Reply to Reviewer 2 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.

General Comments

In this paper, the authors present a suite of dissolved gases measurements conducted along a three-week transect on the east side of the Canadian Arctic in July-August 2017. This data set gives a rare representation of the vertical and horizontal distribution of methanol, acetone, acetaldehyde, dimethyl sulfide and isoprene in the marginal ice zone in this part of the Arctic. The sampling protocols and the analytic technics are well described and appropriate. The results are well discussed and lead to interesting hypotheses regarding the controlling factors of this gases and how they are influenced by the presence of sea ice. The interpretation of the data is slightly too speculative in few instances (see specific comments), but in general, very convincing owing the excellent grasp the authors have on the literature. Overall, this is an interesting and well written paper.

Here I would like to share with the authors two points deserving attention. First, the area covered during the cruise is very large and encompasses different water masses, water circulation patterns, and marine ecosystems. Different ‘regions’ have been obviously sampled and pooling all the results together may be misleading. I am not proposing to change the way the results are presented (i.e. figures), but the potential importance of the characteristics of the three main regions (West Baffin Bay, Smith Sound, Lancaster Sound) on the gases measured should be mentioned in the Discussion. Second, the effect of ice edges on the biogeochemistry of the adjacent waters is very much influenced by the water circulation. Water masses moving out, in, or along ice edges will have different biological and chemical characteristics. This should be taken into account when comparing the ice edges sampled west of Baffin Bay, Smith Sound, and Lancaster Sound. The authors touched that aspect when referring to the recent work my Lizotte et al. (2020), but do not discuss how this may influence their ice edge results.

Many thanks to the reviewer for their input. We agree that a discussion of different regions and the effect of ice edges and water circulation on these gases would be helpful. Following the suggesting by the reviewer, we have divided the cruise track in three sections according to the regions suggested by the reviewer. We computed mean seawater concentrations and fluxes for each of these sections. A table displaying mean concentrations for each of the sections has been added to the supplementary material. Some discussion has been added to explain the differences in mean concentrations in light of the dominant seawater currents in the area and the location of the ice edge.

The following descriptive text has been added to the manuscript:

Sect. 3.2:

To investigate the effect of sea ice edges and water mass circulation on the surface concentrations of these compounds, we calculate mean underway surface concentrations measured in different sampling areas; West Baffin Bay (17.07-23.07), Smith Sound (23.07-31.07) and Lancaster Sound (31.07-07.08). These areas were chosen as they divide the cruise track in three equally representable sections and allow to comment on the effect of water circulation relative to sea ice edges/ice bridges. Means and standard errors of dissolved gas concentrations and some auxiliary data are presented in the supplementary material (Supplement S3). Sea ice bridges are often observed north of Smith Sound and east of Lancaster Sound (Lizotte et al., 2020; McLaughlin et al., 2004). At the same time, surface waters flow southwards and westwards from these sea ice bridges (McLaughlin et al., 2004; Münchow et al., 2015). This makes Smith Sound and Lancaster Sound ideal locations to sample downstream of an ice edge.

The following table has been added to the Supplementary material S3:

Table S1: Mean and standard error (std err) of the underway seawater concentrations of dissolved gases and some auxiliary data. Means are presented for three sections of the cruise. Full section name and sampling period are stated here; West Baffin Bay (West BB)) (17.07-23.07), Smith Sound (23.07-31.07) and Lancaster Sound (31.07-07.08).

	West BB		Smith Sound		Lancaster Sound	
	mean	std err	mean	std err	mean	std err
c(methanol)/(nmol dm^{-3})	23	2	46	3	41	3
c(acetone)/(nmol dm^{-3})	3.4	0.3	10.8	0.5	11.7	0.7
c(acetaldehyde)/(nmol dm^{-3})	1.1	0.4	5.5	0.2	6.0	0.2
c(DMS)/(nmol dm^{-3})	1.61	0.06	1.59	0.06	1.00	0.04
c(isoprene)/(nmol dm^{-3})	0.057	0.005	0.062	0.003	0.066	0.003
f(DMS)/(µmol m^{-2} d^{-1})	1.12	0.08	1.44	0.11	0.52	0.05
f(isoprene)/(µmol m^{-2} d^{-1})	0.041	0.003	0.065	0.005	0.029	0.003
T(sst)/(°C)	0.69	0.15	1.86	0.13	1.13	0.12
c(sss)/(1)	30.4	0.07	30.1	0.8	28.0	0.2
c(Chl *a*)/(mg m^{-3})	0.73	0.07	0.26	0.04	0.18	0.02
c(SIC)/(%)	21	3	8	1	20	2

