Point-by-point responses to Review #1 and 2.

Journal: BG
Title: CO_2 flux over young and snow-covered Arctic sea ice in winter and spring
Author (s): Daiki Nomura et al.
MS No.: bg-2017-521
MS Type: Research article

We thank the reviewers for their valuable comments, which have helped us to improve the manuscript.

For clarity, the authors' responses are inserted as green text.

Anonymous Referee #1
Received and published: 11 February 2018

General comments

Nomura et al present an interesting analysis of rare data capturing CO2 fluxes between sea ice and the atmosphere in Arctic winter, spring and summer as part of the N-ICE project. The methods are robust, the data are of high quality and significant value, and the arguments laid out in the paper will be of wide interest amongst the sea ice and CO2 communities. However, the manuscript comes across as a little rushed in its current form, and I believe it would be improved significantly by adding more detail and explaining more clearly the key points. I recommend acceptance for publication after moderate revisions. Results are presented in summary tables. In general, I find that not enough information is presented for the reader to easily follow the arguments made in the paper, and I think some may even be misleading. For instance, based on Table 3, you argue that Fice is greater than Fsnow and thus make the argument that snow cover reduces flux magnitude. From the table, it appears that this is only demonstrably true for two out of the seven first-year ice stations. Two of the stations appear to have negative fluxes, but this is not addressed in the text at all, but seems to me to be quite important. These factors should be discussed in much greater detail in the text. Given the variability in your results, I think it is necessary to present the actual data, rather than just summary data. This would probably be best as figures, to accompany the summary tables. On a similar note, you have the number of measurements listed for F-snow and F-ff in table 3, but why not F-ice. Please include this information and error estimates. It is also quite difficult in general to follow the flow through and between the different tables, for example discussion of the relationship between flux magnitude and snow thickness or water equivalent. The text needs more detail to guide the reader's understanding and some more figures would certainly help.

We are grateful for your favorable assessment. We have made changes in response to all of your recommendations and edited the text improve the readability of the text.

Now we have indicated the stations for each result (e.g., for stations FI5 and FI6) in the text. In addition, we have added following information about the negative fluxes and reason for single F_{ice} measurement in the text:

"For F_{ice}, there were negative CO_2 fluxes at stations FI3 and FI4 (–0.6 mmol C m^{-2} day^{-1} for FI3 and –0.8 mmol C m^{-2} day^{-1} for FI4) (Table 3). These fluxes corresponded to low or negative$\Delta pCO_{2\ b-a}$ as compared to that in atmosphere (Table 2 and Figure 6). Negative CO_2 fluxes should correspond to negative $\Delta pCO_{2\ b-a}$. Therefore, the uncertainty for the calculation of carbonate chemistry may be one reason for the discrepancy in pCO_2 calculation in these conditions (Brown et al., 2014)."

"During first CO_2 flux measurements (about 30 minutes), ice surface temperature was stable at –5.8°C, suggesting that the effect of removing snow on the variation of sea ice surface temperature was negligible within 30 minutes. The ice surface temperature decreased from –5.8°C to –8.0°C at 200 minutes after removal of snow. Therefore, in this paper, the data of the initial 30 minutes of CO_2 flux measurement after removal of snow or frost flowers was used."

In order to present actual data, we have added relationships between pCO_2 and CO_2 flux in figure showing the relationships between temperature and CO_2 flux (Figure 6). In addition, we have made new figure showing the temporal variation of CO_2 concentration within chamber (Figure 3).

Specific comments

Introduction: it would be useful to include a little more information about what we know about ice-atmosphere CO2 fluxes in the context of ocean-atmosphere fluxes overall in the Arctic, and how they may change in the future. That would set the scene nicely for your statements at the end about ice-atmosphere fluxes being important in the context of a changing Arctic and the broader implications of your work. The final paragraph (line 107) could also be much stronger and punchier.

Thank you for your suggestions.

We have now added some more discussion on the results from other work in the Arctic, and to emphasize the lack of observations in the pack ice:

"In the ice covered Arctic Ocean, storm periods, with high wind speeds and open leads are important for air-to-sea CO_2 fluxes (Fransson et al., 2017), due to the under-saturation of the surface waters in CO_2 with respect to the atmosphere. On the other hand, the subsequent ice growth and frost flowers formation in these leads promote ice-to-air CO_2 fluxes in winter (e.g. Barber et al., 2014). Given the fact that Arctic sea ice is shrinking and shifting from multi-year ice to first-year ice, the area of open ocean and thinner seasonal ice is increasing. Therefore, the contribution of open ocean/thinner sea ice surface to the overall CO_2 fluxes of the Arctic Ocean is potentially increasing. However, due to the difficulty in acquiring observations over the winter pack ice, most of the winter CO_2 flux measurements were examined over the Arctic landfast ice. Therefore, there is a definite lack of information on conditions during wintertime, especially from Arctic pack ice." in introduction.

"Rare CO_2 flux measurements from Arctic pack ice show that two types of ice are significant contributors to the release of CO_2 from ice to the atmosphere during winter and spring: young thin ice with thin layer of snow, and old (several weeks) snow covered thick ice." in abstract.

We have changed from "Arctic sea ice" to "Arctic pack ice" in title.

To emphasize the novelty of our work, we have rewritten the final paragraph;

"The Norwegian young sea ICE (N-ICE2015) campaign in winter and spring 2015 provided opportunities to examine CO_2 fluxes between sea ice and atmosphere in a variety of snow and ice conditions in pack ice north of Svalbard. Formation of leads and their rapid refreezing allowed us to examine air–sea ice CO_2 fluxes over thin young sea ice, occasionally covered with frost flowers in addition to the snow-covered older ice that covers most of the pack ice area. The objectives of this study were to understand the effects of i) thin sea ice and frost flowers formations on the air–sea ice CO_2 flux in leads, ii) effect of snow-cover on the air–sea ice CO_2 flux over thin, young ice in the Arctic Ocean during winter and spring seasons, and iii) of the effect of the temperature difference between sea ice and atmosphere (including snow cover) on the air–sea ice CO_2 flux. ".

Line 125-127: state specifically which stations you are referring to. I assume "young ice", but this should be explicit. That might also help the descriptions of relationships between variables in the discussion, as mentioned in "general comments".

Thank you for this suggestion. We have added the specific information for station "station YI1". For the descriptions of relationships between variables in the discussion, please see your general comments.

Line 155-157: does this not contradict your argument that snow provides insulation? Perhaps it would help to mention timescales of T change/stability.

We agree with your comments. We have added:

"The ice surface temperature decreased from –5.8°C to –8.0°C at 200 minutes after removal of snow. Therefore, in this paper, the data of the initial 30 minutes of CO_2 flux measurement after removal of snow or frost flowers was used." in the text.

Line 162: I think you have air and ice surface the wrong way round.

Correct, well spotted. We have corrected.

Line 172: I think you should distinguish between stations where snow was cleared and where the sea ice surface was naturally snow-free. Given your arguments about the effects of snow cover, I assume this is significant.

We have no station where the sea ice surface was naturally snow-free (unless frost flowers are not considered as snow) (Table 1).

Line 185-187: clarify when temperature was measured.

We have added "during CO_2 flux measurements (approximately 60 minutes after the onset of the CO_2 flux measurement)" in the text.

Line 192-193: why was carbonate chemistry only measured at these four stations? This should be explained. It also means that table 2 looks like there is a lot of data missing; perhaps there is a better way to present these data?

At some occasions there was simply no time to collect the samples right after the flux measurements were taken, due to diverse and challenging conditions in the field. Due to the technical reason, we could not obtain the brine, except for four stations. Therefore, we have no samples for brine carbonate chemistry, except for four stations. We have added "Due to technical reason, data of snow, sea ice, and brine data were not obtained" in Table 2 caption.

Line 220: I think this should be Guildline PORTASAL salinometer Model8410A

Correct. Changed accordingly.

Line 239-240 and 239-250: this strongly suggests that the constants are not valid for your conditions. The following clearly attempts to justify its use, but it is not clear why the 40% uncertainty does not apply to your data, which would mean that none of your calculated values would have statistically significant differences. Please clarify.

