

**Interactive comment on “Distributions and stoichiometry of dissolved nitrogen and phosphorus in the iron fertilized region near Kerguelen (Southern Ocean)”**

**by S. Blain et al.**

**Anonymous Referee #1**

**Received and published: 18 August 2014**

Blain et al. present a subset of the results from the recent KEOPS2 study of the region surrounding the Kerguelen plateau in the Southern Ocean. Analysing both inorganic and organic dissolved nutrients they largely confirm previous observations in the Southern Ocean whereby marked blooms, particularly those dominated by diatoms, tend to be characterised by relatively low N:P uptake ratios. Although the overall result is not especially novel, the study provides a confirmation that the low N:P ratios are also characteristic of the KEOPS2 bloom and the authors provide a useful and interesting extension of previous work to include organic nutrient measurements. The results are well presented and the manuscript is well written. Overall, the manuscript thus represents a useful contribution to the literature, particularly when considered alongside the body of other information collected during the KEOPS2 study. I have a few minor comments/suggestions which the reviewers might wish to consider in revising their manuscript.

Specific points:

Overall the demonstration and discussion of the relatively low N:P drawdown ratios are clear. However, given the extensive data set which is available, as evidenced by the other KEOPS2 papers in the special issue, I was left wondering whether a bit of further investigation/demonstration of the causes couldn't have been carried out. For example, the authors argue that bloom dominance by diatoms was likely the cause of the relatively low N:P removal ratios, but no data on community structure is presented, at least directly within the current manuscript.

**The composition of the diatom community, and the contribution of diatoms to the carbon biomass were both determined during KEOPS2. The results are now presented in Lasbleiz (Phd thesis manuscript). At stations F-L and A3-2 diatoms contributed to ~70 % of the carbon biomass and were dominated by Chaetoceros (Hyalochaete) spp, Pseudo-nitzschia spp and Centric spp. (< 25µm). At other stations, where the contribution of diatoms to carbon biomass was determined, diatoms contributed to less than 45%.**

**The text was modified accordingly : (page and line numbers refer to the BGD version)**

**page 9959 line 18 “A noticeable deviation from this value was observed for a set of data where N\* increased from N\*=-3 µM to N\*=6 µM. All data with N\*>0 are for samples collected in the mixed layer north of the PF, and located in a bloom where diatoms contributed to 70 % of the carbon biomass in the euphotic layer (Lasbleiz, 2014).”**

page 9960 line 4 “...observations because the stations with a nutrient drawdown anomaly were located in an iron fertilized region and the diatom community was not dominated by *Fragilariopsis kerguelensis*, but rather by *Chaetoceros (Hylochaete) spp*, *Pseudo-nitzschia spp* and *Centric sp.* (Lasbleiz 2014).”

page 9962 line 2 “We discuss here the case of stations A3 and E-4W, which had similar chlorophyll concentrations as F-L. Station A3 had also contribution of diatoms to carbon biomass and dominant diatoms species similar to F-L (these features are not available for E4-W) (Lasbleiz 2014) .”

Similarly, (e.g. Page 9962), could you use total nutrient or even DIC drawdown as an index of bloom duration to demonstrate this point? Effectively this is apparent in Figure 9, i.e. the high values of N\* occur as both N and P are progressively depleted in the surface waters, but the authors could perhaps have been more quantitative.

**We thank the referee for this suggestion which in principle could give additional support to our hypothesis of the age of the bloom. The comparison of the age of the bloom based on the nutrient drawdown would require a good estimate of the concentrations of nutrients before the bloom. At A3, we measured nutrient concentrations of NO<sub>3</sub> and PO<sub>4</sub> during the first visit which preceded the bloom, but for F-L the estimate is problematic because we did not visit this station before the bloom, and the location of F-L north of the polar front precludes to derive this value from the nutrient concentration at the depth of the winter water. Additionally, the occurrence of internal waves and episodic deepening of the mixed layer resupplied the mixed layer with nutrients, which lead to large uncertainties in the estimate of the drawdown due to biology. Thus, we prefer not to present this calculation in the manuscript.**

Minor points:

Page 9950, Line 18: I believe you mean ‘...the occurrence of a subsurface minimum of N\*...’

**Correction done**

Page 9952, first paragraph was a bit awkward, rephrase? ??

**The text was modified in the following way:**

**“Our work presents new data on dissolved inorganic and organic nitrogen and phosphorus concentrations from the iron-fertilized regions near the Kerguelen archipelago. We present their spatial and temporal distributions, and we also discuss the stoichiometry of both nutrients.”**

Page 9952, Sampling section: before describing how the samples were collected from the bottles, it would be useful to describe how the samples were collected from the water column.

**Done**

Additionally, information on the collection of a second set of samples which didn't end up being analysed would seem to be a bit redundant?

**We removed this sentence**

Page 9953: Qu erou  et al. 2014 didn't appear in the reference list.

**Added**

Figure 1: There was a lot of information on this figure and it was potentially difficult to distinguish where the stations were. It would be useful if clarity could be improved further.

**A supplementary table with the coordinates and date/time for the stations is added.**

Figure 9 caption: I don't think you mean that different values of rN:P were used in the calculation here. You assume rN:P = 16 throughout.

**Yes, the legend was modified**

**“Figure 9: (a) Comparison of concentrations of  $\text{NO}_3^-$  versus  $\text{PO}_4^{3-}$ . Dots denote the samples and lines show different values of  $\text{N}^* = \text{NO}_3^- - r_{\text{N:P}} \text{PO}_4^{3-}$  (b) Comparison of concentrations of TDN versus TDP. Dots denote the samples and lines show different values of  $\text{TNxs} = \text{TDN} - r_{\text{N:P}} \text{TDP}$ ”**

Figure 10: It would have been useful to have seen the corresponding profiles of N and P (not just N\*).

**The vertical profiles for N and P are already shown in figure 8 for A3 and in figure 7 for TNS6.**

**Interactive comment on “Distributions and stoichiometry of dissolved nitrogen and phosphorus in the iron fertilized region near Kerguelen (Southern Ocean)” by S. Blain et al.**

**Anonymous Referee #2**

**Received and published: 10 September 2014**

**General comments:**

This is an interesting study with a good dataset that presents vertical distributions of both inorganic and organic nitrogen. Overall, the manuscript is well organized although there are some sections that need attentions either in the presentation or the use of English language. This paper should be published after some improvements are made.

