Using barium ion chemistry to assess the photoproduction of carboxylic acids from crude oil-seawater systems under solar irradiation

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Oil spilled in aquatic systems is exposed to sunlight, resulting in important photochemical processes. Photochemistry likely plays a major role in the fate of oil spilled in areas with sunlight exposure, especially since high molecular weight aromatics are readily photodegraded but are resistant to biodegradation. Previous studies have showed that a wide array of photoproducts are generated during natural photochemistry of crude oil under solar irradiation. In studying the photochemical mechanisms of oil transformations, previous studies have seen that the aldehyde and ketone photoproduct concentration in the aqueous phase increased with solar irradiation time.[1] Another important class of these photoproducts is the formation of carboxylic acids, including naphthenic acids. Naphthenic acids, widely found in crude oil, are important due to their prevalence in oil contaminated sites and chronic toxcitiy as well as their persistence in the environment and their important role in biogeochemical cycles. Other carboxylic acids produced from photooxygenation are also important in the fate, transport, and toxicity of oil. Herein, we report a thorough investigation of time on the dependence of carboxylic acid photoproduct generation in the aqueous phase under oil exposed to simulated sunlight. Oil samples were spread over seawater in a jacketed beaker held at 27 °C and exposed to simulated sunlight for various exposure times. The aqueous phase was collected after irradiation and derivatized with 0.1 mM barium acetate. Isolation of carboxylic acids using barium acetate derivatization produce barium adducts, which are selectively ionized in positive mode. These results provide insight into the photochemical degradation products of oil in marine systems and have important implications for management of oil spills.

[1] Cao, X et al. (2017) Environ. Sci. Technol. *51* (20), 11858-11866