Photochemical reaction at the air-water interface and effect on atmospheric nitric oxide

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Interfaces coated by organic material exposed to the atmosphere are ubiquitous and can include aerosol particles, cloud droplets, built surfaces and oceans. We hypothesize that photochemical interactions occur at these interfaces impacting sources and sinks of various compounds, and thus atmospheric composition.

The oceans cover the majority of the Earth, and the interactions potentially taking place at their surface may play an important role on the air-water exchange of trace gasses. The sea surface microlayer (SML) is concentrated in reactive light absorbing organic material, such as dissolved organic matter (DOM) with a high proportion of functional groups such as carbonyls and carboxylic acids. Photochemical reactions taking place there may lead to unique chemical pathways and products not previously considered or observed in the overlying gas phase or underlying bulk.

Here, we present an investigation of photochemistry at the air-water interface using nonanoic acid as a model carboxylic acid surfactant. Irradiation by UV light results in products released both to the gas and aqueous phases, with and without a photosensitizer in solution. This photochemistry also leads to the formation of saturated and unsaturated aldehydes along with other oxygenated photo-induced products (Rossignol *et al.*, 2016; Tinel *et al.*, 2016). Two different aspects of that chemistry will be discussed i.e., peroxy radicals production at the air-water interface and their impact on NO deposition, and VOC production from natural biofilms.

In fact, the reaction mechanism producing aldehydes and oxygenated products passes through the formation of peroxy radicals (Rossignol *et al.*, 2016). In turn, peroxy radicals may react with nitric oxide (NO) to form nitrogen dioxide (NO_2) and organonitrate compounds (Finlayson-Pitts and Pitts, 1999). Thus, we pose the question: could the photochemistry at the ocean surface, or at any other air-water interfaces, be a new path of NO loss in the atmosphere? Here we show that NO loss is induced when an air-water interface coated with nonanoic acid is irradiated. Experimental data will be presented concerning the impact of environmental conditions on this loss and the products formed by this chemistry as a function of temperature, pH, salt solution concentration, and the nature of surfactant. Formation of organonitrates is specifically investigated by off-line UPLC-HESI-HRMS (Ultra-performance liquid chromatography – Heated Electrospray – High Resolution Mass Spectrometer) analysis of the aqueous phase.

Marine biological processes are known to be important contributors to water and SML composition. Thus, we use a suspension of biofilm material as a natural surrogate in some experiments. Irradiation of biofilms with a Xenon lamp results in volatile gas phase compounds. The organic compounds formed were monitored using a PTR-ToF-MS (Proton Transfer Reaction-Time of Flight-Mass Spectrometer). Those compounds in water were analysed by UPLC-HESI-HRMS. The nature of the photochemical reactions occurring and their impacts will be discussed. In addition, the formation of secondary organic aerosol (SOA) precursors is investigated by means of an aerosol flow tube which allows the reaction of released volatile organic compounds (VOCs) with ozone or hydroxyl radical. Particle concentrations were monitored using a fine-mode condensation particle counter (CPC). These data will aide in our understanding of trace gas and aerosol particle budgets in the marine boundary layer.

Overall, we highlight some specificities of the chemistry taking place at the air-water interface.

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Finlayson-Pitts, B. J., and Pitts Jr, J. N. (1999) *Chemistry of the upper and lower atmosphere,* Academic Press.

Rossignol, S., Tinel, L., Bianco, A., Passananti, M., Donaldson, J. D., Brigante, M., and George, C. (2016) *Science*, under review.

Tinel, L., Rossignol, S., Bianco, A., Passananti, M., Perrier, S., Wang, X., Brigante, M., Donaldson, J. D., and George, C. (2016) *unpublished work*.