Review 1

General Comments

This manuscript presents the first in situ observations of surfactant accumulation in the sea-surface microlayer (SML) of the Fram Strait during the onset of Arctic sea ice melt (spring 2023), coupled with CH_4 and N_2O measurements. The study addresses an important knowledge gap: the influence of short-term surface processes on climate-relevant trace gas fluxes in polar oceans. The novelty lies in linking surfactant dynamics, algal bloom development, and greenhouse gas (GHG) emissions, providing new insights into how the SML may act as a natural regulator of CH_4 and N_2O fluxes in rapidly changing Arctic environments.

The manuscript is generally well-written, logically structured, and supported by robust datasets from a challenging field campaign. Figures are clear and informative, and the interpretations are scientifically sound. Overall, the study is valuable and has strong potential for publication, but the current manuscript requires several important clarifications and improvements as detailed below.

We sincerely thank Il-Nam Kim for the thoughtful and constructive comments. We greatly appreciate the recognition of the novelty and significance of our study, as well as the suggestions for clarifications and improvements. We have revised the manuscript based on the reviewer's comments and provided our response to each comment in blue italics.

Specific Comments

1. Abstract (p.2, lines 24–31): The conclusion that surfactants reduced CH_4 and N_2O emissions is compelling but somewhat overstated. Please add quantitative uncertainty ranges for this reduction with specific numbers.

Quantification of the reduction of sea–air gas fluxes by SAS in the SML was not possible because direct flux measurements were lacking, and SAS likely accumulated on the downwind side of the lead. Therefore, the SAS concentrations near the ice edge were most likely higher than in the central part of the lead. An estimate based on the measured SAS concentrations may have overestimated the reduction in sea-air fluxes. Consequently, we restricted our interpretation to reporting the observed SAS accumulation in the SML of two leads, which may have contributed to a reduction in gas fluxes. To clarify that we are only referring to a potential reduction in sea–air fluxes, we added the term "potentially" in line 28. Additionally, we revised the title to "Biogeochemical Shifts During Arctic Spring: Potential Reduction of CH_4 and N_2O Emissions Driven by Surfactants in the Sea-Surface Microlayer" for clarity.

2. Introduction (p.3, lines 79–87): The introduction nicely describes CH_4 and N_2O sources/sinks in the Arctic. However, the information about the role of EPS and algal-derived surfactants is likely to be insufficient here. Please provide more information about the background of EPS in polar environments and their potential to form slicks, and etc.

We revised this paragraph and added information about the role of EPS in the Arctic, particularly in the context of SAS accumulation in the SML:

> *"In polar environments, extracellular polymeric substances (EPS) are an important component of the SAS accumulating in the SML, where they contribute to the formation of biofilms (Gao et al., 2012; Orsi et al., 1995). EPS are produced by phytoplankton, primarily diatoms, and by bacteria as cryoprotectants and are therefore abundant in sea ice and brine (Aslam et al., 2012; Krembs et al., 2002; Underwood et al., 2013). During melting, EPS are released into the surface ocean, providing a source of organic carbon (Riebesell et al., 1991; Riedel et al., 2006). Due to*

cross-linking of their polymers, which mainly consist of polysaccharides, EPS can form marine gels and aggregates that influence particle sinking rates and act as potential sources of cloud condensation nuclei (CCN) (Orellana et al., 2011; Riebesell et al., 1991; Verdugo, 2012). Additionally, these aggregates can serve as hotspots of microbial activity (Simon et al., 2002)."

3. 2.3 section (p.5, lines 135–136): Please clarify why poisoning was done with different $HgCl_2$ volumes for CH_4 (125 µL) vs N_2O (50 µL).

The different volumes of $HgCl_2$ were used due to the different sample volumes of CH_4 and N_2O (50 mL and 20 mL, respectively). The greater sample volume for CH_4 was chosen to avoid a CH_4 fraction below the detection limit of the gas chromatograph.

4. 2.3 section (p.5, lines 143–147): The time lag between sampling at leads/ice holes and sample poisoning is critical. I consider this the major weakness of the manuscript, and the authors should provide scientifically robust evidence to validate this assumption.

