

Reply to Reviewers Comments:

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We thank to the editor and both reviewers for taking time to critically review our paper and for their constructive comments, which no doubt go to improve the paper. Our responses to each of the referee's specific comments are listed below:

Response to the comments of Anonymous Referee # 1

**Title:** will be changed to: **Coexisting methane and oxygen excesses in nitrate-limited polar water (Fram Strait) during sea ice melt and modelled constraints for this paradox**

**Figure 1:** has been modified

**Chapter 3:** title is changed to: Sampling and analytical procedures

**Line 95:** *specify used oxygen sensor; has the sensor been Winkler verified during the cruise?*

The SBE43 dissolved oxygen sensor SN43 is used and calibrated using Winkler titration. The text has been modified accordingly.

**Line 98:** "towed in through" "in" has been deleted

**Line 129:** "...in ice covered as well in ice-free..." has been deleted to avoid misunderstanding

**Line 144:** *In the ice-covered regions light transmission was only reduced in the upper 20 m?*

Yes, in comparison to the AW where the light transmission is reduced up to 60 m. These differences are due to the different bloom situations.

**Line 145:** *crated different - WHAT-WORDS MISSING – under ice* : is rewritten

**Line 154:** *CUT "increasing" : correlated with oxygen concentrations:* has been changed

**Line 158:** *cannot see the stringence of the argument. If you start with N-limitation and continue with Redfield-conform PP, this will further drive the remaining nutrients away from the Redfield ratio. Please strengthen – or revise your statement concerning the need for additional nitrogen sources*

We agree and the statement has been changed to:

The almost constant nitrate/phosphate ratios, which correlated with oxygen concentrations, substantiate this observation (Fig. 2E and H). By comparison, a shift from new to regenerated production was obviously evident in nitrate-limited PSW. The PSW on the East Greenland shelf is

generally characterized by low initial nitrate concentrations (Kattner and Budéus, 1997). In summer the surface waters are extensively nitrate exhausted, and ammonium uptake becomes more important (Smith et al., 1997). The pronounced oxygen enhancement in the PSW combined with a highly variable nitrate/phosphate ratio showed the importance of both new and regenerated production, probably dependent on the ice cover.

***Line 173: the paragraph is very vague. DMSP concentrations close to those in the ice free AW bloom are explained with ice algae, and the fact that PSW waters are DMSP poor even close to the ice edge is explained is eaten up by bact. consumption. Neither the one nor the other effect in vicinity of ice is really constrained by the data, and also not really important for the stories of the paper. Consider to remove, or make stronger.***

We removed and restrict our statement to DMSP in the form that for methane formation, DMSP may act as a potential precursor

***Line 184: concentration in equilibrium with the atmospheric partial pressure (between 3 and 3.5 nM, depending on T and S).***

has been modified

***Lines 199 to 200: here, the authors directly translate the enhanced methane concentration into a hotspot of methane production. This needs justification. The high concentrations occur under the partly ice-covered region, i.e. in the area of reduced air-sea exchange. On top of that, it is the only area with strongest upper water column stratification (see Fig 2A). Both tend to diminish escape of the methane produced. I do not argue that the authors are right, but this has to be considered in the argumentation.***

This point will be added to the text.

***Line 237 in connection to line 263: is this not the diffusion coefficient of water in the cell which has to be considered here? Which is not per se the same than in the surrounding water (off course of minor importance for the argumentation)***

This is correct it is the diffusion coefficient of water in the cell, which has to be considered here. We have used the value of seawater for both the diffusion coefficient of water in the cell and in the surrounding water. Inside the cell the salinity is probably slightly lower than in the surrounding seawater as part of the osmotic pressure of the cell is established by means of organic osmolytes. However, at 0°C, a salinity change from 35 (in seawater) to about 30 (in the cellular interior) has only a minor impact on the diffusion coefficient for oxygen ( $S=30-35$ :  $D = 1.0580-1.0503 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (Ramsing and Gundersen, 1994).

There is one universal aspect of the cellular interior, however, that is largely neglected — the fact that it is highly crowded with macromolecules. Inside the cell macromolecules, can occupy a large proportion of the volume of the cell, which reduces the volume of solvent that is available for diffusive transport processes within the cytosol. Reducing the available volume decreases the effective diffusion coefficient, probably also for O<sub>2</sub>.