A little bit of discussion has been added in regards to this for each compound. In square brackets we share sentences that have not been added as response to this reviewer comment, but have been included here for context.

Sec. 4.1 Methanol

[Underway methanol concentrations do not appear to vary with on SIC itself (Fig. 9). The presence or absence of sea ice at the time of sampling appears to influence methanol concentrations more strongly.] This is further supported by the fact that higher methanol seawater concentrations were measured in the relatively ice-free Smith Sound (46 nmol dm^{-3}) and Lancaster Sound (41 nmol dm^{-3}),

compared to the more ice covered west Baffin Bay (23 nmol dm^{-3}). Our underway methanol measurements support dominant biological cycling of methanol, while oxidation rates probably exert a strong influence on dissolved concentrations.

Sec. 4.2 Acetone

[Higher concentrations of acetone in partially sea ice covered ocean could be due to exposure of photolabile organic carbon from under the sea ice and the influence of sea ice on light penetration depth, thus further supporting a dominant photochemical source of acetone during this cruise track.] In support of this, we observe in the mean higher concentrations of acetone in Smith Sound (10.8 nmol dm^{-3}) and Lancaster sound (11.7 nmol dm^{-3}), which are both relatively open water areas downstream of sea ice edges, compared to West Baffin Bay (3.4 nmol dm^{-3}).

Sec. 4.3 Acetaldehyde

Similarly, we observe higher concentrations of acetaldehyde in Smith Sound (5.5 nmol dm^{-3}) and Lancaster Sound (6.0 nmol dm^{-3}), compared to West Baffin Bay (1.1 nmol dm^{-3}). Smith and Lancaster Sound are both areas where unbleached organic carbon is exposed to light as it is moved by ocean currents from ice covered waters into ice-free waters. This leads to higher production of acetaldehyde in these areas.

Sec. 4.4 Relationships between oxygenated VOCs

All three oxygenated VOCs (methanol, acetone and acetaldehyde) measured during this cruise generally display lower concentrations during the first week of sampling, which corresponds to sampling the sea ice zone of the more marine-influenced West Baffin Bay area. The slightly higher concentrations of these compounds nearer to land, i.e. in Smith Sound and Lancaster Sound, may be related to terrestrial sources or production of these gases as water masses are exposed to ice-free conditions by ocean currents. Methanol, acetone and acetaldehyde display gradually increasing concentrations as the vessel transects towards the ice edge in Lancaster Sound between 04/08 and 06/08.

Sec. 4.5 DMS

In the mean, higher concentrations of DMS were measured in West Baffin Bay (1.61 nmol dm^{-3}) and Smith Sound (1.59 nmol dm^{-3}) compared to Lancaster Sound (1.00 nmol dm^{-3}). It could be that these differences are due to different stages of the phytoplankton bloom at the different locations. At the same time, it is interesting that Smith Sound displays slightly higher concentrations of DMS compared to Lancaster Sound. This could be because the ice behind the ice bridge in Lancaster Sound tends to be multiyear ice (McLaughlin et al., 2004) which leads to different phytoplankton bloom and DMS dynamics, producing higher DMS concentrations further downstream, compared to first year ice edges (Abbatt et al., 2019; Lizotte et al., 2020).

Sec. 4.6 Isoprene

Average concentrations of isoprene were very similar in West Baffin Bay, Smith Sound and Lancaster Sound. It appears that other factors such as sst, Chl a and SIC at the time of sampling affect isoprene concentrations more strongly than different ocean dynamics in these areas.

