



## **Productions of Volatile Organic Compounds (VOCs) in Surface Waters from Reactions with Atmospheric Ozone**

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Ozone ( $O_3$ ) is a key atmospheric oxidant, greenhouse gas and air pollutant. In marine environments, some atmospheric ozone is lost by reactions with aqueous compounds (e.g. dissolved organic material, DOM, dimethyl sulfide, DMS, and iodide) near the sea surface. These reactions also lead to formations of volatile organic compounds (VOCs). Removal of  $O_3$  by the ocean remains a large uncertainty in global and regional chemical transport models, hampering coastal air quality forecasts. To better understand the role of the ocean in controlling  $O_3$  concentrations in the coastal marine atmosphere, we designed and implemented a series of laboratory experiments whereby ambient surface seawater was bubbled with  $O_3$ -enriched, VOC-free air in a custom-made glass bubble equilibration system. Gas phase concentrations of a range of VOCs were monitored continuously over the mass range  $m/z$  33 – 137 at the outflow of the bubble equilibrator by a proton transfer reaction – mass spectrometer (PTR-MS). Gas phase  $O_3$  was also measured at the input and output of the equilibrator to monitor the uptake due to reactions with dissolved compounds in seawater. We observed consistent productions of a variety of VOCs upon reaction with  $O_3$ , notably isoprene, aldehydes, and ketones. Aqueous DMS is rapidly removed from the reactions with  $O_3$ . To test the importance of dissolved organic matter precursors, we added increasing (milliliter) volumes of *Emiliana huxleyi* culture to the equilibrator filled with aged seawater, and observed significant linear increases in gas phase concentrations of a number of VOCs. Reactions between DOM and  $O_3$  at the sea-air interface represent a potentially significant source of VOCs in marine air and a sink of atmospheric  $O_3$ .