

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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General Remarks

We thank Oliver Wurl for his valuable comments regarding our manuscript. As outlined in some detail below, most of the raised points – especially those associated with sum frequency generation (SFG) spectroscopy, its use for environmental nanolayer studies and the corresponding data interpretation – can be attributed to terminology issues or misunderstanding. Therefore, we will change the manuscript at several places to improve and clarify the text as far as possible. However, in view of the interdisciplinary character of the journal, for technical details and SFG specific spectroscopic issues we

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continue to point the interested reader to our preceding papers.

During recent years we have pushed forward the application of SFG spectroscopy as a new tool to get a deeper insight into the molecular structure of marine interfaces. A guiding principle and motivation of this work is the necessity to properly distinguish between the *nanolayer* (uppermost molecular layer at the interface) and the *microlayer* (uppermost water layer, which is bounded by and feeds into the *nanolayer* at the air/water interface). So far, due to the difficulties to probe the *nanolayer*, environmental studies have almost exclusively focused on microlayer composition and dynamics. Often it has been implicitly assumed that the properties of the *microlayer* strongly correlate with the properties of the *nanolayer*. In contrast to classical *microlayer* studies, SFG enables a closer look to the molecular air-sea interface (i.e., the *nanolayer*) but per se does not yield direct information of the *microlayer* bulk properties. In general, the question arises if seemingly straightforward reasoning based on *microlayer* properties (e.g., high organic matter content implies high surfactant concentration direct at the air-water interface, which in turn implies a potential effect on turbulent air-sea gas exchange by diminishing wave formation) is always applicable. In this regard, being fully aware of the current limitation of our method, it is an important and unexpected finding of this study that high primary productivity as indicated by a strong algal bloom does not necessarily correlate with high *nanolayer* signals. Hopefully, future studies will help to further advance the interpretation of SFG spectra of natural samples and enable us to draw more decisive conclusions. Currently, we address this point by initiating joint studies aiming at a direct comparison of *microlayer* derived biogeochemical parameters and SFG *nanolayer* response. Moreover, dedicated studies would be extremely helpful to test the hypothesis that SFG signal intensity can be directly correlated with air-sea gas transfer efficiency.

Specific Comments

Comment: My basic concern is that the authors assumed that their ex-situ measurements are representative for natural conditions,...

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The concern addresses two valid points. Ex-situ sampling (*i*) may not reflect the instant condition of the natural air-sea water interface and (*ii*) the sample may be altered due to the transport and time delay before analysis in the laboratory.

With respect to the latter we would like to point to an article currently under review for publication in Biogeosciences, which tackles the issue of microlayer sample treatment and storage (Schneider-Zapp et al., Biogeosciences Discuss. 2013, 10, 2835-2855, 2013, doi:10.5194/bgd-10-2835-2013). The authors of this paper came to the conclusion that microlayer samples preserve best over at least several days if stored untreated at 4°C. Hence, our method of sampling at sea and measurement immediately after return, which usually leads to storage times of about 5 hours, can be considered unlikely to introduce errors large enough to bias the reported results notably. In addition, experiments with our own samples (analysis right after return, after one day, after freezing, etc.) did not reveal this treatment as a potential source of problems as well. This was pointed out in our previous publications as well ([Lass2010] Laß et al., Limnol. Oceanogr. Methods 2010, 8, 216, doi:10.4319/lom.2010.8.216; [Lass2011] Laß and Friedrichs, J. Geophys. Res. 2011, 116, C08042, doi:10.1029/2010JC006609).

The other issue of probing a calm and equilibrated water sample in the laboratory instead of performing an instantaneous measurement at sea deserves a closer look. Unfortunately, with state-of-the art laser technology, is it not possible to perform field or even in-situ SFG measurements as yet. Future development of rugged lasers and fiber based instrumentation may overcome this limitation. At present, laboratory based measurements are inevitable. For sure, a one-to-one transferability of laboratory based results to assess the actual state of the natural air-sea interface is not valid. The issue is closely related to the stability of organic films and the time scale of surface nanolayer formation following a wind or wave induced disturbance as well as the wet-to-dry surfactant ratio. As discussed in some detail in our previous paper (Section *Film formation dynamics* in [Lass2010]), we performed simple stirring experiments to estimate the characteristic time scale of nanolayer formation. It turned out that natural nanolayers