**Specific comments:**

**Abstract:**

Please revise accordingly after revising the other sections.

C5050

**Introduction:**

Page 9951, L17: please use “air-to-sea flux of CO<sub>2</sub>”.

**done**

Page 9951, L24-27: please reword. While it is true that many models do not explicitly simulate the iron cycle, there is a problem in the statement. Besides, one reference does not represent “many”.

**The sentence was modified as follows: “Early modelling studies on the iron hypothesis were conducted using models that did not explicitly represented the iron cycle. The effect of iron fertilization was mimicked using the extreme assumption that iron fertilization results in the complete depletion of N or P in surface waters (Gnanadesikan et al., 2003)”.**

Page 9952, L1-8: the authors could emphasize: (1) there has been evidence of N and P decoupling over various spatial and temporal scales in the Southern Ocean, which is associated with both physical and biogeochemical processes (there are more relevant references, which should be cited);

**The following references were added: Lourey and Trull JGR 2001, Jenkins et al. 1984, and Minas and Minas 1992.**

(2) data of DON and DOP have been lacking.

**We have added here the reference Wang et al. 2003**

**Materials and methods:**

Please provide more information such as sampling time and locations. I would recommend the authors to combine the sampling and analyses sections.

**We have inserted a new paragraph at the beginning of the section " 2.1. Sampling" and in a supplementary table with coordinates and date/time of the stations.**

Page 9953, L11: please reword so readers know that you measured both inorganic and organic N and P. The method for nitrite is also needed.

**We have added a new paragraph in the analytical method section "For  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ , one sample was immediately analyzed aboard with a segmented flow analyzer (Skalar) equipped with colorimetric detection using methods described in Aminot, 2007. The accuracy of the methods was assessed using reference material (Certipur, Merck). The precision was in the range 1-4 %, and the limit of detection was 0.02  $\mu\text{M}$  for  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , 0.03  $\mu\text{M}$  for  $\text{PO}_4^{3-}$ .**

Results:

The first paragraph belongs to the M&M.

**We think that with the addition of the new paragraph in the sampling section (see above), this paragraph can stay at the beginning of the results section because it describes some general characteristics of the stations.**

Please rephrase: page 9953, line 17;

**We have eliminated this sentence, because it repeats what is now stated in the new paragraph of section 2.1. Sampling.**

page 9954, L17-19

**It now reads: Above 150m,  $\text{NO}_2^-$  concentrations were clearly higher at the stations in the polar front zone (PFZ)( $\text{NO}_2^-$  in the range 0.3-0.4  $\mu\text{M}$ ) than at those in the Antarctic Zone (AZ)( $\text{NO}_2^-$  of 0.25  $\mu\text{M}$ ).**

and L23-25;

**At Stations TEW-1, concentrations of  $\text{NH}_4^+$  increased from 0.19  $\mu\text{M}$  (at 10m) to 1.45  $\mu\text{M}$  (close to the bottom). The same trend was observed at TEW-2 (0.17  $\mu\text{M}$  at 10m and 0.39  $\mu\text{M}$  close to the bottom).**

page 9955, L1-3

. It now reads:

**DON concentrations above the Kerguelen plateau at Stations A3-1 and TNS-10 ( $6.0 \pm 1.0 \mu\text{M}$ ) were similar DON concentrations in the meander of the PF  $6.4 \pm 1.7 \mu\text{M}$  (stations TNS-3 to TNS-7). But higher values were detectable north of the PF ( $8.6 \pm 1.2 \mu\text{M}$  for stations TNS-1 and TNS-2)**

