



## **Seasonal variations in vibrational spectra of the sea surface nanolayer and their relation to characteristic parameters for phytoplankton activity**

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The sea surface nanolayer is a very thin organic substance layer, down to monomolecular thickness. It is found on top of the sea surface microlayer, which in turn comprises roughly the uppermost millimeter of the water column. The nanolayer constitutes the actual interface between ocean and atmosphere and plays an important role in all exchange processes of matter and energy between ocean and atmosphere. Nevertheless, knowledge about formation and development of the sea surface nanolayer in the course of the year is very limited. In this study we present surface-specific observations of the sea surface nanolayer development over a period of three and a half years. Samples of the sea surface have been taken monthly at Boknis Eck Time Series Station (Eckernförde Bay, southwestern Baltic Sea) by screen sampling. From surface-sensitive vibrational spectra obtained by nonlinear sum frequency generation spectroscopy (SFG), information on amount, structure and composition of the organic nanolayer material was extracted. SFG has been introduced by us as a new method to study the ocean nanolayer quite recently [1,2]. The abundance of nanolayer material was found to follow a pronounced yearly periodicity, with larger amounts of material present from mid to end of summer. A substantial time lag of about 2.5 months between spring algal bloom maxima and abundance maxima of nanolayer material has been observed. In contrast to common perception, this shows that high phytoplankton abundance and pronounced nanolayers are not directly related to each other. Variations in the appearance of the spectra serve as indicators for changes in structure and chemical composition of the nanolayer. The accumulation of carbohydrate-rich material in late summer provides a possible explanation for the observed spectral changes. We propose that sloppy feeding of zooplankton as well as photochemical and/or microbial processing of organic material present in the microlayer is responsible for the periodicity of nanolayer intensity and its temporal shift with respect to other influential factors.

### References

- [1] K. Laß, G. Friedrichs, J. Geophys. Res. 116 (2011) C08042/1-15
- [2] K. Laß, J. Kleber, G. Friedrichs, Limnol. Oceanogr.: Methods 8 (2010) 216-228