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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.

jiayzhou@ulb.ac.be

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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.

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 O2 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 O2 transport through sea ice. Further, these O2, Ar and N2 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.

REVIEWER1: General comments The authors present seasonal biogeochemical depth profiles in discrete ice cores from land-fast sea ice, treated as a time series. From their data set, they determine the biological and physical contributions to O2 dynamics in bulk sea ice from late winter to early summer, and compute net community production in the form molecular oxygen changes using inert gases to account for physical changes in the gas composition of bulk sea ice. The data set is of good quality, and the topic will be much appreciated in the sea ice scientific community. The main issue with this manuscript is clarity, which is lacking in places, especially in the Discussion, and its lack compounds proper appreciation and evaluation of their data analysis. I recommend it for publication after moderate revision to edit, to clarify, and to sharpen several parts of the Discussion.

We restructured the discussion sections. Sections 4.1 – 4.5 discuss both physical and biological processes that have affected the temporal changes of O2 concentrations in comparison to Ar and N2. In section 4.6, we discuss the potential errors related to the calculation of NCP from O2/Ar or O2/N2 ratio in sea ice. These errors are taken into account in section 4.7 when we provide our conservative estimate of NCP in the impermeable layers and and [O2]bio in the permeable ice layers.

Specific comments (SC):

Reviewer1 (SC #1). P2050, L12-13: Explain what reproducibility means in the context of this study and provide details of how it was assessed using standard gases.

AUTHORS: We injected six different gas standards in the gas chromatograph (GC). Each gas standard has a different injection pressure (respectively 0.5, 1, 2, 3, 5 and 10 torrs). Each gas standard has been injected three times, and we then calculated the variation coefficient on the three injections by dividing the standard-deviation by the mean gas concentrations. The variation coefficient gives a sense to the precision of the GC. Because all our ice samples had an injection pressure exceeding 2 torrs, we took the maximum variation coefficient for all the gas standards exceeding 2 torrs, hence 0.7 % for O2, 2.2 % for Ar and 0.1% for N2. The corresponding reproducibility of the analyses was then respectively 99.3, 97.8 and 99.9 %.

The related paragraph now reads as: "The reproducibility of the analyses (i.e., the precision of the gas chromatograph) was 99.3 % for O2, 97.8 % for Ar and 99.9% for N2. It corresponds to 100 % minus the variation coefficient (in %) obtained from triplicate analysis of four different standards (2, 3, 5, 10 torrs of injection pressures)." (p.5 of the word document, L3-6).

Reviewer1 (SC #2). P2052, L6-8: Dissolved gas evasion into gas bubbles forming in the brine of permeable sea ice should not affect the bulk sea ice O2/Ar. In other words, bulk sea ice gas ratios could not provide information about phase change within sea ice, if I understand this correctly, unless the gas bubbles escape sea ice. I suggest the use of this term, "bulk sea ice gas (e.g., O2/Ar, O2/N2) ratio", throughout the manuscript for clarity when discussing the measurements in the context of gaseous and dissolved gas phases in sea ice. I also suggest use of the latter two terms for clarity too.

AUTHORS: In a closed system, it is true that “dissolved gas evasion into gas bubbles forming in the brine” does not modify the O2/Ar ratio in bulk ice. However, this is not true in a semi-open system (i.e., permeable ice layers before that sea ice consolidates), because of brine convection at the sea ice bottom (Notz et al., 2008). Indeed, assuming an initial signal of O2/Ar in bulk ice at incorporation. On gas bubble formation, the O2/Ar in the gas bubbles should be different to the O2/Ar in the brine; both ratios depend on partition coefficient of O2 and Ar. Then, because brine convection removes the brine from sea ice and replace it by seawater (with the same initial O2/Ar signal), we then have a source of O2/Ar that could support the O2/Ar of gas bubbles to tend toward the atmospheric ratio (22.5).

Reviewer1 (SC #3). P2052, L17-18: Given that O2 could be undersaturated when respiration dominates in sea ice, I suggest replacing ‘supersaturation’ with ‘O2 concentration change in sea ice’.

We understand the concern of the reviewer, but suggest using “saturation” instead of “O2 concentration change in sea ice”, because we also present O2 concentrations in bulk ice and their variations with depth and in time. Therefore, it may be confusing. Further, the term “saturation” implies a comparison of O2 with its solubility value, which is not the case when using “O2 concentration change in sea ice”.

