

# Reply to Reviewer 3 comments for: “Sea ice concentration impacts dissolved organic gases in the Canadian Arctic” by Charel Wohl et al.

Many thanks to the reviewer for taking the time to thoroughly review the manuscript and provide constructive comments. The reviewer provided thought provoking comments, which has helped us to improve the manuscript. Please see our responses below. Reviewer comments are in normal font and author’s replies can be found in italic.

Within the present publication a unique data set of arctic sea water measurement of methanol, acetaldehyde, acetone, DMS and isoprene is presented by the authors. These measurements were conducted during 17/07/2011 to 08/08/2017 onboard of CCGS Amundsen. The measurements are distinguished between different sea ice cover periods and thus provide a very interesting insight in how sea ice cover is able to influence production of organic materials relevant for the atmosphere. From the measured sea water values the corresponding emission fluxes are calculated afterwards. The results of the paper fit very well into the scope of Biogeosciences.

The paper is well structured and the results are logically discussed. A deep discussion of the results with measured values from literature is done, too. However, I think in some parts more discussion is mandatory, especially in the conclusion on the atmospheric oxidation capacity. Furthermore, I find the figures 2 to 6 hard to interpret. I recommend publication after the addressing of my questions and comments.

## General comments

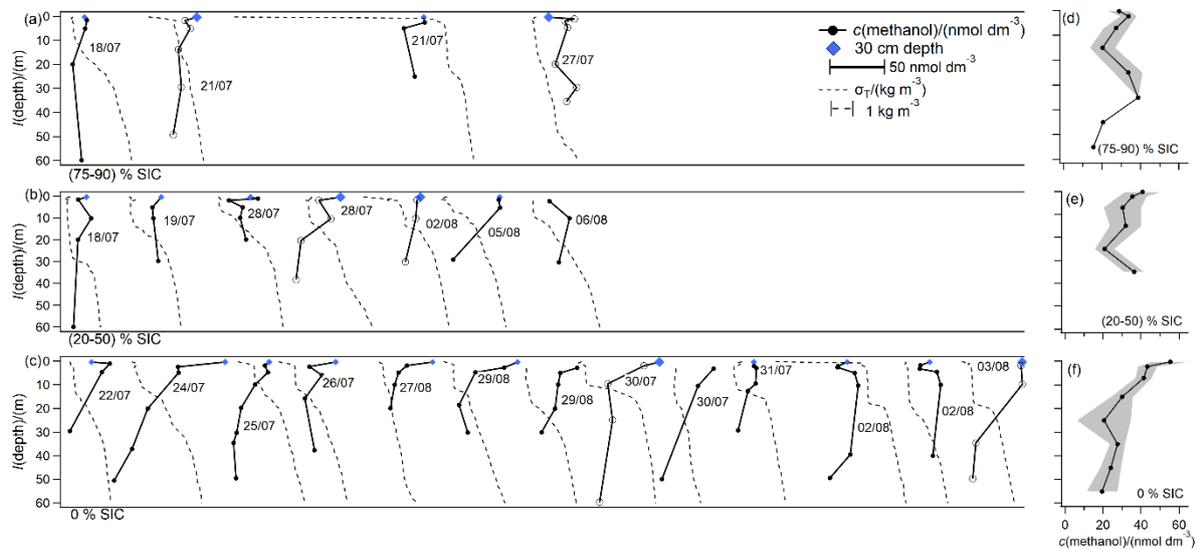
I find it hard to understand the figures 2 to 6 in which the depth profiles are presented. How am I able to know what concentrations was measured? In the legend are bars sketched that represent a certain concentration range, but these are not presented in the figure. These have to be added for the measurement points, otherwise the further discussion cannot be well comprehended.

*Many thanks to the reviewer for highlighting this. The casts have been grouped by sea ice concentration and horizontally offset to show the shape of the dissolved gas distributions with depth. A lot of the discussion focusses on the shape, rather than absolute concentrations. We recognize that it can be difficult to see what absolute concentration has been measured at each depth. We thus agree to add mean vertical profiles grouped according to ice cover and binned in different depth horizons. These mean vertical profiles show mean absolute concentrations at different depths for different sea ice concentrations.*

*The following introductory text has been added to the manuscript:*

*In Figures 2 to 6, panels (d) to (e) indicate mean vertical profiles grouped according to ice cover and binned in different depth horizons. These mean vertical profiles show mean absolute concentrations at different depths for a range of sea ice concentrations. Binning depth horizons were as follows; 0-0.5, 0.5-4, 4-10, 10-20, 20-30, 30-40, 40-50 and 50-60 m. Smaller bins were chosen near the surface to investigate the near surface gradients.*

Figures 2 to 6 have been updated to include a mean vertical profile for different sea ice concentrations. Here we share the updated Figure 2 only to avoid over-crowding this document. References to the additional panels (d) to (f) have been added to the discussion text.



