Geophysical Research Abstracts
Vol. 17, EGU2015-12177-2, 2015
EGU General Assembly 2015

Formation of alkenes and oxygenated VOC from light mediated surface chemistry at the air-seawater interface

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Organic carbon and halogens are relevant in the atmosphere because they influence the reactive chemical removal pathways of climate active gases (i.e. ozone, methane, dimethyl-sulfide), and can modify aerosols that affect Earth's radiation balance. The amount of dissolved organic carbon (DOC) in the world's oceans is comparable to that of atmospheric CO_2. Yet oceans are currently believed primarily to be a receptor for organic carbon emitted over land. Recent field measurements find elevated concentrations of glyoxal ($C2H_2O_2$), the smallest a-dicarbonyl compound, over tropical Oceans (Wittrock et al., 2006; Sinreich et al., 2010; Lerot et al., 2010; Mahajan et al., 2014). More recently, we have measured for the first time Eddy-Covariance fluxes of glyoxal (Coburn et al., 2014), which locate a chemical source within the sea-surface microlayer. Glyoxal over oceans is surprising, given its very short atmospheric lifetime (few hours) and highly solubility (Henry's Law constant, KHeff $\sim$ 4x105 M/atm); over oceans glyoxal remains unexplained by atmospheric models, and is a smoking gun that indicates missing oxygenated volatile organic compounds (OVOC) sources from the oceans.

A series of laboratory experiments have been performed at IRCELYON that studied the light induced surface chemistry of synthetic aqueous mixtures containing NaCl, NaBr, NaI, photosensitizers (humic acids) and an organic surfactant (nonanoic acid) in a photochemical Quartz flowreactor. The air from the flowreactor was transferred to a dark reactor where the products from photosensitized reactions at the air/sea interface were further exposed to ozone. The products were sampled in the presence/absence of light and ozone by Proton Transfer Reaction Time of Flight Mass Spectrometry (PTR-ToF-MS) and Light-Emitting-Diode Cavity-Enhanced Differential Optical Absorption Spectroscopy (LED-CE-DOAS). In the presence of light nonenal formation is observed. Addition of ozone leads to the formation of glyoxal, among other OVOC products. We discuss results in context of the field observations, and discuss atmospheric implications.

References:

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