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## ***Interactive comment on “Physical controls on the storage of methane in landfast sea ice” by J. Zhou et al.***

**J. Zhou et al.**

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REVIEWER 2: This is an interesting and well written paper, which highlights the physical controls on methane dynamics within sea ice and the authors have gone to great lengths to verify their observations and data. Their major conclusion is that methane storage in sea ice is the primary source of elevated methane levels compared to the underlying water and they basically rule out that biological processes lead to elevated methane concentrations within sea ice. At first reading this is indeed a convincing conclusion resulting from the available and presented data. However, I do have some major contentions regarding the way they arrive at these conclusions and their take home message. The authors, in a previous publication on physical and biological properties of landfast sea ice, done at the same locality and during the same period as

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described in this paper and most likely on parallel if not the same cores, have not at all referred to the chlorophyll data obtained during this study let alone considered or discussed these. The authors refer to the previous paper, but only in the context of physical properties and Argon. Nor is any reference made to the other biogeochemical data, particularly the interesting information on nutrients for example (See Zhou et al. 2013). The authors go to great lengths to assess the biological activity by calculation and argumentation. I don't understand why they don't compare the CH<sub>4</sub> bulk measurements with the chlorophyll and nutrient data they have, particularly since there is considerable variability in concentration and distribution between cores, within cores and with season. Furthermore, an analysis and comparison of CH<sub>4</sub> standing stocks is to my mind not an efficient and credible method to exclude biological activity. It is unfortunate that the authors do not have rate measurements to support this, especially since considerable biological activity must have occurred, judging by the Chlorophyll concentrations measured. Needless to say this information would have been crucial, even if it was only to substantiate their major findings. Currently, however, the omission of this available information weakens the paper.

**AUTHORS:** We did not refer to chlorophyll and nutrient data (from Zhou et al., 2013) as we do not see any direct relationship between these data to methane concentration. Although Damm et al., 2008 have shown good correlation coefficient between chlorophyll-a and methane concentration, and Damm et al., 2010 found a good correlation coefficient between phosphate and methane concentrations, there is only a poor correlation between chlorophyll-a and methane (Fig. A) and between phosphate and methane (Fig. B) in the present study. We added the correlation coefficient in the manuscript, and will provide the graphs in the Appendix. Caption of the figure: Relationships between (A) chlorophyll-a (Chl-a) and methane (CH<sub>4</sub>) concentrations, and (B) phosphate (PO<sub>43-</sub>) and CH<sub>4</sub> concentrations, in sea ice. Open and closed circles indicate respectively permeable and impermeable ice layers (i.e., brine volume fraction above or below 5 %). Chl-a and PO<sub>43-</sub> data are from Zhou et al., 2013.

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REVIEWER2: This study is on first year landfast sea ice, which has specific and unique properties that may differ considerably from those of pack ice, both first year and multi-year. One major aspect in this case was the proximity to the sediment underneath, which was 6,5 meters. This has connotations with regard to methane sources, which differ markedly from those under oceanic pack ice, for instance, where different water masses with different methane loads occur, and where the sea ice is multi-seasonal and has a different history. This is not discussed or reflected on in this study. The impression the authors give is that their results reflect that, which occurs in sea ice in general - see conclusion -and that biological activity in sea ice is not likely to play a role in methane production in sea ice anywhere and at any time. This is very misleading and needs to be constrained. One should be careful to extrapolate information gained from landfast sea ice over a water column of 6,5 meters, to the entire Arctic sea ice cover or elsewhere, not that this is what the authors are explicitly conveying, but there is a danger that this may be taken to be a fact. The authors need to account for the uniqueness of the ice they studied as well as the locality relative to other sea ice covered zones.

AUTHORS: We have modified the manuscript accordingly and have emphasized that the conclusions are valid for landfast sea ice in shallow water depth areas.

REVIEWER2: The fact that the authors in their conclusions discuss that CH<sub>4</sub> dynamics in the permeable layers need further investigation, points to the uncertainty as to what role biology may play there. This information is not mentioned in the Abstract. Furthermore it would have been appropriate to distinguish more clearly about the possible differences between processes in the impermeable and permeable layers. This information needs to be in the abstract too. In this context, I also found discrepancies between the Figure 13 in Zhou et al. 2013 and Fig 4 of this paper where the zone of permeability in the former is shown to reach the ice surface, whereas it does not do so in the latter Figure. There is an apparent transition zone during May, shown in the former figure, which is not displayed in this paper where the impermeable zone extends

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well into May. This is a little disturbing and needs to be clarified, particularly since there are differences in processes in these layers.