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recovered within the time resolution of the experiment (few seconds). In contrast, artificial samples of dry surfactants showed equilibration times on the order of minutes. These results are in line with the conclusion drawn from our semiquantitative analysis of the wet-to-dry surfactant ratio (presented in some detail in [Lass2011]) showing that wet surfactants dominate at our sampling site (wet/dry \approx 12). In this spirit, in comparison with a virtual in-situ field experiment, our procedure yields a significant enrichment of the dry surfactants but a realistic picture of the wet surfactant abundance. Although the fraction of dry surfactants in the actual natural nanolayer is low, due to a 12.5 fold enrichment of our sampling procedure, about half of the nanolayer SFG signal may arise from dry surfactants (see comment below).

In the current version of the paper, all the above mentioned points have been already addressed by referring to our previous work. However, motivated by the comments of the referee, in the revised version of the paper we will elaborate the intricate dependencies of sampling procedure, the wet-to-dry surfactant ratio, and SFG signal intensity more clearly (see comment below).

Comment: My basic concern is that the authors assume ... that oxygen in surface water (1 m depth) is a good proxy for primary productivity. Page 3186, Line 25 I disagree that oxygen concentration maxima in surface water (1 m depth) is a good indicator for spring algal bloom. How to ensure that the oxygen maxima are not due to storm events commonly occurring in spring? The wording is awkward ... how can a coincidence be a good indicator? According to the Figure 2, some of the chlorophyll maxima occurred in Dec 2009, and February 2011. It seems rather early, and I am wondering if the authors correctly plotted the data. Oxygen maxima occurred in February during the whole study period ... again a season of probably more storm events. I suggest to present wind and oxygen data during sampling period (not monthly average value).

Please note that we do not present monthly average values. We present data from sampling cruises which take place once a month. This is clearly stated on page 3182, lines 24–26.

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Storm events indeed can enhance O₂ concentrations by injecting bubbles into the water column. Please note, however, that the period with high winds at Boknis Eck already starts in fall (October to December). February is not known to be a month with an extraordinarily high number of storm events. Thus, the regularly occurring enhanced O₂ concentration/saturation in February are very unlikely caused by irregularly occurring storm events.

The paragraph in question by no means claims any general direct connection between oxygen concentration and algal blooms. Note that – as expected – the overall seasonal trend of oxygen is dominated by the temperature dependent solubility of oxygen. In contrary to the comment, it is clearly emphasized in the text that the regular coincidence of oxygen maxima and spring algal bloom is a special feature of the sampling station BE (backed by an appropriate citation). We will adjust the wording of lines 23–26 in order to point this out more clearly: “At BE sampling site, the oxygen saturation typically exhibit well pronounced maxima in spring. As it was shown in a previous publication (Smetacek et al., Rapp. P.-V. Reun. Cons. Int. Explor. Mer. 1984, 183, 126), these maxima are related to the annual spring algal bloom and coincidentally coincide with the oxygen concentration maxima. This coincidence makes the much more pronounced O₂ concentration maxima a more suitable spring algal bloom indicator than the oxygen saturation level itself.”

The mentioned irregular behavior of the chlorophyll data are a typical feature of BE as well. As stated in the text, chlorophyll data only partly reflect the actual phytoplankton productivity at BE station. Note that our analysis of the time resolved data does not rely on the scattered chlorophyll or Secchi depth data.

Comment: Abstract – Revise carefully and provide a concise summary of the manuscript. Description of sampling station and period should not be part of the abstract, but of the methodological section

We disagree. We think that the abstract should give the reader a brief but meaningful

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overview about the major points of the ms. This, of course, includes naming of the sampling station and stating of the sampling period. Especially in the light of similar studies which often rely on (too) sparse sampling, the quite extensive and unique sampling period presented here should be mentioned in the abstract.

Comment Page 3179, Line 5: I think that the nanolayer is much too thin to consider it as a place of particle enrichment. The sea-surface microlayer is a better description for floating particles.