For F_{ice}, there was negative CO_2 flux for stations FI3 although $\Delta pCO_{2\,b-a}$ was positive. Negative CO_2 fluxes should correspond to negative $\Delta pCO_{2\,b-a}$. Therefore, the uncertainty for the calculation of carbonate chemistry may be one reason for the discrepancy in pCO_2 calculation in these conditions (Brown et al., 2014).".

We have added "For F_{ice}, there were negative CO_2 fluxes at stations FI3 and FI4 (–0.6 mmol C m^{-2} day^{-1} for FI3 and –0.8 mmol C m^{-2} day^{-1} for FI4) (Table 3). These fluxes corresponded to low or negative$\Delta pCO_{2\,b-a}$ as compared to that in atmosphere (Table 2 and Figure 6). Negative CO_2 fluxes should correspond to negative $\Delta pCO_{2\,b-a}$. Therefore, the uncertainty for the calculation of carbonate chemistry may be one reason for the discrepancy in pCO_2 calculation in these conditions (Brown et al., 2014).".

Line 253-254: please give enough information for the reader to understand this calculation, without having to dig out an old reference.

We have added newer reference "Petrich and Eicken, 2010". This is a rather standard method for sea-ice, thus we would not like to use space to explain the derivation of porosity in more detail than referring to the source.

Petrich, C. and Eicken, H.: Growth, structure and properties of sea ice, in Thomas, D. N. and Dieckmann, G. S. eds., Sea Ice, 2nd ed., Oxford, Wiley-Blackwell, 23–77, 2010.

Methods: please include information about how atmospheric pCO2 was measured. It comes later as a footnote to a table, but should be included here.

We agree with your comment. We have added "The pCO_2 of atmosphere was calculated from CO_2 concentration (ppmv) at Ny-Ålesund, Svalbard (http://www.esrl.noaa.gov/gmd/dv/iadv/) taking into account saturated water vapor and atmospheric pressure during sampling day." in the text.

Line 275-276: state which stations you are referring to. This would help in general in various places in the text.

Agree. We have added "at station YI1" in the text, and also in other locations in the text to make the reasoning easier to follow.

Line 279-280: I think it would help to demonstrate this point if you plotted air temperature on figure 4, so that the relation is clear.

We have added air temperature on Figure 5a.

Line 285-286: can you highlight on figure 4b which measurements are from frost flowers?

We have changed the range of salinity in Figure 5b and added arrow to indicate frost flower data.

Line 292 and table 2: you present data from the top 20 cm, which presumably means your top two 10cm slices. Why do you only present the top 20cm when most cores are longer? Would it be better to present profiles to show downcore variability? If not, please justify presenting only the top 20 cm and provide error/uncertainty estimates from averaging of values from two core slices.

We have used average temperature for top 20 cm sea ice because the environmental information at the top of sea ice were important parameters regulating the CO_2 flux at sea ice surface. Unlikely the conditions deeper down in the ice will be important for such a short period of measurement given fluxes in the ice would be diffusion driven. We have added the range of temperature at top 20 cm sea ice in Table 2.

Line 322: "except for station OI1". Should this also say YI1 as it does in section 3.2?

Correct. We have added YI1 in the text.

Line 324: "..and in cases the thick insulating snow cover". Does not make sense. In certain cases? In cases where. . .?

We agree with your comments. We have changed to ", except for station OI1 (Tables 1 and 2)".

Line 355-358: this statement is only true for FI5, FI6 and YI1. Same comment for line 372-373.

Correct. We have added ", especially for stations FI5 and FI6".

Line 357: Where you state that one value or group of values is lower than another, please provide relevant statistical details (e.g. t-test, z-test etc.)

We agree with your comments. We have deleted "mean" and added ", especially for stations FI5, FI6, and YI1." in the text.

Line 372-382: This paragraph is an example of where a lot more detail is required to demonstrate your points. Flux direction, magnitude and relationships between variables all need to be discussed for the different stations.

We have added information of flux direction, magnitude and relationships between variables (F_{snow}/F_{ice} ratio and water equivalent) all need to be discussed for the different stations. New paragraph is:

"The magnitude of positive F_{snow} is less than F_{ice} for stations FI5 and FI6 (Table 3) indicating that the potential CO_2 flux from sea ice decreased due to the presence of snow. Previous studies have shown that snow accumulation over sea ice effectively impede CO_2 exchange (Nomura et al., 2013; Brown et al., 2015). Nomura et al. (2013) reported that 50–90% of the potential CO_2 flux was reduced due to the presence of snow/superimposed-ice at the water equivalent of 57–400 kg m^{-2}, indicating that the snow properties are an important factor that controls the CO_2 exchange through a snowpack. Comparisons between stations FI5 and FI6 for F_{snow}/F_{ice} ratio (0.2 for FI5 and 0.0 for FI6) and water equivalent (11 kg m^{-2} for FI5 and 127 kg m^{-2} for FI6) indicate that the potential CO_2 flux is reduced (80% for FI5 and 98% for FI6 of the potential CO_2 flux) with increasing water equivalent. Although the magnitude of the potential CO_2 flux through the sea ice surface decreased by the presence of snow for stations FI5 and FI6 (Table 3), the snow surface still presents a CO_2 source to the atmosphere for low snow density and shallow depth conditions (e.g., +0.6 mmol C m^{-2} day^{-1} for FI5)."

Line 380: reference to table 3. You need to be specific about what you are referring to that shows that flux is reduced by the presence of snow. If you compare FI5 and FI6, FI6 shows a much greater potential flux but actually has a greater snow thickness and water equivalent than FI5. This should be incorporated into your comparisons.

We agree with your comments. We have added "for stations FI5 and FI6".

Line 396-399: How will footprint size make such a big difference? If it arises from small-scale heterogeneity in time and/or space, this should be stated. Are there any other reasons worthy of mention?

To clarify we have added the following "The eddy covariance method reflects a flux integrated over a large area, that can contain several different surface types. Therefore, eddy-covariance appears to be more useful for understanding fluxes at large special and temporal scales. On the other hand, the chamber method reflects the area where chamber was covered, and it is useful for understanding the relationship between fluxes and ice surface conditions on smaller scales. The different spatial scales of the two methods may be therefore one reason for the discrepancy in CO_2 flux measurements."

Line 401-406: your fluxes are at the lower end of positive values – this should be stated, and elaborated on to discuss negative fluxes as well as positive ones (as per my earlier comment).

We have added "of positive values".

We have added "For F_{ice}, there were negative CO_2 fluxes at stations FI3 and FI4 (–0.6 mmol C m^{-2} day^{-1} for FI3 and –0.8 mmol C m^{-2} day^{-1} for FI4) (Table 3). These fluxes corresponded to low or negative$\Delta pCO_{2\ b-a}$ as compared to that in atmosphere (Table 2 and Figure 6). Negative CO_2 fluxes should correspond to negative $\Delta pCO_{2\ b-a}$. Therefore, the uncertainty for the calculation of carbonate chemistry may be one reason for the discrepancy in pCO_2 calculation in these conditions (Brown et al., 2014)." in the text.

Line 406: should be "up to +11.8" or somehow make it clear that this is the maximum value.

We agree with your comments. We have added "up to".

Line 432-461: this section emphasises the importance of the temperature gradient in modifying fluxes and gives the impression that this is the most important variable. In fact, the correlation between temperature difference and flux is less strong than the correlation with pCO2 difference between the ice and atmosphere (given in line 310). This would be much clearer and more reflective of what the data show, if both variables were discussed here in terms of their relative importance overall and such a strong emphasis on temperature dampened. I also think it would help to add to figure 5 a panel which plots pCO2 difference vs. flux, to show the two relationships directly.