**AUTHORS:** In response to a comment of the REVIEWER2, we provide new plots in the supplementary material. Because Damm et al., 2008 and 2010 have suggested potential transformation of methylated compounds into CH<sub>4</sub> and have found correlation between chlorophyll-a and methane concentrations, and between phosphate and methane concentrations, we assume that the pathway that they have suggested does not exist in our ice samples, as we only found poor correlation coefficient between chlorophyll-a and methane, and between phosphate and methane in this study. About the discrepancies between the Figure 13 in Zhou et al., 2013 and Figure 4 in the manuscript: the impermeable layers are based on Zhou et al., 2013. Hence, the upper ice layers of May were theoretically permeable according to Golden et al., 1998, but our observations indicate that they were not (Zhou et al., 2013). We have modified the Figure 4 accordingly.

**REVIEWER2:** Some additional points: Fig 3: How do you explain the higher methane concentrations in the water column during June?

**AUTHORS:** The most obvious explanation for this high methane concentration is riverine input as a consequence of continental snow melting.

**REVIEWER2:** Analyses were done within one year, which means cores were stored for long periods at -30°C. Can it be ruled out that such storage has no effect on gas bubbles and brine within cores. The cores were frozen to prevent brine drainage, but what about brine expulsion at -30°C? When sea ice is frozen under these temperatures, brine can be expelled, particularly from the first few centimetres along the edges of the core. Where were analyses carried out and how were cores transported. Was there an uninterrupted cooling chain at -30°C? The authors stored their cores at -30°C to limit biological activity-what were they concerned about? That biological activity could affect the measurements? At what temperatures were the cores really

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stored? -35°C as in Zhou et al. 2013 or as described in this paper -30°C?

**AUTHORS:** The ice cores were collected in Alaska and stored in the laboratory in Barrow (BASC) at -35 °C. Then they were transported by plane from Barrow to Anchorage, then shipped from Anchorage to Antwerpen (Belgium) in a reefer (-30°C), then trucked to the cold storage facilities of Nobert Dentressange, and then to the laboratory of glaciology (Brussels, Belgium). Multiple temperature sensors were transported with the ice cores, and according to the records of these temperature sensors, the cooling chain was interrupted for 4 hours during the transport from BASC to Anchorage but the temperature remained below -20 °C all the time. Then in our laboratory of glaciology (Brussels, Belgium), the ice cores were stored between -30°C and -35 °C. We would like to highlight that the transport and storage of the ice cores followed the same procedures as for the continental ice cores. Furthermore, that transportation at low temperature is required as we also expected to measure other biogenic gas as O<sub>2</sub>, CO<sub>2</sub> on the ice cores. So it is important to limit biological activities.

Because of the low temperature of the ice, humidity of the air may induce slight freezing at the surface of the cores, but as we removed the outer parts of the ice samples before each analysis, to avoid contamination of our CH<sub>4</sub> concentrations in sea ice by the CH<sub>4</sub> of the surrounding atmosphere.

We believe that we have put considerable effort and money to ensure the quality of our data, but we are open to any additional suggestions that the reviewer may have on good practices for the future transport and storage of our sea ice samples.

**REVIEWER2:** Line 13 Page 6 “Providing that there is no CH<sub>4</sub> in the pure ice matrix”. This needs some explanation or reference.

**AUTHORS:** According to Week (2010), the crystallographic structure of sea ice, hence the arrangement of the water molecules in space does not allow the incorporation of impurities in general. Sometimes, we may find defects in the ice structure, but only a few number of foreign atoms and molecules (HF, F<sup>-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup> and NH<sub>4</sub>F), which have

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the appropriate charge and size, may be incorporated in the pure ice structure (i.e., pure ice matrix). In addition, CH<sub>4</sub> incorporation in ice matrix is possible in clathrates, but requires high pressure, and we thus do not expect to find this in sea ice. Further, our CH<sub>4</sub> concentrations in brine (that are deduced using CH<sub>4</sub> concentrations in ice and brine volume fractions) were similar to the observed CH<sub>4</sub> concentrations in seawater; this would not be observed if there CH<sub>4</sub> in the ice matrix. Therefore, it is very likely that there is no CH<sub>4</sub> in the pure ice matrix.

REVIEWER2: Line 5-10 page 7 “This is allowed providing that the relationship of Wiesenburg and Guinasso (1979) is valid for the ranges of brine temperature and –salinity”. Is the relationship valid or not? Important conclusions are not well represented in the abstract.

AUTHORS: From the best of our knowledge, there is no study on gas solubility for the ranges of brine temperature and salinity in ice. Therefore we generally assume that the temperature and salinity-dependent gas solubility (that is established for seawater) is valid for sea ice. This is what we have done for argon in Zhou et al., 2013. In the same paper, we have demonstrated that the extrapolation of the relationship of gas solubility to sea ice temperature and salinity does not significantly affect our estimate of gas solubility in ice.

REVIEWER2: In the conclusions, “seems” is used more than once i.e that CH<sub>4</sub> did not seem to be affected by biological processes. This reflects uncertainties, which weaken the final conclusions. Be more succinct. I recommend publication of the paper after significant revision, taking into account the questions and problems mentioned above.