Well, as already outline above, it is important to properly distinguish the *microlayer* and *nanolayer*. We will rephrase the paragraph to avoid any ambiguous interpretation: “Material scavenged from deeper layers by bubbles is enriched, and insoluble (“dry”) surfactants as well as bouyant particles accumulate at the interface . . . The microlayer boundary to the atmosphere is formed by an even thinner layer (1 – 10 nm), the so-called nanolayer. It can be as thin as one molecular layer formed by surface-active substances.

Comment Page 3179, Line 8-14: The statements here are contradicting stating first that the nanolayer has only a minor effect on air-sea gas exchange, and subsequently discussing its role in wave damping and further to its role in climate due to imparing gas exchange.

The statements of this paragraph are by no means contradictory and are accepted in the literature for a long time (e. g., Liss and Duce (eds.), *The Sea Surface and Global Change*, Cambridge, 1997). However, the separation of the effects of the diffusional barrier and the change of the visco-elastic properties may be pointed out more clearly: “The nanolayer also has an effect on the air-sea gas exchange. It imposes (i) an additional diffusion barrier and (ii) influences the visco-elastic properties of the water surface. While the first effect is more important for aerosols, the latter impairs the gas exchange between ocean and atmosphere by wave damping and hence diminished turbulent gas transport (Liss and Duce, 1997).”

Comment Page 3180, line 7: As the community starts to understand the role of sea-surface

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micro- layers in air-sea interactions, the claim that nanolayers are "prerequisite for an improved parameterization of its role in the context of climate models" is extremely speculative and should be removed.

On a molecular level, air-sea gas transfer ultimately takes place directly at the water-air interface. Moreover, even a monomolecular layer of organics is known to significantly change the surface tension and visco-elastic properties of the surface. Nevertheless, in the large body of literature on the importance of organics for air-sea gas exchange, the possibly different roles of the nanolayer and microlayer composition and structure have not been properly worked out so far. Therefore, we again stress the necessity to distinguish carefully between *microlayer* and *nanolayer* when discussing its influences on the gas exchange. As already outlined above, we plan to address the mutual interdependencies of both layers by direct comparisons of microlayer derived biogeochemical parameters and SFG nanolayer response. We agree with the referee that the community starts to understand the role of the microlayer (which in the common usage of the word often combines the effects of micro- and nanolayer), however, the possibly distinct role of the nanolayer should not be overlooked. The wording of the phrase in question will be changed as follows: "... , which is an important keystone for an improved parametrization of its role in the context of climate models."

Comment Page 3183, Line 20: Page 3181, Line 20 I do not understand how the theoretical enrichment of 12.5 has been derived? I think the natural enrichment processes, especially at the micro- and nanometer scale is so complex, that assuming ex-situ nanolayers are representative to natural ones are speculative. How about bubble transport, micro-scaled turbulence, atmospheric deposition influencing chemical composition? What means "is expected to re-establish"? How sure are the authors about their statement? In addition, details of the sampling platform (research vessel, small-sized vessel, zodiac) has not been reported at all, although critical for sampling the micro- and nanolayer

This criticism results from a misconception of the term "enrichment factor". The quoted

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enrichment factor of 12.5 does not refer to the enrichment of organic matter in the microlayer relative to the bulk water phase. It simply refers to the fact that our sampling procedure (screen sampling, collection efficiency, measurement in a lab dish with smaller surface) leads to a corresponding enrichment of insoluble (dry) surfactants on the surface of our lab sample dish. The determination and assessment of this number have been described in detail in our previous publications (Lass2010 and Lass2011). We mention this enrichment factor, because it makes clear that even under typical conditions with dominating wet surfactants, about half of the nanolayer SFG signal can be assumed to arise from dry surfactants. In this spirit, significant changes of the wet-to-dry ratio during the course of the year may somewhat bias the comparability of the absolute SFG signal intensities. However, a comparison of signal intensity ratios for samples pooled from 2, 4, and 6 dips of the sample sieve did not reveal obvious seasonal trends. We conclude that our analysis of the overall seasonal trend and of the time delay between spring algal bloom and maximum SFG nanolayer intensity is not significantly biased by a changing wet-to-dry ratio.

