Sunlight Creates Oxygenated Species in Water-Soluble Fractions of *Deepwater Horizon* Oil

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Results and Discussion

In order to assess the impact of sunlight on oil fate, Macondo well oil from the Deepwater Horizon (DWH) rig was mixed with pure water and irradiated with simulated sunlight. After irradiation, the water-soluble organics (WSO) from the dark and irradiated samples were extracted and characterized by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Liquid–liquid extraction yielded two fractions from dark and irradiated water/oil mixtures: acidic WSOs (negative-ion electrospray (ESI)), and base/neutral WSOs (positive-ion ESI) coupled to FT-ICR MS to catalog molecular-level transformations that occur to Macondo-derived WSOs after solar irradiation. Such direct measure of oil photo-transformation has not been previously reported. The most abundant heteroatom classes detected in the irradiated WSO acid fractions correspond to molecules that contain five oxygens (O_5), while the most abundant acids in the dark samples contain two oxygen atoms per molecule (O_2). Higher-order oxy-gen classes (O_5–O_9) were abundant in the irradiated samples, but <1.5% relative abundance in the dark sample. The increased abundance of higher-order oxygen classes in the irradiated samples relative to the dark samples indicates that photo-oxidized components of the Macondo crude oil become water-soluble after irradiation. The base/neutral fraction showed decreased abundance of pyridinic nitrogen (N_1) con-current with an increased abundance of N_1O_x classes after irradiation. The predominance of higher-order oxygen classes indicates that multiple photochemical pathways exist that result in oxidation of petroleum compounds.

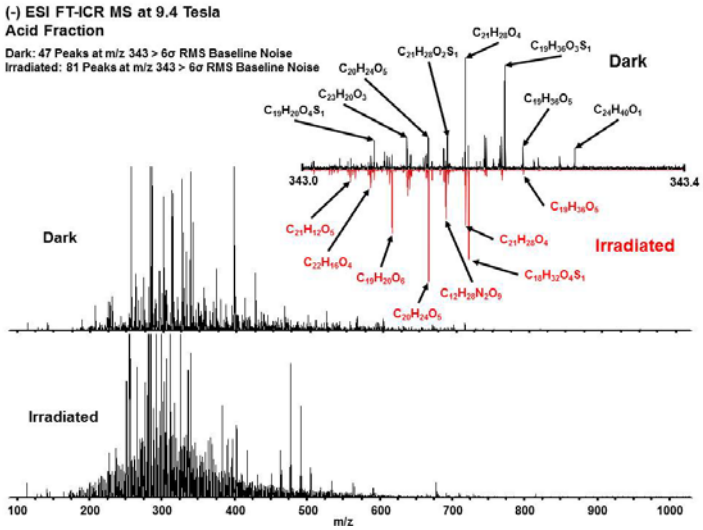

Figure 1. Negative-ion electrospray ionization FT-ICR mass spectra of the WSO acid extracts before (top) and after (bottom) irradiation. The top-right inset shows a 400 mDa mass-expanded window spanning nominal *m/z* 343. A two-fold increase in the number of detected mass spectral peaks with signal magnitude greater than six times the baseline rms noise level highlights the increased spectral complexity observed after irradiation. The most abundant peaks after irradiation correspond to highly oxygenated compounds not observed without irradiation across the same mass range.

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References

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