

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.

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Academic Editor Dr. Stephane Blain Biogeosciences discussion MS No.: bg-2014-342 Attached to this letter I am enclosing a new version of the manuscript “Dissolved greenhouse gases (nitrous oxide and methane) associated with the natural iron-fertilized Kerguelen region (KEOPS 2 cruise) in the Southern”. The manuscript has been modified regarding the main concerns of the reviewers. These modifications briefly comprise: 1) changes in the result section, where serious inconsistency in the results was presented (graphs and legends are not consistent with the interpretation); this was caused by an

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error in layout and designation of Figures; 2) rephrase of numerous paragraphs and the improving of the English language (spelling and grammar errors); 3) and re-structure Introduction and Discussion section. In addition, in this manuscript dissolved Fe data were included and used to perform a new PCA analysis. A new co-author was included because of she is membership in the data of dissolved iron. We have noticed the effort and the time devoted by the reviewers in order to improve our manuscript, reasons by which we are deeply grateful. We hope to have strengthened the manuscript. Yours sincerely,

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Reviewer # 2 Main coment that need to be clarified: 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.

R: the introduction was restructured as the reviewer mentions attending antecedents of factors that regulate recycling in the Southern Ocean and focusing more on the study area, two new references were introduced, after an exhaustive search. In addition. As was mentioned by reviewer # 1, the main objective of this research was included in introduction section. Besides, the introduction section was shortened, the background of gas distributions was updated and focused on Southern Ocean. Spatial dynamics of gases were oriented to the availability of different sources of iron and, the way in which dissolved iron may stimulate microbiological activity, starting from the accumulation of phytoplankton biomass.

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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. It's 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. R: The reviewer is correct; we include dissolved Fe data obtained by Geraldine Sarthou. These data were discussed and used by performing a new PCA by only with environmental data come from transect WE

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.

R: Yes, lines related to DMSP and DMS and their potential substrate for CH₄ generation were very speculative. The discussion about it was substantially reduced.

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 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.

R: Well, there is a high variability of dFe as it was presented Qu  rou   et al., (KEOPS special volume). Regarding the question of the reviewer there is a portion of the water masses found at TEW-7 likely interacted more with both the plateau and shallow coastal waters of Kerguelen Island than the water masses from the recirculation area.

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This theory is consistent with the circulation data discussed by Park et al. (2014) who demonstrated that water masses are carried northwards between the island and the recirculation area and finally looped back east of the recirculation area. However, also exists a significant deep dFe enrichment was observed over the plateau (stations A3) with dFe concentrations increasing up to 1.30 nmol L⁻¹ close to the seafloor, probably due to sediment resuspension and associated pore water release. Thus our point is that CH₄ accumulation is related with Fe input independent on its origin.

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.

R: If the dFe is the main subject of the KEOPS 2 cruise, it should be included as forcing factor for microbial processes involved in GHG cycling. Unfortunately, dFe data was only measured in W-E transect and other stations. So we performed a new PCA including real dFe data, but this analysis was made only for TWE. However, the new graph contains two figures, PCA made with environmental variables from the ML b) with environmental variables from 0-500 m depth water column. The grouping of stations is not substantially different between the two analyzes (except st TWE08 that pivots one little), but the weight of the variables changes as seen through the vectors.

Specific comments:- Page 12533 Abstract - "intense CH₄ cycling" – Whereas there is

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high supersaturation of CH₄ indicative of production there is no evidence presented for methane cycling: R: In the abstract section, we referred to CH₄ accumulation, so we have changed the word by production. However at subsurface waters, we have some evidence of methanotrophy or another consuming process or advection of CH₄ depleted water are taking place ,

Page 12534 Introduction Line 1 “linked” is a bit vague. Could be read as indicating increasing GHGs are causing higher GHGs, R: we changed the mentioned line, we introduced a direct relationship

Line 6 “This means that GHGs play a major role in the Earth’s radiative balance”. Is features in different ocean regions there some doubt in this? R. we removed this line
Line 16 Tilbrok misspelt R: done
Line 25 “or gas sequester” - does this mean under-saturation?; R: we modified the paragraph and we referred to under- or supersaturated gas condition in surface ocean. 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?

R: we rephrased it and included two new references related with dissolved gas distribution in Southern Ocean. They are Chen L et al. 2014 for N₂O and Yoshida et al 2011 for CH₄

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.

