

## ***Interactive comment on “Insights into oxygen transport and net community production in sea ice from oxygen, nitrogen and argon concentrations” by J. Zhou et al.***

**J. Zhou et al.**

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Dear editor,

We are grateful to the reviewers for their thorough comments, which have considerably improved the quality of the revised manuscript. We provide our responses to their specific comments and questions here below.

In general, as both reviewers were concerned about the uncertainty of our measurements, we have provided estimate of the potential uncertainties in the revised manuscript. We have also rewritten the manuscript for precision in the terminology and for clarity.

C2202

We would like to emphasize that we only provide conservative (hence minimum) estimate of the NCP in sea ice. It is true that taking into account gas exchanges in the permeable layers will improve the estimate, but it is impossible in the present study: first, because our O<sub>2</sub> measurements (from optodes) in the under-ice water did not work for unknown reason, and second, because of the current lack of knowledge on how both brine convection and diffusion affect gas transport in sea ice.

Finally, although both of the reviewers appeared focused on the NCP estimate and the related problems, we would like to emphasize that the paper has another objective (as shown in the title), which is providing insights on O<sub>2</sub> transport through sea ice. Further, these O<sub>2</sub>, Ar and N<sub>2</sub> data in bulk ice are the first measurements on natural sea ice cores. Therefore, we hope that the reviewers will also consider the originality of the dataset and the discussion on the physical imprints in gas concentrations for their final decision.

REVIEWER2

General Comments Reviewer2 (general comment #1) This manuscript presents measurements of gas concentrations within sea-ice cores across a seasonal gradient that are used to estimate the net metabolism within sea ice. The method uses the ratios between oxygen and argon and oxygen and nitrogen to separate the physical dynamics of oxygen concentrations from the biological consumption and production of oxygen. The method was adapted from techniques used in the open ocean, however, a key assumption is overlooked in this application to sea ice. The manuscript discusses sea ice as a closed system, and therefore no corrections for the exchange of gases across the ice-water and ice-air interface is included, but the sea-ice was found to be permeable over at least part of the ice during all periods when this methodology was used. Further, the manuscript lacks clarity throughout and consistency in terminology, which make it very difficult to evaluate the methods and results which appear to be very interesting. The discussion could be shortened significantly to highlight the significant results. Related to this, there seem to be no replicate samples, error estimates, or

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statistics with which to weigh the significance of the results. Overall, addressing these issues will likely constitute a re-analysis of the data and an entirely new manuscript.

We agree with the reviewer2 that there is no correction for exchange of gases across the ice-water and ice-air interface. For that reason, we have emphasized that we only provide conservative estimate of NCP. Most importantly, current knowledge on gas exchange through sea ice does not allow us to make appropriate correction. To the best of our knowledge, the first paper on the diffusion coefficients of O<sub>2</sub>, Ar, N<sub>2</sub> derived from observations on sea ice is still under review (Crabeck et al., submitted), and only one publication has addressed the problem experimentally, and only for O<sub>2</sub> (Loose et al., 2001). In addition, to what extent brine convection affect gas transport has not been quantified. Therefore, we could only discuss on the potential changes in O<sub>2</sub>/Ar and O<sub>2</sub>/N<sub>2</sub> due to gas diffusion and gas bubble formation, and provide the potential errors that these changes may cause on our NCP estimates.

In brief, this paper aims to highlight the processes that affect O<sub>2</sub> dynamics in sea ice, showing that NCP estimate from O<sub>2</sub>/Ar seems promising, and pointing out the required improvement to go further with NCP estimate using O<sub>2</sub>/Ar.

Also, we have restructured the discussion sections in our revised ms.

Crabeck, O., Delille, B., Rysgaard, S., Thomas, D. N., Geilfus, N. X., Else, B., and Tison, J.-L.: First "in situ" determination of gas transport coefficient (DO<sub>2</sub>, DAr, DN<sub>2</sub>) from bulk gas concentration measurements (O<sub>2</sub>, N<sub>2</sub>, Ar) in natural sea ice, *Journal of geophysical Research - Oceans*, submitted. submitted. Loose, B., Schlosser, P., Perovich, D., Ringelberg, D., Ho, D. T., Takahashi, T., Richter-Menge, J., Reynolds, C. M., Mcgillis, W. R., and Tison, J. L.: Gas diffusion through columnar laboratory sea ice: implications for mixed-layer ventilation of CO<sub>2</sub> in the seasonal ice zone, *Tellus B*, 63, 23-39, 2010.