We will modify the section on the "Sampling method and procedure" as follows: "... For spectroscopy, the samples were poured into Teflon dishes measuring 14 cm in diameter and were given a rest for at least 20 min prior to measurement to allow for equilibration between interface and aqueous phase. Details of the sampling procedure and consequences for the interpretation of the measured SFG signal intensity are outlined in our previous publications [Lass2010, Lass2011]. Briefly, taking into account the sampling efficiency as well as the ratio of the areas of the field sampler and the spectrometer dish, our specific procedure yielded samples with a theoretical surface concentration of dry surfactants 12.5 times as high as on the original sea surface. In contrast, as it can be concluded from stirring experiments outlined in Ref. [Lass2010], the wet surfactant fraction of the surface-active matter is expected to re-establish surface – bulk phase equilibrium such that the measurement should largely reflect their concentrations as present at sea. The wet-to-dry surfactant ratio can be estimated from SFG intensity ratios measured for samples pooled from a variable number of dips of the sieve. Follow-

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ing the data reduction procedure described in Ref. [Lass2011], we deduced a natural wet-to-dry ratio of 12^{+13}_{-5} from 46 corresponding measurements performed throughout the sampling period. The stated uncertainty corresponds to error of the mean at 1σ confidence level. Taking into account the 12.5 times enrichment of the dry fraction for the laboratory measurements reveals that about half of the SFG signal intensity results from the dry surfactant fraction. Therefore, without independent measurements of the particular wet-to-dry surfactant ratio, the reported SFG intensities are a qualitative rather than absolute measure of nanolayer density. Note that a significant change of the wet-to-dry ratio during the course of the years could have biased the comparability of the SFG signal intensities. However, no obvious seasonal trend of the wet-to-dry ratio were discernible from the variable dip experiments. Also note that the analysis of the seasonal nanolayer trends largely relies on the presence or absence of nanolayer signal rather than on the absolute signal intensities.”

In addition, the missing information on the sampling platform will be provided in the revised paper: “The sieve was mounted on a chain suspension and was submersed from that side of the ship (R/V Littorina, occasionally R/V Polarfuchs and R/V Alkor) that was facing the surface water current induced by wind and waves. Sampling was performed . . .”. As the referee seems to be concerned about a possible contamination of the samples, we would like to stress that we regularly also collected samples which exhibited no detectable surfactant layer. This indicates that the sampling vessel did not act as a serious contamination hazard.

Comment Page 3186, Line 1 and throughout manuscript: What is a overlayer?

The word 'overlayer' combines both artificial (dry surfactants forming monolayers) as well as natural nanolayers (dry and wet surfactants). As we are dealing with natural nanolayers only, we will replace the word 'overlayer' by 'nanolayer' throughout the manuscript.

Comment Page 3185, Line 21 to Page 3186, Line 12: A signal at 3700 cm-1 is also

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present in August (see Fig.1) and contradicts the interpretation that the broad signal between 3400-3500 cm-1 indicates intensive organic layers. Indeed, the signal at 3700 cm-1 seems to increase from March to Oct/Nov, and then to August.

In fact, in comparison with a “surfactant-free sample” (not shown in Fig. 1) the intensity of the narrow 3700 cm^{-1} feature is significantly reduced. Note that the narrow feature is *superimposed* to the background signal, which stems from the broad OH feature peaking around $3400\text{-}3500\text{ cm}^{-1}$. The remaining, somewhat broadend dangling OH bond intensity is due to the averaging of several spectra, some of which showed residual OH dangling bond signal. For clarification of this issue, we will add a spectrum of a “surfactant-free” water sample from a water depth of 25 m (see supplement to this reply). This spectrum exhibits the intense OH dangling bond feature we are referring to. The caption of figure 1 will be changed accordingly: “Sea surface nanolayer spectra for March, August and October/November. These three spectra are averages representing 4–6 spectra each taken over three years in the respective months. For comparison, the (non-averaged) spectrum of a surfactant-free water samples from a depth of 25 m has been included as well. The labels indicate the different vibrational modes.”

Comment Page 3189, Line 5: What is a correlation function? I know functions obtained from regression analysis, but not correlation. Please explain.

A comprehensive description of our data analysis procedure is already presented in the paper (both mathematical and in words). However, we will make some adjustments to the text to make our reasoning more clear. The use of correlation functions as useful indicator to uncover dependencies as a function of time (e.g., to determine time shifts) is common practice. We refer to suitable mathematical textbooks for further details; a quick introduction can be also found on en.wikipedia.org.

