

Interactive comment on “Dissolved greenhouse gases (nitrous oxide and methane) associated with the natural iron-fertilized Kerguelen region (KEOPS 2 cruise) in the Southern Ocean” by L. Farías et al.

Anonymous Referee #2

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The paper describes the distribution of dissolved nitrous oxide and methane in relation to a number of physical and biogeochemical variables in the water column of the Kerguelen plateau, a region that has been previously studied in relation to natural iron fertilisation. The authors report some undersaturation of N₂O in in coastal and certain offshore sites, but conversely very high CH₄ concentrations and emissions that generally exceed those reported for the open ocean. They relate N₂O undersaturation and CH₄ supersaturation to dissolved iron availability and chlorophyll-a, and indirectly attribute CH₄ production to methylophony and N₂O undersaturation to nitrogen fixation.

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They also attribute the high variability in the distribution of dissolved GHGs across the Kerguelen plateau to mesoscale activity.

The paper would benefit from clarification at the end of the Introduction defining the aims and context of the paper. Its not clear that the KPR does provide a natural laboratory, or that the evolution of a phytoplankton bloom is followed in the dataset, and generally the focus of the paper is not well-framed by the Introduction. It needs to be more clearly articulated that the paper focuses on the potential role of iron-fertilised phytoplankton blooms in the Southern Ocean on GHG dynamics. Line 7-8 on Pg 12535 suggests this, but the Introduction largely focusses on N₂O & CH₄ production processes in general.

The dataset is comprehensive but unfortunately the presentation and interpretation does not do it justice. There are a number of format and presentational issues, particularly relating to the figures, that make the interpretation difficult to follow, and observed trends are attributed to processes or parameters for which no data is presented. For example, it is unclear why Fe is only described qualitatively, and how this is then applied in the PCA analysis; this isn't acceptable when Fe is at the centre of the interpretation, so presentation of the Fe data is essential. Its difficult for a reader to be convinced that “natural Fe fertilization did not seem to stimulate N₂O accumulation in surface and subsurface water” (Pg 12548 Line 6-7), when no Fe data is presented, and Fe is only discussed qualitatively. The same goes for the DMSP data in the interpretation of CH₄ distribution and nitrogen fixation regarding the N₂O; if these are the important processes then either show the data, or at least critically evaluate whether these parameters/processes are capable of supporting the observed distributions.

A major issue in the interpretation is that the authors associate the high CH₄ supersaturation with iron-induced phytoplankton production in the water column without considering that the methane, like the iron, could originate in the coastal/shelf region. This is despite recording methane supersaturations that are high relative to open ocean waters and more typical of coastal waters, and also that the high CH₄ supersaturation

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offshore (TEW7) is found at similar low densities to the coastal/shelf water at TEW1. The authors identify the importance of “advection related to mesoscale structures”, but do not extend this idea to transport of CH₄ from the coastal/shelf region near the Kerguelen Islands.

The interpretation of the PCA analysis is incorrect and rather limited. The plots are not identified in the Figure 5 legend but, assuming the upper left plot is a) the W-E transect ML data & and the upper right is b) the W-E entire water column data, then these do not show a similar grouping, contrary to Pg. 12543 Line 1-2. The description of a) from Line 20 Pg 12542 does not match Fig 5a – there are not three “sets “ as one of the sets is only one station, and there is not a close relationship between Fe, CH₄ and Chl-a (in fact quite the reverse). Fig 5b instead suggests the parameters do not explain the majority of the stations, and the trends conflict with that of Fig 5a. If Fe-induced primary production is the source of CH₄, with CH₄ consumption in deeper waters would we expect to see agreement between the ML (5a) and full water column (5b)? It would have been more informative if temperature, salinity and density were included in the PCA analysis.

In places the paper relies on general observations of conditions on the KPR reported in other papers and uses this as evidence to support the conclusions, rather than clearly showing the relationships and factors influencing N₂O & CH₄. I recommend major revision of this paper before publication.

Specific comments:-

Page 12533 Abstract - “intense CH₄ cycling” – Whereas there is high supersaturation of CH₄ indicative of production there is no evidence presented for methane cycling

Page 12534 Introduction Line 1 “linked” is a bit vague. Could be read as indicating increasing GHGs are causing higher GHGs

Line 6 “This means that GHGs play a major role in the Earth’s radiative balance”. Is

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there some doubt in this?

Line 16 Tilbrok misspelt

Line 25 “or gas sequester” - does this mean undersaturation?