For a decreased diffusion coefficient, however, it follows from equation (6) that there is a lower concentration of  $O_2$  in the interior of the cell. Consequently, using the diffusion coefficient of seawater also for the interior of the cell, we obtain a conservative estimate for  $C_{0,max}$ . This means, that the maximum concentration in the environment, which allows anaerobic processes to take place inside the cell is possibly higher than predicted by our model.

***Line 228 AND 257: I strongly recommend to add a Figure 3ab showing in 3a a conceptual scetch of the setting, illustrating the concept, boundaries etc., and in 3b a graph  $C(r)$  vs  $r$  illustrating the solution of equation (6). This would make it easier for the non-modeller.***

We will include the suggested figure. Since the strongest decay of  $C(r)$  occurs across the cell membrane, figure 3b will also include  $C(r)$  for the membrane region.

***Line 278: Though I see no better way the using Spalding and Portis either, I suggest to add a sentence on the limitations of this approach. Membranes can be highly specific in their transport characteristics, so equation 8 cannot be taken for granted at all.***

In order to point out the limitation of Spalding and Portis, we will add the following suggested sentence after equation (8):

*‘... The inverse proportionality between  $P$  and the square root of molecular mass is assumed to represent a useful approximation for gases that permeate the membrane via (passive) diffusion. ...’*

The latter cannot be taken for granted, since highly specific membrane channels, such as aquaporins, might be involved in the transport of gas molecules through the membrane. Aquaporins are a family of membrane proteins specialized in rapid water conduction across biological membranes. Whether these channels also conduct gas molecules and the physiological significance of this potential function is still a matter of debate. To address this question, the permeability of aquaporins to  $O_2$  and  $CO_2$  was investigated by means of molecular dynamics simulations of membrane-embedded aquaporin and of a pure lipid bilayer (Y. Wang et al., 2007). The water pores showed a very low permeability to  $O_2$ , but may contribute to the overall permeation of  $CO_2$  due to its more hydrophilic nature. Hence, the permeability to  $O_2$  is possibly lower than the value predicted by equation (8) (Spalding and Portis). For a decreased permeability to  $O_2$ , however, it follows from equation (4) that there is a stronger decay of  $C(r)$  across the cell membrane, Consequently, using equation (8), we get a conservative estimate for  $C_{0,max}$ .

Y. Wang et al., Exploring gas permeability of cellular membranes and membrane channels with molecular dynamics. J. Struct. Biol. (2007) 157: 534-44.

***Line 282: I understand that it is tempting, but given the uncertainties in the – nice – approach, it is mere coincidence that you end up with the  $C_{max}$  matching the observed data. Also, I would like a sentence on the surrounding surrounding the bacteria (i.e. Roseobacter). Wouldn't the microbes be mostly bound to particles rather than free floating, which again mains that the oxygen***

***concentration  $c_0=c_a$  they would “see” might be lower than the oxygen concentration in the bulk seawater (i.e. Jorgensen 1977).***

In the case that the microbes are attached to particles rather than floating free, the volume of the accessible region of the environment, which can supply  $O_2$  to the cell surface is reduced. Reducing the available volume decreases the effective diffusion coefficient of  $O_2$ .

For a decreased diffusion coefficient in the surrounding water, however, it follows from equation (5) that there is a lower concentration of  $O_2$  at the cell surface ( $r = a$ ) and consequently also in the interior of the cell. Hence, assuming a free floating cell, we obtain a conservative estimate for  $C_{0,max}$ . We will improve the description of our assumptions for the model and add the following sentences to the text preceding equation (1):

*‘... Assuming a free floating cell, the diffusion coefficient ( $D$ ) in the surrounding water is a constant and is given by the value in bulk seawater at  $0^\circ C$  for a salinity of 33. Inside the cell the salinity is probably slightly lower than the one of the surrounding seawater as part of the osmotic pressure of the cell is established by means of organic osmolytes. However, at  $0^\circ C$  a salinity change from 35 to about 30 (cellular interior) has only a minor impact on the diffusion coefficient for oxygen ( $S=30-35$ :  $D = 1.0580-1.0503 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (Ramsing and Gundersen, 1994). Therefore, we assume the diffusion coefficient of seawater ( $D = D_w$ ) for both the water in the cell and the surrounding water ... ’*

We agree with the referee, that the exact agreement of  $C_{0,max}$  with the observed data is probably a coincidence. However, given the uncertainties, we tried to make conservative assumptions for the critical model parameters, such as the membrane permeability to  $O_2$  (see above). Therefore, the maximum concentration in the environment, which allows anaerobic processes to take place inside the cell is possibly higher than predicted by our model. Even, a predicted  $C_{0,max}$  lower than the observed data would not alter the conclusion of our model as long as  $C_{0,max}$  is much higher than zero. We hope that the model is convincing in this respect.