Reviewer2 (general comment #2) P2052 L25-3. This is a big assumption and is contradictory with statements in the MS. During all periods the sea-ice was permeable

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in the lower portions (Figure 5) and this region is where a majority of ice metabolism occurs due to this permeability and exchange of metabolic products, nutrients, and carbon with the seawater. Further, it is unclear if the authors are suggesting sea ice is a closed system? Ice is described as porous (1st sentence of Intro) and both permeable and impermeable at different times of the year / different depths of the ice core. Further, I would argue that the sea-ice system is more complicated with the source of O<sub>2</sub> at the center, so exchange across both the air-ice and ice-water interface would need to be corrected for. Since this was modeled after the oceanic O<sub>2</sub>/Ar method and NCP estimation was only applicable under permeable ice conditions, I find it very troubling that no corrections are included for the transfer across the air-ice and water-ice interface. This is in direct contradiction with the explanation in the methods (P 2052 L25-3) "In a closed system, NCP then corresponds to the changes of O<sub>2</sub>NCP between sampling events. Note that in seawater studies, because of the open system, additional coefficients and equations are required to take into account the diffusion at air-sea interface, the changes in the mixed layer depth and the diffusion of O<sub>2</sub> across the base of the mixed layer (Castro-Morales et al., 2013)." Further, without measurements of below-ice seawater O<sub>2</sub> concentrations and the fact that the sea-ice surface is a region of very high productivity, it is very difficult to evaluate the profile suggested for the permeable ice (Figure 6, P2065 L 20-25).

Sea ice is a composite material, with both permeable and impermeable layers. We understand the concern of the reviewer about the corrections for gas transfer through sea ice. We have tried to measure O<sub>2</sub> in the under-ice water, but the optodes did not work properly. More importantly, as we said in response to the previous comment, current uncertainty about the relative contribution of both diffusion and convection to gas transport, does not allow a proper correction of NCP.

Reviewer2 (general comment #3) The methods also lack detail and make it hard to evaluate the results. What time of day where the ice cores taken, was this consistent across periods? Diel O<sub>2</sub> production / respiration could heavily influence the results.

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Over what timescales are the O<sub>2</sub> rates determined? From core to core? Can it be assumed across these long time periods that NO exchange between the air – ice – water occurs? This is unlikely. Where any replicate samples taken? Error estimate? Statistics comparing results?

No. The ice cores were not sampled at the same time of the day, but between 11AM and 3PM. However, it is unlikely that diel O<sub>2</sub> production/respiration will affect our O<sub>2</sub> measurements in bulk ice. According to the incubation experiments of Mar Fernández Méndez ([https://www.mpi-bremen.de/Binaries/Binary16430/M.Sc.\\_Thesis\\_Mar\\_Fern%C3%A1ndez.pdf](https://www.mpi-bremen.de/Binaries/Binary16430/M.Sc._Thesis_Mar_Fern%C3%A1ndez.pdf), p.27), the net primary production (NPP) of *F. cylindrus* (a typical cold-water species that can be found in Arctic and Antarctic seawater and sea ice) was 1.73  $\mu\text{mol O}_2 \text{ Lincubation water}^{-1} \text{ h}^{-1}$ . Assuming a 12 hours of daylight, we may expect a NPP of 20.76  $\mu\text{mol O}_2 \text{ Lbrine}^{-1} \text{ d}^{-1}$  in the field. Because brine volume fraction approach 20 % in the bottom of the ice where the highest chlorophyll-a concentrations was observed (Figure 3), we may expect a NPP of 20.76 \* 20 %  $\mu\text{mol O}_2 \text{ Lice}^{-1} \text{ d}^{-1}$ , hence 4.15  $\mu\text{mol O}_2 \text{ Lice}^{-1} \text{ d}^{-1}$ . This accounts for 3 to 6 % of the mean O<sub>2</sub> concentrations in bulk ice (ranging from 67.4 to 122.4  $\mu\text{mol O}_2 \text{ Lice}^{-1}$ ). We have added that paragraph in the supplementary material (S1), the numbers in the materials and methods (p.5 L6-8 of the Word document) and have taken into account the maximum uncertainty of 6 % in our total error estimate (p.18 L8 and p.19 L10 of the Word document).

Reviewer2 (general comment #4) In general, I think that some terms used in the MS are misleading and limit the clarity of the MS; some examples: (1) “We present the evolution of O<sub>2</sub> standing stocks, saturation levels and concentrations” – oxygen evolution primarily relates to molecular oxygen production by photosynthesis; the saturation levels are not “evolved”. This is especially important when the physical processes are considered (which are a large component here). I would suggest the use of oxygen exchange or production and respiration or metabolism. Explicitly providing terms for the abiotic and biotic processes would significantly clarify this point.