We agree with your comments. We indicated that both variables ($\Delta pCO_{2\ b-a}$ and temperature difference) affect CO_2 flux. For example, we compared our data (e.g. for station FI6) with a previous study (Nomura et al., 2006) for each variable. The $\Delta pCO_{2\ b-a}$ was similar (297 µatm for Nomura et al., 2006 and 293 µatm for FI6) while temperature difference was not same (4.5°C for Nomura et al., 2006 and 20.2°C for FI6). In addition, the CO_2 flux was +0.7 mmol C m^{-2} day^{-1} for Nomura et al., 2006 and +11.8 mmol C m^{-2} day^{-1} for FI6. These results suggested that temperature difference enhanced the CO_2 flux between sea ice and atmosphere at the same $\Delta pCO_{2\ b-a}$. On the other hand, the variation of $\Delta pCO_{2\ b-a}$ would be modified CO_2 flux as shown in equation ($F_{CO2} = r_b\ k\ \alpha\ \Delta pCO_{2\ b-a}$). For the relationships between CO_2 flux and $\Delta pCO_{2\ b-a}$ as indicated in section 3.4, CO_2 flux values included the effect of the temperature difference. Therefore, it is difficult to divide the relative importance for $\Delta pCO_{2\ b-a}$ and temperature difference.

We have added relationships between pCO_2 and CO_2 flux in figure showing the relationships between temperature and CO_2 flux (Figure 6).

Line 458-459: “for young sea ice likely the frost flower conditions”. Does not make sense.

We agree with your comments. We have changed to “for young sea ice with frost flowers (e.g. station YI1)”.

Line 468-473: from the data presented in table 3, not all stations can be described as showing CO2 sources. Some clearly show sink behaviour (negative fluxes), and for a number of others, the uncertainty on flux estimates cannot confidently be described as a source, e.g. when flux = 0.1±0.1. This is particularly the case given that you state the detection limit as 0.1. This also needs to be considered in your discussion.

We agree with your comments. We have added:

“For F_{ice}, there were negative CO_2 fluxes at stations FI3 and FI4 (–0.6 mmol C m^{-2} day^{-1} for FI3 and –0.8 mmol C m^{-2} day^{-1} for FI4) (Table 3). These fluxes corresponded to low or negative$\Delta pCO_{2\ b-a}$ as compared to that in atmosphere (Table 2 and Figure 6). Negative CO_2 fluxes should correspond to negative $\Delta pCO_{2\ b-a}$. Therefore, the uncertainty for the calculation of carbonate chemistry may be one reason for the discrepancy in pCO_2 calculation in these conditions (Brown et al., 2014).”

Line 476-477: This should not be presented as a conclusion.

We agree with your comments. We have deleted from the text.

Line 485-488: I think you undersell the importance of your work here, and you could make more compelling statements about the role of sea ice in CO2 fluxes in a changing Arctic.

We agree with your comments. We have deleted.

Figure 3. should this cite Hudson et al., 2015?

We agree with your comments. We have added “Hudson et al., 2015” in the Figure 3 caption.

Table 2. Consider adding an extra column for ΔpCO2 (air-sea difference) to aid understanding.

Added as suggested.

Table 3. The key thing that jumps out for me is that natural flux is much higher for frost flowers than snow. I would have thought that’s worth highlighting in your discussion.

We have added “and F_{ff} was higher than F_{snow}, except for station FI1”. We also indicated “Frost flowers are known to promote gas flux, such as CO_2, from the sea ice to the atmosphere (Geilfus et al., 2013; Barber et al., 2014; Fransson et al., 2015).”

Technical corrections
In general, the manuscript is well-written, the technical language is appropriate, and the standard of English is good. However, there are a couple of points to check throughout the text: use of the definite/indefinite article; singular/plural nouns and their following verbs e.g. frost flowers, was/were.

Thank you. During revisions we have tried to have our native-English co authors read through the text to improve the flow.

Line 84: should be transport by molecular diffusion

Changed accordingly.

Line 218: remove hyphens

Changed accordingly.

Line 377: I think 0.0 is a mistake.

F_{snow}/F_{ice} ratio for FI6 was 0.02. Therefore, we indicated it as "0.0".

Table 3: brackets in the top line are confusing.

We have changed.

Anonymous Referee #2
Received and published: 16 February 2018

The manuscript makes interesting observations of CO2 flux through sea ice, but re- quires extensive improvement. It was never articulated how this study is novel. I feel that it perhaps may be novel, but it is unclear how in its current form. Major revisions are needed before this manuscript can be considered publishable. The abstract is borderline uninformative. What are characteristic fluxes? Are these important? Of course CO2 can flux through sea ice, but it's hard for the reader to gage exactly how trivial this is without values in the abstract to justify reading the rest of the paper. The sentence beginning line 61 is a reference dump. What did these studies find and how does it build to the importance (or lack thereof) of the present manuscript?

We are grateful for your assessment of our work. We have now added some more discussion on the results from other work in the Arctic, and to emphasize the lack of observations in the pack ice:

We have added "In the ice covered Arctic Ocean, storm periods, with high wind speeds and open leads are important for air-to-sea CO_2 fluxes (Fransson et al., 2017), due to the under-saturation of the surface waters in CO_2 with respect to the atmosphere. On the other hand, the subsequent ice growth and frost flowers formation in these leads promote ice-to-air CO_2 fluxes in winter (e.g. Barber et al., 2014). Given the fact that Arctic sea ice is shrinking and shifting from multi-year ice to first-year ice, the area of open ocean and thinner seasonal ice is increasing. Therefore, the contribution of open ocean/thinner sea ice surface to the overall CO_2 fluxes of the Arctic Ocean is potentially increasing. However, due to the difficulty in acquiring observations over the winter pack ice, most of the winter CO_2 flux measurements were examined over the Arctic landfast ice. Therefore, there is a definite lack of information on conditions during wintertime, especially from Arctic pack ice." in introduction.

We have changed the final paragraph of the introduction "The Norwegian young sea ICE (N-ICE2015) campaign in winter and spring 2015 provided opportunities to examine CO_2 fluxes between sea ice and atmosphere in a variety of snow and ice conditions in pack ice north of Svalbard. Formation of leads and their rapid refreezing allowed us to examine air–sea ice CO_2 fluxes over thin young sea ice, occasionally covered with frost flowers in addition to the snow-covered older ice that covers most of the pack ice area. The objectives of this study were to understand the effects of i) thin sea ice and frost flowers formations on the air–sea ice CO_2 flux in leads, ii) effect of snow-cover on the air–sea ice CO_2 flux over thin, young ice in the Arctic Ocean during winter and spring seasons, and iii) of the effect of the temperature difference between sea ice and atmosphere (including snow cover) on the air–sea ice CO_2 flux." in introduction.

In the abstract, we have added CO_2 flux values "We found that young sea ice formed in leads, without snow cover, is the most effective in terms of CO_2 flux (+1.0 ± 0.6 mmol C m^{-2} day^{-1}) since the fluxes are an order of magnitude higher than for snow-covered older ice (+0.2 ± 0.2 mmol C m^{-2} day^{-1})." We have added "Rare CO_2 flux measurements from Arctic pack ice show that two types of ice are significant contributors to the release of CO_2 from ice to the atmosphere during winter and spring: young thin ice with thin layer of snow, and old (several weeks) snow covered thick ice.".

68: Sea-ice CO_2 fluxes

Changed accordingly.

On line 81, please see Massman et al. (1995) as the fundamental reference on this topic (https://www.fs.fed.us/rm/pubs_exp_for/glees/exp_for_glees_1995_massman.pdf).

We agree with your comments. We have checked and added.

Somewhat harsh transition before the last paragraph of the introduction. Please state more clearly how the background materials presented tie directly to the proposed study and therefore what makes the present study novel. Material in section 4.3 could help. (note that there are also many reference dumps here. Please explain what the studies found; it is your job to make the reader's job easy (https://www.sesync.org/blog/the- writers-job).

We agree with your comment. Please see our response to your first comment "The manuscript makes interesting observations of CO_2 flux ……and how does it build to the importance (or lack thereof) of the present manuscript?".

on line 132, how was it ensured that placement of chambers did not perturb the pressure gradients in the snow? Creating pressure gradients can push CO2 out (or pull it in).

