Biogeosciences Discuss., 10, C2307–C2314, 2013
www.biogeosciences-discuss.net/10/C2307/2013/

Biogeosciences
Discussions
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Interactive comment on "Seasonal signatures in SFG vibrational spectra of the sea surface nanolayer at Boknis Eck Time Series Station (SW Baltic Sea)" *by* K. Laß et al.

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Received and published: 31 May 2013

We thank the referee for his valuable comments regarding our manuscript. General remark: Our study is not aiming or claiming to present a very detailed picture of the molecular composition of the organic nanolayer. Instead, the measured signal intensities are taken as a rough measure of the abundance of (different classes of) surface active material and hence of the ability of the organic film to reduce air-sea gas transfer by changing the viscoelastic properties of the interface. Moreover, it should be kept in mind that our study is primarily concerned with the nanolayer and not the microlayer. Up to now, a proper distinction between these two different layers and their

interrelations remains difficult. Our surface sensitive VSFG study tries to bridge the gap between â€{œbulkâ€İ microlayer measurements using field samples on the one hand and laboratory studies using artificial surfactant monolayers on the other hand. The paper works out first conclusions regarding overall trends of nanolayer abundance at BE time-series station and proposes tentative explanations for the very unexpected result of low signal intensities during or shortly after the intense spring algal bloom. Of course, much more work is needed to be able to draw definitive conclusions.

1. *Referee comment: Although they do not quote the depth range sampled by this device this can be derived from their method description as being in the range 30 to 50 microns. Nevertheless, i think it would be helpful to the reader if this depth range was formally stated.*

   The wire mesh size â€{œASTM Mesh 16â€İ conforms to the official recommendation for sea surface microlayer sampling given by the IOC in in 1985 (reference is given in the article). The ratio of the sample volume per dip and the screen area for our sampler yields a formal water layer thickness of 400 Âμm. This comprises, next to the actual microlayer sample, also some subsurface water residues remaining under the actual wire mesh on the samplerâ€^{TM}s frame. Although care has been taken to let it run off before recovering the sample, this effect could not be avoided completely with our sampler. We will add this information to our manuscript by adding the following text on p. 3183, line 17: â€{œ. . . , corresponding to an effective sampling depth of about 400 Âμm.â€İ

2. *Referee comment: Regarding sampling, it would be informative if the authors could explain their rationale for selecting the mesh screen in preference to alternatives such as the glass plate and others. Are there any potential implications for sample integrity arising from the choice of sampling protocol?*

   The wire mesh screen as a sampling device was selected for the following reasons:

a. The IOC provides a standardized procedure for sea surface microlayer sampling, using the Garrett screen (see above).
b. As it is important for a long-run times-series experiment, the wire mesh screen is a simple and rugged construction (unlike e.g. the drum sampler). The screen sampler can be employed from a research vessel and does not require a Zodiac for operation. This allows its deployment also under weather conditions which inhibit the use of a Zodiac. At BE, this saves us a few sampling cruises per year.
c. For the dipping prism technique (in the â€{œtraditionâ€İ of Langmuir-Blodgett film preparation, employed by Baier et al. (1984)) it is questionable whether the deposited film represents the original layer on the water surface. For example, surface (i.e. the nanolayer) / bulk solution (i.e., the microlayer) equilibration, which is important for the wet surfactant fraction, cannot be accounted for by the prism dipping technique. Taking samples by leaving the nanolayer on its â€{œaqueous substrateâ€İ is expected to give a more realistic view of the natural organic composition.

Of course, as it would be the case for all other possible sampling methods as well, laboratory analysis does not reflect the natural in situ status of the organic nanolayer. Hopefully, provided that suitable laser systems become available, it will be possible to perform such in situ field measurements in future studies. For now, it can be expected that the recovery of the dry surfactant fraction is somewhat biased. Adsorption processes at the screen mesh or on the walls of the sample bottles provide loss terms whereas surfactants â€{œmixedâ€İ into the bulk phase may accumulate at the surface upon resting of the water in the sample bottles and the laboratory dish and hence act as a source term. We addressed the first point in our previous publication by performing test experiments, i.e. the sampling of artificial dry surfactant monolayers. As it is stated in the paper, the corresponding sampling efficiency has been taken into account. With respect to

the second point, it should be noted that dry surfactants have been found to contribute to the nanolayer composition to a minor extent. Therefore this issue is of minor importance.

