

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

We would like to express our thanks and appreciation for your interest and comments to our manuscript. Please find below the point-to-point responses to your comments. 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

This paper presents a nice data set on CH₄ water concentration profiles in the Ross Sea during the Summer 2020. This is rare data, which, per se, deserves publication. The data set is interpreted in terms of potential driving processes such as water mass mixing, sea ice melting, biological consumption/production and air-ocean exchange processes. I have however reservations on several aspects of the paper, both in terms of structure of the paper, methodology and conclusions.

Response: We appreciate your interest in our manuscript. We agree that the manuscript can be further improved.

My major concern is that the paper argues that CH₄ profiles in the mixed layer demonstrate the impact of sea ice melting on the CH₄ dynamics in the area. First of all, I have doubts on the pertinent use of CH₄ % saturation vs. Salinity plots to demonstrate the impact of mixing processes. I believe several processes are embedded in the saturation level of CH₄: temperature, salinity changes, air-ocean exchanges biogeochemical processes and not only dilution processes by mixing.

Response: We agree with the reviewer that CH₄ saturation was influenced by several aspects. The saturation was intended to be used for convenient comparison with the equilibrium concentration. Now we have changed the saturation to concentration when discussing the impact of mixing processes.

Also, nowhere in the paper is it made reference to existing CH₄ sea ice concentration data in the Antarctic (they are indeed rare, but they do exist). The latter show bulk ice concentration ranges similar to those presented in the water profiles of this paper, which make it very difficult to explain 22% reduction of CH₄ saturation in the whole (25-50m thick) mixed layer from melting contribution of 1m thick sea ice, even when using minimal sea ice values. Plotting CH₄ concentration values vs. Salinity does not show any trend from West to East along the transect, probably due to partial re-equilibration with the atmosphere (on this I agree with the authors).

Response: Thank you for the suggestion. We have cited the Jacques et al. (2021) for the bulk CH₄ concentration in sea ice. We agree with the reviewer that it is difficult to separate the impact of sea ice melting on CH₄ saturation from other processes (e.g., water mixing, microbial oxidation). We have re-evaluated the role of sea ice melting in

CH₄ undersaturation and found that is far more complicated than we thought before. The sea ice may a source for the bulk CH₄ in ambient seawater but sea ice melting may facilitate the local water mixing and enhanced the vertical convention, which eventually lowers the surface CH₄ concentration. Since we have no sea-ice data, we decided to deleted the relevant speculations (sea ice melting) in the text. We have re-written the Discussion, discussed the role of water mixing, oxidation, and gas exchange in CH₄ undersaturation.

The authors also make an overall budget of CH₄ air-ocean fluxes for the Ross Sea, based on a 3-days cruise flux measurements... which I think is a bit overstretched. More precaution should be taken in presenting those results (e.g. no clues on what happens in the winter!). The authors already reckon that the unbalance is rather insignificant for their observation period extrapolated to the whole summer period in the Ross Sea

Response: We agree. Winter data is important in understanding how sea ice works on CH₄ dynamics. In the revised manuscript, we have highlighted that our calculated fluxes are certainly an underestimation since CH₄ measurements in the Ross Sea as well as in the Southern Ocean from other seasons are largely missing. Besides, the discussion of CH₄ flux are more cautious and only constrained in summer. We realize that the size of dataset is too small to give an overall estimation of CH₄ flux in the Ross Sea but we believe that the conclusions of the study are adequate for the dataset. Importantly, one purpose of this study is calling upon future work in the region, or even in the Southern Ocean, since it is the difficulty to access what makes it so difficult to obtain larger spatial and temporal coverage.

There are also a certain number of contradictions at several places in the manuscript, which I have listed more completely in the detailed comments here below. In short, I think the paper is not yet mature for publication in Biogeosciences. My first reaction would be to reject the paper at this stage, but to encourage the authors to rethink the methodology and interpretation of the data and provide us with a new manuscript. Arguments should be presented to dissociate the impact of temperature, salinity, dilution and biogeochemical processes on the observed saturation states, and how these are disentangled from water mass mixing processes.