C2206

What we meant by “evolution”: Changes of O<sub>2</sub> standing stocks over time is a temporal evolution, while changes with depth is a spatial evolution. We have changed the word throughout the text as the reviewer felt uncomfortable with that. The saturation levels also change in time. Within a closed system, the total gas concentration do not change, but gas solubility change due to the changes in ice temperature and brine salinity (= “brine concentration” and “brine dilution” effects). Since the saturation levels depend on the total gas concentration and gas solubility, they will change according to the ice temperature and brine salinity.

(2) P2046 L 17 – “Sea ice is a porous material”, this suggested that fluid gas exchange readily happens in sea ice, but the MS talks at length about impermeable ice layers. The point about impermeable and permeable ice layers should be made explicitly and consistently throughout the MS

We replaced the sentence by “sea ice is a composite material”. However, saying that sea ice is a porous material was not wrong. Brine inclusions, microorganism, gases and even solid precipitates may fill the pores of sea ice (within the pure ice matrix). This is what we meant when we wrote that “sea ice is a porous material”.

Indeed, fluid gas exchange occurs in this porous material, but the rate of that exchange depends on the size of the pores and how well these pores are interconnected (i.e., the brine volume fraction). Golden et al., (1998) have shown that fluid exchange through the columnar ice increases drastically when the brine volume fraction exceeds 5 %. Following that observation, we defined as “permeable” ice layers, the ice-layers with brine volume fraction above 5 %. In contrast, “impermeable” ice layers are the ice-layers with brine volume fractions below 5 %. Therefore, from our point of view, an ice layer that is “impermeable” may be porous (i.e, contains brine inclusions), the ice pores are not well connected enough to allow rapid fluid exchange.

We have clarified the terminology about permeable and impermeable layers in the result section “Figure 5a shows the concentration of O<sub>2</sub> in bulk ice [O<sub>2</sub>], compared to

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the solubility of O<sub>2</sub> in ice. The dashed areas refer to the permeable ice (i.e., layers with brine volume fraction above 5 %, while the non-dashed areas right above refer to the impermeable layers (i.e., with brine volume fraction below 5 %) (Golden et al., 1998)).” (p.8 L13-16).

Golden, K. M., Ackley, S. F., and Lytle, V. I.: The percolation phase transition in sea ice, *Science*, 282, 2238-2241, 1998.

(3) P2051 L3 Equation 1 is described as “Gas saturation levels is described following Craig and Hayward (1987) in seawater” but the equation does not provide the gas saturation “level”; instead it describes the ratio of the difference between the two concentrations (e.g.  $(110/100)-1 = .1$ ). This is another example of a place where clarity can be increased; what does “level” represent here? How do you get to the “saturation levels (%)” show in Figure 4?

Gas saturation is calculated as described in Eq. 1, hence not in percentage. In Figure 4, we simply multiplied the results from Eq. 1 by 100 to express gas saturation in percentage; this facilitates comparison with the literature, where gas supersaturation and undersaturation are generally expressed in percentage. However, we did not explicitly express gas saturation in percentage in Eq. 1 (and similarly in Eq. 2), to avoid confusion in Eq. 3, where gas saturation is used as is, and not in percentage.

We have detailed this in the revised version “Note that for comparison with the literature, gas saturation are given in percentage in the text. Supersaturation and undersaturation are therefore represented by positive and negative percentage values respectively.” (p.5 L25-27 of the Word document). In the caption of Figure 4, we have also indicated that gas saturations calculated in Eq. 1 are given in percentage.

Detailed comments (DC)

Reviewer2 (DC on P 2046) L 5 “dynamics” instead of “dynamic”?; L8 NCP defined as “biological contribution”?, not as defined in line 20; L19 “to survive to” to survive at.

C2208

We revised the manuscript using “dynamic” and “survive at”. NCP is indeed the balance between photosynthesis and respiration (as defined in L20), but photosynthesis and respiration are the biological factors that contribute to O<sub>2</sub> supersaturation (L8).

In the revised version, we have used biological activity or biological O<sub>2</sub> production throughout the text, and only use NCP when we talk about the rate of biological O<sub>2</sub> production/consumption.