Sec. 5 Air-sea fluxes

On average, we observe higher mean DMS fluxes in Smith Sound (1.44 µmol m^{-2} d^{-1}), compared to West Baffin Bay (1.12 µmol m^{-2} d^{-1}) and Lancaster Sound (0.52 µmol m^{-2} d^{-1}). […] Indeed, isoprene

fluxes were higher on average as well in Smith Sound (0.065 µmol m^{-2} d^{-1}), compared to West Baffin Bay (0.041 µmol m^{-2} d^{-1}) and Lancaster Sound (0.029 µmol m^{-2} d^{-1}).

Specific comments

P1, line 21 - …broadly higher concentrations… This is vague. Any numbers or statistics to support this interpretation?

In the main text, mean concentrations with and without sea ice cover as well as linear correlations are presented. This sentence has been changed to:

Underway (3-4 m) measurements showed higher concentrations in partial sea ice cover compared to ice-free waters, for most compounds.

P1, line 31 - …once the ice has melted… Or when under-ice water masses move out of the ice pack (see General Comment)

The following sentence has been added to the abstract to summarise this:

Differences in underway concentrations based on sampling region suggest that water masses moving away from the ice edge influences dissolved gas concentrations.

P11, line 194 - …Here we briefly discuss the effect of sea ice concentration (AND WATER CIRCULATION)… Water masses circulation at the ice edge is also important if one want to understand the impacts of ice edges on water biogeochemistry.

We agree with the reviewer, though in this specific section, we focus on depth profiles. We only discuss the effect of water circulation on underway surface water measurements. See also our reply to the general comment and how this has been addressed.

P11, line 202 - …could be characterised… Since not measured during this cruise.

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

P11, line 207 - …for this region… Which region? West Baffin Bay? Lancaster Sound? The area covered during this study encompassed different 'regions', even if I admit the that term 'region' is vague…

We replaced "for this region" by "for the Canadian Arctic Archipelago".

P11, line 208 - …that that…(typo)

Typo corrected.

P11, line 213 - …in this region… Same comment as above. Please be more specific about the localisation.

We replaced "in this region" by "in the Canadian Arctic Archipelago".

P12, line 227 - …These may be in part due to under ice phytoplankton blooms… Under ice phytoplankton blooms take place 'under the ice', so this statement is confusing in respect of the previous sentence stating that Chl a is lower at full ice cover.

This statement has been changed to:

These may be in part due to ice-edge blooms …

P12, line 229 - …these compounds… Which ones? All the compounds measured during this study?

This has been replaced by:

… the compounds measured in this study, …

P 14, line 271 - …could be… The rest of the sentence is missing.

Thank you for spotting this. The sentence has been completed to read:

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).

P14, line 275 - …phytoplankton SPECIES…¸

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

P14, line 277 - …to be highly variable… I suggest deleting the (a), (b) and (c) since this style is not used elsewhere in the manuscript.

We deleted the (a), (b) and (c).

P14, line 281 - …concentrations more strongly… This paragraph will benefit to have a clear concluding sentence.

A concluding sentence has been added:

Our underway methanol measurements support dominant biological cycling of methanol, while oxidation rates probably exert a strong influence on dissolved concentrations.

P15, line 309 - …it appears that photochemistry… The present data set cannot identify processes (sources/sinks) at play since no rate measurements were conducted. This conclusion is not backed by observations.

This sentence has been changed to:

While it is possible that some of the acetone we observed below ≈ 10 m is derived from biological activity, the near surface gradient of acetone concentration suggest that photochemistry is the dominant source of acetone in the upper 10 m.

Additionally, we introduced this possibility to the reader at the start of the discussion:

Additionally, we speculate in this section on the dominant processes (photochemistry or biologial source or sink) based on variations in concentrations. This speculation could have been more conclusive if we had made concurrent rate measurements.

P16, line 323 - …SLIGHTLY higher concentrations of acetone… For clarity I suggest to had 'slightly' since the difference in the mean concentrations of acetone between ice and ice-free waters, although statistically significant, is small.

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

P16, line 341 - …which also SHOW… Replace 'observe' by 'show'.