We agree with your comment. First, the chamber collar was inserted 5 cm into the snow and 1 cm into ice at frost flowers site to avoid air leaks between inside and outside of chamber. Then, chambers were installed over the collar. Therefore, placement of chamber on collar would avoid creation of pressure gradient. In addition, LI-COR 8100-104 chambers used in this study have carefully designed pressure vents to prevent pressure gradients and wind incursion from outside the chamber (Xu L., et al. 2006).
Xu L., et al. 2006. On maintaining pressure equilibrium between a soil CO_2 flux chamber and the ambient air. Journal of Geophysical Research. 111, D08S10, doi:10.1029/2005JD006435.

on 144, please see Bain et al. (2005) as a relevant reference for wind-induced effects (https://www.sciencedirect.com/science/article/pii/S0168192305001164)

Thank you. We have checked and added.

Frost flowers are first introduced in the paragraph beginning on line 146. One assumes that these are somehow important for CO2 flux? The notion was not previously introduced. (see line 360. This belongs in the intro). I agree with Reviewer 1 that the manuscript was prepared somewhat hastily.

We have added "In addition, Fransson et al. (2015) indicated that frost flowers promote CO_2 flux from the ice to the atmosphere." in the introduction. We also mentioned "F_{ff}" in the method section.

153: what is station FI6? Abbreviations are introduced before they are explained. It would help to explain the geography of the site before the measurements, also to ensure that measurements were made with a random design in mind.

We have changed "Air–sea ice CO_2 flux measurements were done over young ice (YI stations), first-year ice (FI stations), and old ice (multi-year ice) (OI station).". We also referred to the table where all the stations are listed.

Extensive English improvement is needed in section 2.3

We agree with your comment. The native English-speaking co-author has now edited section 2.3 and gone through the text.

On line 266, what does 'near-constant 0 C' mean?

We agree with your comment. We have changed to “near 0”.

60.0 cm sounds rather specific for a measurement of snow which I assume has frequent small undulations, either at the snow surface or snow-ice interface in section 3.4, per day is not a SI unit, and diurnal patterns in the flux may make it difficult to scale from the native measurements (in the SI units of seconds) to the full day.

Snow is variable, but given that these are spot measurement we report to snow depth at site of measurement, as it is the local conditions that will affect the conditions at the measurement site ice surface. We would like to keep unit used in this study because sea ice CO_2 flux community used in the previous studies and it would be convenient for comparisons.

416: the abbreviation F was introduced far earlier.

Correct, (F) deleted from the sentence.

432: this is actually interesting. By focusing on the challenge of estimating gas transfer velocity, the manuscript has some novel features. These might be initial hypotheses for future work if causality can’t be determined, but the mechanisms of sea ice/atmosphere gas exchange make for a more interesting analysis even if remaining questions are left.

We agree with your comments. We estimated gas transfer velocity for station FI6 and tank experiment. The gas transfer velocity for F_{ice} at station FI6 is higher than that of tank experiment examined in Nomura et al. (2006) even with very similar$\Delta pCO_{2\ b\text{–}a}$ and brine volume fraction. Therefore, our results clearly indicated that temperature difference between sea ice surface and atmosphere would produce an unstable air density gradient and upward transport of air, thereby increasing gas transfer velocity. The comparison of the gas transfer velocity would be useful to evaluate the temperature effect on the air-sea ice CO_2 flux.

Figure 4: avoid simultaneous use of red and green in a figure.

We agree with your comments. We have changed.

CO_2 flux over young and snow-covered Arctic pack ice in winter and spring

Nomura Daiki 2018/3/24 0:22
削除: sea

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Abstract

Rare CO_2 flux measurements from Arctic pack ice show that two types of ice are significant contributors to the release of CO_2 from ice to the atmosphere during winter and spring: young thin ice with thin layer of snow, and old (several weeks) snow covered thick ice. Young thin sea ice is characterized by high salinity and then porosity and thin layer of snow. Snow covered thick ice can remain relatively warm (>-7.5°C) due to a thick insulating snow cover despite air temperatures were as low as –40°C. Brine volume fractions of these two ice type are therefore high enough to provide favorable conditions for gas exchange between sea ice and the atmosphere even in mid-winter. Although the potential CO_2 flux from sea ice decreased due to the presence of the snow, the snow surface is still a CO_2 source to the atmosphere for low snow density and thin snow conditions. We found that young sea ice formed in leads, without snow cover, is the most effective in terms of CO_2 flux ($+1.0 \pm 0.6$ mmol C m^{-2} day^{-1}) since the fluxes are an order of magnitude higher than for snow-covered older ice ($+0.2 \pm 0.2$ mmol C m^{-2} day^{-1}).

Mats Granskog 2018/3/23 6:46
削除: We

Bruno Delille 2018/3/27 1:35
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1 Introduction

Arctic sea ice is changing dramatically, with rapid declines in summer sea ice extent and a shift towards younger and thinner first-year ice rather than thick multi-year ice (e.g., Stroeve et al., 2012; Meier et al., 2014; Lindsay and Schweiger, 2015). Although the effects of sea ice formation and melting on biogeochemical cycles in the ocean have previously been discussed (e.g., Vancoppenolle et al., 2013), the effects of sea ice freezing and melting on the carbon dioxide (CO_2) exchange with the atmosphere are still large unknowns (Parmentier et al., 2013).

Recent CO_2 flux measurements on sea ice indicate that sea ice is an active component in gas exchange between ocean and atmosphere (Nomura et al., 2013; Geilfus et al., 2013; 2014; Delille et al., 2014; Brown et al., 2015; Kotovitch et al., 2016). The sea-ice CO_2

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fluxes depend on (a) the difference in the partial pressure of CO_2 (pCO_2) between the sea ice surface and air, (b) brine volume fraction at the ice-snow interface, (c) ice surface condition including the snow deposited on ice, and (d) wind-driven pressure pumping through the snow. For (a), it is known that the air–sea ice CO_2 flux is driven by the differences in pCO_2 between the sea ice surface and atmosphere (e.g. Delille et al., 2014; Geilfus et al., 2014). The brine pCO_2 changes due to processes within the sea ice, such as thermodynamic process (e.g., Delille et al., 2014), biological activity (e.g., Delille et al., 2007; Fransson et al., 2013; Rysgaard et al., 2013), and calcium carbonate ($CaCO_3$; ikaite) formation and dissolution (e.g., Papadimitriou et al., 2012). When the pCO_2 in the brine is higher than that of the air pCO_2, brine has the potential to release CO_2 to the atmosphere. Brine volume fraction (b) controls permeability of sea ice (Golden et al. 1998) and then CO_2 fluxes (Delille et al. 2014; Geilfus et al 2014). The air–sea ice CO_2 flux is strongly dependent on the sea ice surface conditions (c) (Nomura et al., 2010a, 2013; Geilfus et al., 2013; 2014; Barber et al., 2014; Brown et al., 2015; Fransson et al., 2015). Nomura et al. (2013) proposed that snow conditions (e.g., water equivalent) are important factors affecting gas exchange processes on sea ice. In addition, frost flowers promote CO_2 flux from the ice to the atmosphere (Geilfus et al., 2013; Barber et al., 2014; Fransson et al., 2015). For (d), it is thought that for snow cover, the CO_2 flux is affected by wind pumping (Massman et al.,1995; Takagi et al., 2005) in which the magnitude of CO_2 flux through snow or overlying soil (e.g., Takagi et al., 2005) increases due to wind pumping and can increase the transport relative to molecular diffusion by up to 40% (Bowling and Massman, 2011). These results were mainly found over land-based snow (soil and forest), and thus these processes are not well understood over sea ice (Papakyriakou and Miller, 2011).

In addition to the processes described above, the CO_2 flux over sea ice may also be influenced by the temperature difference between the ice surface and the atmosphere. This has been shown in previous studies in dry snowpacks over land surfaces. These studies show that there is an unstable air density gradient due to heating at the bottom producing a strong temperature difference between bottom and top of snow (e.g., Powers et al., 1985; Severinghaus et al., 2010). This produces air flow within the snowpack, which is a potentially significant contributor to mixing and transport of gas

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and heat within the snowpack. We expect that this process would also occur in snow over sea ice, especially during the wintertime when air temperatures are coldest and the temperature difference between sea ice surface (snow bottom) and atmosphere is largest (e.g., Massom et al., 2001). Generally, the sea ice surface under thick snow cover is warm due to the heat conduction from the bottom of sea ice and the insulation effect of the snow cover, and a strong temperature difference between sea ice surface and atmosphere is observed (e.g., Massom et al., 2001). Such a temperature difference would produce an unstable air density gradient and upward transport of air containing CO_2 degassed at the sea-ice surface, thereby enhancing CO_2 exchange between sea ice and atmosphere.

