

## Response to reviewers: Significant methane undersaturation during austral summer in the Ross Sea (Southern Ocean)

We thank the reviewer for the thorough review and constructive suggestions. Please see the point-to-point responses below. The original reviewer comments are in black and our responses are coloured blue. Red texts correspond to the revised manuscript without tracked changes.

### General comments

In this manuscript, the authors present an interesting data set of CH<sub>4</sub> concentration profiles showing the distribution of CH<sub>4</sub> in the water column at 10 locations in the Ross Sea. The measurements were carried out during the austral summer in January 2020 on board of the R/V Xuelong 2. Methane concentration data in the Southern Ocean is scarce, and in this sense, the data set represents a relevant contribution to the community. Nevertheless, the manuscript requires modifications before is suitable for publication.

*Response: Thanks for your interest. We realize that the paper was not clear enough. The paper has been thoroughly modified based on reviewer's comments.*

In terms of the structure of the manuscript, I missed a robust and organized section describing the data collection and methods to support subsequent results and discussion. It is my impression, that the text does not follow a coherent line of thought, jumping back and forth between topics and figures, which makes it hard to trace exactly how the authors arrived to the given results and conclusions. Please see specific comments below.

*Response: Thank you for the comment. The section "Materials and Methods" has now been re-organized and the description of detailed methods were along with the supplement material (Text S1, Table S4-S5, Figure S1). The revised manuscript is focusing on the CH<sub>4</sub> distribution in the Ross Sea and the subsequent consequences of CH<sub>4</sub> uptake during summertime.*

As I mentioned before, the data presented in the manuscript is interesting. However, a deep analysis of the different processes involved in the CH<sub>4</sub> dynamics is missing. The authors focused much of the attention to the dilution effects due to sea-ice melting, leaving aside other relevant processes. I would suggest following a process-based analysis where the relative importance of each mechanisms is assessed, instead of having the melting sea-ice as a central line. Following are my comments, which I hope can contribute to the improvement of this manuscript.

*Response: We do agree with the reviewer that multi-processes cause the CH<sub>4</sub> undersaturation. After re-evaluation of the role sea ice melting in CH<sub>4</sub> undersaturation, we found it is far more complicated than we thought before. The main purpose of this*

*study is reporting CH<sub>4</sub> undersaturation in the Ross Sea. Hence, to keep the manuscript simple and concise, the effect of sea ice melting has been deleted in the revised version. In addition, we have now re-written the “Discussion” to separately discuss the impact of water mixing, vertical convection, CH<sub>4</sub> oxidation, and air-sea exchange on CH<sub>4</sub> distribution. The mass balance calculation has been discussed with Figure 6. Please see our detailed response below.*

### **Specific comments**

#### Abstract:

Is “fresh water injection” considered to be the same process as “advection”? In L.124 is stated that advection is negligible. Please clarify.

*Response: Sorry for this unclear expression. The “fresh water injection” refers to the mixing between ice-melting water and ambient seawater. This sentence has been deleted and the abstract has been re-written.*

L.19-L.21 Please remove the sentence starting with “We estimated that the Southern Ocean...”. This result can be used as part of the discussion to give some perspective to the potential relevance of the region in the global context. However, using three days of data from one specific region to make a final statement about the role of the whole Southern Ocean as a sink or source of CH<sub>4</sub> is not appropriate.

*Response: We agree. This sentence has been deleted.*

#### Introduction:

L.30 I guess “emissions” refer to the “net global oceanic emissions”.

*Response: We have modified as “oceanic CH<sub>4</sub> emissions”.*

L.53 remove “on the basis of our results”

*Response: Done.*

L.54 CH<sub>4</sub> consumption is not mentioned here, while in the abstract is stated to be as equally important as the sea-ice melting. Please clarify and follow a consistent rhetoric throughout the manuscript.

*Response: Thanks for the suggestion. The sentence has been rewritten in the revised version.*

*“the objectives of our study were (i) to determine the distribution of CH<sub>4</sub> in the water column of the Ross Sea, (ii) to decipher the major processes affecting the CH<sub>4</sub> water column distribution and (iii) to determine the role of the Ross Sea as a source or sink of atmospheric CH<sub>4</sub>”*

A paragraph describing the main processes associated with the CH<sub>4</sub> cycle would be very useful to contextualize the discussion and to aid non-expert readers. This could be included after L.31 and could be expressed, for example, using the terms of eq.3 (air-sea flux, diffusion, advection, production/oxidation, etc.), including the relevant aspects of surface CH<sub>4</sub> and water-column distribution.