Reviewer2 (DC on P2047) L2 “evolution”, I would suggest variability or change; L10 “privileged” seems like the wrong word here. We used “change” instead of “evolution”, and “preferred” instead of “privileged”

Reviewer2 (DC on P2048) L7-8 “to discuss on the feasibility to decipher” awkward. L20-25 What time of the day were the ice cores collected? was this consistent for all periods? With O<sub>2</sub> production maximal at midday and the potential build-up of O<sub>2</sub> across the daytime (dependent upon the air-ice and ice-water exchanges which are ignored here) this could significantly alter the calculated NCP rates and the O<sub>2</sub>/Ar ratios.

This comment is related to the general comment #3. Please check our response to your general comment #3.

Reviewer2 (DC on P2049) L 4, again, the use of evolution here is misleading / confusing. I suggest variation or dynamics. We have used the word “variation” in the revised ms. Thank you for your suggestion.

Reviewer2 (DC on P2051) L2 missing colon L10-14 Much stronger support for this would be to use the maximum rates present in Rysgaard 2008 to calculate the maximum change in the N<sub>2</sub> signal that can be provided by denitrification (and annamox). A quick back of the envelope give 0.2  $\mu\text{mol N L}^{-1} \text{d}^{-1}$  per m of ice thickness, which is a small percentage of the signal. This could also be a source of variability in N<sub>2</sub>, especially for the impermeable ice layers?

C2209

We have quantified the impact of denitrification on N<sub>2</sub> variation in the ice, as suggested by the reviewer2. The paragraph reads as “Denitrification was found to occur in sea ice (Rysgaard et al., 2008), but could not have affected significantly the concentrations of N<sub>2</sub> in bulk ice in the present study. The maximum reported denitrification rate (175 nmol N<sub>2</sub> L<sup>-1</sup> d<sup>-1</sup>) was indeed 3 orders of magnitude lower than the average bulk ice N<sub>2</sub> concentrations (248 μmol N<sub>2</sub> L<sup>-1</sup>) presented here. The correlation between N<sub>2</sub> and Ar with a r<sup>2</sup> of 0.98 (Fig. 2) further supports that N<sub>2</sub> is inert like Ar, and can be used to trace physical processes.” (p.6 L3-8 of the Word document). We also think that denitrification is negligible in our study, not only because the denitrification rate is small in comparison to the pool of N<sub>2</sub> in sea ice, but also because our O<sub>2</sub> concentrations in sea ice indicate oxic conditions. Hence, denitrification could only occur in some micro-anoxic niches. If the reviewer refers to the correlation of 0.98 % between N<sub>2</sub> and Ar in the ice, when he/she talked about “source of variability in N<sub>2</sub>” in sea ice, then the difference of solubility and diffusion coefficient between N<sub>2</sub> and Ar, may be two factors that controls the variability of N<sub>2</sub> in sea ice (in comparison to Ar), rather than the denitrification, which is insignificant in our study as the reviewer2 has pointed out.

Reviewer2 (DC on P2052) L 5 and 7, Consistency in significant figures; L23-24 This statement is unclear “in which, [O<sub>2</sub>]<sub>eq</sub>/[Ar]<sub>eq</sub> is the solubility ratio in seawater at equilibrium in Castro-Morales et al. (2013), but the solubility ratio in ice at equilibrium in the present study (Sect. 2.4).”

We don't understand about what the reviewer2 means by “consistency in significant figures”. We have double checked the figures; there is no mistake.

Also, about the solubility ratio, we detailed the problems in the materials and methods: “For seawater, [O<sub>2</sub>]<sub>eq</sub> and [Ar]<sub>eq</sub> are respectively the solubility of O<sub>2</sub> and Ar at saturation. In ice, however, [O<sub>2</sub>]<sub>eq</sub> and [Ar]<sub>eq</sub> may differ from the solubilities due to physical processes such as bubble nucleation, diffusion and convection (see Sect. 2.4 and 4.6).” (p.7 L14-16 of the Word document).

C2210

Reviewer2 (DC on P2053) L9 “thickness” = thickens? Thickness was fine. We meant that the three gas standing stocks varied in the same way over time, but the ice thickness varied differently.

Reviewer2 (DC on P2056) – L9-16, Would it not make more sense to normalize your standing stock by ice thickness for comparison purposes?

Unfortunately, this does not help. . . Indeed, because of the relative abundance of O<sub>2</sub>, Ar and N<sub>2</sub> in ice, the graph of the standing stocks normalized by ice thickness is similar to Figure3, but with different Y-axes.