In the ice covered Arctic Ocean, storm periods, with high wind speeds and open leads are important for air-to-sea CO_2 fluxes (Fransson et al., 2017), due to the under-saturation of the surface waters in CO_2 with respect to the atmosphere. On the other hand, the subsequent ice growth and frost flowers formation in these leads promote ice-to-air CO_2 fluxes in winter (e.g. Barber et al., 2014). Given the fact that Arctic sea ice is shrinking and shifting from multi-year ice to first-year ice, the area of open ocean and thinner seasonal ice is increasing. Therefore, the contribution of open ocean/thinner sea ice surface to the overall CO_2 fluxes of the Arctic Ocean is potentially increasing. However, due to the difficulty in acquiring observations over the winter pack ice, most of the winter CO_2 flux measurements were examined over the Arctic landfast ice. Therefore, there is a definite lack of information on conditions during wintertime, especially from Arctic pack ice.

The Norwegian young sea ICE (N-ICE2015) campaign in winter and spring 2015 provided opportunities to examine CO_2 fluxes between sea ice and atmosphere in a variety of snow and ice conditions in pack ice north of Svalbard. Formation of leads and their rapid refreezing allowed us to examine air–sea ice CO_2 fluxes over thin young sea ice, occasionally covered with frost flowers in addition to the snow-covered older ice that covers most of the pack ice area. The objectives of this study were to understand the effects of i) thin sea ice and frost flowers formations on the air–sea ice CO_2 flux in leads, ii) effect of snow-cover on the air–sea ice CO_2 flux over thin, young ice in the

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Arctic Ocean during winter and spring seasons, and iii) of the effect of the temperature difference between sea ice and atmosphere (including snow cover) on the air–sea ice CO_2 flux.

2 Materials and Methods

2.1 Study area

This study was performed during N-ICE2015 campaign with R/V Lance in the pack ice north of Svalbard from January to June 2015 (Granskog et al., 2016). Air–sea ice CO_2 flux measurements were carried out from January to May 2015 during the drift of floes 1, 2, and 3 of the N-ICE2015 campaign (Figures 1 and 2, Table 1). The ice pack was a mixture of young ice, first-year ice and second-year ice (Granskog et al., 2017), the two latter with a thick snow cover (Merkouriadi et al., 2017; Rösel et al., 2018). Air–sea ice CO_2 flux measurements were done over young ice (YI stations), first-year ice (FI stations), and old ice (multi-year ice) (OI station). In the N-ICE2015 study region modal ice thickness was about 1.3–1.5 m and modal snow thickness was about 0.5 m (Rösel et al., 2018). Formation of leads and their rapid refreezing provided us the opportunity to examine air–sea ice CO_2 fluxes over thin sea ice, occasionally covered with frost flowers at station YI1 (Figure 2 and Table 1). Air temperature and wind speed were measured at a 10 m weather mast on the ice floe installed about 400 m away from R/V Lance (Cohen et al., 2017).

2.2 CO_2 flux measurements

The air–sea ice CO_2 flux was measured with LI-COR 8100-104 chambers connected to a LI-8100A soil CO_2 flux system (LI-COR Inc., USA) (Figure 2). This enclosed chamber method has been widely applied over snow and sea ice (e.g., Schindlbacher et al., 2007, Geilfus et al., 2015). Two chambers were connected in a closed loop to the infrared gas analyzer (LI-8100A, LI-COR Inc., USA) to measure CO_2 concentration

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through the multiplexer (LI-8150, LI-COR Inc., USA) with an air pump rate at 3 L min^{-1}. Power was supplied by a car battery (8012-254, Optima Batteries Inc., USA). Four CO_2 standards (324–406 ppmv) traceable to the WMO scale (Inoue and Ishii, 2005) were prepared to calibrate the CO_2 gas analyzer prior to the observations. CO_2 flux was measured in the morning or in the afternoon during low-wind conditions (Table 2), to minimize the effect of wind on the flux (Bain et al., 2005).

One chamber was installed over undisturbed snow or frost flowers over the ice surface. The chamber collar was inserted 5 cm into the snow and 1 cm into ice at frost flowers site to avoid air leaks between inside and outside of chamber. The second chamber was installed on bulk sea ice after removing the snow or frost flowers. Flux measurements was begun immediately in order to minimize the changes of the ice surface condition. In order to evaluate the effect of removing snow on sea ice surface temperature, ice surface temperature was monitored during CO_2 flux measurements at station FI6. To measure the sea ice surface temperature, temperature sensor (RTR 52, T & D Corp., Japan) was installed in the top of the ice (1 cm) surface after snow removal. During first CO_2 flux measurements (about 30 minutes), ice surface temperature was stable at –5.8°C, suggesting that the effect of removing snow on the variation of sea ice surface temperature was negligible within 30 minutes. The ice surface temperature decreased from –5.8°C to –8.0°C at 200 minutes after removal of snow. Therefore, in this paper, the data of the initial 30 minutes of CO_2 flux measurement after removal of snow or frost flowers was used. The chamber was closed for 20 minutes in a sequence. The 20-minute time period was used because CO_2 fluxes over sea ice are much smaller than over land. The CO_2 concentrations within the chamber were monitored to ensure that they changed linearly throughout the measurement period (example given in Figure 3). The CO_2 flux (mmol C m^{-2} day^{-1}) (positive value indicates CO_2 being released from ice surface to air) was calculated based on the changes of the CO_2 concentration within the headspace of the chamber with LI-COR software (Model: LI8100PC Client v.3.0.1.). The mean coefficient of variation for CO_2 flux measurements was less than 3.0% for CO_2 flux values larger than ±0.1 mmol C m^{-2} day^{-1}. For CO_2 flux values smaller than ±0.1 mmol C m^{-2} day^{-1}, the mean coefficient of variation for CO_2 flux measurements

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was higher than 3.0%, suggesting that the detection limit of this system is about 0.1 mmol C m^{-2} day^{-1}.

In this paper, we express the CO_2 flux measured over the snow and frost flowers as F_{snow} and F_{ff}, respectively, and the flux measured directly over the sea ice surface either on snow-free ice or after removal of snow and frost flowers as F_{ice}. F_{snow} and F_{ff} are the natural flux (snow and frost flowers are part of the natural system), and F_{ice} is the potential flux in cases when snow or frost flowers are removed. While removal of snow and frost flowers is an artificial situation, comparisons between F_{ice} and F_{snow} or F_{ff} provide information about the effect of snow on the CO_2 flux. Therefore, in this study, we examine both situations for CO_2 flux.

2.3 Sampling of snow, frost flowers, brine, and sea ice

For salinity measurements, separate samples were taken for snow only, snow and frost flowers, and sea ice surface scrapes. The samples were taken using a plastic shovel, placed into plastic bags and stored in an insulated box for transport to the ship-lab for further processing. Samples were melted slowly (2–3 days) in the dark at +4°C. The temperature of the snow and frost flowers samples were measured during CO_2 flux measurements (approximately 60 minutes after the onset of the CO_2 flux measurement) using a needle-type temperature sensor (Testo 110 NTC, Brandt Instruments, Inc., USA). The accuracy of this sensor is ±0.2°C. Snow density was obtained using a fixed volume sampler (Climate Engineering, Japan) and weight measurement. The depth of the snow pack and frost flowers was also recorded using a ruler.

