Minor Revision - Response Letter

We thank all reviewers for their thorough reading of the manuscript and for their valuable comments, which we have incorporated into the revised version. Please refer to the redlined revised manuscript and revised Supplementary Information to track the implemented changes/addition.

Reviewer Comments

Reviewer 1:

The sc metric relies on taking square root of integrated SFG area) as proportional to interfacial oscillator number while treating orientational factors as constant across natural samples. Could the authors provide polarization-resolved SFG checks (e.g., ssp vs ppp) or an external standard spike to demonstrate that orientation changes with composition/wind history do not bias sc, especially at low coverage ($< 20\,\%$) where baseline subtraction issues are acknowledged?

Response:

We have already provided a detailed 3-page response to this well justified comment during the open Discussion of the manuscript that we do not wish to repeat it in full here. In short – by pointing to material included in the Supplementary Information, to previous work, and to new measurements of selected samples in ppp polarization – we have explained why it is indeed reasonable to neglect spectral changes attributable to possible molecular orientation effects. This comprises *(i)* an explanation of why we chose the (most commonly employed) ssp polarization combination for our measurements, *(ii)* a discussion of the ppp spectra that we have now recorded in response to the referee's comment, *(iii)* a more detailed consideration of previous work on spectral variations arising from the anticipated variability of the surfactant pool in natural samples, and *(iv)* the experimental confirmation of the linearity of the VSFG response, which was already presented in the original manuscript as Fig. S1 (now Fig. S2) in the Supplementary Information.

Because the main emphasis of this paper is the biogeochemical context and as the spectroscopic part already takes up substantial space, we originally chose not to present all of these details in the main text. Instead, we referred readers to our previous publications and the Supplementary Information. The referee's comment, however, indicates that this strategy did not fully achieve its intended goal in the original manuscript. In response, we have now modestly broadened our discussion of this point, while still avoiding a shift of the paper's central focus toward these (albeit very intriguing) spectroscopic details. Although minor compositional differences between sites manifest as small changes in the relative CH_2/CH_3 intensities, the polarization-resolved measurements and the observed linear scaling behavior (despite variations in composition and surface coverage of the SML during the SURF experiment) indicate that neither orientational nor compositional changes exert a dominant influence on the sc metric within the investigated, environmentally relevant coverage range, which also encompasses low surface coverages. Our pragmatic choice of the reference point for 100% surface coverage ensures that, for environmental SML samples, a measured $sc = 1$ can be interpreted as a fully developed organic nanolayer at the air–water interface. Whether this straightforward operational approach can be generalized remains to be shown in future work. In this context, it would be especially valuable to analyze SML samples from a wide range of biogeochemical provinces—a research direction we intend to pursue further.

Changes: We now provide a brief explanation of the rationale for using ssp polarization in Section 3.1 and more explicitly direct the reader to the Supplementary Information. In addition to Supplementary Fig. S2 (formerly Fig. S1), we have now included a direct comparison between the ssp and ppp spectra in Supplementary Fig. S1. Further details of our expanded discussion can be seen in the redlined versions of the manuscript and the Supplementary Information.

Reviewer 2:

I found the manuscript is very well written on surfactants from the sea surface microlayer (SML). It is worth publication without any corrections.

Response:

Thank you for the favorable evaluation of our manuscript. We intend to make a few minor revisions and additions to address the helpful remarks of the other referee(s); however, the overall scientific content of the paper will remain unchanged.

Further Changes to the Manuscript

Reviewer 3:

During the pre-review stage of the manuscript (not part of the open Discussion), we have received valuable comments from another reviewer. While providing a detailed reply to these comments is not part of the minor revisions requested by the editor, we would like to take this opportunity to briefly address his/her comments as well, as they led us to introduce a few minor modifications to the manuscript.

Comment 1: The study provides a valuable link between nanolayer and microlayer properties, which is a gap in current literature. The global mapping approach is promising but should explicitly state its limitations (e.g., wind speed, temporal variability, surfactant composition diversity).

Response 1: As we already pointed out in the original manuscript, we recognize that the global mapping approach presented here has clear limitations. The primary role of the global maps in this study is to underscore the significance of the correlation between surfactant activity and surface coverage, and to illustrate how this relationship can be used to obtain a rough estimate of the surface coverage *potential* (i.e., in an average sense and under calm conditions) on a global scale. We agree that the factors highlighted by the reviewer are likely to be important at regional scales and should be a central topic of future investigations. In the scope of this paper, however, such detailed analyses are not warranted, given the limitations of our experimental dataset and the simplifying assumptions applied for our first global upscaling attempt.

Comment 2: VSFG and AC voltammetry methods are well-described, but the operational definition of 100 % coverage remains somewhat arbitrary. Consider adding a sensitivity analysis or justification for the chosen reference point. The Langmuir correlation assumes uniform surfactant behavior; discuss potential deviations for different surfactant classes.