**Figure 1** Overview plot displaying the shape of all methanol and density ( $\sigma_T$ ) depth profiles, grouped by SIC and staggered along the x-axis for ease of viewing. Panel labels indicate the SIC bin. The scale bars for methanol and density in panel (a) apply also to panels (b) and (c). Profiles with hollow markers are highlighted in Error! Reference source not found.. Sampling dates are indicated to locate stations using Fig. 1. Panels (d) to (f) indicate absolute concentrations of mean vertical profiles grouped according to ice cover and binned by depth horizons. The shaded area indicates standard error for each depth horizon.

Line 271

Here discussion text is missing.

*Thank you for pointing this out. Discussion text has been added in this place:*

*Another reason for higher methanol concentrations during this cruise could be slower bacterial consumption which has been shown to vary seasonally (Sargeant et al., 2016).*

It would be worth to compare the measured DMS values also with the values in Lana et al. (2011) and Hulswar et al. (2021). These are often used in global models to determine the effect of DMS on climate. I suggest a small discussion of these data in comparison with the measurements due to the possible benefit for the model community.

*A small discussion of our measured DMS values comparing them to these global databases has been added and is copied here:*

*An updated global climatology for DMS (Hulswar et al., 2021) predicts around 2 nmol dm<sup>-3</sup> for this sampling area during our sampling months, while the previous climatology (Lana et al., 2011) predicted around 2.5 nmol dm<sup>-3</sup>. We note that the updated climatology includes new measurements in this sampling area, but still does not reflect these more recent and very high measurements of DMS in the sea ice zone cited above.*

Line 437 and following

In Dani and Loreto (2017) it was stated that “globally (i) marine phytoplankton taxa tend

to emit either DMS or isoprene, and (ii) sea-water surface concentration and emission hotspots of DMS and isoprene have opposite latitudinal gradients". The results presented here reveal that this might not be true for oceans in interaction with sea ice, and coastal areas. A small discussion has been already done, but I miss a bit one in regards to the statement of Dani and Loreto (2017).

*A small discussion has been added in regards to how our measurements fit with the statement by Dani and Loreto (2017). It has been copied over here:*

*Dani and Loreto (2017) suggest opposite latitudinal distributions of isoprene and DMS, with higher concentrations of DMS and lower concentrations of isoprene at the poles. Our data shows surprisingly high isoprene concentrations which does not fit this trend. It is possible that the statement by Dani and Loreto (2017) does not hold in the Arctic, where we suspect that terrestrial influence or the effect of sea ice leads to high isoprene concentrations.*

Regarding the emission calculation of DMS I think it is not so easy to neglect the gasphase concentration. For gas-phase DMS in the Northern Atlantic up to 35 ppt and in the Antarctic more than 200 ppt were measured (see review of Yu and Li, 2021). The Henry's Law coefficient for DMS is 1.55 at 273°K. This results into a steady state water concentration of 0.05 and 0.31 nmol dm<sup>-3</sup>, which is 4% and 22% of the mean measured sea water value. Therefore, it is my opinion that for DMS the gas-phase concentration cannot be easily neglected without some bias that has to be discussed.

*We agree with the reviewer and we decided to recompute our DMS flux. To recompute our DMS flux, we assume 185.5 pptv of atmospheric DMS as measured previously measured in the mean by Mungall et al. (2016) during a similar time of year and at a similar location.*

I think the discussion of the assessment of acetone and methanol towards the lifetime of methane and other pollutants has to be deeper. Regarding the applied background values of methanol and acetone in this study together with the 1.8 ppm methane the first order reaction rate of methane with the OH radical is more than 2000% higher than that of methanol and acetone combined. The possible higher emission rates of DMS and isoprene might have a stronger effect. This discussion has to be done more deeply.