Comment Page 3191, Line 15: Any references for the presence of lipo-polysaccharide and/or TEP like material on the oceans surface?

As it is outlined in the introduction, carbohydrates are known to constitute a major

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fraction of the organics found in surface water. An overview of the different classes of organic material involved in organic microlayer formation has been given recently by Wurl et al. (Biogeosciences 2011, 8, 121) and a detailed literature review about the role of carbohydrates/TEP for surface films has also been given in our previous publication, Ref. [Lass2011]. For the sake of completeness, we will include the recently published review (Cunliffe et al., Progress in Oceanogr., in press) entitled “Sea surface microlayers: A unified physicochemical and biological perspective of the air–ocean interface” as an additional reference in the final version of the paper. In contrast to microlayer/surface ocean work, publications on the presence of particular surfactant classes in the *nanolayer* are “very scarce”. To stress it even more, in fact we are only aware of our own previous publication [Lass2011]. According to this work, the hypothesis that surface-active carbohydrate compounds (such as lipo-polysaccharidea) may play a decisive role in *nanolayer* formation is based on spectroscopic reasoning.

Comment Page 3191, Line28: It seems that Wurl et al (2011) reported a time series of enrichment of total dissolved carbohydrates, but not the absolute concentration. Lowest enrichment was found at times of highest productivity, and it seems wrongly interpreted by the authors.

The publication in question shows a data series (for Saanich inlet station) that indicates highest primary productivity in August and September. Although enrichment factors are reported for a whole year, unfortunately, the underlying TDC concentrations were not published. The referee is right that directly relating enrichment factors and total concentrations is not valid, and hence our original statement is not underpinned by their data. We have to admit that we find their discussion of the role of the microlayer in terms of enrichment factors quite confusing. By no means, the enrichment factor alone is a useful measure for microlayer abundance. At least relative measures for total concentration should be reported as well. We will replace the sentence under question as follows: “To the best of our knowledge, such a seasonal trend has not been reported in the literature so far. In contrast, . . .”

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Comment Page 3192, Line 14 to Page 3193, Line 11: A rather length discussion if oil spills and bathing could have been biased to the results seems to be inadequate. Overall, the discussion requires major revision, and focus on the major statements of the paper rather than on bathing.

We consider the discussion on a possible anthropogenic bias as highly appropriate. We know from discussion with many colleagues that the question of a possibly contaminated surface is coming up regularly. We also think that the comprehensiveness of the corresponding text (approx. 5% of the paper) is not exaggerated. Nevertheless, we will further condense this section in the final paper. The sentences “Note that several public. . . (page 11, lines 333/34)”, “. . . we conclude that this influence is negligible (line 338)”, “No bathing was assumed for an air temperature. . . (lines 347/48)” and “This procedure was necessary. . . (lines 348/49)” will be deleted.

Comment: The authors claim that sloppy feeding by zooplankton may lead to pronounced accumulation of organic material in the nanolayer without reporting any data on zooplankton abundance. I believe such data should be available from the time series station at Boknis Eck.

For sure it would have been helpful to corroborate the role of sloppy feeding by presenting data on the abundance of zooplankton. Regrettably, these data have not been collected at BE station during the sampling period. Several references have been already included in the discussion section to underline the feasibility of our hypothesis that sloppy feeding (and the accompanying DOM release) may be in fact responsible for the observed delay between SFG maximum and the intense algal spring bloom.

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

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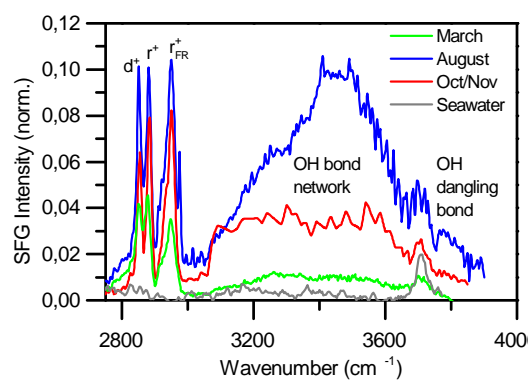


Fig. 1. Figure 1 of the article under discussion in the updated version.