

Review EGUsphere Lange et al.

This manuscript addresses an important topic, trace gas sampling in the Surface Microlayer (SML), through a systematic laboratory approach with the aim to characterize sampling losses when the SML is sampled using a glass plate. The manuscript is generally well written and the authors have well-constructed their argumentation and reasoning. However, the manuscript also demonstrates that the mechanisms regulating air-sea exchange are very complex and not fully understood yet. Therefore, several limitations prevent a wide application of the evidenced sampling efficiencies.

In particular the influence of surfactants is complex and the choice of one surfactant is limiting the general representativeness of the sampling efficiencies, particularly in cases where surfactants are present (as is generally the case in natural environments).

There seems to be a known and recognised bias in the experimental design where the oversaturation of the trace gas in the aqueous phase and zero-air above, will introduce a very strong gradient and may not uphold the well-mixed assumption. While this is discussed in the manuscript, this should be mentioned earlier on, e.g. in the experimental set-up, to better frame the limitations of the sampling efficiencies that are found.

While the manuscript clearly motivates the use of the peak area and not the concentrations of the gases, it would be good to indicate at least the LOD for each gas and the system's sensitivity for each. This will help interpret the magnitude differences for PAs and their ratios discussed and give a better estimation of the environmental relevance of the method. Indeed, without these information, the differences in PA between trace gases explained as different amounts of trace gas in the sample, could also be due to different trapping and ionisation efficiencies between these very different gasses (as for example shown also in Wang et al., 2023, DOI: 10.1016/j.marchem.2023.104206) Therefore, the information on how sensitive the purge and trap GC-MS system is, seems necessary.

Although the influence of the surfactant on the sampling efficiency seem not very high, it remains a relatively badly understood system. The use of the surface activity might be a convenient choice, but the SA might not be the best indicator for the exchange of gases, as it will also highly depend on the nature of the surfactant, which this method does not qualify. Different (mixes) of surfactants will behave differently towards different gas species, depending on their physicochemical nature. As is mentioned in the conclusion, the influence of the surfactants needs to be further studied, but not only with regard to their concentration (which was attempted here) but also their nature (ionic, nonionic). It would be nice to add this nuance in the text, or in the conclusion.

Another suggestion for an additional nuance in the conclusion, would be to consider a non-linear approach to this dataset (or an extended) as well seen the multiple issues with linear assumptions that are not validated and the poor modelling with surfactants.

Further minor comments:

L126-127: The text states that 'Two different tanks were used... ', however table 1 lists 3 different tanks. The incubation bath should also briefly be described in the Experimental setup (2.1)

L306: It is mentioned that on 3 occasions the EF was below 1; it is not clear to me if these values were included in table 2? Do the authors have an idea why these samples are different (First of a set? Temperature?...)

L524: '...dilution by the DBL reduced the PA sampled by the glass plate to about 0.79 of the concentration in the ULW...' : Please clarify what are the units of this 0.79 as I first assumed this was percentage or a ratio but now think it might be absolute reduction in a.u. of the peak area?

Tables and Figures:

Figure 2: difference between different sample types is difficult to see due to small symbols

Table 6: what is the meaning of the asterisks (*) in the table?

For all figure references: in the text is mentioned 'Fig. Figure x' ; this should normally just read 'Figure x'.

Language and editorial :

L77: it's not clear to me what is meant by undersize here. Could you perhaps find a synonym?

L107 : ... experiment A **is** described in Appendix A... please correct

L306: ... was enriched on average EF from 3.7... this sentence does not seem grammatically correct. Please correct.

L625: expectations and findings by : this sentence seems not grammatically correct , please correct.