Response to the comments of Anonymous Referee Review # 2

***The oceanographic settings of the study area are very complex and probably unfamiliar to many oceanographers and biogeochemists, so it is difficult to figure out the oceanographic processes that occur when they are not well explained and the hydrography not included in detail***

The water masses are described by density gradients and the nutrients composition.

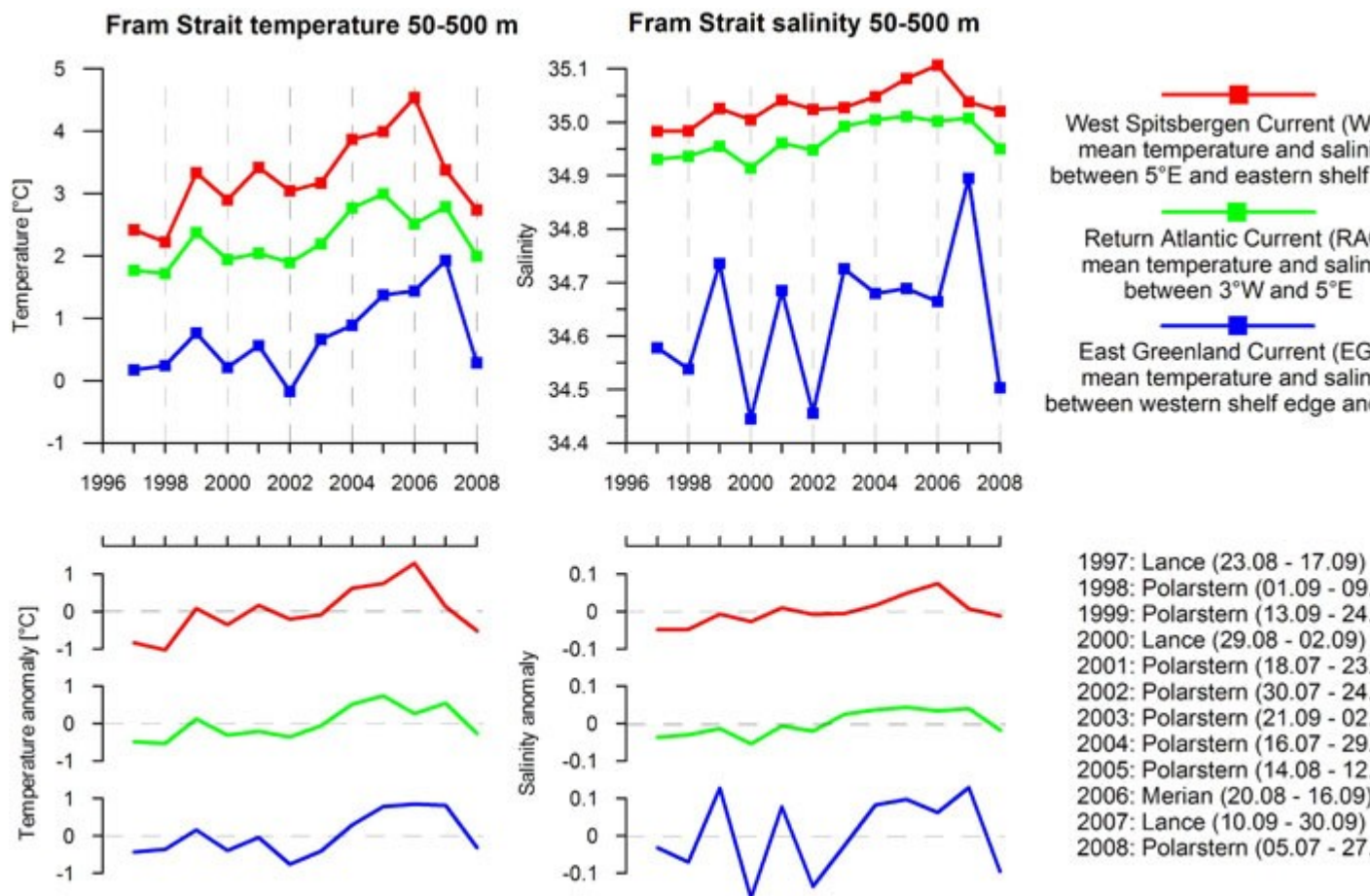
The detailed oceanography of the region has been intensively investigated in the past years and references are provided. Oceanographic processes are not the focus of our paper and hence, hydrographic data in more detail does not supply and further information for our purpose.