Response: We thank the reviewer for pointing out these confusions and encouraging us to revise. We agree that the clarity of the manuscript can be further improved. Below are our point-to-point responses to the concerns.

Detailed Comments

l. 15: Delete sentence “Simple box model...waters.”...this is more like just a mass balance calculation, from the description in the methods...also there is a contradiction with the methodology where it is stated that advection is considered as negligible!(l. 125)

Response: Done. Sorry for the misleading statement. The word “advection” in this sentence has been deleted and the role of advection in CH₄ distribution has been discussed in “Section 4.2 CH₄ dynamics in the surface mixed layer”.

l. 18: add sentence: “Simple mass balance calculations further suggest that CH₄ consumption also contributes to the CH₄ undersaturation.”

Response: Thank you. The sentence has been changed as “the CH₄ concentrations in the mixed layer were mainly driven by air-sea exchange and diapycnal diffusion between surface and subsurface layer, as well as in-situ consumption of CH₄”.

l. 18: Delete “Thus we argue that..” and replace by: “Both CH₄ consumption and sea ice melting are therefore important drivers of CH₄ undersaturation, which implies that the high-latitude area of the Southern Ocean act as a sink for atmospheric CH₄ in the summer.”

Response: This sentence has been deleted.

l. 19-20: This is a summer only budget!... cannot be used as an annual budget”, not knowing what happens in the winter!..

Response: We agree. The sentence has been modified as “the Ross Sea was a significant sink for atmospheric CH₄ during the austral summer”.

l.47-48: “storage of CH₄ in ice crystals is usually a minor source compared to sea ice brines (bubbles or dissolved) and under-ice sea water in the Arctic (..).”

Response: Thank you. Done.

l.53: “we propose that (i)...”

Response: This sentence has been modified as “the objectives of our study were (i) to determine the distribution of CH₄ in the water column of the Ross Sea, (ii) to decipher the major processes affecting the CH₄ water column distribution and (iii) to determine the role of the Ross Sea as a source or sink of atmospheric CH₄”.

l. 54: “..our results from a summer West-East field transect in the Ross Sea...”

Response: This sentence has been deleted.

l. 54: “and (ii) sea ice melting..”

Response: Done.

l. 47-54: This section should refer to the work of Damm et al. on in-situ sea ice CH₄ production and impact on air-sea fluxes in the Arctic

Response: Thank you for the suggestion. The work of Damm et al. (2015; 2018) have been referred in the text.

l. 56: “Hydrographic measurements and..”

Response: Changed to “Study site and hydrographic measurements”.

l. 57: I am missing here the description of the actual measurements!.. CTD, precisions...actually, move material from section 2.2

Response: Done.

l. 57-71: This is not “Method”!.. but more general statements about ocean circulation in the Ross Sea.. This should be moved to “Introduction” (after lines 32-34) , or eventually used in the discussion section

Response: Have been moved to the “Introduction”.

l. 57-58: Figure 2 and Tables S1 are “Results”, not methods

Response: Have been moved to the “Results”.

l. 76: Table S2 and S3 are Results, not Methods

Response: Have been moved to the “Results”.

l. 76-77: not clear what the “total volume” is in this case..

Response: It is the volume of all water masses at a specific station, determine by the water depth.

l. 78: “CH₄ sampling and analysis”

Response: Done.

l. 79-80: “onboard...January 2020”.. move to section 2.1

Response: Done.

l. 85-87: Move to section 2.1

Response: Done.

l. 91: “is calculated by”

Response: Done.

l. 95: “-1.9 to 1.4°C”

Response: Done.

l. 95: “sampling with the atmospheric CH₄...”

