



Investigating the pathway for the photochemical formation of VOCs in presence of an organic monolayer at the air/water interface.

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Recently the surface microlayer (SML) has received growing attention for its role in the deposition and emission of trace gases. This SML is presumably a highly efficient environment for photochemical reactions thanks to its physical and chemical properties, showing enrichment in chromophores [1]. Still, little is known about the possible photochemical processes that could influence the emission and deposition of volatile organic compounds (VOCs) in the SML. A recent study underlines the particularity of the presence of an organic microlayer, showing enhanced formation of peptide bonds at the air-water interface, although this reaction is thermodynamically disfavoured in bulk water [2]. Also, emissions of small gas phase carbonyl compounds formed photochemically by dissolved organic matter have been measured above natural water and glyoxal, for example, measured above the open ocean is thought to be photochemically produced [3, 4].

This study presents the results of a set of laboratory studies set up in order to better understand the role of the SML in the photochemical production of VOCs. Recently, our group has shown the formation of VOCs by light driven reactions in a small quartz reactor (14mL) containing aqueous solutions of humic acids (HA) in the presence of an organic (artificial or natural) microlayer [5]. The main VOCs produced were oxidized species, such as aldehydes, ketones and alcohols, as classically can be expected by the oxidation of the organics present at the interface initiated by triplet excited chromophores present in the HA. But also alkenes, dienes, including isoprene and unsaturated aldehydes were detected and a reaction pathway, initiated by a H-abstraction of the surfactant by the excited HA*, has been proposed. This mechanism infers that the presence of the surface microlayer will enhance protonation and self-reactions, leading to the formation of dimers as suggested in [6]. These products could explain the formation of the unsaturated products observed.

To confirm the hypothesis of an initiative step of H-abstraction, the system was simplified using OH radicals, generated by the photolysis of H₂O₂, in presence of an artificial organic layer of nonanoic acid. The VOCs produced, monitored by PTR/SRI-TOF-MS in NO⁺ and H₃O⁺ ionization mode, were less abundant compared to the system with HA, but the same classes of products could be observed, including oxidation products such as aldehydes but also unsaturated products like dienes. The underlying water was sampled before and after the experiment and analysed by HR-ESI-MS, showing mostly enrichment of oxidative products, such as hydroxy- and keto-acids immediately derived from the photochemical oxidation of the nonanoic acid layer. These products, showing lower volatility and higher polarity, partition preferentially to the bulk water. The results of this simplified system confirm the reaction mechanism proposed and the role an organic layer can play in the photochemical formation of VOCs, which could influence the marine boundary layer chemistry.

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