Page 9955: section 3.2.1 needs improvement, particularly on DON dynamics

**We have modified the description of the DON distributions in this paragraph.**

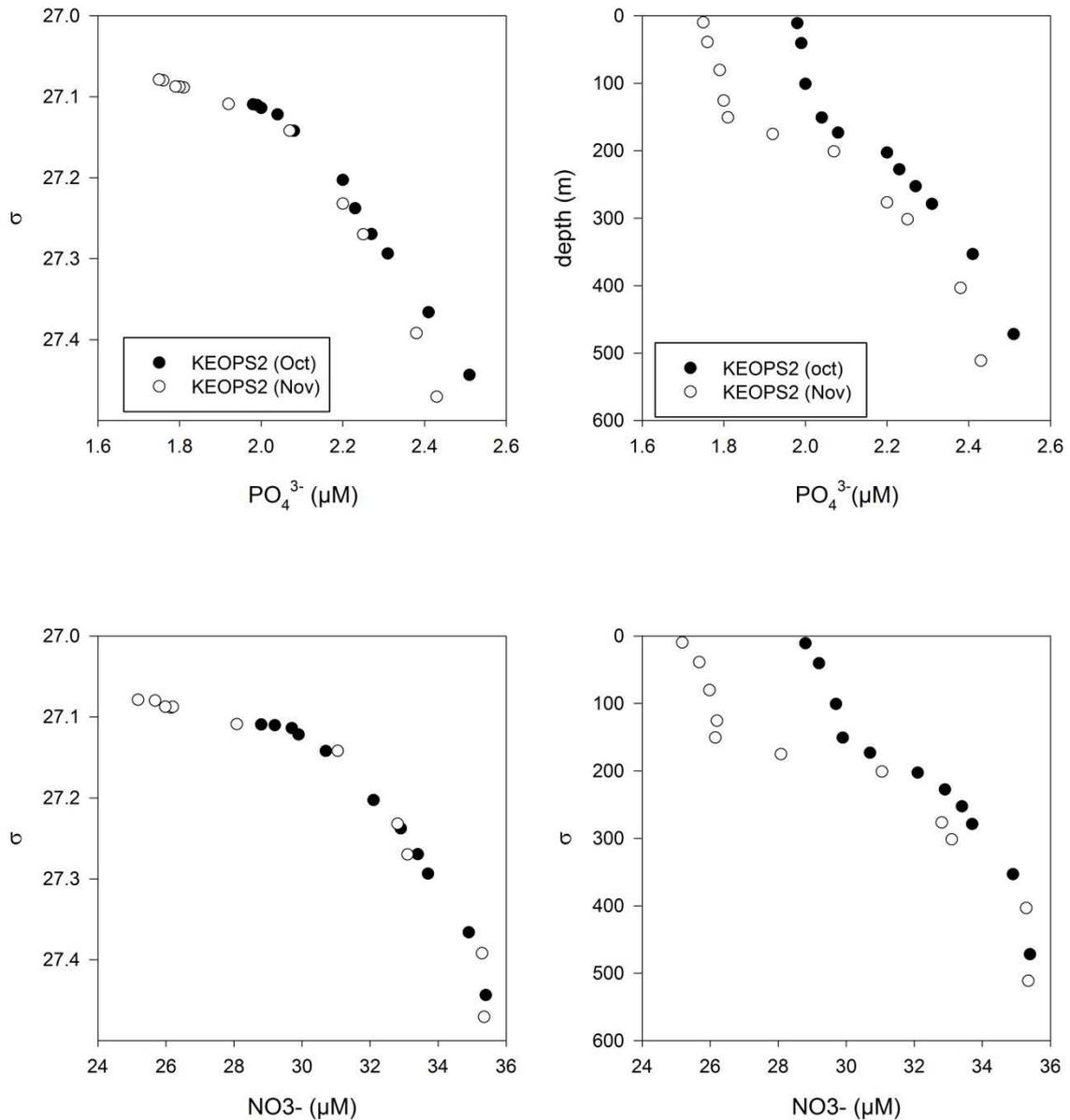
The vertical distribution of different chemical nitrogen species during the two visits at station A3 are detailed in figure 4.  $\text{NO}_3^-$  distributions are discussed in more detail in the section 3.3. Concentrations of  $\text{NO}_2^-$  were, during both visits, homogeneous in the mixed layer and revealed a small maximum below the mixed layer depth (MLD).  $\text{NO}_2^-$  increased from 0.27  $\mu\text{M}$  at A3-1 to 0.33  $\mu\text{M}$  at A3-2 (Fig. 4b).  $\text{NH}_4^+$  concentrations roughly doubled between the two visits (0.1  $\mu\text{M}$  at A3-1 to 0.2  $\mu\text{M}$  at A3-2) and clear maxima were detectable at the base of the mixed layer. Concentrations of DON did not change between visits, however DON accounted for 20% of TDN in the mixed layer at A3-1, and this contribution increased to 25% in the upper 40 m water layer at A3-2. Both  $\text{NO}_3^-$  consumption and DON release during the 4 weeks that separated the two visits explained the increase in the percent DON of TDN. Below 200 m, TDN was higher at A3-1 than at A3-2. This was mainly driven by the differences in DON concentrations that were higher at A3-1 (4.7-6.7  $\mu\text{M}$ ) than at A3-2 (1.8-4  $\mu\text{M}$ ) in the 250-300 m layer (Fig. 4).

Page 9958, section 3.3.2: please make it clear that the Feb data were from 2013, but others from 2011.

**New version : “At Station A3, vertical profiles of changes of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  concentrations were observed between spring and summer (Fig. 8). Albeit the stations were sampled in November 2011 and February 2013, we consider these variations as seasonal changes”.**

I would think that this section could be moved to the discussion section because (1) there may be uncertainties in your estimates of stocks given that there is a considerable difference in  $\text{PO}_4$  concentration below 200 m between Oct and Nov, 2011;

**We agree that there is some variability in the vertical profiles of  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$ , but the reasons for the variation below 200m between October and November 2011 are related to internal waves. This is demonstrated by the plot below where the two profiles are very similar if sigma is considered in place of depth.**



(2) the authors may calculate the ratio of depleted NO<sub>3</sub> and PO<sub>4</sub>, which is relevant (see page 9959, line 20-28).

**We have calculated the ratio of integrated N/integrated P for the three time points. They are quite similar: 14.6 in winter, 14.5 at the first visit, 14.5 at the second visit and 13.6 in February. However, as mentioned in the manuscript it is better to consider N\* or TNxs to address the decoupling between N and P. This approach is presented in Fig 8 and discussed at the end of the discussion section.**

Please pay attention to the tense. There are places with mixtures of present and past tenses.

**done**

Discussion:

Page 9959, L7-10: please reword.

Regarding the  $N^*$  minimum between 100-200 m, I have some comments. I don't think that it is caused by preferential remineralization of OP, which should occur at all the depths. It may be linked to changes in the community structure thus N/P uptake ratio over time and/or space.

**We agree with the referee that preferential remineralization of P versus N should occur at all depths. But our hypothesis was that for the depth layer 100-200 m, organic matter accumulated throughout the season. This could result in the remineralization of more P than N and lead to a minimum value of  $N^*$  compared to other depths. However, we recognize that the accumulation of diatoms with low N:P ratios in this depth layer can also result in a  $N^*$  minimum. In fact both processes might contribute to this minimum of  $N^*$  and our data set does not allow to favor one or the other. Thus we have modified the text accordingly.**

Nitrate to phosphate ratio is often  $<16$  in the Southern Ocean, and there has been evidence of subsurface minimum of  $NO_3:PO_4$  ratio (e.g., in AU9309 and AU9706), which would lead to minimum  $N^*$  in the subsurface.

**We were not able to obtain the data of AU9309 and AU9706, thus this statement is still to be confirmed.**

Figures:

Please use the same orders for labels and sub-plots. For example, in Fig 4, both A3-1 and A3-2 may have an order of  $NO_3$ , DON, TDN, and in labels; Figs 5 and 6 have similar problems; Figs 7 and 8 should use the same order, e.g., (a) nitrate and (b) phosphate.

**Done and legend of figures modified accordingly.**

**Blain et al. Biogeosciences**

**discussion Doi:10.5194/bgd-11-9949-2014**

**Distribution and stoichiometry of dissolve nitrogen and phosphorus in the iron fertilized region near Kerguelen (Southern Ocean)**

**by S. Blain et al.**

**Anonymous Referee #3**

The authors describe and analyze the concentrations of the inorganic and total organic species of nitrogen and phosphorus and their correlations in the Kerguelen area. Some stations were located at HNLC sites, others at an area naturally fertilized by iron, and at the meanders at the polar front, representing different systems. As a whole, the paper is well written although so me English editing should be performed (see below for examples). However, revisions are ne eded before the manuscript is accepted for publication.