Response: Done.

l. 96: South Pole data.. why not use data from closer by?...Arrival Heights?..(<ftp://ftp.niwa.co.nz/CH4/arch>)

Response: Thank you for the suggestion. We believe the data suggested by the reviewer is not necessarily appropriate for this study since it contains integrated values over 120 m above sea level.

l. 101: “2.3 Flux Density Calculations”

Response: Thank you. Done.

l. 107-110: Wind data: I am sure there were true wind data recordings on the Xuelong 2, isn't it?.. It would be more accurate to use those

Response: Thank you for the suggestion, the ship-measured wind data has been used in the revised manuscript.

l. 113: "CH₄ budget in the mixed layer": Is this what you also refer to as "box model" elsewhere in the paper. should be mentioned!.. is it really a "box model"?.. it is indeed more of a mass balance calculation than a "box model"

Response: This sentence has been changed to "CH₄ mass balance calculation in the mixed layer".

l. 114: "In order to give a first estimate of..."

Response: Thank you. Done.

l. 123: This is a true equation for F_{vd}..should have the status of an equation on a separate line

Response: Yes, we agree. Done.

l. 124-125: "advection... negligible".. in contradiction with what is said in the abstract!

Response: Sorry for the misleading statement. The abstract has been modified to avoid contradiction.

l. 127: "sink for the mixed layer"

Response: This sentence has been modified as "Positive values of F_x indicate a production of CH₄ in the mixed layer, while negative values indicate a consumption of CH₄ in the mixed layer".

l. 128: Introduce here figures 1 and 2 and supplementary table with CH₄ concentration... which should actually be grouped with all the rest of the supplementary material!...

Response: Thank you for the suggestion. The supplement has been re-grouped as suggested. Please note that Figure 1a has been separated and as a single figure in the revised text.

l. 130: Figure 1 d should include a plot of $\Delta\sigma$

Response: The density plot has been added (Figure 2c in the revised version).

l. 131: "temperature gradient" .. not differences, given the units..

Response: Done.

l. 141: Introduce also here a few words on the CH₄ concentrations, referring to the table, and indicating low variability overall (1.5-5.2 nM). Figure 1b should also show the CH₄ concentration profiles. Actually Figure 1b deserves to be an isolated figure.

Response: Agree. The sentences have been modified. We also separated Figure 1b as a

new figure. The profile of CH₄ concentration has been added in Figure 2d.

l. 150: “(Figure 2b, Table S2)

Response: Done.

l. 155: “most heterogeneous region”

Response: Done.

l. 156: “was found only closer to the ice sheet and at depth (Table S2)”

Response: Done.

l. 161: “in February 2020”

Response: Done.

l. 164: “ (Figure 3d, stations R1-R5...”

Response: Done.

l. 166-172: This is already “Discussion”

Response: Thank you for the suggestion. These sentences have been moved to the “Discussion”.

l. 163-164: However, CH₄ concentrations are relatively constant in surface waters throughout (ca. 3 nM) so this trend could be S/T impact on saturation rather than dilution through mixing with melted sea ice.

