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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.

K. Laß et al.

lass@phc.uni-kiel.de

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We thank the referee for her/his valuable comments regarding our manuscript. We will address the issues raised by the referee as follows:

General comments:

Referee 2: The authors relate SFG signals from the interface, which they refer to as the nanolayer, to parameters in the underlying water column (1 meter depth) in order to discuss the relation of SFG dynamics with biological activity. The discussion lacks information about a possible discrepancy between the investigated parameters – e.g. Chlorophyll a – in the nanolayer (or microlayer as the underlying interfacial layer) and the bulk phase. Principally,

it is suggested throughout the literature, that material in the interface is dominantly imported from the underlying bulk water. However, there might be short-term effects, changing this dependency (precipitation, turbulent mixing) and leading to remarkably different concentration of organic material between the interface and the bulk water. In this respect, also a discussion about wind speed affecting interfacial concentrations of e.g. Chlorophyll a and DOC given in literature would help along with indications of the wind speed conditions during the monthly sampling of the study presented.

The comment is concerned with the potential influences of short-term effects that may have somewhat biased our data sampling strategy as well as data interpretation.

Our analysis did not reveal any obvious trends of SFG signal intensity with respect to wind speed, wind direction, or wave height. Nevertheless, it may be well speculated that the effects outlined by the referee affect single data points and that the high variability seen in the time-series data are attributable to a superposition of several short-term effects. However, by smoothing of such short-term effects, our analysis of the 3.5 years long time-series study smoothes out such short-term effects and hence allows us to identify annual trends. Note that we only looked for such an annual trend and did not take the bait to overinterpret short-term variability. In order to address this issue we added the following sentence on page 3186, line 19: "As the data did not reveal any obvious trend with respect to wind speed, wind direction, or wave height it is safe to assume that this overall annual trend is not biased by wind and wave induced short-term effects."

Chlorophyll a content has been determined for water column samples from standard water depths only. This is feasible as phytoplankton is preferentially found in deeper water layers. As it is stated in the paper, the Chlorophyll a concentration did not reflect the actual blooms that well. Therefore, the Chlorophyll a data have not been used as a suitable parameter in our analysis. In fact, it is known that Chlorophyll a concentration only partly reflect phytoplankton productivity whereas the oxygen maxima have been shown to be a more robust indicator for the spring algal bloom (at Boknis Eck sampling

site, see section 4.2.1 in the paper).

With respect to the referee comment that DOC enrichment (microlayer vs. bulk concentration) might strongly depend on short-term effects, it is important to note that *(i)* this enrichment has been shown to be rather low to negligible for the Southern Baltic sea anyway (Stolle et al., Biogeosci. 2010, 7, 2975) and that *(ii)* a disturbance of this enrichment by short-term effects is not a crucial issue for our data interpretation. As already outlined above, our analysis relies on (smoothed) annual trends rather than short-term variability. Also note that our analysis is based on absolute signal intensities and not on (relative) enrichment factors (see also our answers to related comments of referee 1 and of referee Wurl).

Referee 2: It would be helpful for the reader in the authors could make some comments on how the SFG signals, both in vibrational modes and intensity, differ (or not?) between the samples taken with the screen or from 1 meter water depth.

For more information on the ratio of organic matter in surface and subsurface water samples, we would like to point to our previous publication [Laß and Friedrichs, J. Geophys. Res. 116 (2011), C08042]. In this publication it has been shown that signal intensities for subsurface samples were much lower and that the overall spectral signatures were similar. We also demonstrated a semi-quantitative analysis of the data revealing that wet surfactants prevail. As no subsurface water samples have been used for the analysis of the annual trend and as a detailed analysis of the surface-to-subsurface intensity ratio would require an advanced treatment of the data (see previous publication), we consider a repeated discussion of these findings dispensible. The following statement will be added at page 3187 line 7 as new paragraph: “In line with our previous publication [Laß and Friedrichs, J. Geophys. Res. 116 (2011), C08042], a comparison of surface water and subsurface water samples revealed a general tendency of much lower signal intensity and hence a depletion of surface active organic material with water depth.”

Referee 2: Moreover, the temporal resolution of the sampling strategy needs some thoughts, especially regarding the conclusions drawn by the authors. I suggest that only monthly sampling prevented the detection of some phytoplankton blooming events, which possibly explains the lacking spring bloom signals in 2009 and 2010. This is especially worth to mention, as in 2010 the SFG signals are highest in spring and decline throughout the year. Thus, at least for this year I don’t follow the authors with the explanation of sloppy feeding being the main driver for SFG signal variability in the nanolayer.
and
Referee 2: Page 3187 lines 23-25: for the air-water interface, bulk material which is settling downwards is most likely not relevant, but its degradation and the resulting production of dissolved material would be. So the authors should go a bit deeper into the discussion here, including bacterial turnover of organic material. (See also general comments above).

