



UNIVERSITÀ
DEGLI STUDI
FIRENZE

UGO SCHIFF
DIPARTIMENTO
DI CHIMICA

Dear Editor,

I'm sending you the revised version of the paper: "**Factors controlling atmospheric DMS and its oxidation products (MSA and nssSO_4^{2-}) in the aerosol at Terra Nova Bay, Antarctica**" by Silvia Becagli et al.

Referees' suggestions are all appreciated and accepted, I thank both the referees for their support to this paper.

The point-to-point answer to the referee's comments and the related changes made to the manuscript are reported in the specific answers to each referee, here only the answers to the main comments are reported.

The main criticisms are expressed by referee 2 and in summary are: (i) the missing data of DMS in sea water and (ii) a deep discussion on the fate of atmospheric DMS to better explain the trend of measured concentration of DMS, MSA and nssSO_4 in the atmosphere at the sampling site.

Regarding the first point, I completely agree, but unfortunately we don't have such measurements, therefore in several parts of the paper (including in the abstract and in the conclusion) I stress about the need for DMS measurements in sea water to better understand the DMS concentration trend into the atmosphere. Besides, according to the referee suggestions I improve the discussion on the sea-to-atmosphere DMS transfer as function of wind speed also referring to the published paper suggested by the referee.

"Besides processes in the water column, ocean-air DMS flux has a more of a linear relationship with wind speed, as it is largely transported by interfacial exchange and it is not as influenced by bubbles (i.e. whitecaps, Bell et al., 2017; Zavarisky et al., 2018) as other more insoluble gases. Vlahos and Monahan (2009) evidenced that at wind speed higher than 10 m/sec DMS transfer rates decreases due to the amphiphilic nature of DMS that leads to transfer delay because higher wind speeds cause a higher concentration of sinking bubbles by whitecapping of the ocean surface. Anyway, Marandino et al. (2007) demonstrate that most of the variance in the fluxes can be accounted by variations in DMS sea surface concentration (37%) than wind speed (19%).

.....

Therefore, large differences in the DMS sea to air transfer velocity do not seem to occur and are not expected to be the cause of the different behavior of DMS evolution in the two ACs. Unfortunately, we do not have measurements of DMS in sea water, that could have confirmed this hypothesis, but it is consistent with previous modeling and experimental evidences assessing that the large year-to-year



variability of atmospheric DMS concentrations can not be explained by changes of meteorological processes controlling the k_w factor or by changes of atmospheric oxidants, but most likely by changes in oceanic DMS concentrations (Sciare et al., 2000; Kettle and Andreae, 2000; Marandino et al., 2007; Bock et al., 2021)."

To answer to second point a figure reporting the scheme of the processes leading to the measured concentration of DMS, MSA and nssSO₄ is added and discussion is enlarged referring to this figure and other published results suggested by the referee.

"These processes can be summarized by the simple model reported in Fig. 5, where the box represent the atmosphere over the sampling site (and relative concentration of DMS, MSA and nssSO₄²⁻). F_{DMS} , F_{MSA} , and F_{nssSO_4} are the flux of DMS, MSA and nssSO₄²⁻ incoming (F-in), outgoing (F-out) or formation (Fox). DMS_{sw} and DMS_{LR} represent the concentration of DMS in sea water and from sea water far from the sampling site (long range) respectively. MSA_{LR} and $nssSO_4^{2-}_{LR}$ represent the concentration of long range transported species and $nssSO_4^{2-}_{volc.}$ represent the volcanic nssSO₄²⁻.