Reviewer2 (DC on P 2056) L23-25 Saying gas exchanges with the atmosphere (as well as the water below) suggests that a correction is required for both of these losses of gas before NCP can be calculated. Therefore, whenever the brine volume is above 5% (Golden et al. 1998) (if assuming gas is behaving the same as a fluid), these exchanges need to be accounted for, as in the air-water flux in the open ocean (Castro-Morales et al., 2013). The much lower NCP rates reported here (P2063 L 29) compared to other measurements suggest some of these losses may be significant.

We agree that we need to suggest that a correction is required to take into account gas loss in the impermeable layers.

The low NCP rates reports in P2063 L29 refer to the impermeable layers where chlorophyll-a concentrations were lower than in the bottom of the ice, and nutrient refill is much less efficient as well. We are not aware about NCP in impermeable layers for comparison, what do the reviewer mean by the “other measurements”? What we have done in the revised ms is a comparison with NCP values from melt ponds (Lee et al., 2012) where similar chlorophyll a concentrations are found.

Lee, S. H., Stockwell, D. A., Joo, H.-M., Son, Y. B., Kang, C.-K., and Whittedge, T. E.: Phytoplankton production from melting ponds on Arctic sea ice, *Journal of Geophysical Research: Oceans*, 117, C04030, 2012. Further, these impermeable layers are layers

C2211

with brine volume fraction below 5 %, hence limited gas exchange.

Reviewer2 (DC on P2058) L5 awkward. L12 “reminds” awkward. Due to the new structure of the discussion sections, this paragraph has been removed.

Reviewer2 (DC on P2062) L22 “Therefore, to test the feasibility of using O<sub>2</sub>/Ar to estimate NCP ice, we calculated the changes of standing stocks of O<sub>2</sub>NCP” confusing, again consistency in terms would clarify. O<sub>2</sub>NCP was defined as “NCP-related O<sub>2</sub> concentrations” earlier. Should it read: changes of O<sub>2</sub> standing stocks due to O<sub>2</sub>NCP? Due to the new structure of the discussion section, this paragraph has been removed.

Reviewer2 (DC on P2063) L2 delete “much”. Done

Reviewer2 (DC on P2065) L11 – does not seem to follow above. We forgot the subject “We” in the sentence. Sorry for that mistake.

Reviewer2 (DC on P2065) L24 It is very confusing to me to present NCP rates per m<sup>2</sup> while separating this over different heights in the ice. The m<sup>2</sup> suggests two dimensions in a planar surface, while a third dimension is including by comparing different heights of ice (3 dimensions). I would suggest a per volume (m<sup>3</sup> or L) would be clear and more accurate here, as is commonly done with ice core incubations. That paragraph has been removed in the revised version.

Reviewer2 (DC on P2066) L 24 “from the atmosphere” carbon uptake is not examined here / occurring in the atmosphere, should read “from uptake rates determined across the ice-air interface.” L23-27 This suggest a significant transfer across the ice-water interface which needs to be accounted for – see earlier comments. That paragraph has been removed in the revised version. The reason is: after the submission of our paper, a recent publication (Rutgers v.d. Loeff, JGR2014) suggests that gas diffusion through sea ice may be very slow. Hence, the assumption of steady state that we have made in our previous paper, where NCP = diffusion, may be not correct. Therefore, we removed equations 4 and 5 in our revised version and provide [O<sub>2</sub>]bio, which is

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the concentration of O<sub>2</sub> in sea ice due to biological activity rather than NCP (i.e. O<sub>2</sub> production per unit of time).

Rutgers van der Loeff, M. M., N. Cassar, M. Nicolaus, B. Rabe, and I. Stimac (2014), The influence of sea ice cover on air-sea gas exchange estimated with radon-222 profiles, *J. Geophys. Res. Oceans*, 119, doi:10.1002/2013JC009321.

Reviewer2 (DC on Figure 5) – Unreadable, unfortunately the automatic journal format makes this figure very small, but even at a full page size this figure would still be too small (I had to blow it up to 300% to read). This is the most important figure in the MS and needs to be redone, or possibly split to make this very important figure useful. We removed some the axes to enlarge the figure; We will also ask during the typesetting to rotate or split the figure in the revised version for “landscape” format publishing. Otherwise, the figure should be readable in a A4-size sheet in “portrait” format.

Reviewer2 (DC on Figure 6) – Carbon “uptake” incorrect (you cannot have a negative uptake), should read carbon exchange or flux. That figure does not exist anymore in the revised version.

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Interactive comment on Biogeosciences Discuss., 11, 2045, 2014.

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