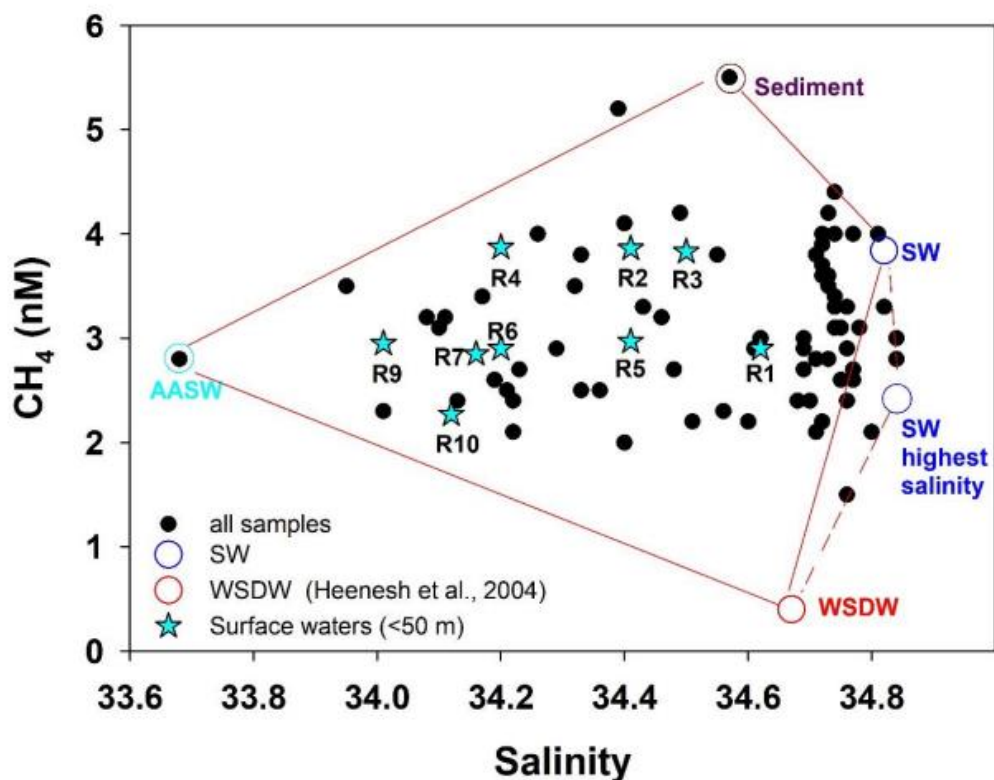
Response: Thank you for the suggestion. We agree that the S/T can influence CH₄ saturation. However, in our cases, this impact is limited because the changes in S (33.7-34.8) and T (-1.8-1.4 °C) are small. Please see the Table below. We used the highest and lowest T and S, with a constant CH₄ concentration, to calculate the saturation that yields a maximum difference of 9% (which is mainly caused by the T differences). In contrast, 1.1 unit differences of salinity yield only 1% difference in saturation. In our study, the mean temperature at the surface (<5 m) in the west and east were 0.1 vs. -0.1 °C and therefore the impact of temperature on CH₄ saturation is limited. Instead, the differences in CH₄ concentrations (3.4 nM in the west vs. 2.8 nM in the east) were mainly caused by convection, water mixing (with 0.2-unit differences in salinity), and air-sea gas exchange. We have now indicated both concentration and saturation in the text.

CH ₄ conc.	T	S	Saturation*
3.4 nM	-1.8	34.8	90%
	1.4	34.8	98%
	1.4	33.7	97%
	-1.8	33.7	89%
2.8 nM	-1.8	33.7	73%

*Calculated from Wiesenburg and Guinasso (1979)

1. 170-172: “We found...”.. Where is the blue arrow in Figure 3e coming from?.. If I understood correctly, you are using the numbers from Figure 3d, correct?...But there, the change in saturation level could also result from the combination of other processes such as the effect of temperature and salinity on solubility (which is used to calculate the saturation) or exchanges with the atmosphere, correct?..

In fact I am a bit disturbed by the use of a % saturation vs. salinity plot to discuss mixing processes, while obviously temperature and salinity changes should also affect the saturation numbers. Why not use simply a CH₄ concentration vs. salinity plot, as shown here below (built from the values in the supplementary table, in the same way you built your Figure 3e)?



There you see a similar arrangement than in your figure 3e, but clearly the concentration of the mixed layer waters (same criteria as yours – all 50 m depth in this case), shows no trend with salinity... dynamics of CH₄ does not indicate dilution from melting sea ice... the CH₄ bulk concentration of which could be close to SW (and not negligible!).. see further comments..

Response: Yes, there are multiple processes that affect CH₄ concentration and saturation. Thank you for your suggestion, we have re-built the Figure 3e (in the revised manuscript it is Figure 5) by using concentration rather than saturation. We have been also re-written the discussion part with regard to this figure.

