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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.

1. Peter S. Liss, R.A.D., ed. *Sea Surface and Global Change*. 1997, Cambridge University Press: Cambridge. 509.
2. Griffith, E.C. and V. Vaida, In situ observation of peptide bond formation at the water-air interface. *Proceedings of the National Academy of Sciences*, 2012. 109(39): p. 15697-15701.
3. Sinreich, R., et al., Ship-based detection of glyoxal over the remote tropical Pacific Ocean. *Atmospheric Chemistry and Physics*, 2010. 10(23): p. 11359-11371.
4. Kieber, R.J., X.L. Zhou, and K. Mopper, Formation of carbonyl-compounds from uv-induced photodegradation of humic substances in natural-waters - fate of riverine carbon in the sea. *Limnology and Oceanography*, 1990. 35(7): p. 1503-1515.
5. R. Ciuraru, L. Fine, M. van Pinxteren, B. D'Anna, H. Herrmann, C. George, Unravelling new processes at

interfaces: chemical isoprene production at the sea surface. submitted.

6. Griffith, E.C., et al., Photoinitiated Synthesis of Self-Assembled Vesicles. *Journal of the American Chemical Society*, 2014. 136(10): p. 3784-3787.



Interfacial Water Structure from Freshwater to Saltwater Brines

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Water at solid-liquid interfaces commonly differs from the bulk phase by adopting a polar, ordered structure. Electrolytes can act to perturb this structure, and as such, interfacial water in freshwater environments is not only different from its bulk counterpart, but also from counterparts in brackish, seawater, and sea-ice brine environments. In this study, sum-frequency generation spectroscopy, a surface-sensitive technique, is used to monitor electrolyte-induced changes of interfacial water structure. Solution ionic strength was varied over five orders of magnitude and spectra were collected from two mineral surfaces (fused silica and calcium fluoride) and two polymer surfaces (polystyrene and poly(methyl methacrylate)). Analysis of the spectra reveals both striking similarities and differences between these four aqueous interfaces. Spectral response at each of the four interfaces to salt addition is examined in the context of a model of charged interface nonlinear susceptibilities. From this analysis, inferences of interfacial structure and behavior are made.



Sum-Frequency Generation Spectroscopy for Studying Organic Layers at Water-Air Interfaces: Microlayer Monitoring and Surface Reactivity

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The sea surface microlayer, according to commonly accepted terminology, comprises the topmost millimetre of the oceanic water column. It is often enriched with organic matter and is directly influenced by sunlight exposure and gas exchange with the atmosphere, hence making it a place for active biochemistry and photochemistry as well as for heterogeneous reactions. In addition, surface active material either is formed or accumulates directly at the air-water interface and gives rise to very thin layers, sometimes down to monomolecular thickness. This “sea surface nanolayer” determines the viscoelastic properties of the seawater surface and thus may impact the turbulent air-sea gas exchange rates. To this effect, this small scale layer presumably plays an important role for large scale changes of atmospheric trace gas concentrations (e.g., by modulating the ocean carbon sink characteristics) with possible implications for coupled climate models.

To date, detailed knowledge about the composition, structure, and reactivity of the sea surface nanolayer is still scarce. Due to its small vertical dimension and the small amount of material, this surfactant layer is very difficult to separate and analyse. A way out is the application of second-order nonlinear optical methods, which make a direct surface-specific and background-free detection of this interfacial layer possible. In recent years, we have introduced the use of vibrational sum frequency generation (VSFG) spectroscopy to gain insight into natural and artificial organic monolayers at the air-water interface.

In this contribution, the application of VSFG spectroscopy for the analysis of the sea surface nanolayer will be illustrated. Resulting spectra are interpreted in terms of layer composition and surfactant classes, in particular with respect to carbohydrate-containing molecules such as glycolipids. The partitioning of the detected surfactants into soluble and non-soluble (“wet” and “dry”) surfactants will be discussed. Furthermore, the application of a combined VSFG/Langmuir trough experiment to investigate the reaction kinetics of heterogeneous oxidation processes will be highlighted. The ozonolysis of monolayers of unsaturated fatty acids serves as model system for natural aging processes of surfactant layers at the sea surface. Finally, a VSFG time series study of the sea surface nanolayer at a western Baltic Sea near-shore sampling station will be presented. The observed seasonality reveals a significant temporal shift with respect to the spring algal bloom showing that high organic material content in the microlayer does not necessarily correlate with high nanolayer abundance. This interesting finding and implications for the formation of surfactant material by degradation of biological material will be discussed briefly.



Linking the Presence of Surfactant Associated Bacteria on the Sea Surface and in the Near Surface Layer of the Ocean to Satellite Imagery

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Several genera of bacteria residing on the sea surface and in the near-surface layer of the ocean have been found to be involved in the production and decay of surfactants. Under low wind speed conditions, these surfactants can suppress short gravity capillary waves at the sea surface and form natural sea slicks. These features can be observed with both airborne and satellite-based synthetic aperture radar (SAR). We have developed a new method for sampling the sea surface microlayer that has reduced contamination from the boat and during lab handling of samples. Using this new method, a series of experiments have been conducted to establish a connection between the presence of surfactant-associated bacteria in the upper layer of the ocean and sea slicks. DNA analysis of in situ samples taken during a RADARSAT-2 satellite overpass in the Straits of Florida during the 2010 Deepwater Horizon oil spill showed a higher abundance of surfactant-associated bacterial genera in the slick area as compared to the non-slick area. These genera were found to be more abundant in the subsurface water samples collected as compared to samples taken from the sea surface. The experiment was repeated in the Straits of Florida in September 2013 and was coordinated with TerraSAR-X satellite overpasses. The observations suggest that the surfactants contributing to sea slick formation are produced by marine bacteria in the organic matter-rich water column and move to the sea surface by diffusion or advection. Thus, within a range of wind-wave conditions, the organic materials present in the water column (such as dissolved oil spills) can be monitored with SAR satellite imagery. In situ sampling was also performed in the Gulf of Mexico in December 2013 during RADARSAT-2 and TerraSAR-X satellite overpasses. Areas near natural oil seeps identified from archived TerraSAR-X imagery were targeted for in situ sampling. A number of samples from this location have been analyzed to determine the presence and relative abundance levels of one genus of surfactant-associated bacteria. Determining the effect of surfactant-associated bacteria on the state of the sea surface may help provide a more complete global picture of biophysical processes at the air-sea interface and uptake of greenhouse gases by the ocean.