1. Materials and Methods.

a. There are no explanations as to when and where the sampling took place. The only mention appears in Figure 1 and it is not enough. For example, stations A3 were occupied twice during the experiment and then again in February 2013. This section should be expanded b.

b There is no explanation as to how the water was sampled (except that Niskin bottles were used). Which CTD, rosette were used? Who collected the physical data and where are they presented? The authors also use in the text  $\theta$  and  $\sigma$  (I assume potential temperature and density anomaly) but there are no explanation as to what they represent. Explanations should be added.

**A paragraph has been added at the beginning of the sampling section and a supplementary table provides the information for the positions and date/time of the stations.**

**“During KEOPS2, the samples were collected at the stations presented on the map in Fig.1. The coordinates and time of sampling are summarized in sup table 1. Additional samples were collected during the cruise KEOPSMOOR in February 2013 at stations A3 and at station TNS-6 (sup table 1). The samples for dissolved nitrogen and phosphorus analysis were collected with 22 12 liter Niskin bottles mounted on a rosette equipped with using a Seabird SBE911-plus CTD unit. In this work we used potential temperature ( $\theta$ ) and density anomaly ( $\sigma$ ) to characterize the hydrology of the stations. A more complete description of the hydrology and the circulation is presented in Park et al. 2014.”**

c. There is no explanation or reference as to the methods used for the determination of nitrate, nitrite and phosphate. Aminot, 2007 is referred to in the DON-DOP analysis.

**This point is clarified. We now mention that the analysis were done “with a segmented flow analyzer (Skalar) equipped with colorimetric detection using methods described in Aminot, 2007”**

d. In addition to Skalar, it should be mentioned that the method used is colorimetry, using a segmented flow analyzer .

**done, see response to comment c.**

e. Considering the DON-DOP analysis. It should be explained that DON and DOP are actually calculated values from TDN-TDP minus the inorganic species. This should be changed across the manuscript

**Modified according to the recommendations of the referee :**

**In the method section**

**“This provides the concentrations of Total Dissolved Nitrogen (TDN) and Total Dissolved Phosphorus (TDP). The concentrations of DON and DOP were calculated as follows;  $\text{DON} = \text{TDN} - [\text{NO}_3^-] - [\text{NO}_2^-]$  and  $\text{DOP} = \text{TDP} - [\text{PO}_4^{3-}]$ ”**

**in the discussion section**

**“In the case of KEOPS2, the contribution of DON and DOP to TDN and TDP could reach 30%. We have therefore considered TDN and TDP at all KEOPS2 stations where these measurements were available (Fig. 9b).”**

**see also response to comment 2.e.**

f. A paragraph should be added explain the quality control/quality assurance of the nutrient determination, including detection limit and uncertainty.

**Done**

g. The authors stated that they did take duplicates to be run in the laboratory at home but it was not needed due to “the good quality and analysis performed aboard”. Please explain how that was determined. This is very important in particular when minima or maxima in the depth profiles were determined based on one point only (for example figures 4 and 5)

**During the cruise, the accuracy of the measurement was assessed using reference material Certipur (Merck).**

**Following the recommendation of referee #1, the mention of the second set of samples that was finally not analyzed back in the lab was removed.**

2. Results

a. First paragraph. The author state the chlorophyll concentrations were low/ high. Please give concentrations.

**done: “( ~0.3 mg m<sup>-3</sup>) (Lasbleiz et al. 2014)”**

I assume that the values appear in Queroue et al 2014-reference that is missing and in Lasbleiz et al., 2014 – submitted to the special issue?

**Yes**

b. Figures 2-3. Please consider exchanging the legend to vertical section or Cross section instead of two dimensional distribution

**Done**

c. Section 3.2.1, third line. Instead of the name of the section, add 3.3

**Done**

d. Section 3.2.1, ninth line. There is no percentage in figure 4

**We have now added for % of DON at station A3 , data not shown**

e. Section 3.2.1, 13<sup>th</sup> line. It should be rephrased. TDN is the measured parameter and DON the calculated one. The correction should be performed across the whole manuscript.

**The sentence was modified as follows :**

**“Below 200 m, TDN was higher at A3-1 than at A3-2. This was mainly driven by the differences in DON concentrations that were higher at A3-1 (4.7-6.7 μM) than at A3-2 (1.8-4 μM) in the 250-300 m layer (Fig. 4 ).”**

**See also other changes already mentioned in response to comments 1.e.**

f. Section 3.2.2, 2<sup>nd</sup> line. Is 0.39 uM significantly different from 0.22 uM NO<sub>2</sub>?

**The precision of measurement of NO<sub>2</sub><sup>-</sup> is around 4%. Thus we think these values are significantly different.**

g. Section 3.2.2. Figure 5 is unclear. Please check if correct. F-L appears in one panel and F-S in three.

**That is true, because TDN and TDP were only determined at F-S**

Also, in the text there is a reference to Figure 5b and in the figure, the panels are not marked with a, b, c, etc.

**The panels are marked with a, b, c, d. they are now printed in bold.**

h. The separation of section 3.2 and 3.3 (Dissolved nitrogen alone and nitrate and phosphate, respectively) is confusing. I suggest to combine the two sections into one.

**We prefer to maintain the separation between the two sections because the section 3.2 is dedicated to the description of the spatial variability and the section 3.3 is more focused on the temporal variability.**

i. Section 3.3.1. The KEOPSMOOR profile (Feb 2013) should appear in the Methods section or given a reference as the ANTARESS 3

**This is now done in the new paragraph added at the beginning of the section "Sampling".**

j. Section 3.3.1. The authors should explain why the NO<sub>3</sub> concentrations from ANTARESS 3 are acceptable/intercomparable with the present study. They mention only why PO<sub>4</sub> is not.