Given that these points have already been addressed in previous publications or fall outside the scope of the present paper, we address the issue of sampling method choice only briefly by adding the following sentence on page 3183 line 6: â€{œThis method has been selected basically due to its simplicity of use and reliability with respect to deployment conditions and apparatus treatment.â€İ

3. *Referee comment: The authors (also) state that some samples were returned to the laboratory for analysis within a few hours while others were stored frozen for up to 2 weeks. It would be helpful to know which specific samples were subject to each of these treatments as the issue of storage bias should be considered here. In their response to the other reviewer (Wurl), who also raised the issue of sample integrity, the authors cite the recent submission to BGD of Schneider-Zapp et al which concludes that no sample treatment and minimal storage at* $4\,^{\circ}C$ *was optimal. However, Schneider-Zapp et al also found potentially substantial changes on freezing and I therefore feel that given that some samples were subjected to this treatment, this point is not adequately addressed by the authors. Can they provide comparative analyses of samples processed in these two different ways?*

Though it is general desirable to treat every sample exactly the same way, it was not always possible to perform the analysis right after return (e.g., due to technical problems and availability of spectrometer time). In advance to the actual sampling series, a preliminary lab study has been performed to assess the stability of the samples. For example, spectra recorded for freshly taken sample and the same sample after one week of frozen storage did not reveal significant differences. The change in averaged CH intensities for this sample was less than 10 %. This is well below the observed natural variability of replicate samples taken during the same day. Therefore, storage times on the order of one week are considered

safe with respect to sample alteration. In contrast, for storage times of several months up to half a year considerable to complete loss of VSFG signal has been observed.

In order to answer the actual question raised by the referee, the Figure shown below compares the integrated SFG intensity of the CH modes and with the corresponding storage times. Neither considerably more scatter nor obviously different intensities have been observed for samples that have been stored for some time. Plotting the intensities as function of storage time (and thereby ignoring any superimposed seasonal trends) revealed an apparent slight trend to overall lower signals for higher storage times, which is not significant ($R^2 = 0.03$, slope is indistinguishable from zero at a confidence level of 0.95). We will include these findings in the manuscript by adding the following sentences in the manuscript on page 3183 line 25: â€{œThe data points acquired from samples subject to storage in frozen state did not exhibit any prominent behaviour and generally blended well within the other data points.â€İ

4. *Referee comment: In section 4.2 the authors state that the structure of a broad band between 3000 and 3600 per cm "is still subject to ongoing discussion". While the authors cite some publications, for clarity it might be helpful to also briefly outline in a couple of sentences, what the most likely possible explanations of this structure are.*

   Our previous publication was concerned with the detailed analysis of sea surface nanolayer SFG spectra and contains a more elaborate explanation of this topic. The assignment of water bands and their attribution to water molecules in specific molecular environments is not trivial and is subject to ongoing fundamental physicochemical research. Although measured for the first time about 20 years ago, the interpretation of the VSFG spectrum is still subject to discussion. One of the problems is the fact that standard VSFG measures the square of the susceptibility tensor and hence the phases of the different signal components get lost. Not until recently, advanced methods of VSFG spectroscopy