Brine was also collected at stations FI3–6 for salinity, dissolved inorganic carbon (DIC) and total alkalinity (TA) measurements. Brine was collected from sackholes as described in Gleitz et al. (1995). The sackholes were drilled using a 9 cm diameter ice corer (Mark II coring system, Kovacs Enterprises, Inc., USA) to a depth of 30 cm. The sackholes were then covered with a lid of 5 cm-thick urethane to reduce heat and gas transfer between brine and atmosphere. When brine accumulated at the bottom of the

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sackholes (approximately 15 minutes), it was collected with a plastic syringe (AS ONE Corporation, Japan) and kept in 500 mL unbreakable plastic bottles (I-Boy, AS ONE Corporation, Japan) in order to facilitate safe transport to the sampling sites in cold and harsh conditions. The brine bottles were filled without head-space and immediately stored in an insulated box to prevent freezing. Immediately after return to the ship, the brine samples were transferred to 250 mL borosilicate bottles (DURAN Group GmbH, Germany) for DIC and TA measurements using tubing to prevent contact with air. The samples were preserved with saturated mercuric chloride ($HgCl_2$, 60 µL for a 250 mL sample) and stored in the dark at +10°C until analyses was performed at the Institute of Marine Research, Norway.

Sea ice was collected by same ice corer as described for brine collection and at the same location as snow and frost flowers were collected. Sea ice temperature was measured by same sensor as described for snow. For the ice cores, the temperature sensor was inserted in small holes drilled into the core. The core was then cut with a stainless steel saw into 10 cm sections and stored in plastic bags for subsequent salinity measurements. The ice core sections were kept at +4°C and melted in the dark prior to measurement.

2.4 Sample analysis

Salinities for melted snow, frost flowers, sea ice, and brine were measured with a conductivity sensor (Cond 315i, WTW GmbH, Germany). For calibration of salinity measurement, a Guildline PORTASAL salinometer Model 8410A, standardized by International Association for the Physical Sciences of the Oceans (IAPSO) standard seawater (Ocean Scientific International Ltd, UK) was used. Accuracy of this sensor was ±0.003.

Analytical methods for DIC and TA determination are fully described in Dickson et al. (2007). DIC in brine was determined using gas extraction of acidified sample followed by coulometric titration and photometric detection using a Versatile Instrument for the Determination of Titration carbonate (VINDTA 3C, Germany). TA of brine was

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determined by potentiometric titration of 40 mL sample in open cell with 0.05 N hydrochloric acid using a Titrino system (Metrohm, Switzerland). The average standard deviation for DIC and TA, determined from replicate sample analyses from one sample, was within ±2 μmol kg^{-1} for both DIC and TA. Accuracy of the DIC and TA measurements were ±2 μmol kg^{-1} for both DIC and TA estimated using Certified Reference Materials (CRM, provided by A. G. Dickson, Scripps Institution of Oceanography, USA). The pCO_2 of brine ($pCO_{2\ b}$) was derived from in situ temperature, salinity, DIC and TA of brine using the carbonate speciation program CO2SYS (Pierrot et al., 2006). We used the carbonate dissociation constants (K_1 and K_2) of Mehrbach et al. (1973) as refit by Dickson and Millero (1987), and the KSO_4 determined by Dickson (1990). The conditional stability constants used to derived pCO_2 are strictly only valid for temperatures above 0 °C and salinities between 5 and 50. Studies in spring ice indicated that seawater thermodynamic relationships may be acceptable in warm and low-salinity sea ice (Delille et al., 2007). In sea ice brines at even moderate brine salinities of 80, Brown et al. (2014) found that measured and calculated values of the CO_2 system parameters can differ by as much as 40%. On the other hand, because the CO_2 system parameters are much more variable in sea ice than in seawater, sea ice measurements demand less precision than those in seawater. Fransson et al. (2015) performed one of few detailed analyses of the internal consistency using four sets of dissociation constants and found that the deviation between measured and calculated DIC varied between ±6 and ±11 μmol kg^{-1}, respectively. This error in calculated DIC was considered insignificant in relation to the natural variability in sea ice.

The pCO_2 of atmosphere was calculated from CO_2 concentration (ppmv) at Ny-Ålesund, Svalbard (http://www.esrl.noaa.gov/gmd/dv/iadv/) taking into account saturated water vapor and atmospheric pressure during sampling day.

The water equivalent was computed for snow by multiplying snow thickness by snow density (Jonas et al., 2009). Brine volume of sea ice was calculated from the temperature and salinity of sea ice according to Cox and Weeks (1983) and Petrich and Eicken (2010).

3 Results

3.1 Air temperature

Air temperature is shown in Figure 4. During the study period, air temperature varied significantly from a low of –41.3°C (30 January) to a high of +1.7°C (15 June) (Hudson et al., 2015). Even in wintertime (from January to March), rapid increases of air temperature from below –30°C up to –0.2°C (e.g., 18 February), were observed. In springtime (from April to June), the air temperature increased continuously, and from 1 June, air temperatures were near 0°C, although rapid increases (and subsequent decreases) of air temperature to near 0°C were observed on two occasions in mid-May (Cohen et al., 2017).

3.2 Characteristics of snow, sea ice, and frost flowers

The snow and ice thickness at the observation sites ranged between 0.0 and 60.0 cm and between 15.0 and >200 cm, respectively (Table 1). The thin snow and ice represent newly formed ice in leads at station YI1. The thickness of the frost flowers ranged from 1.0 to 2.5 cm.

Figure 5 shows vertical profiles of snow and ice temperature and salinity in the top 20 cm of ice. Temperatures within the snowpack depended on the air temperature at the time of observation. However, the bottom of the snow and the surface of the sea ice were relatively warm (T>–7.5°C), except for the frost flowers station YI1 and the multi-year ice station OI1 (Figure 5a and Table 2). High salinities (S>18.6) characterized the bottom of the snow and the surface of the sea ice except for the multi-year ice station OI1 (Figure 5b). At the multi-year ice station OI1, salinity was zero through the snow and top of sea ice. Salinity of frost flowers was up to 92.8 for the thin ice station YI1 (Figure 5b). Snow density and water equivalent ranged from 268 to 400 kg m^{-3} and 11 to 180 kg m^{-2}, respectively.

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3.3 Physical and chemical properties of brine

The brine volume fraction, temperature, salinity, DIC, TA, and calculated pCO_2 are summarized in Table 2. Brine volume fraction in top 20 cm of ice was from 9 to 17%, except for the value of 0% at the multi-year ice station OI1 (Table 2). Brine temperatures and salinity ranged from −5.3 to −3.3°C and 51.8 to 86.6, respectively. DIC and TA of brine ranged from 3261 to 4841 µmol kg^{-1} and 3518 to 5539 µmol kg^{-1}, respectively. The pCO_2 of brine ($pCO_{2\ b}$) (334−693 µatm) was generally higher than that of atmosphere ($pCO_{2\ a}$) (401 ± 7 µatm), except for station FI4.

3.4 CO_2 flux

Table 3 summarizes the CO_2 flux measurements for each surface condition. For undisturbed natural surface conditions, i.e. measurements directly on the snow surface (F_{snow}) or the frost flowers (F_{ff}) on young ice, the mean CO_2 flux was +0.2 ± 0.2 mmol C m^{-2} day^{-1} for F_{snow} and +1.0 ± 0.6 mmol C m^{-2} day^{-1} for F_{ff}. The potential flux in cases when snow or frost flowers had been removed (F_{ice}) was +2.5 ± 4.3 mmol C m^{-2} day^{-1}. The air–sea ice CO_2 fluxes measured over the ice surface (F_{ice}) increased with increasing difference in pCO_2 between brine and atmosphere ($\Delta pCO_{2\ b\text{–}a}$) with significant correlation ($R^2 = 0.9$, $p < 0.02$), but this was not the case for F_{snow} ($R^2 = 0.0$, $p < 0.96$) (Figure 6).