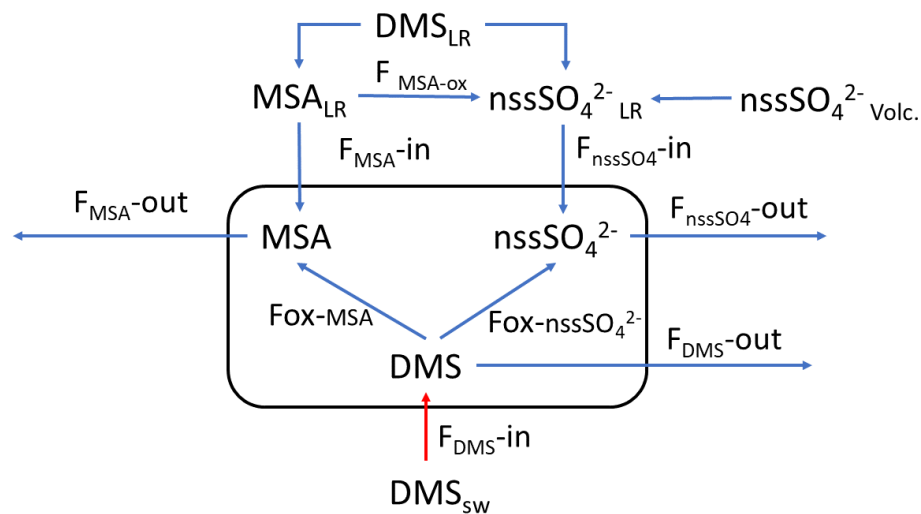


Figure 5. Schematic representation of the processes related to the measured concentration of DMS, MSA and nssSO₄²⁻ at MZS. See text for the abbreviations meaning.

.....
.....
.....

Looking at the scheme in Fig. 5, from 16 to 17 December 2019 we assumed that F_{DMS-in} is constant and quite high; at the beginning of DMS emission (16 December 2019) F_{ox-MSA} and $F_{ox-nssSO_4}$ just started therefore the concentration of DMS in the box depend by the equilibrium between F_{DMS-in} and $F_{DMS-out}$.



At this wind speed $F_{\text{DMS-out}}$ is probably low respect to $F_{\text{DMS-in}}$ as the concentration DMS_{sw} (driving the sea-air flux) is high. In these conditions, the DMS concentration reached a maximum of 32.8 nMol/m^3 on 16 December (average over the period 9:00-21:00 LT). Due to the constant wind speed and direction (Fig. 6) we can assuming that DMS emission from the ocean remains constant also in the following days ($\text{DMS}_{\text{emitted}}$), when UV radiation increase in the following 24 h stimulated the DMS oxidation processes, $F_{\text{ox-MSA}}$ and $F_{\text{ox-nssSO}_4}$ become relevant and at constant $F_{\text{DMS-in}}$ and $F_{\text{DMS-out}}$, the concentration of MSA and nssSO_4^{2-} increases and DMS decreases. MSA and nssSO_4^{2-} reached the maximum concentration on December 17 (8.3 and 9.9 nMol/m^3 for MSA and nssSO_4^{2-} , respectively, for the sampling time 9:00-21:00 LT), when the DMS concentration was 12.6 nMol/m^3 .

Therefore, the December 17 in the box of Fig. 5 we should have:

$$\text{DMS}_{\text{emitted}} = \text{DMS}_{\text{lost}} + \text{DMS}$$

If DMS emitted = 32.8 nMol/m^3 and DMS in the box is 12.6 nMol/m^3

$$\text{DMS}_{\text{lost}} = 32.8 - 12.6 = 20.2 \text{ nMol/m}^3$$

But the DMS_{lost} is due to the formation of MSA and nssSO_4^{2-} therefore:

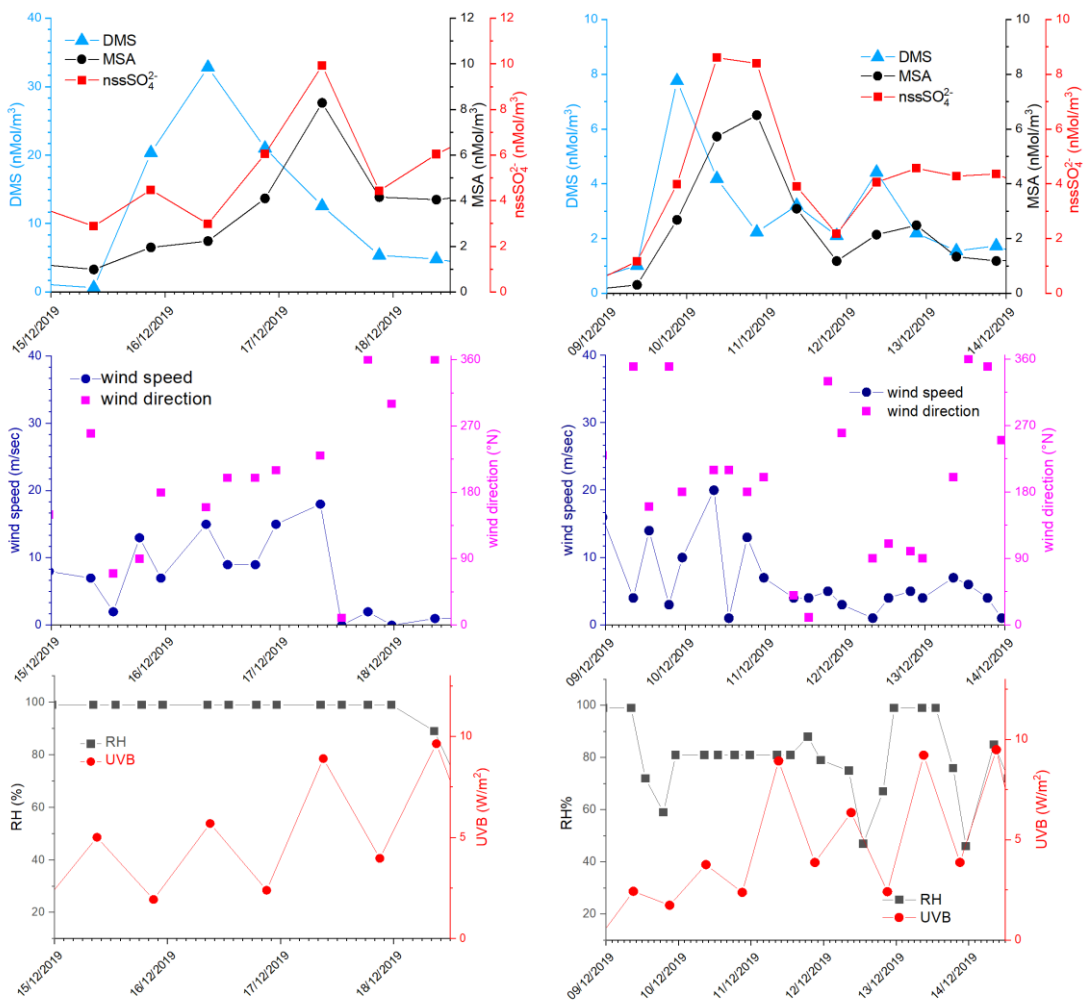
$$\text{DMS}_{\text{lost}} = \text{MSA} + \text{nssSO}_4^{2-} = 8.3 + 9.9 = 18.2 \text{ nMol/m}^3 \text{ that is in agree with the value of } 20.2 \text{ previously calculated with the approximation of the constant DMS emission in these days.}$$

Therefore, in this situation of constant wind speed and direction the 17 December we can suppose that F_{MSA} and F_{nssSO_4} in and out are negligible and the concentration of MSA and nssSO_4^{2-} in the box are mainly due to the $F_{\text{ox-MSA}}$ and $F_{\text{ox-nssSO}_4}$, for this reason reflecting the MSA/ nssSO_4^{2-} ratio of freshly formed biogenic aerosol.

In the following day (18 December) the abrupt change of wind direction (Figure 5) transport on the sampling site different air masses, therefore progressively increasing $F_{\text{DMS-out}}$, $F_{\text{MSA-out}}$ F_{nssSO_4-out} leading to a MSA, nssSO_4^{2-} and DMS concentration decreases in the box of Fig. 5. ”

Referee 1 suggests to give more importance to the sea ice melting in area far from the sampling site to explain early concentration peaks of biogenic aerosol (“...At this time MSA and nssSO_4^{2-} were very likely transported from areas far from the sampling site (i.e. MSA_{LR} and $\text{nssSO}_4^{2-\text{LR}}$ -Fig.5) where an early phytoplankton bloom was taking place likely due to the sea ice melting in the external boundary of sea ice belt around Antarctica (Gabric et al., 2005; Gabric et al., 2018).”) and to modify the figure in order to easily read them. This is accomplished by re-drawing the pictures with different and enlarged symbol for each parameter (now not only differing by colour) when necessary.

Here an example of the new aspect of figure 6.



Finally, the paper was revised for English language and checked for references.
I hope the paper is now acceptable for publication on ACP.

Best regards,
Silvia and Co-Authors