**NO<sub>3</sub> concentration in the deep water, including in the winter water, were very similar for ANTARESS3 and KEOPS2. There was no systematic shift observed for nitrate as observed for phosphate. Therefore, NO<sub>3</sub> concentrations of ANTARES were considered as "oceanographically" consistent.**

3. Discussion.

a. Second paragraph. Please add reference to Redfield's ratio

**Done**

b. Page 9960, paragraph starting in line 19. The authors argue about the necessity to look at TDN vs TDP ratios. However, the contribution of the organic part to the total concentration is small. A sentence should be added explaining why this contribution is necessary

**We have added a sentence giving the range (in %) of the contribution of DON and DOP to TDN and TDP. This shows that this contribution is not always negligible.**

c. Figure 9b. Please make the line notations as in 9a, - which line corresponds to which N.

**Done**

d. Page 9962 – First paragraph – the English should be reviewed

**Done**

**"During KEOPS2 rapidly growing diatom blooms were also sampled at other stations located south of the PF, but anomalies similar to those at F-L were not observed. We discuss here the case of stations A3 and E-4W, which had similar chlorophyll concentrations as F-L. Station A3 had a contribution of diatoms to carbon biomass and dominant diatom species similar to F-L (these features are not available for E4-W) (Lasbleiz 2014). There is no reason that the physiological features of exponentially growing diatoms as revealed for station F-L do not apply to the diatoms growing at stations A3 and E4-W. It is, however, possible that the resulting effect is not large enough to translate into N\* or**

**TN<sub>xs</sub> anomalies. A possible explanation could be the differences in the age of the blooms. The stoichiometry would be less affected in a younger bloom as compared to a bloom of longer duration. This hypothesis cannot be fully verified due to the poor temporal resolution of the satellite ocean color images available. Another or complementary explanation is the difference in the mixed layer depths that were 50 m and 150 m at stations F-L and A3-2, respectively”.**

e. Page 9962 – First paragraph. The anomalies at stations A3 and E-4W should be shown in Figure 9.

**The text mentions that there is no anomaly at A3 and E-4W.**

f. Page 9962 – The Sampling during Feb 2013 should appear in the methods.

**Done**

1 **Distributions and stoichiometry of dissolved nitrogen and phosphorus in the iron**  
2 **fertilized region near Kerguelen (Southern Ocean).**

3

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9

10 **Abstract**

11

12 During KEOPS2 (Kerguelen Ocean and Plateau Compared Study 2), we determined  
13 dissolved inorganic and organic nitrogen and phosphorus species in the naturally fertilized  
14 region of Kerguelen Island (Southern Ocean,). Above 150m, stations were clearly separated  
15 by the Polar Front (PF), with concentrations of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{PO}_4^{3-}$  overall lower north than  
16 south of the PF. Though less pronounced, a similar trend was detectable for dissolved organic  
17 nitrogen (DON) and phosphorus (DOP). At all stations offshore and above the plateau, a  
18 subsurface maximum of  $\text{NH}_4^+$  was observed between 50 and 150 m. We examined nutrient  
19 stoichiometry by calculating the linear combination  $\text{N}^* = [\text{NO}_3^-] - 16 [\text{PO}_4^{3-}]$ . The majority of  
20 stations and depths revealed  $\text{N}^*$  close to  $-3 \mu\text{M}$ , however, for surface waters north of the PF  
21  $\text{N}^*$  increased up to  $6 \mu\text{M}$ . This suggests a preferential uptake of  $\text{PO}_4^{3-}$  versus  $\text{NO}_3^-$  by fast  
22 growing diatoms. Using the tracer  $\text{TN}_{\text{xs}} = [\text{TDN}] - 16[\text{TDP}]$  revealed that the dissolved  
23 organic fraction significantly contributed to changes in  $\text{TN}_{\text{xs}}$ .  $\text{TN}_{\text{xs}}$  were negative for most  
24 stations and depths, and relatively constant in the layer 0-500m. As for  $\text{N}^*$ , the stations north

25 of the PF had higher  $TN_{xs}$  in the layer 0-100m. We discuss this stoichiometric anomaly with  
26 respect to possible external sources and sinks of N and P. Additional data collected in  
27 February 2013 at two sites revealed the occurrence of a subsurface minimum of  $N^*$  located  
28 just below the pycnocline that denotes a layer where remineralization of particulate organic  
29 matter with low N:P ratio P, possibly associated with preferential remineralisation of P versus  
30 N, persists throughout the season~~preferential remineralization of P versus N persists~~  
31 ~~throughout the season.~~

## 32 1. Introduction.

33 The first scientific expeditions in the Southern Ocean discovered high concentrations of major  
34 nutrients such as nitrate ( $NO_3^-$ ) and phosphate ( $PO_4^{3-}$ ) in surface waters south of  $50^\circ S$  (Hart,  
35 1942). The general meridional overturning circulation that brings deep water to the surface at  
36 the southern limits of the Antarctic circumpolar current (Marshall and Speer, 2012) is the  
37 major mechanism supplying surface waters with  $NO_3^-$  and  $PO_4^{3-}$ . Most of the nutrient-rich  
38 upwelled waters are transported northward and they leave the surface north of the polar front,  
39 through their transformation into intermediate and mode waters. Despite the several months  
40 long northward transport during which the  $NO_3^-$  and  $PO_4^{3-}$  rich waters are exposed to sunlight,  
41 little phytoplankton biomass develops. This system was characterized as “high nitrate low  
42 chlorophyll” (HNLC). The major consequence of the HNLC status of the Southern Ocean is  
43 that large amounts of unused nutrients are transported back into the ocean interior where they  
44 feed the main thermocline and finally supply low and mid latitude surface waters with  
45 essential nutrients (Sarmiento et al., 2004). Another consequence is that similarly to  $NO_3^-$  and  
46  $PO_4^{3-}$ , large amounts of upwelled dissolved inorganic carbon (DIC) are not converted to  
47 particulate organic carbon (POC) and remain in contact with the atmosphere for time periods  
48 long enough to degas carbon dioxide ( $CO_2$ ) with important consequences on climate (Sigman  
49 and Boyle, 2000).