4 Discussion

4.1 Effect of snow cover on the physical properties of sea ice surface

In this study, we examined CO_2 fluxes between sea ice and atmosphere in a variety of air temperature conditions from –32 to –3°C and diverse snow and ice conditions (Table 2). The bottom of the snow pack and the surface of the sea ice remained relatively warm (>–7.5°C) (Figure 5a, Table 2), except for stations OI1 and YI1, even though air temperature was sometimes below –40°C (Figure 4). Relatively warm ice temperatures were likely due to the upward heat transport from the bottom of the ice and in some cases the thick insulating snow cover, except for stations OI1 and YI1 (Table 2). Therefore, snow acted as thermal insulator over sea ice, and in general the snow depths observed during N-ICE2015 point towards this being representative for first-year and second-year or older ice in the study region in winter 2015 (Rösel et al., 2018). The young and first-year ice surfaces were characterized by high salinities (Figure 5b). During sea ice formation, upward brine transport to the snow pack occurs (e.g., Toyota et al., 2011). In addition, brine within the sea ice was not completely drained as compared to that of multi-year ice. Furthermore, formation of frost flowers and subsequent wicking up of surface brine into the frost flowers also provides high salinity at the surface of sea ice (Kaleschke et al., 2004; Geilfus et al., 2013; Barber et al., 2014; Fransson et al., 2015) as observed in this study (S>92) (Figure 5b). Snowfall over the frost flowers would have preserved the high salinity at the bottom of snow pack and top of sea ice for young and first-year ice.

As a result of the combination of the relatively high temperature and high salinity at the top of sea ice, brine volume fractions in the upper parts of the sea ice were high, up to 17% (Table 2). It has been shown that ice permeability increases by an order of magnitude when brine volume fraction > 5%, which would correspond to a temperature of –5°C for a bulk ice salinity of 5 – the so called "law of fives" (Golden et al., 1998; Pringle et al., 2009; Zhou et al., 2013). Because sea ice temperatures were low and thereby reduced permeability in winter season, generally, air–sea ice CO_2 flux is at its minimum in the winter (e.g., Delille et al., 2014). However, in our study, the brine volume fractions were generally >9%, except for station OI1 with fresh ice at the surface, providing conditions for active gas exchange within sea ice and between sea ice and atmosphere. This situation was likely made possible due to the thick snow cover and relatively thin and young sea ice.

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4.2 CO_2 fluxes over different sea-ice surface types

The CO_2 flux measurements over different surface conditions indicate that the snow cover over sea ice affects the magnitude of air–sea ice CO_2 flux, especially for stations FI5 and FI6 (Table 3). For undisturbed natural surface conditions, the CO_2 flux measured directly over snow-covered first-year ice and young ice with frost flowers (F_{snow} and F_{ff}) was lower in magnitude than that for potential flux obtained directly over the ice surface after removing snow (F_{ice}), especially for stations FI5, FI6, and YI1.

F_{ff} indicates that the frost flowers surface on young thin ice is a CO_2 source to the atmosphere and F_{ff} was higher than F_{snow}, except for station FI1. Frost flowers are known to promote gas flux, such as CO_2, from the sea ice to the atmosphere (Geilfus et al., 2013; Barber et al., 2014; Fransson et al., 2015). At multi-year ice station OI1, neither snow or ice surface acted as a CO_2 source/sink. The surface of multi-year ice did not contain any brine (Figure 5b and Table 2), and the top of the ice was clear, colorless and very hard, suggesting superimposed formation at the top of sea ice. This situation would be similar as for freshwater-ice and superimposed-ice as these non-porous media block gas exchange effectively at the sea ice surface (Delille et al., 2014). Snow-ice and superimposed-ice were frequently found in second-year ice cores during N-ICE2015 (Granskog et al., 2017), so the 'blocking' of gas exchange in second-year and multi-year ice may be a widespread process in the Arctic.

The magnitude of positive F_{snow} is less than F_{ice} for stations FI5 and FI6 (Table 3) indicating that the potential CO_2 flux from sea ice decreased due to the presence of snow. Previous studies have shown that snow accumulation over sea ice effectively impede CO_2 exchange (Nomura et al., 2013; Brown et al., 2015). Nomura et al. (2013) reported that 50–90% of the potential CO_2 flux was reduced due to the presence of snow/superimposed-ice at the water equivalent of 57–400 kg m^{-2}, indicating that the snow properties are an important factor that controls the CO_2 exchange through a snowpack. Comparisons between stations FI5 and FI6 for F_{snow}/F_{ice} ratio (0.2 for FI5

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and 0.0 for FI6) and water equivalent (11 kg m^{-2} for FI5 and 127 kg m^{-2} for FI6) indicate that the potential CO_2 flux is reduced (80% for FI5 and 98% for FI6 of the potential CO_2 flux) with increasing water equivalent. Although the magnitude of the potential CO_2 flux through the sea ice surface decreased by the presence of snow for stations FI5 and FI6 (Table 3), the snow surface still presents a CO_2 source to the atmosphere for low snow density and shallow depth conditions (e.g., +0.6 mmol C m^{-2} day^{-1} for FI5).

For F_{ice}, there were negative CO_2 fluxes at stations FI3 and FI4 (–0.6 mmol C m^{-2} day^{-1} for FI3 and –0.8 mmol C m^{-2} day^{-1} for FI4) (Table 3). These fluxes corresponded to low or negative$\Delta pCO_{2\ b\text{–}a}$ as compared to that in atmosphere (Table 2 and Figure 6). Negative CO_2 fluxes should correspond to negative $\Delta pCO_{2\ b\text{–}a}$. Therefore, the uncertainty for the calculation of carbonate chemistry may be one reason for the discrepancy in pCO_2 calculation in these conditions (Brown et al., 2014).

4.3 Comparison to earlier studies on sea-ice to air CO_2 flux

The CO_2 fluxes measured over the undisturbed natural surface conditions (F_{snow} and F_{ff}) in this study ranged from +0.1 to +1.6 mmol C m^{-2} day^{-1} (Table 3), which are at the lower end of the reported range based on the chamber method and eddy covariance method for natural and artificial sea ice (–259.2 to +74.3 mmol C m^{-2} day^{-1}) (Zemmelink et al., 2006; Nomura et al., 2006, 2010a, 2010b, 2013; Miller et al., 2011; Papakyriakou and Miller, 2011; Geilfus et al., 2012, 2013; 2014; Barber et al., 2014; Delille et al., 2014; Sørensen et al., 2014; Brown et al., 2015; Kotovitch et al., 2016). Direct comparison to previous studies is complicated because CO_2 flux measurements with both chamber and eddy covariance techniques were used during different condition for season and ice surface characteristics. In addition, discrepancies between chamber and eddy covariance measurements of air-ice CO_2 fluxes have been repeatedly observed. The footprint size of CO_2 exchange measured with the two approaches (Zemmelink et al., 2006, 2008; Burba et al., 2008; Amiro, 2010; Miller et al., 2011; Papakyriakou and Miller, 2011; Sørensen et al., 2014; Miller et al., 2015) may be one reason for the large

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difference. The eddy covariance method reflects a flux integrated over a large area, that can contain several different surface types. Therefore, eddy-covariance appears to be more useful for understanding fluxes at large special and temporal scales. On the other hand, the chamber method reflects the area where chamber was covered, and it is useful for understanding the relationship between fluxes and ice surface conditions on smaller scales. The different spatial scales of the two methods may be therefore one reason for the discrepancy in CO_2 flux measurements.

Comparison of the natural CO_2 flux range (+0.1 to +1.6 mmol C m^{-2} day^{-1} for F_{snow} and F_{ff}) (Table 3) with previous estimates derived from the chamber method (–5.2 to +6.7 mmol C m^{-2} day^{-1}) (Nomura et al., 2006, 2010a, 2010b, 2013; Geilfus et al., 2012, 2013; 2014; Barber et al., 2014; Delille et al., 2014; Brown et al., 2015; Kotovitch et al., 2016) (these studies include both natural and potential fluxes) shows that CO_2 fluxes during NICE2015 experiment are at the lower end of positive values. However, our potential CO_2 flux (F_{ice}) was a larger CO_2 source (up to +11.8 mmol C m^{-2} day^{-1}) than reported in previous studies (+6.7 mmol C m^{-2} day^{-1}). In our study, the maximum potential flux (e.g., +11.8 mmol C m^{-2} day^{-1}) was obtained for F_{ice} at station FI6 (Table 3). In this situation, $\Delta pCO_{2\ b\text{–}a}$ (293 µatm) was the highest (Table 2 and Figure 6), and it is reasonable to consider this as the highest magnitude of positive CO_2 flux within our study. However, a previous study by closed chamber method showed that even for a similar $\Delta pCO_{2\ b\text{–}a}$ (297 µatm) and magnitude for the brine volume fraction (10–15%), the CO_2 flux was +0.7 mmol C m^{-2} day^{-1} for artificial sea ice with no snow in the tank experiment (Nomura et al., 2006).