AUTHORS: We have reformulated the conclusion following the recommendation of the reviewers. The conclusion now reads as “We reported on [CH<sub>4</sub>] evolution in landfast sea ice and in under-ice water from February through June 2009 at Barrow (Alaska). Our [CH<sub>4</sub>] in sea ice and [CH<sub>4</sub>] in seawater are consistent with records from the area with CH<sub>4</sub> release from sediment and gas hydrate destabilization (Kvenvolden et al.,

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1993; Lorenson and Kvenvolden, 1995; Shakhova et al., 2010). As summarized in Fig. 4, gas exchange likely took place during initial ice growth between sea ice and the atmosphere, and the formation of cracks could lead to a decrease of CH<sub>4</sub> at the very surface of the ice. Then when sea ice reached ca. 25 cm of ice thickness, gas bubble formation triggered by strong solubility changes could have favoured CH<sub>4</sub> accumulation in ice. CH<sub>4</sub> retention in the ice was twice as efficient as that of salt. However, as sea ice thickens, temperature and brine salinity gradient were no more sufficient to trigger bubble nucleation, and CH<sub>4</sub> was then trapped in the dissolved state, as salt did. The subsequent evolution of [CH<sub>4</sub>] in sea ice layers mainly depended on physical processes, as chlorophyll-a and phosphate concentrations did not support in situ CH<sub>4</sub> production, and as CH<sub>4</sub> oxidation was likely insignificant. Abrupt changes in [CH<sub>4</sub>] in sea ice occurred when sea ice became permeable; these were associated with the release of gas bubbles to the atmosphere. Therefore, the main role of our landfast sea ice in the exchange of CH<sub>4</sub> from seawater to the atmosphere was its control on the amount of CH<sub>4</sub> that it is able to store in its impermeable layers and the duration of such storage. Although gas incorporation and sea ice permeability are two dominant factors driving CH<sub>4</sub> concentrations in sea ice in our study site, the magnitude of these processes may be different in the other polar oceans. Indeed, the contribution of the ebullition fluxes of CH<sub>4</sub> from sediment to the concentration of CH<sub>4</sub> in bulk ice, the transport of CH<sub>4</sub> through the ice, the significance of physical versus biological controls on CH<sub>4</sub> dynamics rely on the nature of the sediment, the water depth, the physical parameters of the ice and biological activity within the ice, which may vary depending on the location. In case of a higher mix of physical and biological controls on CH<sub>4</sub> concentrations in bulk ice, we would recommend to measure: (1) the carbon and hydrogen isotopes of CH<sub>4</sub> in sea ice, as isotopic fractionation is highly sensitive to biological processes, and (2) the same isotopes in the sources (e.g., organic matter). Indeed, previous studies have suggested that biogenic CH<sub>4</sub> within anoxic sediments may have carbon isotopic values as negative as -110 ‰ (Whiticar, 1999), in comparison to that formed by CH<sub>4</sub> oxidation (-10 to -24‰ (Damm et al., 2008; Schubert et al., 2011)), but

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few of them have considered that the measured isotopic values in the sediment or in seawater also depend on the isotopic composition of the sources.”

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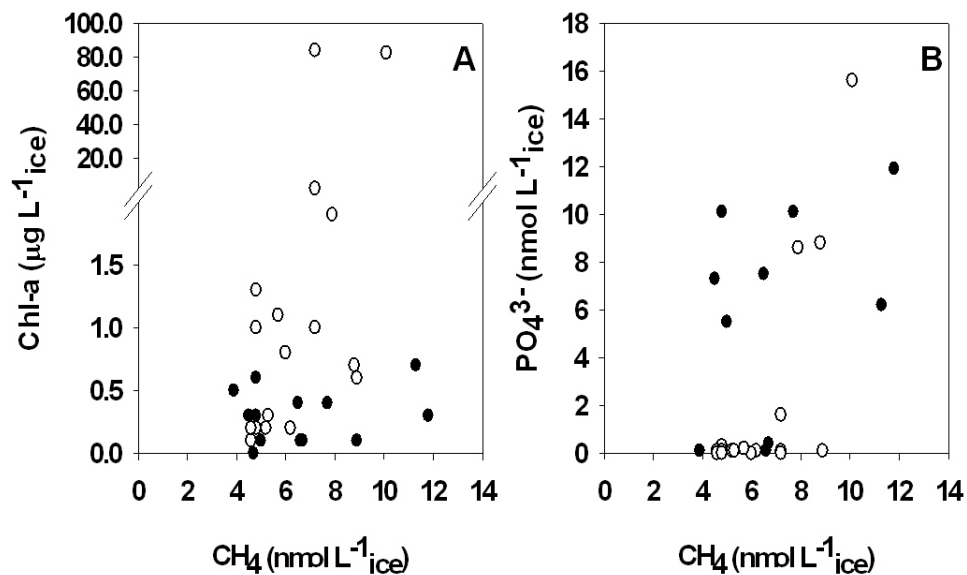
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**Fig. 1.** Relationships between (A) chlorophyll-a and CH<sub>4</sub> concentrations, and (B) phosphate and CH<sub>4</sub> concentrations, in sea ice.

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