*Response: A paragraph has been added in the “Introduction”, please see the revised version.*

Materials and Methods:

L.55 I suggest renaming this section to “Data and Methods”.

*Response: Agree. The title has changed as “Methods”. The data report in this section has been moved to the section “Results”.*

After L.55 start by describing the study site and measurements.

L.56 re-name this section as “Hydrographic data and water mass classification”

*Response: Agree. The section has been re-organized and the title was replaced by “2.1 Study site and hydrographic measurements”.*

L.57-L.58 looks more like results (including Fig.2).

L.58 the definition of the different water masses as described in the literature (including Table S1) should be moved further down in the methods section.

*Response: Agree. The sentence (including Fig. 2 and Table S1) has been moved to the “Section 3.1” according to another reviewer’s suggestion.*

L.59-L.71 is not methods. Should be moved to introduction.

*Response: Agree. Done.*

L.72-L.77 this paragraph should be moved further down. Please first describe the site and measurements, before addressing how the data was analyzed.

*Response: Done. It was moved in the section “2.5 Water mass abundance calculation”.*

L.74 what do you mean by sectional area? Aren’t the measurements taken at individual locations each time? Please clarify.

*Response: To calculate the contribution of each water mass, we need to know the total volume of this specific water mass. The measurements were taken as a point, but the calculation on volume needs an “area”. So, assuming the water column at each station is a cylinder, then the “point” can represent the “area” and the volume can be calculated by water depth (the “high”) and the assuming sectional area (surface).*

L.78 please rename. There are two sub-sections named “sampling and analysis”. Make sure an adequate name is given to each section and sub-section.

*Response: Sorry for the typo. Has been corrected as “2.3 Flux density calculations”.*

L.80-L.81 refer to Fig.1 after the sentence “The CH<sub>4</sub> distribution was measured...”. Also please specify at which nine stations where the samples taken.

*Response: Thank you for the suggestion. Done.*

*“The samples for the determination of dissolved CH<sub>4</sub> concentrations were collected at nine stations (R1-R7 and R9/R10) on a transect along 75°S from 164°E–182°E (Figure 1)”*

L.82 even if a detailed description of the sampling method is given in Zhan et al. please include relevant information here, such as sampling depths, measurement times, etc.

*Response: The sampling depth has been mentioned in the section 2.1. The sampling method has introduced after the reference.*

*“seawater was transferred to 250 mL borosilicate glass bottles with standard taper stoppers (Corning PYREX<sup>®</sup>, USA), which were sealed with Apiezon grease (Sigma-Aldrich<sup>®</sup>, USA) and stored in the dark at 4 °C after 180 µL of saturated HgCl<sub>2</sub>(aq) solution was added. Samples were analysed immediately after shipment to the home laboratory (storage time < six months)”*

L.85 move the sentence “Hydrographic data were collected...” to the section “Hydrographic data and water mass classification”, which should follow this section.

*Response: Done.*

L.101 please re-name (see previous comment for L.78)

*Response: Done. Has been titled as “2.3 Flux density calculations”.*

L.108 why use an average wind speed for the gas transfer velocity? This might introduce significant biases in the flux calculations. If wind data are not available during the research cruise (which I would find strange), there are other resources with sufficient resolution that could be used for the analysis. Please reconsider using other alternatives for the  $k_w$  calculations or provide the necessary information to support your decision, including discussion of the uncertainty associated to the calculation using the mean wind value.

*Response: Thank you for the suggestion. We have now used the ship-measured wind speed to calculate the  $k_w$ , which yields a mean flux of  $-0.44 \mu\text{mol m}^{-2} \text{day}^{-1}$ . It is well known that air-sea gas exchange is depending on the variability of the wind and on the choice of the wind speeds. Moreover, air-sea gas exchange is mainly influenced by the choice of the model for  $k_w$ . We did not discuss it in the text because we would like to focus on the topic of CH<sub>4</sub> undersaturation in the Ross Sea.*

L.124-L.125 why is it advection considered negligible? This statement contradicts the text in the abstract (L.16) where advection is considered as one of the two mechanisms leading to the depletion of CH<sub>4</sub> in surface waters. Please explain.

