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Supplement of

Sea ice concentration impacts dissolved organic gases in the Canadian Arctic

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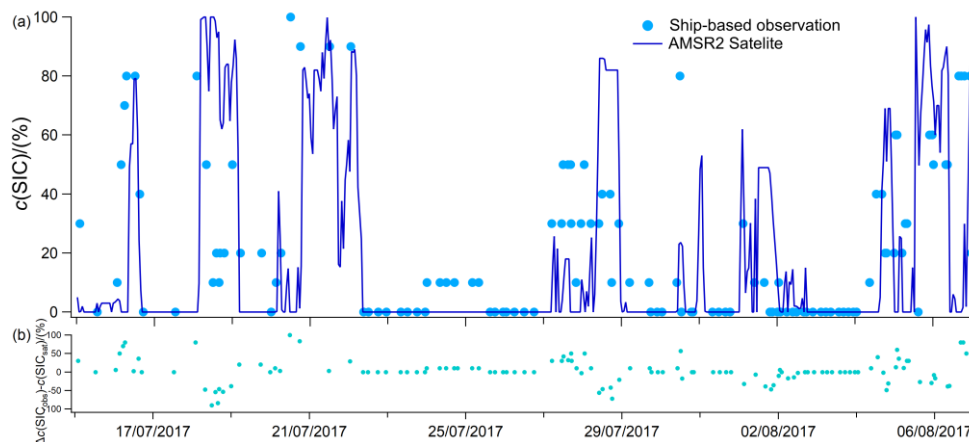**Charel Wohl et al.**

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Supplement S1

Figure S1 shows the underway SIC deduced from the AMSR2 satellite product and infrequent visual observations from the ship. The mean difference between these two SIC estimates is only 6 %, suggesting there is no major systematic bias.

Figure S1 (a) SIC during the cruise estimated from satellite and ship-based observations and (b) the difference between two estimates.

20 **Supplement S2**

The calibration slopes and measurement backgrounds specific to this deployment are laid out here. Additionally, we share our most recent insights regarding VOC measurement backgrounds. For further details about the calculation of dissolved gas concentrations, please refer to Wohl et al. (2019).

During installation on board, the PTR-MS was calibrated using a certified gas standard. Results from this calibration, similar
25 to those from post-cruise gas calibrations, were applied to the cruise measurements. Post-cruise water phase calibrations of the SFCE in the lab have shown that the equilibrator fully equilibrates for the soluble gases acetone, acetaldehyde, methanol and DMS and has a mean equilibration efficiency of 68% for isoprene (Wohl et al., 2019). These equilibration efficiencies were used to calculate dissolved concentrations. The concentrations of acetone and methanol reported here were calculated using an experimentally determined solubility from Wohl et al. (2020).

30 The choice of measurement background is crucial, due to (a) the high and variable backgrounds of seawater VOC measurements when using PTR-MS and (b) a small contamination of methanol and acetone from the PTFE jar trap used for this deployment (see Wohl et al. (2019) for more information on this contamination). Two VOC measurement backgrounds were determined daily during this deployment – a wet equilibrator blank and a zero air blank. These blanks are laid out in detail in Wohl et al. (2019) and in the supplement of Wohl et al. (2020). Here, we use slightly different blanks compared to
35 the preliminary data presented in Wohl et al. (2019) to incorporate an improved understanding from later deployments and lab experiments. The zero air blank, bypassing the SFCE system and measuring the zero air carrier gas directly, was used to

calculate isoprene and acetone concentrations. This is similar to the Pt-catalyst blank used in Wohl et al. (2020). To calculate methanol concentrations, the zero air blank was used and corrected for the influence of humidity on the methanol background. This is similar to the humid air blank used in Wohl et al. (2020). Thus, the blanks used for acetone and methanol do not

40   explicitly account for the PTFE jar contamination. In fact, the small contamination from the PTFE jar appears to be greatly suppressed during normal water measurement thanks to the very high solubility of methanol and acetone. This is consistent with the fact that methanol and acetone concentrations measured far below the mixed layer are relatively low (data not shown) and comparable to limited existing observations (Beale et al., 2013; Williams et al., 2004). Still, methanol and acetone concentrations reported for this deployment could be slightly biased high due to this contamination.

45   For acetaldehyde, the wet equilibrator blank was used, which is identical to Wohl et al. (2020). Later experiments have shown that the acetaldehyde background displays a strong sensitivity on CO_2, and this sensitivity is specific to PTR-MS and not accurately captured by the wet equilibrator blank nor the zero air blank. We decided to compute acetaldehyde concentrations from this deployment using the wet equilibrator as a background in order to maintain consistency with previous measurements. However, this means that acetaldehyde concentrations from this deployment is likely biased high (estimated as around 65 %

50   from lab experiments) due to this unquantified interference of CO_2 with the background. We note that previous seawater measurements of dissolved acetaldehyde using PTR-MS (Kameyama et al., 2010; Wohl et al., 2020; Yang et al., 2014b) do not explicitly account for this and could thus suffer from the same artefact. This interference appears to be more established in breath studies using PTR-MS (Herbig et al., 2009; Trefz et al., 2018) or ambient air measurements (Warneke et al., 2003). The discussion of the acetaldehyde measurements here thus largely focuses on the shape of the depth profiles and the range/relative

55   concentrations measured in the underway measurements, which we believe are of value. The concentration of CO_2 within the 60 m near the surface is not expected to vary drastically (Beaupré-Laperrière et al., 2020; Shadwick et al., 2011) and thus should not substantially impact the shape of the acetaldehyde depth profiles discussed here.

The limit of detection (LOD) and measurement noise (σ) were determined using the method described in Wohl et al. (2020). Data were analysed in 6 minute segments as this was the duration for which discrete samples were analysed for. The 6 minute

60   blank measurements were detrended for instrument drift using a smoothed interpolation. The standard deviation of the residual of this interpolation is converted to a seawater concentration using calibration slopes specific to this deployment. To calculate the noise in hourly averaged underway measurements, this value is divided by the square root of three because each hourly average contains three continuous 6 minute segments (the PTR-MS was not used for water sampling for the other part of the hour). To calculate the measurement noise in isoprene concentration, an additional 20 % uncertainty is applied to account for

65   variable water flow into the equilibrator (see Wohl et al. 2019), which was not extensively monitored during this deployment. The measurement noise and limit of detection for underway measurements specific to this deployment are listed in Table S1. To calculate the measurement noise of a single 6 min discrete CTD measurement, the values in Table S should be multiplied by the square root of three (≈ 1.73).

Table S1 Measurement noise and limit of detection (hourly average) for each compound specific to this deployment.

compound	σ /(nmol dm⁻³)	LOD /(nmol dm⁻³)
isoprene	0.0012	0.0036
methanol	4	12
acetone	0.4	1.2
acetaldehyde	0.8	2.4
DMS	0.04	0.12

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In Wohl et al. (2019), we highlight that DMS concentrations in the underway water inlet are slightly higher compared to measurements from the 5 m CTD. After detailed analysis of the depth profiles, we attribute this to differences in sampling depths. Thus underway DMS data presented here are not corrected for this difference.