*Also, the study area appears to be very dynamic at an inter-annual scale, with a clear long term trend driven by global warming. This is of tremendous importance in the sense that that it is undergoing rapid changes. The concentration of gases may be very sensitive to these changes; if gases are being produced and exchanged with the atmosphere in this region, they act as a positive feedback mechanism for global warming.*

We do not entirely agree with this statement. The increase of methane concentration in the atmosphere of the northern high latitudes has more or less come to halt in the decade between 1998 and 2008 (Dlugokencky e. al., 2009). Therefore both submarine released methane and in situ produced methane in the water column is not likely to increase the sea to air flux due to global warming. However to identify the sink(s) of these marine methane sources will be a topic of future research.

As far as the study area is concerned: the variability in temperature and salinity between 1996 and 2008 shows that there is no clear trend in the warming of the upper water column in the study area (see figure below, weblink: [\temperature-salinity-and-volume-fluxes-in-the-fram-strait](#)). Temperatures have increased between 2002 and 2007 but decrease again clearly in 2008, the year we did our investigation. Also the salinity shows no clear trend in this time span but there is clear drop in salinity in 2008 compared to 2007. However, this change increases the solubility of gases and does not act as a positive feedback for global warming.

Dlugokencky, E. J., L. Bruhwiler, J. W. C. White, L. K. Emmons, P. C. Novelli, S. A. Montzka, K. A. Masarie, P. M. Lang, A. M. Crowell, J. B. Miller, and L. V. Gatti: Observational constraints on recent increases in the atmospheric CH<sub>4</sub> burden. (2009), Geophys. Res. Lett. VOL. 36, L18803, doi:10.1029/2009GL039780.



*As MS' title mentioned, results report a hot spot of CH<sub>4</sub> in nitrate limited and oxygen excess water during on-going sea ice melting. First of all, nitrate limitation is a concept that comes from the biological community. Neither physiological studies, nor biogeochemical community indices (such as N:P or P\*, Chl-a) are included and analysed with sufficient depth. Let include some biological data*

That is correct, nitrate limitation is a concept that comes from the biological community, but what is wrong with this concept? It adequately describes the stage of oligotrophy for our purpose. It remains unclear to us which biological data and for what purpose it should be included.

*Secondly, oxygen excess is not an appropriate term. Usually surface water are supersaturated in O<sub>2</sub>; here, no saturation percentage was estimated and due to the different salinity and temperature of the present water mass (i.e., PDW and ADW), I deduce that saturation percentage may be similar along the zonal transect. Author should indicate saturation percentage values*

The saturation percentage is not similar along the zonal transect. In surface water, temperatures are equally low in both water masses and only salinity differs (between 31 and 33) which results in a solubility difference of 1.4 % (31=368.5μmol/l and 33=363.4μmol/l) between both water masses, while the oxygen concentration increases up to 410 and 360 μmol/l in PW and AW, respectively. Hence the differences in oxygen saturation are that AW is nearly saturated while PW is clearly oversaturated (up to 11%). We will add the saturation percentage values in the reviewed text.

***The MS did not described data clearly, tables are not included, it is only possible to follow by observing one figure, but which lacks sufficient resolution.***

We do not agree with this statement. There is one figure which shows the region where transect was including where the polynya is localized. A second figure is divided into 8 sub-figures where i.e. the density profiles, the phosphate and nitrate distribution, the light transmission, the oxygen, methane and DMSP concentration provide a detailed picture of the situation in the surface water. The data will be available in the data bank “Pangea”.