50 The iron hypothesis (Martin and Fitzwater, 1988) was a major advancement for our  
51 understanding of the HNLC paradox. More than two decades of intense research have  
52 confirmed that increasing iron supply stimulates primary production, major nutrient utilization  
53 and the air-~~to~~-sea flux of CO<sub>2</sub> in surface waters. Nutrient utilization in surface waters is  
54 therefore a diagnostic of the efficiency of the biological pump of CO<sub>2</sub>. Nitrate utilization has  
55 also received much attention in paleoceanographic studies, because it can be inferred from the  
56 isotopic composition of N in bulk material or specific compounds of fossil organisms  
57 preserved in the sediment. Recent results provide support to the enhanced NO<sub>3</sub><sup>-</sup> utilization  
58 related to higher dust deposition during the ice ages in the sub Antarctic region (Martinez-  
59 Garcia et al., 2014).

60 Early modelling studies ~~Many modelling studies~~ on the iron hypothesis were  
61 conducted, using models that did not explicitly represented the iron cycle. The effect of iron  
62 fertilization was mimicked using, ~~were realized with~~ the extreme assumption that iron  
63 fertilization results in the complete depletion of N or P in surface waters (Gnanadesikan et al.,  
64 2003). However, this was never observed during artificial iron fertilization (Boyd et al.,  
65 2007), iron addition during deck incubations (Moore et al., 2007) or in naturally iron fertilized  
66 regions (Blain et al., 2007). For most previous research in this context, it was assumed that  
67 NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> behave in a similar way. This is only true at first order because interesting  
68 differences were noticed (Jenkins et al. 1984, Minas and Minas 1992, Louret and Trull 2001).  
69 ~~For example~~, Weber and Deutsch (Weber and Deutsch, 2010) used zonal mean distributions  
70 of NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> in the Southern Ocean to reveal that the differential utilization of both  
71 nutrients is likely related to the composition of the phytoplankton community. Detailed  
72 investigations of blooms in varying regions of the Southern Ocean confirm different  
73 utilization of NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> depending on the dominant species in the phytoplankton  
74 community (Arrigo, 1999; De Baar et al., 1997; Moore et al., 2007). In addition, the possible

75 role of DOP and DON for N and P decoupling has not been investigated, although modeling  
76 studies suggest that these is organic forms may significantly contribute to the cycling of N and  
77 P in the Southern Ocean (Wang et al. 2003).

78 Our work presents new data on dissolved inorganic and organic nitrogen and phosphorus  
79 concentrations from the iron-fertilized regions near the Kerguelen archipelago. We present  
80 their spatial and temporal distributions, and we also discuss the stoichiometry of both  
81 nutrients.

82 ~~Our work aims to present a new data set of dissolved nitrogen and phosphorus concentrations,~~  
83 ~~including both inorganic and organic pools. Most of the results are from iron fertilized~~  
84 ~~regions near the Kerguelen archipelago. Besides the presentation of the distributions and their~~  
85 ~~spatial and temporal variations, we also discuss the stoichiometry of both nutrients.~~

## 86 **2. Material and methods**

### 87 **2.1 Sampling**

88 During KEOPS2, the samples were collected at the stations presented on the map in Fig.1.  
89 The coordinates and date of sampling are summarized in suppl table 1. Additional samples  
90 were collected during the cruise KEOPSMOOR in February 2013 at stations A3 and at station  
91 TNS-6 (suppl table 1). The samples for dissolved nitrogen and phosphorus analys~~is~~  
92 collected with 22 12 liter Niskin bottles mounted on a rosette equipped with ~~using~~ a Seabird  
93 SBE911-plus CTD unit. In this work, we used potential temperature ( $\theta$ ) and density anomaly  
94 ( $\sigma$ ) to characterize the hydrology of the stations. A more complete description of the  
95 hydrology and the circulation is presented in Park et al. (2014).

96 For  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and nitrite ( $\text{NO}_2^-$ ), syringes (50 mL) were directly connected to the spigot of  
97 the Niskin bottles. The samples were drawn through a 0.45  $\mu\text{m}$  Up-tidisc adapted to the  
98 syringe. Duplicate samples were collected. ~~One sample was immediately analyzed aboard.~~

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99 The second sample (25 mL) was poisoned with mercuric chloride ( $\text{HgCl}_2$ , 20 mg  $\text{L}^{-1}$ , final  
100 concentration) and stored in the dark at room temperature for later analysis. ~~of the analysis~~  
101 ~~performed aboard.~~

102 For ammonium ( $\text{NH}_4^+$ ), samples were collected from Niskin bottles in two 50 mL Schott  
103 glass bottles. Following rinsing, the bottles were filled with 40 mL of seawater and closed  
104 immediately to avoid contamination by air. Back in the aboard laboratory the oxidative  
105 reagent (Holmes et al., 1999) was added.

106 For dissolved organic nitrogen (DON) and phosphorus (DOP) analysis the samples were  
107 collected from Niskin bottles in 100 mL Schott glass bottles. The Schott glass bottles were  
108 rinsed with HCl (10%) and several times with ultrapure water between casts. The samples  
109 were then filtered through 2 combusted GF/F filters. 20 mL of the filtered samples were  
110 transferred to 20 mL PTFE vials and poisoned with 100  $\mu\text{L}$  of  $\text{HgCl}_2$  (4 g  $\text{L}^{-1}$ , working  
111 solution) before storage at 4°C. All analyses were performed aboard as described below.

## 112 2.2 Analytical methods

113 ~~For  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ , one sample was immediately analyzed aboard with a~~  
114 ~~segmented flow analyzer (Skalar) equipped with colorimetric detection using methods~~  
115 ~~described in Aminot, 2007. The accuracy of the methods was assessed using reference~~  
116 ~~material (Certipur, Merck). ~~The precisions was for in the range 1-4 %, and the limit of~~~~  
117 ~~detection was 0.02  $\mu\text{M}$  for  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , 0.03  $\mu\text{M}$  for  $\text{PO}_4^{3-}$ .~~

118 Samples for DON and DOP ~~analysis-determination~~ were spiked with 2.5 mL of the oxidative  
119 reagent (boric acid + sodium hydroxide + potassium peroxodisulfate), and then heated at  
120 120°C during 30 min. After cooling, the concentrations of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  were determined  
121 ~~using continuous flow analysis (Aminot, 2007) with a Skalar instrument as mentioned above.~~  
122 ~~This provides the concentrations of Total Dissolved Nitrogen (TDN)- and Total Dissolved~~

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123 Phosphorus (TDP). The concentrations of DON and DOP were calculated as follows:

124  $DON = TDN - [NO_3^-] - [NO_2^-]$  and  $DOP = TDP - [PO_4^{3-}]$ .