R: Indeed, these lines were confusing; we rephrased and include more pertinent references.

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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). R: We eliminated these lines a relocated them within the end of introduction section.

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. R: This was modified in the revised version

Pg 12357 Line 23 “air” should be a defined CH₄ concentration R: done

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? R: more details about methodology were included i.e., The samples were taken in triplicate in 20 mL vials and carefully sealed to avoid air bubbles. They were then preserved with 50 μ L of saturated HgCl₂ and stored in darkness until analysis. N₂O was analyzed by creating 5 mL of ultra-pure Helium headspace followed by an equilibration in the vial, and then quantifying N₂O by a gas chromatograph (Shimadzu 17A), using an electron capture detector maintained at 350°C, and using a capillary column operated at 60°C. This instrument was connected to an autosampler device. The calibration curves were made with 5 points using He, 0.1 ppm, air, 0.5 ppm, and 1 ppm N₂O standards (Mathison gas mixture). The ECD detector lineally responded to this concentration range

Line 27 The analytical error is unlikely to be the same for all nutrients, so which does the error given apply to? R: the analytical error for the N₂O measurements for this study was about 3%. The uncertainty of the measurements was calculated from the

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standard deviation of the triplicate measurements by depth. Samples with a variation coefficient higher than 10 % were not taken into account for the N₂O database. For nutrients, analytical error for each was specified and referenced to original authors

Figure 1 “Antarctic” misspelt R: done

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. R: indeed, as reviewer #1 mentioned, the order of figures were inconsistent with text and caption, We apologized for that mistake

Fig 3 & 4 labels are mixed up. Fig 3 is the meridional transect between 45-51S, and Fig 3 the zonal transect between 69-75E; R: yes, they were mixed, in the new version that fact was corrected and the figures were improved.

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 accumulation at these stations supported the growth of a bacterial N₂O sink. The authors cite Lasbleiz et al., (2014) to justify the link between high TCH_{1a} & 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. R: This paragraphs highlights that sites of high dFe input provoke high particle accumulation (both presented a excellent correlations and this state has been one of most important conclusion of KEOPS 2 cruise. The best represented sites are, undoubtedly, TWE01 and TWE07 Although both maintained high biomass, the inventories of N₂O (an also fluxes) were lower relatively to surrounded stations. This may insight that a local consumption is working on and it may be associated with N fixation. Any way, we

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rephrased that paragraph

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): R: we introduce potential source of dFe as was stated out by Queroue et al. riverine source from island is a probable source however the most likely is sediment input via diagenesis and release (fide Queroue et al in prep).

4.2 The case of N₂O – this title is unclear; the case for what? R: yes, this subtitle was changed.

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? R: I would say that it is a paradigm for N fixation. N fixation is not only a process associated with tropical and subtropical waters; It is a ubiquitous process and has been recently reported in the LOMROG cruise in the Arctic Sea. We detected fixation rates, and nif genes (see Diez et al., 2012 and unpublised). During KEOPS2, N₂ fixation was detected in all process stations and down to 150 meter depth. Rates were correlated to primary production although the role of iron is hypothesised to be indirect. The ms is currently published as a discussion paper in Biogeosciences (Nitrogen fixation in the southern ocean: A case of study of the Fe-fertilized Kerguelen region (KEOPS II cruise) Author(s): M.L. Gonzalez, V. Molina, L. Florez-Leiva, A.J. Cavagna, F. Dehairs, L. Farias, and C. Fernandez MS No.: bg-2014-576). The relationship between N₂ fixation and N₂O has been explored recently. It was discovered that diazotrophs can actively fix N₂O in marine environments (Farias et al 2013). However, the capacity for simultaneous or alternate substrate fixation is an open question. Nevertheless,

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given the patched distribution in the N fixation, we could ensure that subsaturated condition in surface waters are caused by biological processes; there is a recent work that also measured undersaturation in Southern Ocean, but they argued by the effect of ice melting (see Chen et al 2014). Differences in nitrous oxide distribution patterns between the Bering Sea basin and Indian Sector of the Southern Ocean (Acta Oceanol. 33, 9–19) So, we weighted all arguments and rephrased that paragraph. We should also state that nitrification rates during KEOPS2 were significant and could lead to N₂O accumulation in the water column (Cavagna et al, in prep). Nitrification is likely to produce N₂O, particularly if uncoupling between NH₄ and NO₂ oxidation occurs (this was observed during KEOPS2, Fernandez unpublished data). This evidence suggest that N₂ fixation is likely to act as a N₂O removal process in the southern ocean; otherwise concentrations would be homogeneously distributed in the study area and higher values would have been observed in some stations.

