



Surface-Sensitive Methods for Marine Nanolayer Time-Series Studies

Florian-David Lange^{1,2}, Nhat-Thao Ton-Nu¹, and Gernot Friedrichs^{1,3}

¹Christian-Albrechts-Universität zu Kiel, Institut für Physikalische Chemie

²GEOMAR Kiel, HOSST Helmholtz Research School for Ocean System Science and Technology

³KMS Kiel Marine Science Centre for Interdisciplinary Marine Science

The interface between air and sea, the sea surface microlayer, covers a large part of the earth's surface and is enriched by amphiphilic organic molecules. It is a zone of very active chemistry and biology. The uppermost molecular layer directly at the air-sea interface, the so-called nanolayer, has a significant impact on wave dynamics by changing the viscoelastic properties of the interface and hence modulates air-sea gas exchange.

To answer the question if nanolayer abundance can be directly correlated to primary productivity, a close collaboration between biology and physical chemistry in the spirit of fundamental surface sciences is necessary. This contribution reports a showcase example how to apply a physico-chemical laser spectroscopic tool as a valuable contribution to such an interdisciplinary field. The described non-standard experiments yield fresh insight into a complex environmental system and shed light on non-obvious relations between variable biological activity and the physical properties of the air-sea interface. In the end, this is of particular interest for the assessment of the global role of the North Atlantic to act as a sink for anthropogenic CO₂ emissions. Here, strong algae blooms take place, but if they go along with an immediate or delayed nanolayer formation is largely unknown.

From an analytical point of view, the investigation of the very thin organic layer at the air-water interface is challenging and has to rely on surface-sensitive techniques with the ability to distinguish between nanolayer and bulk water signal contributions. In this study, two complementary methods have been applied to measure both enrichment and abundance of natural sea surface films. Both laser spectroscopic Vibrational Sum Frequency Generation spectra (VSFG) and Langmuir compression isotherms yield information about the presence of surface-active compounds. Whereas the latter essentially measures surface tension changes, VSFG as a vibrational type of spectroscopy supplies additional information about the chemical nature of the interfacial molecules. Based on laboratory studies of organic nanolayer proxies, it was also possible to define a numerical index related to the surface coverage, hence simplifying the use of such measurements for other disciplines.

More precisely, natural samples were taken at the Boknis Eck time series station (BETS) in the Baltic Sea over ten years, complemented by a comprehensive data set obtained during two

consecutive research cruises in the framework of the Baltic Gas Exchange (Baltic GasEx) experiment. Enrichment of surface-active organic material in the microlayer could be confirmed by both methods, indicating the expected tight connection between micro- and nanolayer signal. In agreement with earlier preliminary data (Biogeosciences 10 (2013) 5325), a seasonal trend of nanolayer abundance has been identified that does not directly correlate with chlorophyll concentration and the approximate time of the spring algae bloom at Boknis Eck. This interesting finding implies that primary productivity is not necessarily linked with nanolayer formation and that photochemical and microbial processing of organic precursor compounds play a role for the observed seasonality. More measurements along those lines are needed, in particular for the open Atlantic Ocean, to validate these findings.