***Two main conclusions arise from the MS, not based on the results obtained, 1.- “methane production occurred during regenerated production in Pacific derived water” and 2.- methanogenesis takes place in bacterial cells. In my view, it is very difficult to reach such conclusions based only on oceanographic data. Except for phytoplankton composition, neither biogeochemical rates nor microbial biomass and abundance are included.***

1. Regenerated production occurs in Pacific derived water. This is shown by the specific nutrient composition, i.e. nitrate depletion in combination with oxygen excess clearly above the saturation level. In this point our results are in agreement with previous data sets from Pacific derived water in the Arctic Ocean and references are given. In addition, a clear methane excess has been previously detected in Pacific derived water. Both aspects combined allow us to conclude that methane production is a process, which may occur during regenerated production.
2. In Damm et al, 2010, the results of an experiment for methane production are given. This experiment was carried out with seawater from the Fram Strait in 2008, where the microbial community is also described.

So both main conclusions are based on data from this manuscript or by citations of Damm et al, 2010.

***This means that it is not possible to determine any causal relationships due to the lack of biological measurements (bacterial abundance by epifluorescence microscopy or flow cytometry and even molecular characterization). In the same sense, it is very speculative to assume that microbial cells (model approach) can support (perform) anaerobic pathways if there is no cell abundance available for the studied transect in order to associate them with high methane concentrations. I believe that the model is out of context.***

The statement that microbial cells can perform anaerobic pathways is a hypothesis (not a proof). The latter is based on a microcosm experiment (not a model approach) with Arctic surface water (where the cell abundance was available) as described in Damm et al. (2010). The purpose of the model is to propose a mechanism for the maintenance of anaerobic conditions inside bacterial cells, despite enhanced oxygen concentrations in the environment. The model is applied to answer the question which arose in context with the observed data presented in the ms: Contemporary methane and oxygen excess – a paradox?

***On the other hand, the concept of new and regenerated production methods are based on the origin of the nitrogen nutrients, but not on carbon sources; so the statement that DMSP released during the melting of the ice in the PW potentially favours regenerated production is not correct or is not well explained.***

Yes, the concept of regenerating production is based on nitrogen nutrients and we have used this concept in this context. DMSP is exclusively discussed as a potential precursor for methane production which may be favoured during regenerated production (in contrast to new production where methane is in equilibrium concentration). The sentence “DMSP as an additional carbon source” is not clear and will be corrected to “DMSP as potential precursor for methane formation”

***The author convincingly introduced a mechanism of CH<sub>4</sub> production in the central Arctic (Damm et al. 2010). They discussed the potential role of DMSP (dimethylsulfoniopropionate) degradation products as precursors for methane formation and propose methylotrophic methanogenesis as the principal pathway, using direct (spike experiments) and indirect evidence; but this explanation is not explored in the MS, only an inverse relationship between DMSP and CH<sub>4</sub> concentration is mentioned (without any statistical support).***

The inverse relationship was found in Storforden (Svalbard region), Damm et. al, 2008). As a consequence we discussed a mechanism of methane production and the potential role of DMSP as precursor for methane formation in Damm et. al, 2010. This mechanism was also confirmed by spike experiments (Damm et. al, 2010). In this MS we focus on the fact that comparable environmental conditions exist in the Fram Strait where Pacific derived water occurs and where we have also found the methane excess.

***Other important physical mechanisms that should be considered, is the effect of sea ice melt. Gas concentration (i.e., O<sub>2</sub> or N<sub>2</sub>O) in sea ice is lower than in the water column, so a CH<sub>4</sub> “enriched” or “poor” layer could be the effect of sea ice melting or formation, and gas distribution could be associated with the distribution of polynyas.***

Assuming lower gas concentration in sea ice than in the water, melting would decrease the methane concentration in surface water. But in PW, a methane excess was detected below the melting sea ice. Additionally, in AW sea ice melting had occurred, but there methane is in equilibrium with the atmosphere. Both aspects together confirm that the methane excess in PW is produced in situ.  
...gas distribution could be associated with the distribution of polynyas.

The effect of polynyas on gas distribution is coupled to convection of water masses, which occur during winter, autumn and spring (Damm et al., 2007). In late summer, surface water is highly stratified, which in contrast clearly restricts the gas exchange. This is by the way one of the reasons why we measured a methane excess.