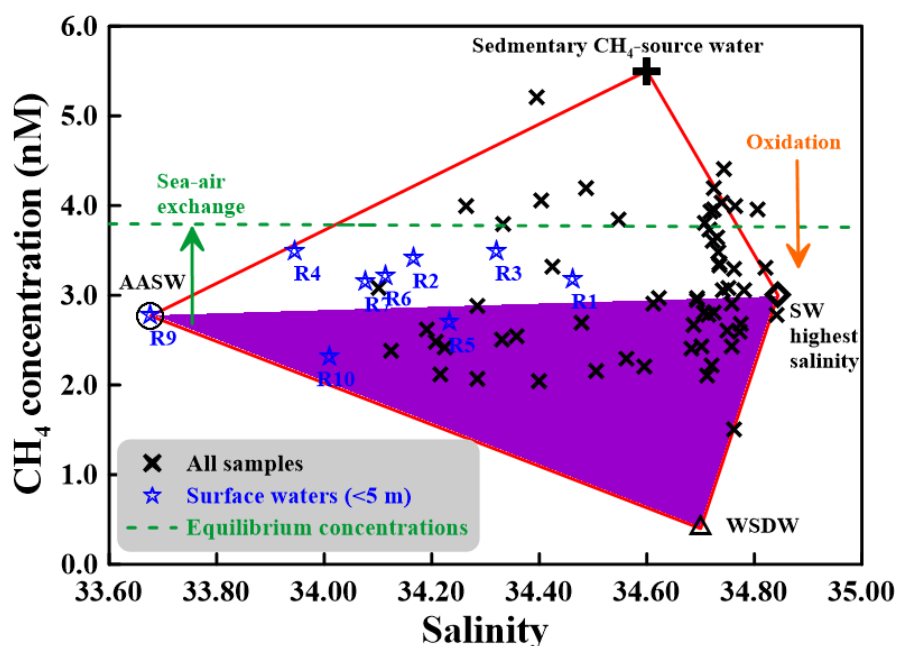


Figure 5: Mixing diagram between salinity and CH₄ concentration on the Ross Sea shelf. Black crosses are all samples and blue stars are samples from the surface layer. Arrows represent controlling processes (green for air-sea exchange, orange for microbial oxidation, and red for water mixing). The green dashed line represents CH₄ in equilibrium with respect to the atmosphere at a constant temperature (mean of all samples: -1.4 °C). The open circle represents the endpoint of AASW that was obtained from station R9 with the lowest salinity; the plus represents the endpoint of sediment-influenced water that was obtained from the near-bottom water (200 m) at station R7; the diamond represents the endpoint of SW (highest salinity) that was obtained from the bottom water (1018 m) at station R3; the triangle represents the endpoint of WSDW (Weddell Sea Deep Water) that was obtained from Heeschen *et al.* (2004). The purple shading indicates the mixing results for MCDW and MSW.

l. 173: “Contribution of Production/oxidation from mass balance calculations”... this is not really a box model, and you are talking about those biogeochemical processes in this section

Response: Agree. This head title has been changed as “Contribution of advection and production/oxidation from mass balance calculations”.

l. 187: “Figure 3e” .. there is no MSW in Figure 3e

Response: The word “MSW” has been changed to “SW and AASW”. The MSW is also modified from the mixing between SW and CDW.

l. 189: “in a negative CH₄ gradient..” a gradient is a slope.. I don’t think you are tracking changes of slopes

Response: Thank you. This sentence has been deleted.

l. 190: Figure S2 is tricky to interpret.. it is strange that linear correlations come out while 4 end members are involved (?).. Is it that mixing of AASW is mainly with SW,

and not CDW (which would inverse the trend)

Response: The AASW is also mixed with MCDW in shallow water depth. This figure has been deleted.

l. 191: “Hence, superimposed to the effect of microbial oxidation of CH₄ (section 3.4)...”

Response: Thanks, done.

l. 192-194: Why supersaturation, then?...and why limited to the stations R1 to R4?.. Clearly the distribution of supersaturation in Figure 1b (top 100m) “roots” into the coastal areas.. could there be enrichment from shallow sedimentary sources (e.g. triggered by tidal forcing?) Another source might be ISW (in contact with sediments upstream), but there doesn’t seem to be higher CH₄ at those depths in your profiles..