Page 12535 Line 2-3” the polar front zone (PFZ), is characterized by marked biogeochemical gradients, most of which are driven by Fe availability (Law and Ling, 2001; Walter et al., 2005)” - do either of these cited papers actually show this?

Line 4-7 “N₂O sinks and/or sources can be observed occasionally in different regions of the ocean (Butler et al., 1989; Law and Ling, 2001; Charpentier et al., 2010), whereas CH₄ sources have always been found in all the world’s oceans (Forster et al., 2009)”. I think the authors are trying to say that the surface ocean is always supersaturated with CH₄, but this is not the case for N₂O; in which case this should be clarified. Forster et al (2009) only focus on the Atlantic, not the global ocean.

Line 7 “Thus, this study. . .” The use of “Thus” is unclear as the preceding sentences do not mention natural fertilisation events. Perhaps a better way to frame this would be to discuss what is known about the relationship between N₂O & CH₄ and nutrients in the Southern Ocean including the observations from artificial fertilisation experiments (Walter et al; Law & Ling).

Line 21-26 Sentence too long and structure incorrect, & dimethylsulphide misspelt. In keeping with the previous sentence this sentence should focus on CH₄ production mechanisms that could occur in the Southern Ocean.

Page 12357 Line 23 “air” should be a defined CH₄ concentration

Line 25. More methodological details are required. How was the headspace transferred volumetrically from the sample bottle – by syringe, or flushing onto a sample loop? What are the reproducibility estimates based on – all samples? Where they collected in duplicate or triplicate?

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Line 27 The analytical error is unlikely to be the same for all nutrients, so which does the error given apply to?

Figure 1 “Antarctic” misspelt

Figure 2. The Figure legend is only partially complete and is incorrect. a) & b) are T & S for the N-S transect, c) and d) are T& S for the E-W transect and e) and f) are T-S diagrams for the N-S & E-W transects respectively. It is not specified what the arrows in a) –d) indicate, and it is unclear what “third station (purple)” is referring to. f) is missing the station profile key.

Fig 3 & 4 labels are mixed up. Fig 3 is the meridional transect between 45-51S, and Fig 4 the zonal transect between 69-75E

Pg 12453

Line 1 The interpretation of the PCA relationships between the ML & full water column for the E-W transect is overly simplistic. The text suggests “ a close relationship between N₂O and nutrients and CH₄, Fe and Chl a” where none exists, and a) and b) show clear differences in relationship between N₂O & nutrients and also CH₄, Fe and Chl.

Line 10 “which are being sunk” – deepening?

Line 17 – what are “certain” Fe levels?

Line 18 – Unclear what is meant by “immersed in SAMW” ?

4.1 Physical characteristics – this section only discusses physical characteristics for half a paragraph before switching to biogeochemical characteristics

Line 27 – Chl a levels do not look to be less than 0.005 $\mu\text{g/L}$ at Station R in Fig 6

Line 28 – “Remarkably...” – Unclear why this is remarkable, as a CH₄ max at the base of the ML, and increasing N₂O concentration with depth, are relatively common

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features in different ocean regions

Pg 12456

Line 3 “These structures” - This sentence needs to be rewritten for clarity

Line 6. The eddies provide the physical mechanism of horizontal transport & vertical isolation that contribute to development of a bloom; however they can only “create fertilisation” if they are transporting nutrients & iron supplied by intense vertical mixing or another external source (shelf, atmospheric deposition etc) or by horizontal mixing from another water mass.

Line 8. What is “acid silicate nutrient”?

Line 10 notes that N₂O shows a close relationship with N species and not Fe in the PCA analysis, but then Sentence 15 indicates there may be dependence of N₂O production on a Fe-containing enzyme”, and so the second statement appears to contradict the PCA analysis.

Line 25 “It is important to note that stations with high TChl a levels are dominated by micro-phytoplankton with high biogenic silica content (Lasbleiz et al., 2014) and therefore susceptible to being rapidly exported to the base of the mixed layer (Jouandet et al., 2014), which explains the highest CH₄ levels found”. This doesn’t explain why the microphytoplankton accumulate in this region, as opposed to sinking through the water column, as suggested by other studies (Smetacek et al, 2012).