On the one hand, the referee raises the issue of (a too low) sampling frequency. We agree that monthly sampling bears the risk of missing events happening on a shorter timescale. The sampling period, however, was basically limited by resource issues (predominantly research vessel availability). On the other hand, the referee addresses the existence of more than one “peak” in the SFG signal in spring and summer 2011. Such an interpretation (which implicitely would neglect any short-term effects) should be treated with extreme caution, as the data exhibit substantial scatter due to natural variability and short-term effects. As it already has been outlined above, our 3.5 years long study was designed to identify annual trends but not short-term effects.

The notion of the referee that SFG signals in 2010 are highest in spring is definitely not supported by our data, which show highest intensities in June for this year. Therefore we cannot follow the criticism in this respect.

Referee 2: If sloppy feeding remains the hypothesized main driver, I also follow the suggestions by the reviewer O. Wurl to have a closer look at zooplankton data available for the sampling station. As zooplankton data for this period of investigation is not available (as can be read in the authors comments), a closer look at “historical” data might help – if available.

Basically each year investigated showed a different seasonal SFG signal: 2009 – one peak in summer, 2010 – one peak in spring, 2011 – two peaks in spring.

"Taking a look at historical data" is exactly what we have done: Historical zooplankton data can be found in the publication by Smetacek et al., which already has been cited in our article. The issues of (apparent) multiple peaks and natural variability have already been discussed in the comments above.

Referee 2: Other biological factors should also be considered, such as heterotrophic bacterial "blooms" (as shortly but not sufficiently discussed by the authors) and their turnover by protists. I bet that such data is also available for the sampling station.

We thank the referee for this helpful comment. We agree with her/his suggestion of bacterial blooms and protozoan grazing of bacterial blooms representing an alternative source for surfactants. Unfortunately, measurements of bacterial abundance and productivity are only available from 1987 to 2007, see article by Hoppe et al. in the same BE special issue. Hoppe et al. nicely showed that bacterial abundance at BE is correlated to water temperature implying that bacteria should have a maximum of abundance in summer. Indeed this could influence the SFG signal we see. Protozoan grazing of bacterial blooms has been investigated in the northern Baltic Sea but not at BE. We modify the text as follows (starting on page 3190 line 10): "Although the order of the maxima suggests otherwise, the possibility should be taken into account that the increased appearance of organic surfactant material is related to generally increasing microbial productivity as result of the warmer surface water: Bacterial abundance at BE is closely related to water temperatures (Hoppe et al., Biogeosci. Disc. 2012, 9, 18655) implying that during summer the bacterial abundance is enhanced. Thus, we speculate that bacteria blooms and the associated grazing by protozoans (see e.g., Kuosa and Kivi, Mar. Ecol. Prog. Ser. 53 (1989), 93 and Kuuppo-Leinikki, Mar. Ecol. Prog. Ser. 63 (1990), 227) may affect the appearance of organic surfactants in summer. Unfortunately, neither measurements of bacterial abundance nor experiments about protozoan grazing are available for BE during the sampling period discussed here.

Specific comments:

Referee 2: Page 3179 lines 8-14: I also had some difficulties with this paragraph and the clarification given by the authors in response to the review by O. Wurl is definitively needed.

This issue has already been addressed in the response to criticism by referee Wurl. The text has been updated to clarify this paragraph.

Referee 2: Page 3180 line 23: Check explanations for the abbreviations. The authors need to switch words.

OK, we switched the words to "GOM = gelatineous organic material".

Referee 2: Page 3185 line 19: For the reader refer to section 4.2.2 that this feature is discussed later.

A cross reference was added on line 19: "..., which is addressed in more detail in section 4.2.2."

Referee 2: Page 3187 line 21: from the data presented the "generally high layer intensity in June and July" is not only restricted to these months. (See also general comments above)

We used the term "general" to allude to an average/representative behavior, without excluding high intensities in neighbouring months. For clarification we changed the text (page 3187 line 22): "...(June and July), with higher intensities also occurring in the neighboring months."

Referee 2: Fig. 3: why are August samples highlighted?

Figure 3 is part of the discussion in section 5.2, which deals with the possibility of an increased carbohydrate abundance in summer. The spectral anomaly in the OH stretch vibration range was observed in particular in August (see Fig. 1). Therefore, the corresponding data points are highlighted in Fig.3. We altered the caption of Fig. 3 to clarify this issue: "Analysis of spectral trends potentially related to carbohydrate abundance. ...The grey areas highlight samples taken in August (see discussion in

sections 4.2.2 and 5.2)."

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