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

P16, line 344 - …by freshwater input from melting sea ice…AND RIVERINE INPUT As mentioned in the Introduction (P 3, line 73), river runoff is also an important source of turbidity in the Arctic

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

P17, line 376 - …These RESULTS suggest common sources…

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

P17, line 376 - …qualities are poor… I suggest deleting 'quite'.

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

P18, line386 - …The slightly higher…may be… This interpretation is very speculative and not supported by the data. In addition, the two sampled regions are separated by many kilometers and were not sampled at the same time. Other processes may be at play.

Indeed, the discussion has been changed to reflect water circulation patterns and the presence of ice edges – see our response to the general comment.

P18, line 390 - …This could be related to phytoplankton at the bottom of the ice… Replace 'phytoplankton' by 'ice algae'.

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

P18, line 385 (line 397) - …We generally observed… This last statement at the end of the paragraph needs to be discussed. Why mentioning that here and what are the implications?

A discussion has been added here:

We generally observe similar concentrations of DMS at 2 m and at 30 cm, except in near full ice cover (75 to 90 % SIC) (Fig. 5a, d) where concentrations at 30 cm are slightly higher than at 2 m, possibly due ice algae and the associated microbial web rapidly producing DMS.

P18; line 400 - The references to Mungall et al. and Abbatt et al. are appropriate, but the authors should also refer to the more detailed and ocean-focused paper by Lizotte et al. (2020), Biogeosciences.

A reference to Lizotte et al. (2020) has been added here.

P18, line 402 – The authors should also compare their results with those reported in the recently published paper by Galí et al. (2021) for the western Baffin Bay ice edge zone. Galí et al. DMS emissions from the Arctic marginal ice zone. Elementa: Science of the Anthropocene (2021) 9 (1): 00113.

Thank you for pointing us to this reference. We added a few references to this publication in this section.

P18, line 408 – Refer to Lizotte et al. (2020).

A reference to Lizotte et al. (2020) has been added here.

P18, line 411 – Excluding...however. I suggest deleting this part of the sentence and to directly state: 'No significant correlation could be observed BETWEEN DMS CONCENTRATIONS AND SEA ICE CONCENTRATIONS DURING THIS STUDY.'

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

P18, line 413 - …dependent on biological settings, presence/absence of under-ice bloom, water masses circulation in respect to the ice edge, time of the year, and type of sea ice.

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

P19, line 423 - …This frequently… Any statistics?

This has been changed to:

In the casts shown in Fig. 7, this frequently coincides with higher oxygen concentrations at the same depth, suggesting that gases produced at this depth from biological activity are not efficiently vented to the atmosphere.

P19, line 432 - …This suggests…

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

P19, line 442 - …have suggested… Replace 'suggested' by 'calculated'.

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

P20, line 454 – …These depth profiles… What is mentioned in this paragraph is relevant to all gases measured in this study. So, it should not be at the end of the section on Isoprene. I see two options: the concerns mentioned here could be addressed in the different sections of the Discussion as relevant, or the whole paragraph (with some modifications) could be moved to the very beginning of the discussion as a warning.

The whole paragraph has been moved to the beginning of the discussion with some modifications. It reads now like this:

The depth profiles and underway data discussed in the following section represent measurements at different times and locations. Therefore, differences are possibly not only due to sea ice coverage but could also be due to the oceanography of the area (McLaughlin et al., 2004). We recognise that sea ice is a very heteogenous environment with respect to ice thickness (Hayashida et al., 2020), the presence of melt ponds (Gourdal et al., 2018; Park et al., 2019), and types of sea ice (e.g. first year vs. multiyear ice (Lizotte et al., 2020)). This heterogeniety likely leads to very dfferent biogeochemistry, affecting trace gas cycling. Most of the discussion that follows here focusses largely the effect of on sea ice concentration on these gases and does not always explicitly take into consideration the effect of these variables, which is worthy of future research.

Additionally, we speculate in this section on the dominant processes (photochemistry or biologial source or sink) based on variations in concentrations. This speculation could have been more conclusive if we had made concurrent rate measurements.

P23, line 535 - …impact the overlying atmosphere…BY… This idea should be further developed. What will be the impact?

We decided to delete this sentence as, the claim made in this sentence is beyond the scope of this manuscript.

END