Response: Agree. 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 CH₄ value, which was attributed to CH₄ release from the sediments. Any discussion on the origin of this high CH₄ is speculative so we decide to focus the CH₄ undersaturation in the main text.

Indeed, we have cautiously discussed these CH₄ 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 CH₄ 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 CH₄ sources in the Ross Sea. Thank you for your suggestion. This part has been modified and further speculation has been deleted to keep the manuscript simple and concise.

l. 196: “caused by dilution”... but, as mentioned before, undersaturation could also result from T/S changes, where is the balance with dilution?

Response: Please see our response above. The concentrations were different between ice-free and ice-covered areas. We have modified the expressions in the text. In addition, since we have no sea ice data, the revised manuscript is highlight in the observation of CH₄ undersaturation but light in the role of sea ice melting in CH₄ distributio.

“Surface CH₄ concentrations ranged from 2.3 to 3.5 nM and are at the lower end of the range of CH₄ concentrations (1.5-7.4 nM) reported for bulk CH₄ concentration in sea ice in the McMurdo Sound (Jacques *et al.*, 2021). It is reasonable to assume that freshwater from melting ice mixes with the ambient seawater. Provided that CH₄ consumption (i.e. F_x) was constant at all stations the resulting CH₄ flux by advection (F_{ad}) is in the range from 0.05 to 1.26 $\mu\text{mol m}^{-2} \text{day}^{-1}$ (except for station R5 where the most pronounced air-sea exchange occurred), indicating that F_{ad} is a source for CH₄ in the mixed layer. 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 CH₄-enriched water while the ice-covered conditions may favour lower transport of CH₄-enriched waters to the mixed layer.”

l. 202-205: same comment as above! You should estimate the contribution of each process to demonstrate that dilution is indeed the main factor!... Looking at the figure above, there is no trend in surface waters with the decrease of salinity... but of course, there exchange with air might have blurred the signature...

Response: Estimation of the contribution of each process to CH₄ undersaturation is difficult based on limited data at current stage. However, we have tried discuss the effect of mixing and did not imply it was the main driver. Please see the “section 4.2 CH₄ dynamics in the surface mixed layer” in the revised version.

“we found that in the west, the uptake by air-sea exchange accounts for about 59% of the CH₄ while CH₄ oxidation was the main process (96%) to remove CH₄ from the surface mixed layer. In the east, the downward diffusion of CH₄ accounts for 84% of the CH₄ removal from the surface mixed layer, becoming the most important process to maintain the status of surface CH₄ undersaturation.”

l. 211: “box model” ... rather “Mass Balance calculation”?

Response: Have been changed.

l. 212: “increased its contribution in the east” ... isn't this in contradiction with Figure 3d?

Response: Sorry for the unclear expression. We mean the contribution of air-sea exchange accounts for 40-70% in the west and 90% in the east that was compared with the contribution of vertical diffusion. This sentence has been deleted. Please also note that it is the low CH₄ concentration at the air-sea interface that determines the strong air-sea flux, not inverse. Indeed, the F_{air} was stronger in the east due to free of sea ice. However, other processes, such as dilution via water mixing between AASW and SW (strong in the east, Figure 2b), vertical diffusion into deeper waters and microbial oxidation offsets the influence of air-sea exchange on CH₄ concentrations, resulting a relatively low CH₄ in the east. This, in turn, explains the influence of sea ice melting on CH₄ uptake: more sea ice melting-enhanced water mixing-lower CH₄ concentration at the surface-stronger gas exchange-more CH₄ uptake from the air.

l. 215: “In the west...” not east

Response: Sorry for the typo. Has been modified.

l. 216: “injected freshwater”...If I understood correctly from previous saying in the paper, this refers to sea ice melt, correct?.. I am a bit surprised that it would have affected the whole mixed layer: sea ice is maximum 1m thick, the mixed layer is 25-50m. Sea ice CH₄ concentrations in the Antarctic are not very well documented, but they do exist. Jacques et al., 2021 report on a range of 1.5 to 7.4 nM for bulk CH₄ concentration in McMurdo Sound, with a mean around 3 nM. This value is similar to

the values for waters in this paper (1.7 to 5 nM). I am therefore not convinced of the impact of dilution from melting sea ice on mixed layers concentrations. Even supposing a minimum sea ice concentration of 1 nM, it would be a factor 3 to 5 lower than SW values, while the mixed layer is a factor 25-50 thicker!...again, plotting CH₄ concentration vs. salinity does not show any trend..

