

## **Ketone and aldehyde photoproducts from solar exposed crude oil on water**

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Photochemistry plays a key role in the fate and transport of oil spilled in aquatic systems. The formation of oxygenated photoproducts has been observed by high resolution mass spectrometry [1], and the presence of aldehyde and ketone photoproducts has recently been assessed with mass spectrometric techniques [2]. The formation of oxygenated photoproducts creates water soluble compounds that have increased bioavailability and transport. In addition, photoproducts with both polar and non-polar functionality can act as emulsifying agents and alter the chemical, physical, and biochemical behavior of oil slicks. In this study, oil samples were placed over seawater and irradiated with simulated sunlight under various conditions. Aqueous phase material was collected after irradiation and derivatized with 2,4-dinitrophenylhydrazine (selective for aldehydes and ketones). Prior to analysis, the derivatized carbonyl compounds were washed and enriched by solid phase extraction. Collected products were analyzed by negative ion electrospray ionization mass spectrometry. MS-MS allowed identification of molecular masses of aldehyde and ketone photoproducts and aided in structural classification of the products, many of which had more than one oxygen functional group. Carbonyl photoproducts were observed over a wide range of molar masses. Utilization of an internal standard allowed for semi-quantitative analysis, revealing that aqueous aldehyde and ketone concentrations increased in a near linear fashion with irradiation time. Additional studies have investigated the impact of atmospheric oxygen content in controlling the kinetics and distribution of photoproducts. Gaining a more complete understanding of the mechanisms and controlling factors for photochemically driven oil oxygenation is necessary to understand the geochemical cycling of petrogenic carbon released to the surface of aquatic systems. This work was supported by the U.S. National Science Foundation.

[1] Ray, et al. (2014), *J. Haz. Mat.* 280, 636-643. [2] Cao & Tarr (2017), *Environ. Sci. Technol.* 51, 11858-11866.