We agree that the reviewer raises an important point, since the time lag between sampling and preservation can indeed influence the gas concentrations. We have added more details about the storage between sampling and preservation (lines 144–149), explaining that the samples were kept cold and in the dark, and that samples from CTD casts (immediately poisoned) from the same day showed no significant difference in gas concentration:

> *"Samples from the ice and off-ship stations were kept cold and in the dark, and returned to the ship within a maximum of two hours after sampling. Back on board, they were immediately poisoned with 125 µL (CH_4) and 50 µL (N_2O) saturated aqueous solution of mercury chloride ($HgCl_2$). Samples collected during CTD casts were poisoned immediately after sampling. The stations at which samples were taken both from CTD and ice stations (1 June and 5 June) show good agreement in gas concentration, despite the difference in the time elapsed between sampling and preservation (see Figure 4)."*

Under these temperatures, and considering that all other procedures were conducted in accordance with international standards (see Wilson et al., 2018), the microbial rates could be expected to be low. Since the storage was done in cold conditions, solubility changes are not expected. Hence, we can be confident that the measurements are correct despite the lag.

5. 2.5 section (p.7, lines 187–188): The thresholds of >200 and >1000 µg Teq L^{-1} originate from studies conducted in non-Arctic conditions (e.g., Wurl et al., 2011; Mustaffa et al., 2020). Since physical conditions in Arctic leads differ substantially, the authors should provide justification for applying these temperate thresholds to Arctic environments.

We acknowledge the reviewer's concern that these thresholds were derived from non-Arctic studies. We have revised the paragraph to clarify that these values were used as comparative thresholds, but that deviations may occur due to differences in SAS composition and hydrographic conditions in Arctic leads. As no Arctic-specific data on gas transfer reduction by SAS are currently available, we applied these estimates to show that a suppression of sea-air fluxes due to the accumulation of SAS in the SML has been previously quantified, with increasing reduction for higher SAS concentrations. Such effects are therefore likely to occur in the Arctic Ocean as well. Quantifying the actual reduction in gas transfer velocity would require direct flux measurements, which were not available in our study. Following the revised paragraph:

> *"In previous studies conducted under temperate conditions, SAS concentrations exceeding 200 µg Teq L^{-1} have been associated with a reduction in gas transfer velocities by approximately 60%, while concentrations above 1000 µg Teq L^{-1} have been classified as slicks (Mustaffa et al.,*

2020; Wurl et al., 2011). Maximum suppression of gas exchange rates was in a similar range in laboratory and wind-wave tunnel experiments using artificial monolayers and natural seawater (Brockmann et al., 1982; Broecker et al., 1978; Pereira et al., 2018; Ribas-Ribas et al., 2018; Salter et al., 2011). We used these values as a comparative threshold, as no Arctic-specific measurements are currently available. However, deviations from this relationship are possible due to potential differences in SAS composition and wind-wave interactions in Arctic leads."

Literature in this comment:

Brockmann, U. H., Huhnerfuss, H., Kattner, G., Broecker, H. C., & Hentzschel, G. (1982). Artificial surface films in the sea area near Sylt 1. Limnol. Oceanogr., 27(6), 1050-1058.

Broecker, H. C., Petermann, J., & Siems, W. (1978). The influence of wind on CO2-exchange in a wind-wave tunnel, including the effects of monolayers. J. Mar. Res., 36(4), 595-610.

Pereira, R., Ashton, I., Sabbaghzadeh, B., Shutler, J. D., & Upstill-Goddard, R. C. (2018). Reduced air–sea CO2 exchange in the Atlantic Ocean due to biological surfactants. Nature Geosci., 11(7), 492-496

Ribas-Ribas, M., Helleis, F., Rahlff, J., & Wurl, O. (2018a). Air-sea CO2-exchange in a large annular wind-wave tank and the effects of surfactants. Front. Mar. Sci., 5, 457.

Salter, M. E., Upstill-Goddard, R. C., Nightingale, P. D., Archer, S. D., Blomquist, B., Ho, D. T., ... & Yang, M. (2011). Impact of an artificial surfactant release on air-sea gas fluxes during Deep Ocean Gas Exchange Experiment II. J. Geophys. Res. Oceans, 116(C11).