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? R: yes, undersaturation is a process that may result if the water cools faster than it can be equilibrated not by high solubility in cold water. Please see new explanation

Line 12 – “freshening of up to 10” - 10 what? 10 psu, but in strict term salinity has not unit (relative units) R: 10 psu but salinity does not have unit.

4.3 The case of CH₄ – again, why a “case for”? R: idem Subtitle changed

Pg 12550 Line 10-16. Again reference to other publications for the Fe data is not enough; qualitative descriptions of iron, such as a “high” and “moderate”, is insuffi-

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cient; R: We included values and PCA analysis was made with real data.

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 R: the production of CH₄ in zooplankton gum, pellet and other particles were early noticed : for example “Karl and Tilbrook found that the amount of methane released by the sinking materials is enough to account for the elevated methane levels leading to the ocean methane paradox. They hypothesized that methanogens produce methane in the guts of some plankton and, for a brief period of time, in the anaerobic “microenvironments” of plankton feces. The methane is then released into the ocean from the droppings. Karl and Tilbrook’s results were supported by both previous and subsequent studies that found methanogens living in plankton and fish fecal pellets, as well as other particulate matter”. We improved the paragraph

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 R: paragraph related with DMSP/DMS were shorten and part of them eliminated due to speculative nature

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

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 R: as mentioned we reduced these lines and eliminated speculation regarding it.

Pg 12552 Line 6-7. Please explain “Given highly variable wind velocities, with averages not exceeding 4ms⁻¹, LM86 was the more appropriate approach to calculate air–sea gas fluxes” given that all winds used-gas exchange parameterisations cover the

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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. R: Indeed, we improved this concept and referred to LM86 as more conservative and W93 as overestimated parameterization, respectively, both widely used in this kind of studies. In addition we include a reference of how at wind speed range measured during Keops II, LM86 is more appropriated.

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? R: we changed it, there was a mistake in the concept, we referred to mixing and advection processes.

Line 21. "N₂O subsaturation and its concomitant influx were registered" – this should read "N₂O undersaturation and a concomitant influx was calculated/estimated" R: done
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. R: the reviewer is right, We only had some evidence in the Polar front but not precisely with eddies as was observed in the recirculation section (central part of TWE). To conclude some about the temporal evolution of eddies and gas levels we had to do Lagrangian experiments

Line 9 "Some insight into N fixation may have been provided" but N fixation data was not presented in this paper. R: similar to previous observation, see above

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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. R: done

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. R: Paragraph considered as implication was totally changed and all speculative sentence were modified.

Line 8. What is "acid silicate nutrient"? R: It was changed 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. R: PCA analysis was made again and reinterpreted

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) R: there really is a controversy on the effect of fertilization by iron and carbon export, which does not necessarily translate into a net carbon sequestration. We read (Smetacek et al, 2012) and they present good arguments related to the fate of phytoplankton bloom. Given that ML was shallow, we believe that part of CH₄ and N₂O accumulated at pycnoclines could be provoked by an accumulation of sedimented particles. So we re-oriented that paragraph

Please also note the supplement to this comment:

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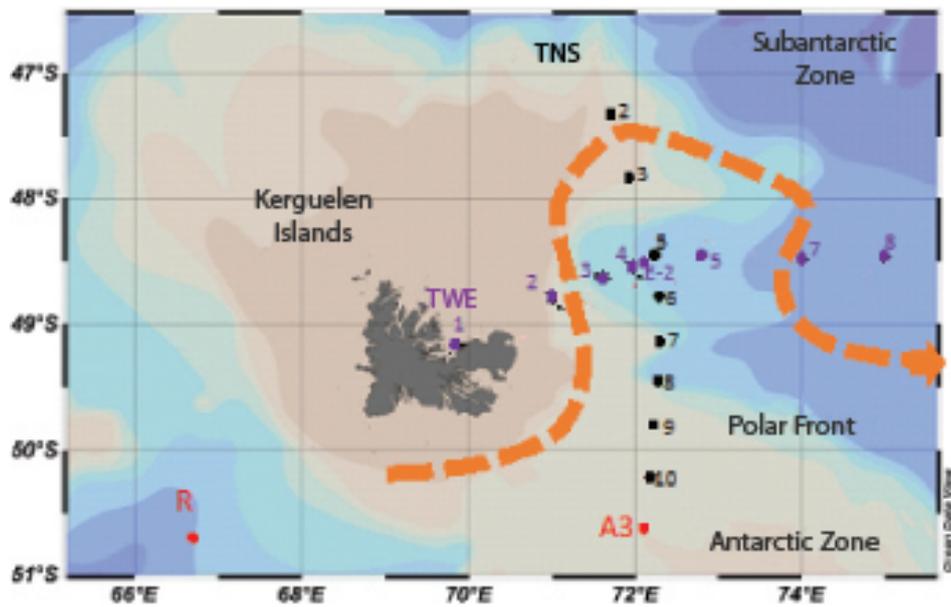


Fig. 1.

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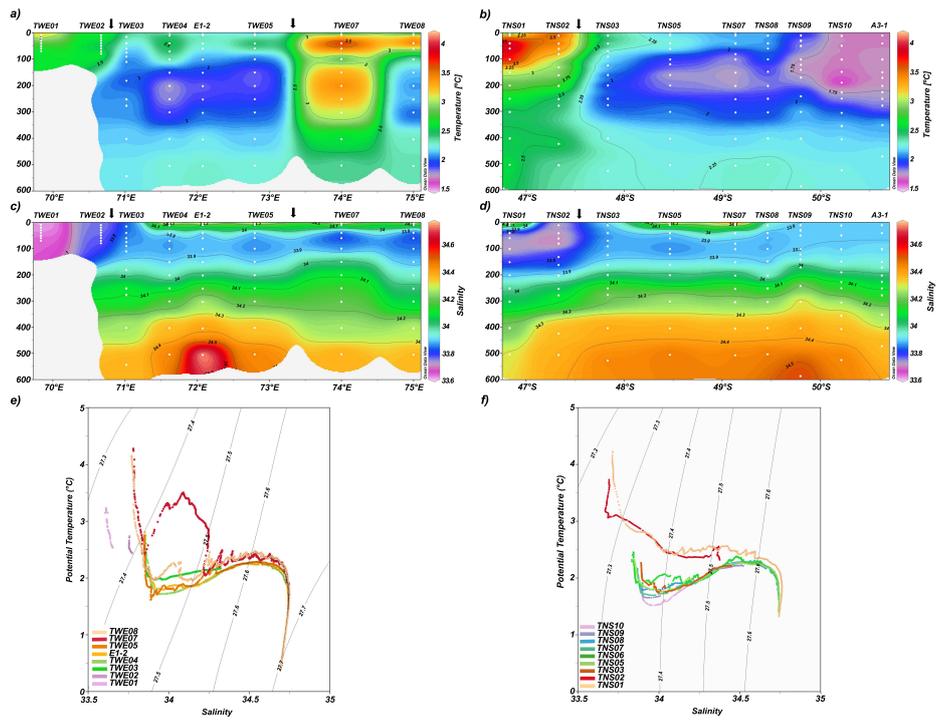


Fig. 2.