Reviewer1 (SC #4). P2055, L16 (and throughout the text): Explain what ‘sensitive’ means in this context and to what the gas ratios are compared to deduce ‘sensitivity’.

We initially used the term “sensitive” for qualitative interpretation. We compared the vertical variations of both O2/N2 and O2/Ar in ice, and observed that O2/N2 varied less vertically than O2/Ar. An alternative method to compare both ratios quantitatively is to compare the deviation of the standard deviation from the mean value, and expresses it in percentage, for each ratio. We have added the percentages in the revised manuscript.

“Although both O2/N2 and O2/Ar in ice have similar coefficient of variation (respectively,

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49 and 46 %, n=121), O2/N2 only exceeded once its abiotic range between BRW2 and BRW8, while O2/Ar exceeded its abiotic range from BRW4 onwards (Figs. 5c and 5d)." (p.9 of the word document, L19-21)."

Reviewer1 (SC #5). P2056, L17-19: Explain how warming may, or may not, have contributed to the sharp decrease in total gas supersaturation.

The sharp decrease in total gas supersaturation is related to warming, because of the relationship between warming (i.e., increasing ice temperature) and: - The brine volume fraction: Increasing ice temperature will increase the brine volume fraction, and hence the permeability of sea ice, which allow gas exchange (gas bubble escape and diffusion), and hence reducing gas supersaturation - ice melt : meltwater that percolates in the brine network adds freshwater into brine, which will cause a decrease of gas concentrations in bulk ice, which induce a lower gas saturation level.

Reviewer1 (comment #6). P2057, L4: Replace '0%' with 'saturation' and 'negative' with 'undersaturation'. Done

In L10, clarify whether it is total gas content or the gaseous gas component. We referred to the accumulation of gaseous O2 in bulk ice. It is reformulated now.

The text in L11-14 is unclear and, in the manner written, implies that (i) gases are incorporated in sea ice brine as a result of a temperature gradient of unspecified location in the air-ice-seawater system, and (ii) the decrease in gas solubility (where?) is a consequence of an unspecified agent. In L14, specify which component of the total gas it is that gases preferentially accumulate

The paragraph now reads as : "If the entrapment of gases in sea ice was constant during ice growth, we should expect a constant [O2] in ice with depth. The slight decreasing [O2] in ice from the surface to the bottom of the impermeable ice layers (2 to 4.9 % of brine volume fraction) (Figure 5) then indicate a decrease in the entrapment efficiency during ice growth. That decrease in the incorporation efficiency has been suggested for Ar in Zhou et al. (2013) and is also valid for CH4 (Zhou et al., 2014). Briefly, when sea ice forms, gas concentration increases in parallel with salinity (this is the so-called "brine concentration"). At the same time, because of the temperature gradient at the beginning of ice growth, brine salinity increases above seawater salinity, leading to the decrease of gas solubility in brine. Both increasing gas concentration and decreasing gas solubility lead to gas supersaturation, and eventually gas bubble formation. Whatever the ice depth where gas bubble formation take place, the formed gas bubbles may then ascend due to their buoyancy and accumulate under the impermeable ice layers. Because gas bubbles move upwards due to their buoyancy, while dissolved compounds are subject to gravity drainage (i.e., downward movement), gas bubble formation favors gas accumulation in sea ice in contrast to the dissolved compounds. However, as sea ice thickens, the temperature gradient (i.e., brine salinity gradient) decreases in the ice, and gas bubble formation due to solubility changes becomes less efficient. This mechanism explains the slight decreasing trend in [O2] in ice from the surface to the bottom of the impermeable ice layers." (p. 10 L25 – p.11 L13 of the word document)

and in L15 replace 'in comparison to' with 'in contrast to' following degassing of supersaturated brines. Done

In L19-20, I understand that the 'accumulation of gas' refers to 'accumulation of gas in the gas phase of sea ice' and the 'low gas solubility' refers to the low gas solubility in brine', while the 'induced high O2 supersaturations' could do better if it were replaced by 'can account for the high total O2 supersaturations observed in the impermeable (coldest) upper sea ice layers'. Done

The whole of this paragraph calls for heavy editing along these lines and requires a good, careful re-write and is one of many similar muddled paragraphs throughout the Discussion. In L21, in the next paragraph, specify that the extent of saturation discussed here refers to the 'total' gas content. I suggest careful combing of the whole manuscript to insert this type of identifiers; left as it is, the discussion is confusing. We have restructured the discussion section.