125 Samples for  $NH_4^+$  determination were incubated for at least 3 hours in the dark, at ambient  
126 temperature, before fluorescence measurements ( $\lambda_{exc}=370$  nm  $\lambda_{emi}=460$  nm ) with a  
127 fluorimeter (Jabsco).

128

### 129 3. Results

130 All the stations used in this work are presented in figure 1. Most of the stations are located  
131 south of the Polar Front (PF), with the exception of the coastal stations TEW-1-2 and the  
132 offshore stations TNS-1-2, TEW-7-8 and F-L that were located north of the PF (Fig.1).

133 Station R-2, located west of the plateau had low chlorophyll concentrations in surface water

134 throughout the season ( $\sim 0.3$  mg  $m^{-3}$ ) (Lasbleiz et al. 2014), an observation that is explained

135 by the low iron supply (Qu erou  et al. this issue). By contrast, all other stations were

136 characterized by the development of large spring blooms consistent with higher iron supply

137 (Lasbleiz et al., 2014). However, the development of the blooms within the iron fertilized

138 region was not homogenous in time and space. A3-1, and stations TNS-1 to TNS-10 of the

139 North-South transect, sampled at the beginning of the spring bloom, were characterized by

140 low chlorophyll concentrations only slightly higher than that at station R-2. Stations TEW-1

141 to TEW-8 of the East-West transect, stations E-2 to E-5, and station A3-2 (second visit at

142 station A3), were sampled a few days later, when the bloom rapidly developed with large

143 spatial heterogeneity. The largest stocks of chlorophyll *a* within the 0-200 m layer were

144 observed at stations F-L north of the PF and at station A3-2 above the plateau. Based on the

145 trajectories of 2 surface drifters (Zhou et al., 2014), stations E-1, E-2, E-3, E4-E and E-5, are

146 assumed to evolve in a quasi Lagrangian framework and their succession in time can be

147 considered at the first order as a time series.

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148 **3.1 Two dimensional distributions of dissolved nitrogen and phosphorus.**

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149 In the upper 200m of the water column, concentrations of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  were  $\geq 19 \mu\text{M}$  and  
150  $\geq 1 \mu\text{M}$ , respectively (Fig. 2 and 3). Concentrations were higher west of the PF (transect EW,  
151 Fig. 2) and South of the PF (transect NS, Fig. 3) and lower in surface subantarctic waters,  
152 north and east of the PF. Concentrations of  $\text{NO}_2^-$  were the highest above 150m, and below this

153 depth  $\text{NO}_2^-$  decreased rapidly to reach values close to the limit of detection at 200m. Above  
154 150m,  $\text{NO}_2^-$  concentrations were clearly higher at the stations in the polar front zone  
155 (PFZ)( $\text{NO}_2^-$  in the range 0.3-0.4  $\mu\text{M}$ ) than at those in the Antarctic Zone (AZ)( $\text{NO}_2^-$  of 0.25  
156  $\mu\text{M}$ ).

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157 ~~Above 150m, the PF clearly separated the stations located in Antarctic Zone (AZ)( $\text{NO}_2^-$  of~~  
158 ~~0.25  $\mu\text{M}$ ) from the stations located in the polar front zone (PFZ)( $\text{NO}_2^-$  in the range 0.3-0.4~~  
159  ~~$\mu\text{M}$ ).~~ Along the transect EW, the highest  $\text{NO}_2^-$  concentrations were measured at TEW-1 (0.31-  
160 0.34  $\mu\text{M}$ ). Contrasting with the  $\text{NO}_2^-$  distribution observed along the transect NS, the stations  
161 of the AZ (i.e. west of the isocline  $\sigma=27$ ) had higher concentrations than those of the

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162 PFZ.  $\text{NH}_4^+$  concentrations were highest at the coastal stations. At Stations TEW-1,  
163 concentrations of  $\text{NH}_4^+$  increased from 0.19  $\mu\text{M}$  (at 10m) to 1.45  $\mu\text{M}$  (close to the bottom).  
164 The same trend was observed at TEW-2 (0.17  $\mu\text{M}$  at 10m and 0.39  $\mu\text{M}$  close to the bottom).  
165 ~~At Stations TEW-1 and TEW-2,  $\text{NH}_4^+$  concentrations increased from 0.19  $\mu\text{M}$  and 0.17  $\mu\text{M}$~~   
166 ~~(at 10m), respectively, to 1.45  $\mu\text{M}$  and 0.39  $\mu\text{M}$  (close to the bottom), respectively.~~ At all

167 stations offshore and above the plateau, a subsurface maximum of  $\text{NH}_4^+$  peaking at 0.5-0.6  
168  $\mu\text{M}$  was observed between 50 and 150 m. The DON distribution was characterized by a north-  
169 south gradient in the 0-150 m layer. DON concentrations were lowest above the Kerguelen

170 plateau at Stations A3-1 and TNS-10 (6.0 $\pm$ 1.0  $\mu\text{M}$  7  $\mu\text{M}$ ) were similar than in the meander  
171 of the PF 6.4 $\pm$ 1.7  $\mu\text{M}$  (stations TNS-3 to TNS-7). But higher values were detectable north of  
172 the PF (8.6 $\pm$ 1.2  $\mu\text{M}$  for stations TNS-1 and TNS-2). Intermediate values were found within

173 ~~the PF meander (Stations E-1 to E-5; XX  $\mu\text{M}$ ) and highest DON concentrations were~~  
174 ~~detectable north of the PF (6-10  $\mu\text{M}$ ).~~  
175 DON concentrations were lowest at Stations A3-1 and TNS-10 (4-7  $\mu\text{M}$ ) above the Kerguelen  
176 plateau. Intermediate values were found within the PF meander and highest DON  
177 concentrations were detectable north of the PF (6-10  $\mu\text{M}$ ). For DOP, the latitudinal gradient  
178 was less pronounced, but DOP concentrations were lower above the Kerguelen plateau than at  
179 any other sites.