The CO_2 flux between the sea ice and overlying air can be expressed by the following equation,

$$F_{CO_2} = r_b\, k\, \alpha\, \Delta pCO_{2\ b\text{–}a},$$

where r_b is the ratio of surface of the brine channel to sea ice surface, and we assume that the value of r_b is equal to brine volume fraction, k is the gas transfer velocity, α is the solubility of CO_2 (Weiss, 1974), and $\Delta pCO_{2\ b\text{–}a}$ is the difference in pCO_2 between

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brine and atmosphere. The equation is based on the fact that CO_2 transfer between seawater and air is controlled by processes in the near-surface water (Liss, 1973). The gas transfer velocity (k) calculated from F, r_b, α and $\Delta pCO_{2\ b\text{–}a}$ was 5.12 m day^{-1} for F_{ice} at station FI6 and 0.29 m day^{-1} for the tank experiment examined in Nomura et al. (2006). This result clearly indicates that the gas transfer velocity for F_{ice} at station FI6 is higher than that of tank experiment examined in Nomura et al. (2006) even with very similar $\Delta pCO_{2\ b\text{–}a}$ and brine volume fraction.

Here, we surmise that the gas transfer velocity and thereby CO_2 flux is greatly enhanced by the temperature difference between sea ice surface and atmosphere. Previous studies indicate that there is an unstable air density gradient in a dry snowpack due to basal heating and the strong temperature difference develops between bottom and top of snow (e.g., Powers et al., 1985; Severinghaus et al., 2010), which enhances the flow of air through the snowpack. We propose that the mixing and transport of gas within the snowpack could also occur over sea ice. Because temperatures at the bottom of snow and the top of sea ice were relatively warm due to a thick insulating snow over sea ice, there was a strong temperature difference between sea ice surface and atmosphere when air temperature was low (Figure 5a and Table 2). For station FI6, temperature difference between sea ice surface and atmosphere was 20.2°C after snow removal. On the other hand, in the tank experiment by Nomura et al. (2006), the temperature difference between sea ice surface (top 1.5 cm) and air in the headspace was only 4.5°C.

Figure 6 shows the relationship between mean air–sea ice CO_2 fluxes and temperature difference between ice and atmosphere. The strong dependence of CO_2 flux with temperature difference (T_{ice}–T_a) was observed, especially for F_{ff} and F_{ice} ($R^2 > 0.7$, $p < 0.01$) (Figure 6). Due to the high brine volume fractions (Table 2), sea ice surface had enough permeability for gas exchange. In addition, ice temperatures were similar for young and first-year ice (Figure 6, Table 2), indicating that pCO_2 at the top of sea ice and CO_2 flux would be of similar order of magnitude if thermodynamic processes dominated. Therefore, our results suggest that the CO_2 fluxes even over the frost flowers as a natural condition, would be enhanced by the upward transport of air containing high CO_2 from the surface of sea ice to the atmosphere due to the strong

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temperature difference between sea ice surface and atmosphere. Although the presence of snow on sea ice has potential to produce a larger temperature difference between sea ice surface and atmosphere and promote the upward transport, the magnitude of the CO_2 flux decreased due to the presence of snow. However, for young sea ice with frost flowers (e.g., station YI1), ice surface temperature was warm (Table 2), suggesting that CO_2 flux would be enhanced by the large temperature difference between sea ice surface and atmosphere.

5 Conclusions

We measured CO_2 fluxes along with sea ice and snow physical and chemical properties over first-year and young sea ice north of Svalbard in the Arctic pack ice. Our results suggest that young thin snow-free ice, with or without frost flowers, is a source of atmospheric CO_2 due to the high pCO_2 and salinity and relatively high sea ice temperature. Although the potential CO_2 flux from sea-ice surface decreased due to the presence of snow, snow surface still presents a modest CO_2 source to the atmosphere for low snow density and shallow depth situations. The highest ice to air fluxes were observed over thin young sea ice formed in leads. During N-ICE2015 the ice pack was dynamic, and formation of open water was associated with storms, where new ice was formed. The subsequent ice growth in these leads becomes important for the ice-to-air CO_2 fluxes in winter due to the fact that the flux from young ice is an order of magnitude larger than from snow-covered first-year and older ice.

6 Data availability

Data used in this paper will be available at Norwegian Polar Data Centre (data.npolar.no).

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Figure captions

Figure 1. Location map of the sampling area north of Svalbard during N-ICE2015. Image of the sea ice concentrations (a) and station map (b) were derived from Special Sensor Microwave Imager (SSM/I) satellite data for mean of February 2015 and from Sentinel-1 (Synthetic Aperture Radar Sensor) satellite data, respectively.

Figure 2. Photographs of the CO_2 flux chamber system at station YI1 north of Svalbard on Friday 13 March 2015. CO_2 flux chamber was installed over the frost flowers on the new thin ice in the refreezing lead.

Figure 3. Example of the temporal variation in CO_2 concentration (ΔCO_2) in the chambers installed at station YI1 that is use to calculate the CO_2 flux. ΔCO_2 indicates the change in CO_2 concentration inside the chamber since the chamber was closed.

Figure 4. Time series of air temperature measured at the weather mast over the ice floe (10 m height) (Hudson et al., 2015). Blank period indicates no data. Colored symbols indicate the date for the chamber flux measurements. The horizontal dashed line indicates air temperature = 0°C.

Figure 5. Vertical profiles of temperature (a) and salinity (b) in snow and sea ice (top 20 cm). The horizontal line indicates snow–ice interface. Shaded area indicates sea ice. The triangle in (a) indicates the air temperature for each station. For stations FI7 and YI2 and 3, we have no salinity data.

Figure 6. Relationships between mean air–sea ice CO_2 fluxes and temperature difference between ice (T_{ice}) and atmosphere (T_a) (circle) and ice temperature (Tice) (top 20 cm) (cross) for F_{snow} (blue), F_{ff} (black) and F_{ice} (red) for young and first-year sea ice. Relationships between mean air–sea ice CO_2 fluxes and the difference of pCO_2 ($\Delta pCO_{2\ b–a}$) between brine ($pCO_{2\ b}$) and atmosphere ($pCO_{2\ a}$) (triangle) for F_{snow} (solid gray) and F_{ice} (open gray).

Table captions

Table 1. Station, date for CO_2 flux measurement, position, floe number, surface condition, ice type and thickness of snow, frost flowers, and sea ice.

a. Sea ice coring and snow sampling was conducted on 5 March 2015.

b. Sea ice coring and snow sampling was conducted on 10 March 2015.

Table 2. Station, snow density and water equivalent, brine volume fraction, and temperature for sea ice (top 20 cm), brine temperature, salinity, DIC, TA, pCO_2 ($pCO_{2\ b}$), and atmospheric temperature, wind speed, pCO_2 ($pCO_{2\ a}$)[a] and $\Delta pCO_{2\ b–a}$.

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a. $pCO_{2\,a}$ (μatm) was calculated from CO_2 concentration (ppmv) at Ny-Ålesund, Svalbard (http://www.esrl.noaa.gov/gmd/dv/iadv/) taking into account saturated water vapor and atmospheric pressure during sampling day.

b. Mean values for snow column.

c. "−" indicates no data. Due to technical reasons, data of snow, sea ice, and brine were not obtained.

Table 3. CO_2 flux measured over the snow (F_{snow}), frost flowers (F_{ff}), and ice surface (F_{ice}). Values measured directly over undisturbed surfaces (either with frost flowers or on snow surface) at a given station are indicated in bold.

a. Data of first CO_2 flux measurement after removal of snow or frost flowers.

b. "−" indicates no data.

c. Number of measurements in bracket.

d. Data from station OI1 was not included.

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