Reviewer1 (SC #7). P2057, L23-25: Could the undersaturation be the result of warming and freshening of the internal brines in the upper ice layers? Equally, how much of the drop in the extent of saturation can be explained by these physical processes? Explain the causality allude to here between the enlargement if the brine channels (increase in brine volume fraction) and bubble escape to the atmosphere.

Mean Ar solubility has increased from 1.9 (in BRW8) to 2.8 μmol L-1ice (in BRW10), i.e. by 50 %. Hence, in a closed system, the saturation levels should decrease by 50 %. This is the so-called "brine dilution". Meanwhile, mean Ar saturation has decreased from 263 % (in BRW8) to -15 % (in BRW10), i.e. by 106 %. Hence, changes in Ar solubility are not large enough to explain the changes in the saturation levels, and about 56 % of the decrease in Ar saturation is associated to the escape of gas bubble, gas diffusion, and the additional snow meltwater.

For O2, things are slightly different due to biological activity: Mean O2 solubility has increased from 38 (in BRW8) to 57 μmol L-1ice (in BRW10), i.e. by 50%. Hence, in a closed system, the saturation levels should decrease by 50 %, as for Ar. Meanwhile, mean O2 saturation has decreased from 280 % (in BRW8) to 58 % (in BRW10), i.e. by 79 %, which as lower than the 106 % observed for Ar. The difference 106 % – 79 % = 27 % is likely the contribution of biological activity to the O2 supersaturation.

This is an important point that we have not discussed in our previous manuscript. We have added this in the revised manuscript, on p.14 L3-14 of the word document.

Reviewer1 (SC #8). P2058, L1-4 & L5-14: The point of these statements was unclear to me.

We described that superimposed ice formation may induce large O2 concentrations at the surface of BRW10, despite the fact that sea ice is theoretically permeable (brine volume fraction exceeding 10% at all depths). This paragraph does not exist anymore in the revised manuscript.

Reviewer1 (SC #9). P2058, L22: Clarify which gas component of the measured total gas standing stock was exchanged upon warming and permeability increase. Written as is, it alludes to either gaseous or dissolved gas exchange or both, and, therefore, two different mechanisms. Both gaseous and dissolved gases are exchanged.

Reviewer1 (SC #10). Title of Section 4.2 & 4.2.2: Clarify 'sensitivity'. We modified the titles due to the new structure of the paper. Thus, these titles do not exist anymore.

Reviewer1 (SC #11). P2061, L13 & L19-28 & P2062, L1-11: Clarify and justify the validity of applying the calculations discussed here to the results of this study. Gas partitioning between the gaseous and aqueous phase of sea ice should not affect the total (bulk sea ice) gas content measured here and, therefore, the gas ratios, unless the gas bubbles are lost from sea ice. Further, in the statement in L13-17, it is unclear how the diffusivity difference amongst the investigated gases affects the 'sensitivity' of the two total gas ratios to record biologically-driven changes in the total O2 content of sea ice.

The main idea is that the O2/Ar and O2/N2 ratios in an ice layer upon consolidation (i.e. when it becomes impermeable) may be not the same ratios as in seawater. We described the potential changes associated with gas diffusion and gas bubble formation when the ice layer was still permeable, and use the results to estimate potential errors in our NCP (calculated using O2/Ar and O2/N2). Because gas bubbles may move upwards owing to buoyancy (as long as sea ice remains permeable), gas partitioning will affect the gas ratios.

Reviewer1 (SC #12). P2063, L29: State how you calculate NCP-O2 in mmol m-2 d-1 from the oxygen volumetric concentration units in eq. 4.

We multiplied the measured O2 concentration per volume of crushed ice (mol L-1) by the thickness of our sample (5 cm, i.e. 0.05 m) to obtain the equivalent O2 per square

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meter (mol m-2). We have added a new paragraph in the materials and methods to clarify this : "Multiplying the [O2]bio obtained in equation 3 (in mol O2 L-1ice) by the ice thickness of the samples (generally 5 cm) gives a production of O2 in mol O2 m-2. Then assuming an O2/C ratio of 1.43 (Glud et al., 2002) and the molar mass of C, we can get the equivalent C uptake in gC m-2. The change of that C uptake over time gives the NCP." (p.7 L17-20 of the word document).

Reviewer1 (SC #13). P2064, L15-16: Clarify 'obvious', 'O2 exchanges', and 'retrieving'.