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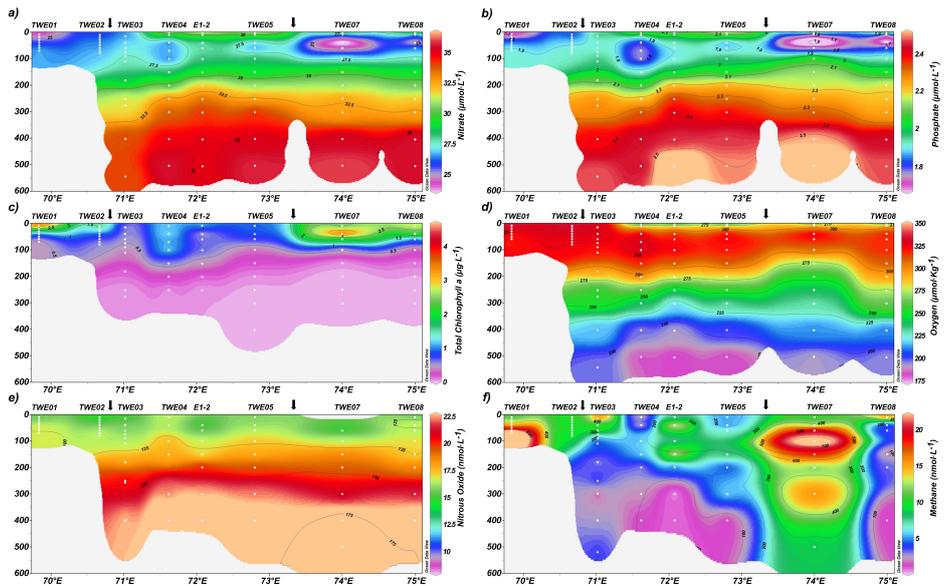


Fig. 3.

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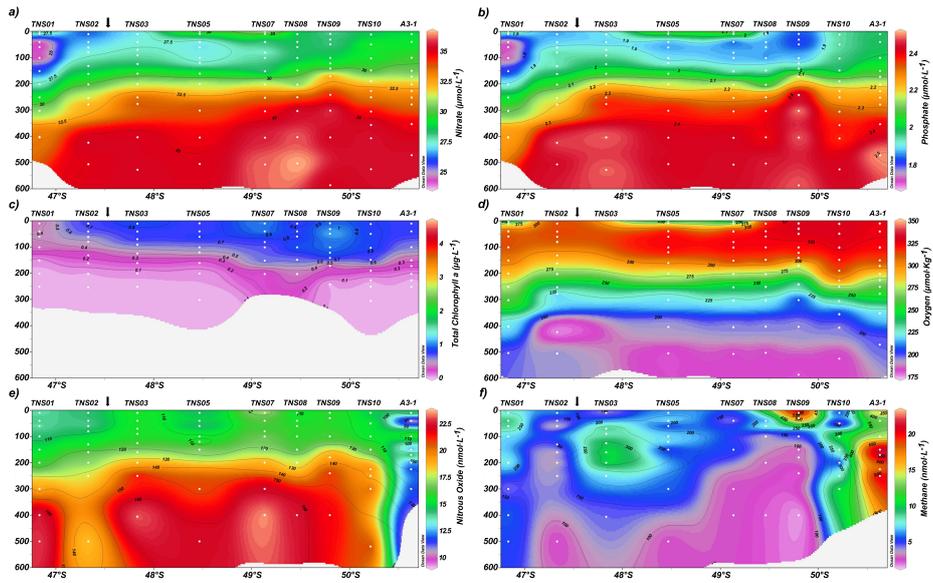


Fig. 4.

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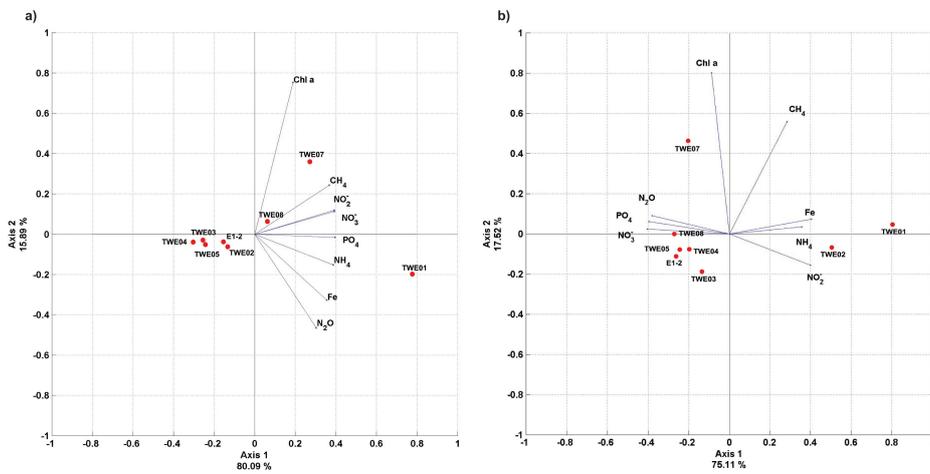


Fig. 5.

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