Response: Thank you for your suggestion. The reference (Jacques et al., 2021) has been cited in the text. We agree that the impact of dilution from melting sea ice on CH₄ is difficult to track in this study, so we have rephrased the words and sentences in the revised version (the sea ice melting part has been deleted.). The specific mixed layer depths have been given in the Table S3, which demonstrates the mixed layer depth ranged from 7 m to 39 m.

l. 218: “exposition to the air”

Response: This sentence has been deleted.

l. 218: “30 days ice free period in the east”... but this is where Fig. 3d shows minimum supersaturation, correct?.. contradiction?

Response: Please see the response to Line 212. Air-sea exchange is not the only factor that influence the CH₄ concentration in the mixed layer. Instead, strong water mixing with AASW in the mixed layer (compared with that in the west) and vertical convection together caused a low CH₄ concentration at the surface, which in turn, leads to a strong CH₄ uptake from the air. Longer timescale of absorption of CH₄ from the air did not equal to higher CH₄ concentration in the mixed layer because the presence of CH₄ removal. Please see the revised manuscript. However, we believe this is speculative and has been deleted.

l. 222: “suggests”.. why not only continuous dilution?

Response: These sentences has been deleted.

l. 223: “previous study” references?

Response: Heeschen et al. (2004) has been added in the text.

l. 229: “the compared results among stations”... I don’t understand. Please rephrase!...

Response: Sorry for the unclear expression. The sentence has been rephrased as “in the west, CH₄ oxidation was the main process (96%) to remove CH₄ from the surface mixed layer”.

l. 231: rather “Summer CH₄ uptake in the Ross Sea”

Response: We have highlighted that the CH₄ flux were only calculated in summer and emphasized the importance of CH₄ data from other seasons.

l. 255-256: you should also insist on the fact that no CH₄ data is available today, which hampers the possibility of providing an annual flux budget!..

Response: Thank you for the suggestion. Done.

l. 260: “sea ice melting is likely to enhance..”.. this is actually not demonstrated by the CH₄ data in this paper..

Response: Agree. The sea ice melting is far more complicated than we thought before. The sea ice may a source to dissolve CH₄ but the sea ice melting may facilitate the local water mixing (e.g., increase in AASW from west to east, see section 3.1, Figure 2b), increase the vertical convection of CH₄, and increase the timescale of surface area exposition to the air, which eventually leads more uptake of atmospheric CH₄. This part has been deleted because it can-not be solved at present by our data alone.

l. 265: “which underlines the potential significance..”

Response: Thank you. Done.

Suppl. Table CH₄: please use contrasting background to better define the stations data

Response: Thank you for the suggestion. Done.

Figure 1: should show ISW out of the Ross Ice Shelf

Response: Please notice the green line that shows the ISW out of the Ross Ice Shelf.

Figure 1b, should be a separate figure

Response: Done.

Figure 3 caption:

a) define “surface”

b) Heeschen et al. do not give CDW values, if I remember correctly, but WSDW with a minimum of 0.4 nM CH₄

Response: Thank you for the suggestion. The Figure has been modified, please see above response (Line 170-172).

Figure S3: where is this scheme commented in the text?.. Maybe I missed it!..

Response: At the end of “Discussion”. It is an assumed mechanism that shows how CH₄-undersaturated water forms during different seasons. We do not have winter data so at this stage it may a speculation to some extent. It is our purpose that appeal more attentions on CH₄ dynamics in the Southern Ocean to deeply understand the mechanism.