Response 2: As the title of our manuscript indicates, the central aim of this paper -— and a key motivation for our study -— is to directly tackle these intriguing issues. Accordingly, substantial portions of the manuscript and the comparative analysis involving natural samples, DPPC, and TX-100 are dedicated to showing that our operational definition of a fully covered organic nanolayer is sound, and that it enables us to condense highly complex interrelationships into a single parameter. Inevitably, such a parameterization entails the loss of certain details – but this is, of course, equally true for the established approach of determining surfactant activity via AC voltammetry.

Just to name a few points that we have worked out in the manuscript as a justification for using DPPC at the specified surface concentration as a suitable reference compound: *(i)* DPPC surface behavior begins to show strong structural reorganization at concentrations higher than those chosen for reference point (see Supplementary Information, Section B). This is expected for surface concentrations so high that the molecules need to escape from repulsive forces by structural reorientation (i.e., lining up of alkyl chains). Therefore, the chosen reference point just at the onset of such strong molecular reorientations corresponds to a situation where the DPPC molecules "touch" each other but are not yet compressed so much that formation of a well-structured 2D phase takes place. This is fully consistent with our concept of 100% surface coverage in natural systems. *(ii)* Unlike TX-100, the ssp spectrum of DPPC shows very similar spectral features compared to the VSFG spectra of natural samples. *(iii)* VSFG spectroscopy is a non-linear laser technique. Therefore, it is important to check the spectrometer performance on a daily basis. In this context, chosing DPPC as a reference compound is advantageous because the preparation of DPPC monolayers with a given surface concentration is straightforward by established monolayer spreading procedures that are routinely employed in VSFG laboratories.

Finally, it has been demonstrated in the paper that saturation effects are observed in the SURF data. The associated spectral area in the VSFG spectra happened to be consistent with our operationally defined reference point, again suggesting that it is representative choice for natural SML systems. It also turned out, that our reference point is a reasonable choice for the Helgoland samples as well as VSFG measurements performed earlier at the Aeolotron wind-wave tank experiment reported in Engel et al. [1]. In Ref. [1] we also demonstrated the effect of surfactant surface coverage on wave damping (see below).

Comment 3: Figures 4–8 are central to the argument. Ensure captions are fully explanatory and include units where missing. The discussion on global maps (Fig. 9) should clarify that these represent potential coverage under calm conditions, not actual dynamic states.

Changes 3: We corrected the description of Fig. 4 by replacing DPPC with TX-100 and also mention the free molecular area given as the upper axes of Figs. 4 and 5. We also include the information that the global maps in Fig. 9 represent the surface coverage *potential* under calm conditions.

Comment 4: Expand on how these findings could improve air–sea gas exchange parameterizations in climate models. Briefly address how surfactant-induced wave damping might interact with other physical processes (e.g., turbulence, wind stress).

Response 4: A full discussion of air-sea gas exchange in climate models would clearly have been beyond the scope of this paper. However, we now have added Section E in the Supplementary Information showing that surfactant-induced wave damping is directly related to the sc metric. In the published data from Engel et al. 2025 [1] it is clearly seen that (at wind speeds below 6 m/s) wave damping is dependent on surfactant surface coverage, with strongest wave damping effects observed for the samples with sc values above 74%.

Changes 4: In Section 3.4, we now refer to the recently published work of Engel et al. (2025) [1] and have included their wind-speed dependent wave damping data to demonstrate the close relation of our sc metric with the wave damping capability of surface films (Supplementary Information, Section E).

Comment 5: The manuscript is well-organized, but the introduction could better highlight the novelty compared to previous studies (e.g., Engel et al., 2018; Elliott et al., 2018).

Changes 5: We have updated the Introduction and have added a short paragraph to emphasize the role of the global maps and how they synergize with the maps presented by Elliott et al. (2018) [2].

Minor linguistic corrections:

We have carefully reread the text and corrected several spelling errors and made a few minor language adjustments (including those suggested by reviewer 3). These revisions do not affect any of the scientific content. All modifications are marked in the redlined manuscript.

References

[1] A. Engel, G. Friedrichs, K. Krall, B. Jähne, Wind-induced collapse of the biopolymeric surface microlayer induces sudden changes in sea surface roughness, EGUsphere 2025 (2025) 1–36. doi:10.5194/egusphere-2025-5375.
URL `https://egusphere.copernicus.org/preprints/2025/egusphere-2025-5375/`

[2] S. Elliott, S. Burrows, P. Cameron-Smith, F. Hoffman, E. Hunke, N. Jeffery, Y. Liu, M. Maltrud, Z. Menzo, O. Ogunro, L. Van Roekel, S. Wang, M. Brunke, M. Jin, R. Letscher, N. Meskhidze, L. Russell, I. Simpson, D. Stokes, O. Wingenter, Does marine surface tension have global biogeography? addition for the oceanfilms package, Atmosphere 9 (6) (2018) 216. doi:10.3390/atmos9060216.
URL `http://dx.doi.org/10.3390/atmos9060216`