*Response: Sorry for the misleading. The abstract has been modified to avoid contradiction. As you can see from Figure 3 (in the revised version Figure 4), the study site was surrounded by the Ross Ice Shelf and sea ice during our sampling period. Hence, to simplified the mass balance calculation, we assumed that there was no advection at station R3 (90% ice condition and near the coast) in the surface mixed layer (7-39 m, Table S3 in the revised version). The discussion has been mentioned in the section 4.2.*

L.126-L.127 The sentence “Positive values represent...” is confusing. I suggest

“Positive values of  $F_x$  represent transport of CH<sub>4</sub> from the mixed layer to the surroundings, while negative values represent transport into the mixed layer” or similar, if that is what you meant. As I said, it is a bit confusing.

*Response: Sorry for the unclear expression. This sentence has been revised.*

“Positive values of  $F_x$  indicate a production of CH<sub>4</sub> in the mixed layer, while negative values indicate a consumption of CH<sub>4</sub> in the mixed layer.”

### Results:

L.131 here you recognize the relevance of wind as a mixing processes affecting the upper oceanic layer. Why not taking this effect into account when calculating the gas transfer velocity ( $k_w$ ) and the fluxes? Also, the stratification effects caused by the density changes might be more relevant at low wind speeds. While at higher wind speeds, large part of the flux is most probably driven by wind-induced mixing. This is of course not evident if the mean wind speed is used for the gas transfer velocity calculations.

*Response: Thank you for the suggestion. We have now used the instantaneous wind speed to calculate the CH<sub>4</sub> flux. The impact of wind speed on CH<sub>4</sub> flux has been discussed in section 4.3 in the revised paper.*

L.136 Here “Lateral transport of water masses...” is discussed. Is this lateral transport not associated to CH<sub>4</sub> advection? How is CH<sub>4</sub> advection negligible but advection of water masses relevant? Please explain.

*Response: Sorry for the misleading statement. We have now re-built the mass balance calculation followed the reviewer’s suggestions. The advection has been now evaluated and discussed in section 4.2.*

L.139 “Consequently, for the eastern-most stations (R7-R10), the water column...”

*Response: Done*

L.145-L.147 why is the high concentration in R7 only observed at the bottom and not in the whole water column, even when the “warm” temperature is observed from the surface to the bottom? Can this be CH<sub>4</sub> from the sediments in the sea floor? It would be interesting (maybe in the discussion) to briefly explain why this is input from sediments is observed in R7 and not in the other “shallow” stations.

*Response: Thank you for the comment. From limited data, we should say that this question cannot be fully addressed with our data and one of the purposes of this paper is to call upon more observations in the Southern Ocean. Thus, in our paper, we proposed the most probable origin of the high CH<sub>4</sub> value, which was attributed to CH<sub>4</sub> release from the sediments. Any discussion on the origin of this high CH<sub>4</sub> is speculative so we decide to focus the CH<sub>4</sub> undersaturation in the main text.*

*Indeed, we have cautiously discussed these CH<sub>4</sub> concentration anomalies and did not treat them as outliers because 1) the analytical method is reliable (please see Supporting Information), with a low limit of detection (0.04 nmol/L, Table S4) and good*

*precision (5%) and accuracy (0.3 nmol/L) (Table S5). Together with the cautious sampling, storage, and transport of seawater, we believe that the CH<sub>4</sub> data are highly reliable and reflected the field situation; 2) those values have been double-checked and analysed at least 2–3 times; 3) We cannot exclude the possibilities of the presence of other CH<sub>4</sub> sources in the Ross Sea.*

L.148 this section should go together with paragraph in L.130 to L.140, as water masses are also discussed there. Maybe start with a sub-section on water masses, followed with another separate subsection about CH<sub>4</sub> in the water column (i.e. moving L.141-L.147 further down).

*Response: Thank you for the suggestion. The paragraph has been re-organized*

L.151 “would it be expected”, does that mean that SW (contrary to what was expected) is not trapped in deep troughs? Or it is, actually, trapped?

*Response: Sorry for the unclear expression. The sentence has been changed to “SW was trapped in deep troughs (>400 m)”, which is related with the calculation of bulk CH<sub>4</sub> concentration in the SW in the section 4.1.*

L.156 “...was found only near the ice sheet (stations R1-R3), where supercooled...”

*Response: Done.*

L.160 the sea-ice data source is only included in the legend of Fig. 3. It should also be included in the methods.

*Response: The sea-ice data source has been described in “Methods”.*

L.163 “...at the Mawson Bank (stations R1 to R5).”