6. 4.2 section (p.13, lines 340–350): The authors interpret the June 5 CH_4 increase and N_2O decrease as possibly driven by shifts in microbial pathways. However, this explanation remains speculative without direct evidence (e.g., microbial rate measurements or isotopic signatures). The authors should present this more cautiously and highlight the need for the validation.

The reviewer raised an important point, and we have revised the sentence for more clarity:

"As inorganic nutrients were depleted on 5 June, but organic material from the algal bloom was available, a shift in microbial processes to use alternative nutrient sources may have occurred, although this cannot be confirmed without supporting data such as gene expression or isotopic signatures."

7. Table 2 (p.9): Negative CH_4 fluxes were observed at some stations. These are important and should be discussed in more depth.

We have added a sentence in the result section emphasizing the observed CH_4 undersaturation and revised the last paragraph of the discussion, including possible explanations for the undersaturation:

"On 18 May, 8 June, and 11 June, negative fluxes and therefore CH_4 uptake by the ocean were observed."

"An observed drop in total bacterial abundance on 5 June may suggest a decrease in microbial CH_4 oxidation potential, which could contribute to the elevated CH_4 concentrations on this day. In the EGC, lower surface saturations, close to equilibrium, were observed and are possibly a result of higher CH_4 oxidation rates. However, since data on active gene expression are not available from our study, this is no direct evidence. The drop in both CH_4 and N_2O from 9 to 11

June, reaching CH_4 undersaturation, was likely caused by dilution with meltwater, as it coincided with rising air temperatures above 0°C, which likely enhanced sea ice melt, particularly surface melt."

8. Fig. 5 (p.10): The extremely high SAS concentration observed on June 5 is remarkable, approximately an order of magnitude higher than typical values. Moreover, the discrepancy between filtered and unfiltered samples is unusually large. This phenomenon requires a more thorough explanation.

We agree that the SAS concentration, particularly in the unfiltered sample from June 5, is extraordinarily high and that the manuscript would benefit from a more detailed explanation. We have added the following paragraph:

"Underwood et al. (2010) reported high concentrations of EPS in sea ice, particularly in brine, while Gao et al. (2012) observed EPS accumulation in the SML of Arctic leads, with a high fraction of colloidal EPS. These findings suggest that in our study, EPS may have been released during the onset of sea ice melt and brine rejection. The substantial difference in SAS concentration between the filtered and unfiltered samples, particularly on 5 June, indicates that a large fraction of colloidal EPS accumulated in the SML, consistent with the observations of Gao et al. (2012). The extraordinarily high SAS concentration of 11788 µg Teq L^{-1} likely resulted from a combination of EPS release from melting sea ice, in situ production during the phytoplankton bloom, and physical accumulation at the lead side. EPS from the SML in open leads can become aerosolized by bubble-bursting and contribute to the formation of CCN (Leck & Bigg, 2005; Orellana et al., 2021)."

9. 4.1 section (p.11, lines 265–275): The authors apply the parametrization of Butterworth & Miller (2016), which was developed for open oceans and marginal ice zones. Please elaborate on the limitations of using this parametrization in semi-ice-covered Arctic leads, where turbulence, wind fetch, and ice-edge effects may differ substantially.

We have revised the paragraph to clarify the limitations of the parametrization used and to emphasize that the results are representative of the sampling area rather than specific to open leads.

"The parametrization used in our study by Butterworth & Miller (2016) accounts for SIC in the area but does not distinguish between lead and under-ice conditions. Consequently, the results provide flux estimates for the broader sampling area rather than fluxes specific to the open lead. In our study, the difference between F_{open} and F_{SIC} ranged from 17–94%. On average, the sea-air fluxes were reduced by approximately 72% due to sea ice coverage. Although our flux estimates are based on parametrizations and no direct measurements were available, the results are in good agreement with previously measured reductions in sea-air fluxes by SIC in comparable sea ice settings. For high SIC (>80%), our calculations showed an average reduction in gas transfer velocity of 88%, compared to the approximately 90% reduction measured by Rutgers Van Der Loeff et al. (2014). For lower SIC (<80%), the calculated reduction was on average 33%, which is consistent with the approximately 30% reduction measured by Prytherch & Yelland (2021). Since CH_4 and N_2O were subject to the same physical drivers, but negative sea-air fluxes (i.e., uptake by the ocean) were only observed for CH_4, it is likely that different factors influenced the fluxes."