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Photosensitized reactions at the sea surface microlayer

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The sea surface microlayer is the organic-enriched layer present at the air-sea interface which has different physical and chemical properties than that of subsurface waters. The chemical analysis of this microlayer is of great interest for many reasons including its major influence to reduce air–sea gas exchange by impeding molecular diffusion across the interface and by influencing the characteristics of water motion at the interface. Surface seawater contains a variety of substances which act as photosensitisers. They include components of the dissolved organic matter known also as humic acids. The sea surface microlayer is the primary recipient of the solar energy. Since the microlayer is enriched in chemicals and biota, it is probable that a number of processes are more effective here than in the rest of the water column. These include changes in the chemical composition of the living cells of phytoplankton and the photodegradation of organic matter.
The focus of this study is to quantify if the organic film acts as a hydrophobic barrier for the air-sea gas exchange and to identify and characterize the gaseous emissions from the surface due to the photochemical processing of the sea surface microlayer. Synthetic mixtures (aqueous solution containing NaCl, NaBr, NaI), photosensitizers (humic acids) containing an organic surfactant (hexanol, otanol, nonanoic acid) have been irradiated by a Xe lamp, the gaseous products being further identified and analyzed by a High Resolution Proton Transfer Reaction – Time of Flight Mass Spectrometer and the particulate phase by a Condensation Particle Counter.
It has been observed that the presence of a thick organic film on the salt solutions reduces the transfer from the aqueous solution to the gas phase.
A net isoprene formation was observed under irradiation. The isoprene is formed only in the presence of the organic surfactant with the need for the photosensitizer. The dependence of the isoprene concentration with the photosensitizer is shown. A reaction mechanism of the isoprene formation is proposed. Furthermore, the oxidation products of isoprene and of the organic surfactant are identified.