*A discussion of the effect of these emissions is beyond the scope of this paper as indeed, we have made no measurements or modelling to comment on the effect of these emissions. We agree though that in some instances we have not made this very clear. We only suggest that our measurements will be useful to assess the impact of these fluxes on the oxidative capacity of the atmosphere. We have subsequently removed any suggestions that our methanol and acetone fluxes affect lifetimes of methane and other pollutants.*

#### **Minor comments**

Line 124

What method has been used to correct the 16m wind speed to the 10 m neutral wind speed?

*We converted the 16 m ASL Gill wind speed to 10 m ASL using the following standard method based on a logarithmic wind profile:*

$$U_{10} = (u_*/\kappa) \ln(10/z_0)$$

where  $u_* = (\tau / \rho)^{1/2}$  is friction velocity ( $m s^{-1}$ ),  $\kappa$  is the von Karman constant of 0.4,  $z$  is measurement height, and  $z_0$  is roughness length (m) calculated as  $z_0 = z \exp[-\kappa U(z)/u_*]$

This has been changed in the manuscript to:

Wind speed was measured from a meteorological tower (approximately 16 m) located on the foredeck of the ship, similar to that described in Ahmed et al. (2019). The measured wind speeds at 16 m above sea level were converted to 10 m wind speed (U10) based on a logarithmic wind profile (Kaimal and Finnigan, 1994) and corrected for speed of ship passage.

I would recommend to add a table into the supplement that displays the physico-chemical characteristics of the gases for the air-sea flux calculation.

A table has been added to the supplement listing mean physico-chemical characteristics required for the air-sea flux calculation. We have copied it over in this document as well:

#### Supplement S4

A table listing the cruise mean physico-chemical characteristics required for the air-sea exchange calculation is displayed here.

**Table S1: Mean physico-chemical characteristics required for the air-sea exchange calculation. The values presented here have been calculated for the mean seawater temperature of 1.2 °C, and a cruise mean wind speed at 10 m (U10) of 4.8 m s<sup>-1</sup>. Henry solubility values are defined here as dimensionless water over gas solubility in ambient seawater. Waterside Schmidt numbers have been calculated using the supplementary R code from Johnson (2010) at a seawater salinity of 35. Waterside transfer velocities ( $k_w$ ) for isoprene have been calculated using the equation from Nightingale et al. (2000). Waterside transfer velocities for methanol, acetone and DMS have been calculated using the parametrisation by Yang et al. (2011). Airside transfer velocities for methanol, acetone, DMS and isoprene have been computed using the equation proposed by Yang et al. (2013).**

	methanol	acetone	DMS	isoprene
$H/(1)$	14215.6	2010.2	28.5	1.4
$S_{cw}/(1)$	2364.2	3403.2	3386.8	3723.7
$k_w/(\text{cm h}^{-1})$	3.7	3.1	3.1	3.0
$k_a/(\text{cm h}^{-1})$		1501.84		

Line 375

I suggest to delete are significant, as this has already been stated.

The manuscript has been changed here according to reviewer's suggestion.

References added by the reviewer

Lana, A., et al. (2011), An updated climatology of surface dimethylsulfide concentrations and emission fluxes in the global ocean, Global Biogeochem. Cycles, 25, GB1004,

doi:10.1029/2010GB003850.

Hulswar, S., et al. (2021), Third Revision of the Global Surface Seawater Dimethyl Sulfide Climatology (DMS-Rev3), Earth Syst. Sci. Data Discuss. [preprint], doi:10.5194/essd-2021-236, in review.

Dani and Loreto (2017), Trade-Off Between Dimethyl Sulfide and Isoprene Emissions from Marine Phytoplankton, Trends in Plant Science, 22, 361-372, doi: 10.1016/j.tplants.2017.01.006.

Yu and Li (2021), Marine volatile organic compounds and their impacts on marine aerosol – A review, Sci. Total Environ., 768, 145054, doi: 10.1016/j.scitotenv.2021.145054.

*Additional References added as reply to reviewer's comments*

Mungall, E. L., Croft, B., Lizotte, M., Thomas, J. L., Murphy, J. G., Levasseur, M., Martin, R. V., Wentzell, J. J. B., Liggio, J. and Abbatt, J. P. D.: Dimethyl sulfide in the summertime Arctic atmosphere: Measurements and source sensitivity simulations, Atmos. Chem. Phys., 16(11), 6665–6680, doi:10.5194/acp-16-6665-2016, 2016.