

Interactive comment on “Assessing the potential for DMS enrichment at the sea-surface and its influence on air–sea flux” by C. F. Walker et al.

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Below we reproduce the comments from reviewer 1 and reply to these:

We thank the reviewer for their informed response and recognition of the value of our data.

1. For the methodology, what is the precision for the continuous DMS measurements using an atmospheric pressure chemical ionization mass spectrometer equipped with a porous membrane equilibrator?

The mean relative standard error on the 5 min averaged SOAP data was $\pm 5\%$. We have now included this in the methods section 2.3.1. A detailed description of the miniCIMS can be found in Bell et al. 2013, as referenced in the manuscript.

C1

2. Gas phase DMS was cryogenically concentrated on 60/80 Tenax TA in a 1/8" Restek Sulfinitert-treated stainless steel trap at -20°C . Usually, the dry ice-ethanol liquid at -78°C or liquid nitrogen liquid at -190°C were used to trap DMS more efficiently. According to my previous studies, the temperature of -20°C is not high enough to trap all the DMS.

As the reviewer points out, there are a number of methods for trapping DMS; we have previously used both liquid nitrogen cold trap as well as the stated method with Tenax. Our laboratory first adopted the Tenax preconcentration method 18 years ago, following the well established procedures used by DMS measurement experts at NOAA and UEA UK. The trapping capacity of a Tenax trap is design dependent, primarily determined by the air flow rate through the trap and the mass of Tenax, which control the trap breakthrough volume which is strongly temperature dependent. Our findings for trap capacity are consistent with Kroupa et al (2004) who only tested to -10°C . For our trap set-up at -20°C we have a breakthrough volume of 40 Litres per gram (DMS) and for the flow rate used, our trapping phase was 10 minutes which is well within the 50% retention time of 40 minutes. Recent interlaboratory comparisons (Swan et al, 2014) and previous studies have confirmed the accuracy of our trapping method.

3. In section 3.5 DMS production rates in the SSM, the authors assumed that other DMS loss terms (photolysis, bacterial oxidation and vertical diffusion to subsurface water) were negligible. However, it should be pointed out, that this hypothesis might produce some bias because the photochemical oxidation rates and bacterial oxidation rates of DMS are also main sinks in actual oceans. The authors need to point out how this affects the results.

The reviewer is correct that these processes are potential DMS sinks, but as we did not measure either in the sea surface microlayer, we have no confirmation of their contribution. However, as the SSM photoproduction rate calculation does not include these processes, it is perhaps misleading to say that these are negligible, and so we have clarified this in the following revised text:

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"This approach assumes that DMS production in the SSM was the source of the 'excess' air-sea flux in B1. Other potential DMS loss processes such as photolysis and bacterial oxidation, may have also been significant DMS sinks (Kieber et al., 1996; Gali et al., 2013); however as these rates were not quantified they are not considered, and so the estimate of PRSSM may represent an underestimate."

As this raises further questions regarding DMS production in the SSM, so we have also added in the Discussion:

"To maintain the observed and calculated enrichment in the SSM, DMS production must dominate over loss terms such as photolysis and bacterial oxidation, and occur at a significantly greater rate than previously reported for the open ocean (Simo, 2004)."

4. In section 4 Discussion. In this study, DMS did not show any gradient in near-surface waters (see Fig. 4). This result is a little strange. Please explain this point using chlorophyll-a and phytoplankton species data. Did chlorophyll-a distribute uniformly as well in the near-surface waters?

The absence of a near-surface DMS gradient would be expected, unless near-surface production or consumption rates were significant. As mentioned in the Discussion, previous observations (Zemmelink et al, 2005) have identified a near-surface DMS gradient which they attributed to degassing. However our observations of no significant DMS gradient between 1 and 1.6m are indicative of a balance between production and loss processes, in agreement with the other reported studies, as stated in the Discussion. We did not obtain measurements of chlorophyll or phytoplankton species data in the microlayer, only in the 1cm depth RHIB sample and the 2m CTD sample which would not provide robust data on near-surface gradients. This paper focuses on DMS concentration and flux data, whereas the biogeochemical data from near-surface waters will be presented in another paper.

5. "Furthermore, the presence of surfactants may have suppressed ventilation across the air-sea interface (Salter et al., 2011) under these conditions, leading to accumu-

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lation of DMS in the SSM". Please add data or references to support the presence of surfactants in the microlayer.

Surfactant measurements were not obtained; however, other related parameters were measured at 1cm depth and 1.6m. These include chlorophyll-a, which showed a mean enrichment of 1.4 at 1cm, CDOM which showed a mean enrichment of 1.3 at 1cm, and DOC which showed no significant enrichment. However, the enrichments in B1 for CDOM and chlorophyll-a were not significantly greater than mean values for the entire dataset. As mentioned above, the biogeochemical data from near-surface waters will be presented in another paper.

We have rephrased the sentence in question to read:

"Furthermore, if surfactants were present, they may have suppressed ventilation across the air-sea interface (Salter et al., 2011) under these conditions, leading to an accumulation of DMS in the SSM."

6. In addition, we have added the following information to the Discussion on Pg 12, L 31:

"The coincidence of elevated phytoplankton DMS production, inhibition of bacterial DMSP consumption, and tolerance of bacterial DMSP degradation under elevated UV-A reported for BATS (Levine et al., 2012), provides further support for potential DMS accumulation in the SSM."

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