment at nominal m/z 500 for (top) Macondo well oil (MWO) and (bottom) June 30, 2010 Pensacola Beach contaminant (5.5–7.0 cm depth). Contaminant species not present in MWO are shown in red. The higher compositional complexity can be more effectively visualized for high-resolution FT-ICR data through mass scale-expanded segments that span a fraction of a single nominal mass (0.2 Da at m/z 500). For positive ESI, 10 peaks are detected for the MWO (top) and 32 for the contaminated beach sediment extract (bottom), whereas no peaks $\geq 6\sigma$ are observed from either the environmental or the analytical blank across the same mass segment (data not shown). Peaks detected from the Pensacola Beach sand extracts but not detected from the MWO are highlighted in red and expose the primary source of the increased complexity as oxidation.

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References [1] Ruddy, B.M. *et al*., Energy Fuels, **28**, 4043-4050 (2014)