Fig 5. Identify what a-d are in the legend

Pg 12547

Line 4-5 “reflecting in some way consumption by local microbiological communities that support high particle matter accumulation”. As written, this suggests that bacteria responsible for N₂O consumption are also responsible for particulate matter accumulation which is unlikely. Perhaps the authors meant to say that organic matter accu-

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mulation at these stations supported the growth of a bacterial N₂O sink. The authors cite Lasbleiz et al., (2014) to justify the link between high TCHla & particulate matter at stations A3, TEW07 & TWE01 and explain the elevated CH₄; however there is no contrasting depletion of N₂O at TEW01 & 07 (in Fig 4) as suggested in Lines 1-2.

Lines 10-17 discusses sources of iron, but does not refer to the freshwater inputs that are mentioned in the following section (Pg 12548 Line 12)

4.2 The case of N₂O – this title is unclear; the case for what?

Line 15-19. The authors infer that nitrogen fixation may represent a sink for N₂O, based on their own observations (Farias et al, 2013). The authors previous work identified N₂O consumption in Fe-deplete warm waters, where nitrogen fixation would be expected; conversely it seems somewhat counter-intuitive that nitrogen-fixers would be active in the cold waters nitrate-replete waters in this study, so further evidence is required to support this. The cited Gonzalez et al paper is not yet published. Were the nitrogen fixation rates significant enough to support the inferred N₂O consumption?

Pg. 12549

Line 5-6 “there is no convincing explanation for undersaturation, which would go against the enhanced solubility of gases due to low seawater temperatures.” – the enhanced solubility of gases at lower temperatures is not the issue; increased solubility in colder waters will result in higher N₂O concentration but not saturation resulting from equilibration with air. The authors are perhaps suggesting that more N₂O would have to be consumed in colder waters for significant undersaturation to be apparent?

Line 12 – “freshening of up to 10” - 10 what?

4.3 The case of CH₄ – again, why a “case for”?

Pg 12550

Line 10-16. Again reference to other publications for the Fe data is not enough; quali-

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tative descriptions of iron, such as a "high" and "moderate", is insufficient

Line 24-26. “Phytoplankton bloom. . . create a proportional amount of organic particles that can host anoxic microhabitats for CH₄-producing bacteria.” If there is any evidence of a relationship between phytoplankton abundance, anoxic microhabitats, and CH₄-production this should be cited. Bacterial abundance, and attached bacteria, are not evidence of anoxic microsites

Pg 12551

Line 1 DMS & DMSP production was not substantial in the iron experiments, but there was an increase relative to the external control stations.

Line 3 “Fertilization experiments in the Southern Ocean. . .” is this referring to the iron experiments in the previous sentence, or other experiments?

Lines 12-19 indicate low transfer efficiency of DMSP to DMS in the KPR region, which appears to contradict Lines 4-13 on Pg 12551 which suggest that methylotrophic degradation of DMS may be the source of the methane.

Pg 12552

Line 6-7. Please explain “Given highly variable wind velocities, with averages not exceeding 14ms⁻¹, LM86 was the more appropriate approach to calculate air–sea gas fluxes” given that all windspeed-gas exchange parameterisations cover the range of 15 m/s or less, and some of these were developed for the open ocean and so are just as, if not more, appropriate than LM86.

Pg 12553

Lines 8-10. “the gas inventories in the ML reflect not only the effect of wind stress, supplying gases and nutrients into the ML”. Wind stress does not supply gases and nutrients; the authors perhaps mean exchange of gases through wind-driven wave-breaking and nutrients via wind-induced turbulence?

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Line 18 what does “with other phytoplanktonic blooms” mean or refer to?

Line 21. “N₂O subsaturation and its concomitant influx were registered” – this should read “N₂O undersaturation and a concomitant influx was calculated/estimated”

Pg 12553

Lines 5-8. “This study suggests that mesoscale structures play a significant role in surface CH₄ production and subsequent air–sea gas exchange. This was not found in the case of artificial fertilization experiments, indicating that the turnover and evolution of microbial communities in this structure are fundamental for the development of substrates and conditions for CH₄ regeneration” - The previous iron experiments have often used mesoscale features such as eddies; however they weren’t designed to look at the effects of these features relative to surrounding water. In considering mesoscale structures, this paper should consider the interaction of eddies with coastal water. Also there is not sufficient evidence presented in this paper to support the latter part of this sentence.

Line 9 “Some insight into N fixation may have been provided” but N fixation data was not presented in this paper.

In a number of the figures the text is very small and barely legible in some cases (Fig. 5 & 6 for example), and details are missing in figure legends.

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