Supplementary material to the response to referee #2 in the interactive comments on "Dimethylsulfide dynamics in first-year sea ice melt ponds in the Canadian Arctic Archipelago"

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This material is to be viewed in complement to the response to the comments of the second referee on the manuscript bg-2017-432 (https://doi.org/10.5194/bg-2017-432) under revision in Biogeosciences Discuss.

Here, we detail the calculations used to reply to the specific comments P8, L5 and P12, L27 – P13, L14 .

Specific comment P8, L5: Is any fractionation expected during storage?

Response: Isotopes fractionation may be caused by differences in rates of reaction or diffusion, or by differences in equilibrium constants. Fractionation during prolonged (several months) storage has been noted before in nitrogen cycle studies, even for frozen samples (Thayer, 1970; Granger et al., 2006). According to kinetics theory, kinetic energy (K.E.) is the same for all gases at a given temperature, which can result in greater velocities of lighter isotopes compared with their heavier counterparts (Sharp, 2007). Applying K.E. equations to the isotopes of interests (e.g. DMS m/z 62 and 63), this would result in the following calculation:

$$\text{K.E. (DMS m/z 62)} = \text{K.E. (DMS m/z 63)} \tag{1.1}$$

and

$$\text{K.E.} = \tfrac{1}{2}mv^2 \tag{1.2}$$

where m is mass and v is velocity. Substituting the masses of the DMS isotopes equation (1.1) becomes

$$\tfrac{1}{2}(62)(v62)^2 = \tfrac{1}{2}(63)(v63)^2 \tag{1.3}$$

$$v_{62} = \sqrt{(63/62)}v63 = 1.008v_{63} \tag{1.4}$$

Average velocity of DMS (m/z 62) is 0.8% greater than the average velocity of DMS (m/z 63) molecules in the same system. Following the same calculation steps, average velocity of DMS (m/z 62) is 4.7% greater than the average velocity of DMS (m/z 68) molecules in the same system. Finally, average velocity of DMS (m/z 63) is 3.8% greater than the average velocity of DMS (m/z 68) molecules in the same system.

According to the above calculations, a negligible maximum fractionation of 5% is expected during storage. Preserved samples and standards were compared against standard curves and fractionation during storage was not observed.

Specific comment P12, L27 – P13, L14: [...] you definitely need to include brine volume fraction, Rayleigh number, and brine salinity here in the discussion [...].

Response: Because of the apparent advanced desalination of sea ice in the ice cores presented, we did not include the Rayleigh (Ra) number results. We still present the calculation in the following paragraph intended only as a response to the specific comment P12, L27 – P13, L14 in order to clarify our process.

Sea ice can be mathematically described as a mushy-layer medium (e.g. Hunke et al., 2011) a multicomponent multiphase medium where interstitial liquid can flow within the porous medium (e.g. Worster and Kerr, 1994). Borrowed from the metallurgy industry, mushy layer theory has been increasingly adopted in sea ice studies because it advantageously provides one set of equations for various sea ice micro-structure configurations. Within the mushy-layer framework, calculation of Ra allows for the description of the onset and strength of gravity drainage (winter). Vertical density gradients, caused by the presence of highly salted brines on the top layers of sea ice, cause instability within the mushy-layer. Ra can thus be used as a proxy for the onset and the intensity of gravity drainage (Carnat et al., 2013). Multiple parameterizations of Ra can be found in the literature (Notz et al., 2009, Carnat et al., 2013 ; Vancoppenolle et al., 2013). They all yield different results leading to different interpretation of ice core data (Vancoppenolle et al., 2013). Field based observations suggest that full depth gravity drainage can be initiated when Ra value reaches 3 (Carnat et al., 2013). A Ra threshold value greater than 10 as suggested in Notz and Worster (2008) is most likely too high for brine convection in situ. Nevertheless, Ra addresses sea ice undergoing gravity drainage, a winter process that influences brine-rich sea ice. Ra has already been used in studies including warming sea ice (e.g. Carnat et al., 2013), but reported values of bulk sea ice salinity and temperature indicate a less advanced stage of sea ice melt in Carnat et al. (2013) than here. During our study, we most likely passed the point of full-depth desalination of warming sea ice given the low salinities observed throughout the ice profiles (Fig. 3). For such highly permeable sea ice, brine loss during sampling may lead to an underestimation of bulk salinity up to 20 g kg^{-1} (Notz et al., 2005) and thus increase the uncertainty of Ra number calculation (VanCoppenolle et al., 2013).

Ra was calculated for sea ice (T > -2ºC) following the formula presented in Carnat et al. (2013):

$$Ra = \frac{\Delta z g \beta (S_{\mathrm{b}}(z) - S_{\mathrm{OC}}) \Pi (V_{\mathrm{b}}/V_{\mathrm{min}})}{\kappa \eta}.$$

As reported in Carnat et al. (2013) : $g = 9.81$ m^{-2} is the acceleration due to gravity; $\beta = 0.78$ kg m^{-3} ppt^{-1} is the haline expansion coefficient of sea water at 0ºC (Fofonoff, 1985); $S_{b\ (z)}$ is the salinity of brine at depth z (depth increasing from zero in the bottom ice to the top of sea ice) calculated using Lepparanta and Manninen (1988), z is given as the distance from a specific level in the ice to the ice-ocean interface ; S_{OC} is the salinity of sea water; $\Pi(V_b/V_{min})$ is the effective sea ice permeability (m^2) calculated using the formula below (Notz et al., 2009 parametrization of Π was also used for comparison) ; $\kappa = 1.3 \times 10^{-7}$ m s^{-2} is thermal diffusivity of brine (Sharqawy et al., 2010) ; and $\eta = 2.55 \times 10^{-3}$ kg m s^{-1} is the dynamic viscosity of brine.

The formula used to calculate the effective sea ice permeability Π was found in the technical discussion paper by Vancoppenolle et al., 2013 (www.the-cryosphere-discuss.net/73209/2013/), after Eicken et al., 2004:

$$\Pi = \begin{cases} 4.708 \times 10^{-14} \cdot \exp(76.90e), & e \leq 0.096 \\ 3.738 \times 10^{-11} \cdot \exp(7.265e), & e > 0.096. \end{cases}$$

e expresses the brine volume fraction and is calculated as follows:

$$e \approx S/S_{br}$$

Where S is bulk ice salinity and S_b is brine salinity calculated using Lepparanta and Manninen (1988). In our study, *e* values ranged between 0.113 and 0.478. Accordingly, the second equation for sea ice permeability Π was used. Because of the high in situ ice temperatures and the low brine salinities, two terms used in Ra computation, we found negative values of Ra. Given that errors in Ra are largest for warm and permeable sea ice (Vancoppenolle et al., 2013), we decided to exclude these calculations in the reviewed version of the paper.

With winter gravity drainage, flushing is the dominant desalination process for fully formed sea ice. Flushing is the three dimensional (i.e. both vertical and laterally in all directions) washing out of salty brine from the structure of porous sea ice and its replacement with a mix of seawater and melt water (Hunke et al., 2011). With our averaged bulk salinity < 4.00 throughout the ice, we agree that sea ice had most likely undergone full-depth salinity drainage and brine flushing before our sampling.