have been used to elucidate the sign of the measured susceptibility tensor elements. Nevertheless, detailed experimental and theoretical analyses of the spectra still offer two different alternative explanations. According to the first interpretation (the â€{œShenâ€İ view), the left and right signal bands at 3200 cm^{-1} and 3400 cm^{-1}, respectively, reflect water molecules in hydrogen-bonded networks that are similar to the molecular structure of ice (3200 cm^{-1}, tetrahedral coordination, ice-like band) or liquid water (dominated by three-coordinated water molecules, liquid-like band). This interpretation is consistent with molecular modeling simulations of the hydrogen-bond network, however, the exact outcome of such simulations heavily depend on the chosen water model (SPC-E, TIP3P, etc.). Conversely, the second interpretation (the â€{œBonnâ€İ view) claims a water interface with a lower degree of structural order. From isotope dilution experiments it is known that the VSFG spectrum HDO exhibits only one peak in contrast to the two-peak structure observed for H_2O. This is consistent with an interpretation that assigns the double-peak feature of H2O to a Fermi resonance of the symmetric stretch vibration and the overtone of the bending vibration. No such Fermi resonance exists for HDO.

As the paper is targeting the biogeochemistry and marine chemistry communities, a lengthy discussion of this issue is not required. A detailed assignment of the water hydrogen bond network spectral feature is not essential for the conclusions drawn in this paper. Instead, the following, more general comments will be included on page 3185 line 24: â€{œDespite extensive experimental and theoretical work, the origin of the band is still subject of ongoing research. Briefly, two alternative interpretations for the two-peak feature are discussed either assigning it to water molecules in â€{œice-likeâ€İ (around 3200 cm^{-1}) or â€{œliquid-likeâ€İ (around 3400 cm^{-1}) hydrogen bonding molecular environments (Tian and Shen, CPL 2009, 470, 1-6 and references therein) or a Fermi resonance between the symmetric stretch and the overtone of the H_2O bending vibration (Nihonyanagi et al., JACS 2011, 133,16875 and references therein).â€İ

5. *Referee comment: I do find the discussion of possible anthropogenic effects rather weak and perhaps distracting from the main focus of the paper and that it should be shortened somewhat.*

   This point has also been raised by referee Wurl. As outlined in the reponse to this referee, we will shorten the paragraph and limit the discussion to the most important points. However, as we know from many discussions with colleagues, the issue of possible contamination is often raised and clearly needs to be addressed in the paper adequately.

Interactive comment on Biogeosciences Discuss., 10, 3177, 2013.

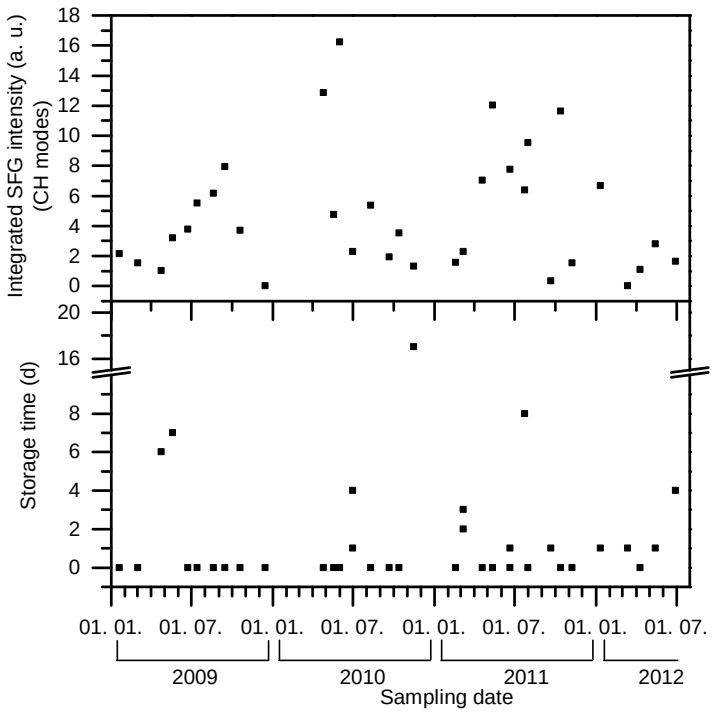

Fig. 1. CH mode SFG intensity and storage time as a function of sampling date.