Utö Atmospheric and Marine Research Station - a new Baltic Sea ICOS-site for sea-atmosphere research

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Atmospheric research has developed a concept of focused, multidisciplinary, automated observation platforms with continuous high time resolution observations. This approach containing state-of-the-art equipment has enabled research on physical, chemical and biological processes and seasonal variability and showed up new, previously unknown phenomena. New technical and engineering solutions allowing, such approach is also state-of-the-art in marine research through projects like US Ocean Observatories Initiative (OOI), European Multidisciplinary Seafloor Observatory (EMSO), JERICO-NEXT and Japanese DONET.

At the Baltic Sea, on Island of Utö (59° 46'50N, 21° 22'23E), Finnish Meteorological Institute has observed meteorology since 1881, marine parameters since 1900 and a diversity of atmospheric chemical and physical variables since 1980. Recent years the stations has also been upgraded with aerosol observations, and together with Finnish Environment Institute, on marine observations.

The current and observations under construction at Utö Atmospheric and Marine Research Station (en.ilmatieteenlaitos.fi/uto).

Marine observations: surface waves, ice-cover radar, temperature and salinity and oxygen at different depths, chlorophyll, cyanobacteria, underwater flows, turbidity, pCO₂ and nutrients.

Atmospheric observations: T, WS, WD, visibility, cloud height, boundary layer wind profiles and turbulence, weather and underwater camera, aerosol particle size distributions, aerosol light scattering and absorption, SO₂, NO_x, CO, O₃, CO₂, CH₄, sea-atmosphere CO₂- and heat fluxes.

In our presentation, we present for the first time some 100 years of climate relevant atmospheric and marine observations from Utö.



Constraining the climatology of CO₂ ocean surface flux for North Atlantic and the Arctic

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The ocean sink is an important part of the anthropogenic CO₂ budget. Because the terrestrial biosphere is usually treated as a residual, constraining the net flux into the ocean sink is crucial for understanding the global carbon cycle. The air-sea interface flux is calculated from millions of measurements of CO₂ partial pressures. However the regional and temporal means depend on parametrization of gas transfer velocity as well as on the wind/waves fields used for calculations.

A recently developed tool, FluxEngine, created within the ESA funded (SOLAS related) OceanFlux Greenhouse Gases project, creates an opportunity to create an ensemble of regional CO₂ flux climatologies for the North Atlantic and Arctic waters using multiple combinations of forcing fields and gas transfer velocity parameterizations. The aim of the study is to provide constraints on the regional monthly averages for the chosen area for the whole "climatology ensemble". This approach is similar to the one used by IPCC for the whole model ensemble used for modeling of the climate. Doing a regional study provides an additional test of the parameterizations because the local flux averages may differ even for parameterizations giving similar global averages.

We present the methodology and CO₂ flux climatology constrains for selected regions and seasons, the preliminary results of a study which aim is to cover the whole North Atlantic and ice-free areas of Arctic Ocean. The study is done within the new ESA funded OceanFlux Evolution project we are part of and at the same time is part of a PhD thesis funded by Centre of Polar Studies "POLAR-KNOW" (a project of the Polish Ministry of Science).



Using eddy covariance and Earth observation products to investigate the Indian Ocean as a source/sink of trace gases to the atmosphere

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According to well known climatologies for CO₂ and DMS, the southwest Indian Ocean shows strong seasonality in surface water concentrations. Available CO₂ observations show values around equilibrium from November to April, followed by a strong decrease that results in an undersaturation of around 80 μatm in July/August. Consequently, this area is an important sink for atmospheric CO₂. In contrast this region is predicted to be a hotspot for DMS emissions. Maximum surface concentrations are expected in northern hemisphere winter (NH). However, the air-sea gas exchange is largely influenced by the monsoon circulation, hence it is computed to peak in June/July. Furthermore these climatologies are based on low spatial and temporal resolution observations, which is especially important when dealing with a seasonally reversing ocean-atmosphere system. Given the evidence that the Indian Ocean is changing faster than other ocean basins, it is important to understand the mechanisms that drive air-sea exchange in this significant sink/source region.

Here we present preliminary data obtained during a cruise starting in Durban, South Africa and ending in Male, Maldives, from July to August 2014. For the first time, eddy covariance air-sea fluxes and concentration gradient measurements for CO₂ and DMS were obtained simultaneously in the southwestern Indian Ocean. We will derive gas transfer coefficients (k) from these direct measurements and correlate with wind speed (u) and other parameters measured on board in order to investigate the mechanisms behind gas transfer. Furthermore, we will examine the intercomparison of DMS and CO₂ so as to focus on the effect of solubility on gas exchange. In addition, we will use a range of outputs from remote sensing platforms to assist the interpretation of the in situ data (e.g. significant wave heights, existence of diurnal warming, impact of SST skin on the CO₂ fluxes, rain frequency and intensity, existence of SST fronts). The correction of k values for the ocean skin temperature and the effect of rain on gas transfer processes are of special interest in this region, given the high degree of warming and the monsoon circulation in the Indian Ocean.