Photochemical Degradation of Petroleum-Derived Water-Soluble Organics into Dissolved Organic Matter

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Introduction

Oil spills in the marine environment have broad environmental impacts. Petroleum begins a complex series of physical transformations and chemical reactions immediately upon entering the aquatic environment. The reactivity of identifiable oil components in the environment depends on the rate and degree of degradation. The two degradation pathways are driven by either microbial (biotic) or photochemical (abiotic) processes. Factors such as the initial composition of the oil and environmental conditions dictate degradation pathways, rates and product end-members. Previous studies show that highly oxygenated water-soluble organic (WSO) photoproducots are created when crude oil is irradiated on water. While initial research focused on the formation of WSO photoproducots from oil where the oil serves as a persistent source of material for product formation, there is current interest in the environmental fate of petroleum-derived WSO photoproducots in the absence of oil and how these products incorporate into the dissolved organic matter (DOM) pool. Here, we generated WSOs from Macondo crude oil that was released into the Gulf of Mexico as a result of the Deepwater Horizon explosion in 2010 and a heavy fuel oil released into the San Francisco Bay by the MV Cosco Busan in 2007. These two oils have drastically different chemical properties that allow us to determine if WSOs generated from these oils will photodegrade to an extent where the WSOs are indistinguishable from the background dissolved organic matter composition from the Gulf of Mexico (GoM) and San Francisco Bay (SFB).

Methods

20 g of Macondo crude oil and heavy fuel oil (NIST 2717a) were added to 150 mL of filtered/UV treated seawater from the GoM. Water-soluble organics from each oil sample were generated by irradiating the samples for 48 h in jacketed beakers that were covered with aluminum foil so that only the oil layer was irradiated while the water remained shielded. The oil and water were separated in a separatory funnel and 30 mL aliquots of the aqueous layer were subsequently irradiated in the absence of oil for 1, 2, 4, 8, 12, 24, 36, 48, 60, and 72 hours. The WSO from each sample was concentrated by a solid-phase extraction method described by Dittmar et al. DOM from the GoM and SFB was extracted to compare with the irradiated WSO products. Each extract was analyzed by negative-ion electrospray (ESI) ionization 9.4 Tesla Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).

Results

The results show that petroleum-derived WSOs experience additional photodegradation in the absence of a persistent oil source. The composition of WSOs from the Macondo oil continue to change after 72 h of irradiation (equal to 18 days of natural sunlight) while those from the heavy fuel oil reach a steady-state after 36 h. These results provide preliminary evidence that the rate of degradation and composition of the product end-members are dependent on the initial composition of the oil. Moreover, the composition of the degraded WSOs from the Macondo oil appear to be trending toward the background DOM. Additional experiments are required to determine the bioavailability of the aliphatic photoproducots formed from both sources.

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References