Transformations of dissolved petroleum compounds at a natural asphalt seep in the Gulf of Mexico

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Water-soluble hydrocarbons from natural sources or from anthropogenic pollution can remain in seawater over long periods of time, where they have the potential to enter the marine food web and bioaccumulate [1]. In this study, we investigated the release of oil-derived dissolved organic matter (DOM) from natural deepwater asphalts by using microcosm experiments. Non-biodegraded asphalt samples collected at the Chapopote asphalt volcano in the Southern Gulf of Mexico [2] were incubated aerobically in artificial seawater over a four-week period.

The molecular composition and changes in DOM were monitored with ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) to determine the molecular composition of the water-soluble fraction of asphalt-derived DOM and excitation-emission matrix spectroscopy to characterize fluorescent DOM (FDOM).

Biodegradation released three times higher amounts of dissolved organic carbon into the water than the killed controls, reaching concentrations in the milimolar range. Solid-phase extracted DOM [3] consisted of small molecular masses, including potentially harmful polycyclic aromatic compounds and polycyclic aromatic sulfur heterocycles, as well as humic-acid like FDOM and an increasing proportion of polyphenols. Killed controls exhibited DOM with higher molecular masses and a specific molecular fingerprint that may be used for determining abiotic asphalt weathering in natural samples. In both biotic and abiotic experiments, >50 % of the molecular formulae consisted of sulfur species, which seem recalcitrant to microbial degradation on the time scales of our experiments. Our findings indicate that sulfur-rich hydrocarbon seeps may present an overlooked contribution to the dissolved organic sulfur pool in the ocean.

[1] D'Adamo *et al.* (1997) *Mar. Chem.* **56**, 45-49. [2] MacDonald *et al.* (2004) *Science* **304**, 999-1002. [3] Dittmar *et al.* (2008) *Limnol. Oceanogr. Methods* **6**, 230-235.