*Response: Done. In the revised manuscript, we compared the CH<sub>4</sub> concentrations at most- western (R1–R4) and eastern stations (R7–R10) in discussing the role of sea ice condition in CH<sub>4</sub> uptake.*

L.163-L.165 refer to Fig.3d

*Response: Done. In the revised manuscript Figure 4d.*

L.170-L.172 it seems here that all other processes involved in the dynamics of CH<sub>4</sub> in the mixed layer have already been discarded. I think the sentence “We found that mixing ... is responsible for the CH<sub>4</sub> undersaturation in the shelf sea” is farfetched at this point of the manuscript. Please present a thorough assessment of the relevant mechanisms involved in the distribution of CH<sub>4</sub> or as you call it “budget in the mixed layer” before presenting such strong statement.

*Response: Thank you for the constructive suggestion. We have re-organized and re-written the “Discussion”. The mechanisms involved in the distribution of CH<sub>4</sub> undersaturation has been separately discussed in the revised version.*

L.173 I assume “box model calculation” refers to what is described in Sect. 2.4 as the

CH4 budget in the mixed layer. At some point it is also refer to as “mass balance”. Please make use of the terminology in a consistent manner throughout the text.

*Response: Thank you for the suggestion. We have been used the term “mass balance” in the text.*

L.175 “...calculated two box models...”, please refer to Sect. 2.4, Eq. 3.

*Response: Done.*

L.177 “If we assume that lateral transport of CH4 is zero”, why? Please clarify, as in some parts of the manuscript (i.e. the abstract) advection is stated as one of the “important drivers ...” while in other parts of the text is described as “negligible”.

*Response: This is unclear expression. We have added Figure 6 and section 4.2 to discuss the “Surface mixed layer CH4 dynamics”. Please see the revised version.*

L.178 what about measurements in station R7?

*Response: In the revised version, the specific mixed layer depths were given in Table S3 and the mass balance calculation for R7 has been added in the text.*

#### Discussion:

L.183 “The fate of CH4...” use “distribution”, instead.

*Response: The “Discussion” has been re-written.*

L.186 “Hence, the CH4-poor CDW may play an important role...” why is it then that this mechanisms is not given the same importance as sea-ice melting? To me it seems like the main focus is to highlight seaice melting as the cause of CH4 undersaturation, while different mechanisms were also found to be significant for CH4 dynamics. I suggest to not over-focus on one single process as these results are all relevant! Please explore all possibilities.

*Response: Thank you for the comment. We have now re-evaluated the involved processes. We agree with the reviewer that water mixing is important in determining the CH4 undersaturation. After the detailed discussion, we found that the water mixing is the primary factor that determines the distribution of CH4 undersaturation in the Ross Sea, superimposed to the prerequisite of CH4 oxidation. Meanwhile, the level of CH4 undersaturation in the subsurface water is the key factor that determines the rate of vertical transfer and how much CH4 could be uptake from the atmosphere during ice-free periods. These have now been discussed and concluded in the text.*

L.194 the phrase “...may originate from surface water that is sufficiently exposed to the air...” is confusing as, at least during 2020, this western region (stations R1-R5) is the one that was cover with ice for the longest time (Fig. 3). Please explain. Also, could it be the other way around? That this region is most of the time cover by ice and, therefore, with very little interaction with the atmosphere. Thus, CH4 is being stored there due to sediment CH4 production for example (in comparison to the more “open waters” which experience more air-sea exchange). Then again, as I said before, air-sea

gas fluxes (and other mechanisms) might also be relevant!

*Response: We agree that the sentence is misleading so that we have deleted it in the revised version. We thank for the reviewer's detailed the discussion that lighting our thoughts. Please noted that the direction of air-sea exchange was up-to-down, which means more CH<sub>4</sub> would be added in the surface waters when experience longer ice-free periods. We believe that the air-sea exchange is an important factor that influences the CH<sub>4</sub> distribution in surface waters, the interesting thing is that most-eastern stations were more undersaturated with CH<sub>4</sub> even they experience more air-sea exchange. This suggest other factors, such as mixing with CH<sub>4</sub>-poor water, microbial oxidation, and vertical convection, together with gas exchange would determine the degree of CH<sub>4</sub> undersaturation. The corresponding discussions have been added in the revised manuscript.*

L.195- L.208 I do not think these statements are really supported by your observations. This paragraph is confusing but most of all, it is misleading as the main focus seems to be to justify the relevance of sea ice melting. I suggest making a detail assessment of the relative importance of each process involved in the distribution of CH<sub>4</sub> in the region, and then discuss the role of all the relevant mechanisms.