We changed that paragraph.

Reviewer1 (SC #14). P2064, L22-23: Explain 'physical O2 supersaturation' and why it should be negligible.

O2 supersaturation due to physical processes (gas bubble formation or solubility decrease) is unlikely in BRW10, because the ice was completely permeable (brine volume fraction exceeding 10 % throughout the ice cover) and Ar was at saturation, or even undersaturated due to the additional snow meltwater.

Reviewer1 (SC #15). P2065, L6: Based on eq. 4, another, implicit, assumption in eq. 5 is that Ar/Areq = 1.

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 [O2]bio, which is the concentration of O2 in sea ice due to biological activity rather than NCP (i.e. O2 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.

Reviewer1 (SC #16). P2065, L24: Explain how you calculate the NCP in carbon units. We converted NCP in carbon units based on the O2/C ratio of 1.43 following Glud et al., (2002), as described earlier in the text. But as we said in response to SC#12, we have added this in the materials and methods.

Reviewer1 (SC #17). P2065, L26: How discernible from zero (no biological activity) are the calculated NCP values with depth in the ice in BRW10? In other words, what is the uncertainty in the calculations? We have performed an uncertainty estimate using Monte-Carlo procedure in the revised version. The paragraph reads as "We estimated the propagation of errors on [O2]bio (calculated from equation 3), using the Monte Carlo procedure and neglecting the error on gas diffusion (i.e., assuming equivalent diffusivities for O2 and Ar in sea ice as in Crabeck et al. (submitted)), we used random values of the measured parameters (T, S and O2/Ar) between the mean ± SD over 1000 iterations, assuming a maximum error of 9.9 % on [O2]eq/[Ar]eq due to gas bubble formation and an absolute error of 0.1 for T and S (Table 2). The calculated maximum uncertainty on [O2]bio is then 34 %." (p.16 L28 – p.17 L3).

Reviewer1 (SC #18). P2066, L23-24: Clarify where and when (season) the Nomura et al. (2010) rate was observed. In L25-27, explain why an additional source of dissolved inorganic carbon (DIC) is required in the under-ice seawater for photosynthetic production in the bottom sea ice when there is DIC in the brine of the biologically active sea ice layers; also, add 'primary production' or 'photosynthetic production' or something along these lines for clarity at the end of L27.

The measurements of Nomura et al. (2010) took place in late May, and the maximum C uptake we referred to in our manuscript was measured the 26th of May 2008, hence about the same time of the sampling date of BRW10 (5th of June), one year before. However, since our previous assumption was not correct (see SC#15), that part has been removed in the revised ms.

Technical comments (TC):

Reviewer1 (TC #1). P2050, L15: Replace ‘determined’ with ‘computed’, as no experiments were performed in this study to determine the solubility of the investigated gases. Done

Reviewer1 (TC #2). Figure 5 is unreadable in print. It needs substantial enlargement. We removed some the axes to enlarge the figure; We will also ask to rotate or split the figure in the revised version if it is in “landscape” format. Otherwise, the figure should be readable in a A4-size sheet in “portrait” format.

Reviewer1 (TC #3). P2055, L20: Replace ‘showed the atmospheric values’ with ‘were close to their respective the atmospheric values’. Done

Reviewer1 (TC #4). P2052, L26, P2053, L1-3: This is irrelevant information and I suggest removing it. Done

Reviewer1 (TC #5). P2058, L17: Replace ‘remove’ with ‘alleviate’. Done

Reviewer1 (TC #6). P2059, L16: Replace ‘mismatched’ with ‘did not coincide’ Done

and in L22, insert ‘diffusive’ before ‘transport’. We inserted “diffusive and convective” before transport.

Reviewer1 (TC #7). P2060, L13: Replace ‘bacteria activities’ with ‘bacterial activity’. In L20, replace ‘from’ with ‘to’. Done

Reviewer1 (TC #8). P2064, L7: Replace ‘witness’ with, for example, ‘suggest’. Done

Reviewer1 (TC #9). P2065, L11-13: This is a fragment of a sentence and does not make sense. The subject “We” was missing. Sorry for that mistake.

Reviewer1 (TC #10). Caption of Fig. 6: I suggest replacing ‘assuming equilibrium between the diffusion and NCP’ with ‘assuming a (transient) steady state depth distribution of bulk sea ice O2 (gaseous + dissolved) content’. We have replaced that figure in the revised version.

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