*Response: Thank you for the comment. We have now re-evaluated these mechanisms and re-written the "Discussion".*

L.200 "when sea ice melts in the summer, seawater with undersaturated CH<sub>4</sub> concentrations then continues to be diluted...which in turns leads to a continuous decrease ...within the surface layers" this is, to my understanding, contradicting the previous sentence in L.192 "the oversaturation of CH<sub>4</sub>...may originate from surface water...".

*Response: Sorry for the misleading sentence. We may consider two stages of sea ice melting. (1) Sea ice melting-induced decrease in CH<sub>4</sub> may occur at the initiation of melting that enhance the concentration gradient at the ocean-atmosphere interface. (2) No further melt of sea ice (ice free), the surface CH<sub>4</sub> either close to the equilibrium concentration with the atmosphere with low gas exchange rates, or keep undersaturated status due to other processes (which is our case). The unclear expressions in Line 192 have been deleted and this part has been re-written.*

*"The calculated  $F_{ad}$  was negatively correlated with the ice conditions ( $r^2=0.67$ ,  $p<0.05$ , Figure 6b), which implies a free-ice conditions may enhance the advection of CH<sub>4</sub>-enriched water while the ice-covered conditions may favour lower transport of CH<sub>4</sub>-enriched waters to the mixed layer"*

L.203 "we found that the CH<sub>4</sub> saturation was decreased by 22% at the Pennel Bank...compared to that at the Mawson Bank" can you really conclude this from your observations? Why?

*Response: Since we have no CH<sub>4</sub> data in sea ice, we deleted this point.*

L.205-L.208 "As the ice-free areas increase, ... due to mixing and ...and/or exchange



with the atmosphere. Thus, the magnitude of sea-ice melting may determine the degree...” this sounds much more reasonable. The conditions of the ice may actually affect several biogeochemical and physical processes! But not only changes in CH<sub>4</sub> due to dilution effects.

*Response: Thank you for the suggestion.*

L.211 is it really a box model?

*Response: Has been modified as “mass balance calculation”.*

L.212 “...were influenced by air-sea exchange (40-70%) in the west...(90%) in the east.” These contributions seem relevant, don’t they? Again, I do not understand why the speech along the manuscript is around the dilution due to sea ice melting, when other interesting results are also found.

*Response: Sorry for the misleading sentence. The role of sea ice melting has been deleted and other processes have been discussed in the revised version.*

L.213 maybe add some numbers of the relative importance of the vertical diffusion, similar to what is done for air-sea exchange (in percentage, for example).

*Response: Done. Please see the revised manuscript.*

L.216 is it east or west?

*Response: Sorry for the typo, it is west. Has been modified.*

L.216 this “rapid decline in CH<sub>4</sub>” is not really seen in the west side (if that is what is meant), is it? How? From the data shown here, it seems like the highest saturation values are found in the western side where no decline in CH<sub>4</sub> saturation is observed. I also think that in order to reach such a conclusion, measurements capturing the temporal variability of CH<sub>4</sub> in each station are necessary, which are not provided here.

*Response: We agree that this sentence may cause ambiguity and therefore it has been deleted.*

L.229 what is it meant with “regulations”?

*Response: Sorry for the unclear expression. This paragraph has been modified.*

Technical corrections:

L.15 remove “Simple”

*Response: Done.*

L.31 “...the Southern Ocean in the global CH<sub>4</sub> cycle”

*Response: This sentence has been deleted.*

L.80 “The CH<sub>4</sub> vertical distribution...”

*Response: This sentence has been modified as “the determination of dissolved CH<sub>4</sub> concentrations...”.*

L.87 “Triplicate or duplicate CH<sub>4</sub> subsamples...”

*Response: Done.*

L.114 remove “roughly”

*Response: Done.*

L.122 in the equation of the Fick’s first law, it looks strange to me to express the gradient using subscripts. I would suggest using  $dC/dh$  instead of  $dc/dh$ .

*Response: Done.*

L.123 K<sub>z</sub> (in italics)

*Response: Done.*

L.135 “stations R9”

*Response: Done.*

L.155 “...heterogeneous region”

*Response: Done.*

L.214 “The sea ice distribution may be responsible...”

*Response: This sentence has been deleted.*

L.215 “...melting or incompletely partially melting...”

*Response: This sentence has been deleted.*

L.218 “...after completely a complete melting of ...”

*Response: This sentence has been deleted.*

L.233 “..., which will result in a net take up uptake of CH<sub>4</sub>...”

*Response: This sentence has been modified.*

L.263 “Our measurements of CH<sub>4</sub>...”

*Response: Done.*

Throughout the text, refer to figures and tables when introducing and discussing the results.

*Response: Done.*