## 180 3.2. Speciation of dissolved nitrogen at selected sites.

### 181 3.2.1. The Kerguelen plateau station A3

182 The vertical distribution of different chemical nitrogen species during the two visits at station  
183 A3 are detailed in figure 4.  $\text{NO}_3^-$  distributions are discussed in more detail in the section  
184 ~~“Temporal evolution of vertical distributions of nitrate and phosphate”~~3.3. Concentrations of  
185  $\text{NO}_2^-$  were, during both visits, homogeneous in the mixed layer and revealed a small  
186 maximum below the mixed layer depth (MLD).  $\text{NO}_2^-$  increased from 0.27  $\mu\text{M}$  at A3-1 to 0.33  
187  $\mu\text{M}$  at A3-2 (Fig. 4b).  $\text{NH}_4^+$  concentrations roughly doubled between the two visits (0.1  $\mu\text{M}$  at  
188 A3-1 to 0.2  $\mu\text{M}$  at A3-2) and clear maxima were detectable at the base of the mixed layer.  
189 Concentrations of DON did not change between visits, however DON accounted for 20% of  
190 TDN in the mixed layer at A3-1, and this contribution increased to 25% in the upper 40 m  
191 water layer at A3-2 (~~data not shown~~). ~~This was due to~~ Both,  $\text{NO}_3^-$  consumption and DON  
192 release during the 4 weeks that separated the two visits explained the increase in the percent  
193 DON of TDN. Below 200 m, ~~the differences in the contributions to~~ TDN was higher at A3-1  
194 than at A3-2. This was ~~are~~ mainly driven by the differences in DON concentrations that were  
195 higher at A3-1 (4.7-6.7  $\mu\text{M}$ ) than at A3-2 (1.8-4  $\mu\text{M}$ ) in the 250-300 m layer (Fig. 4).

### 196 3.2.2. Stations F-S and F-L north of the Polar Front

197 Distinct vertical profiles of  $\text{NO}_2^-$  and  $\text{NH}_4^+$  were observed at station F-S. Concentrations of  
198  $\text{NO}_2^-$  decreased from 0.39  $\mu\text{M}$  at 10 m to 0.22  $\mu\text{M}$  at 93 m. However, we note a remarkably  
199 low value of 0.15  $\mu\text{M}$  at 79 m (Fig. 5a). The  $\text{NH}_4^+$  profile presented the same anomaly,  
200 resulting in two subsurface maxima. This feature contrasts with most other stations where a  
201 single subsurface maximum was observed, as for example at station F-L (Fig. 5b) located a  
202 few nautical miles away from F-S. We suggest that this anomaly is due to the position of F-S  
203 within the polar front where a complex mixing event at small scale could have occurred. The  
204 contribution of DON to TDN at F-S decreased continuously from 34% at 20 m to 9% at 120  
205 m. However, close to the surface the contribution of DON was only 17% (Fig. 5d).

### 206 **3.2.3. The HNLC station R-2**

207 The vertical distribution of  $\text{NO}_3^-$  and DON revealed small variations between the surface and  
208 200 m (Fig. 6a). DON accounted for 19% to 24% of TDN, representing intermediate values as  
209 compared to the range observed in the fertilized region. Concentrations of  $\text{NO}_2^-$  and  $\text{NH}_4^+$   
210 presented similar vertical distributions, decreasing rapidly below the mixed layer (Fig. 6b).  
211 Concentrations of  $\text{NH}_4^+$  in the mixed layer (0.07  $\mu\text{M}$ ) were at least two fold lower than at any  
212 other stations, and  $\text{NO}_2^-$  concentrations in the mixed layer (0.3  $\mu\text{M}$ ) were similar to those of  
213 the mixed layers in the fertilized regions.

### 214 **3.2.4. Lagrangian sites E**

215 All stations were characterized by similar vertical distributions of  $\text{NO}_2^-$  and  $\text{NH}_4^+$ .  
216 Concentrations in the mixed layer were in the range 0.25-0.3  $\mu\text{M}$  decreasing to 0.02-0.03  $\mu\text{M}$   
217 below 200 m. The vertical distributions of  $\text{NH}_4^+$  are characterized by a subsurface maximum  
218 with concentrations (0.4-0.65  $\mu\text{M}$ ) two fold higher than at the surface (0.2-0.3 $\mu\text{M}$ ).  $\text{NO}_3^-$   
219 distributions are described in more detail in the next section. The contribution of DON to  
220 TDN in the mixed layer was in the range 15-25%. No clear temporal evolution was  
221 detectable.

222 **3.3. Temporal evolution of the vertical distributions of nitrate and phosphate**

223 **3.3.1. The Lagrangian sites E**

224 The vertical profiles of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  concentrations in the upper 200 meters of 5 stations  
225 located in the center of a meander of the PF are presented in Fig. 7. In addition, we show data  
226 from two other cruises. Samples collected in early October 1995 during the cruise  
227 ANTARES3 (Blain et al. 2001) provide data typical of winter conditions. Samples of the  
228 KEOPSMOOR profile were collected in February 2013, representing post bloom conditions.  
229 Concentrations of  $\text{NO}_3^-$  are almost identical among visits at 150 m (mean  $27.5 \pm 0.8 \mu\text{mol L}^{-1}$ ,  
230 Fig. 7a). Above 150 m,  $\text{NO}_3^-$  concentrations change along the season. In winter,  
231 concentrations are homogenous from surface to 150 m, resulting in a mean integrated stock of  
232  $4.22 \pm 0.08 \text{ mol m}^{-2}$ . In spring, the KEOPS2 profiles qualitatively cluster in two groups. The  
233 first cluster is composed of stations TNS-5, TNS-6, E-1, E-2 and E-3, with higher  $\text{NO}_3^-$   
234 concentrations (mean integrated stock 0-150m of  $4.10 \pm 0.05 \text{ mol m}^{-2}$ ) than in the group  
235 formed by stations E4-E and E-5 (mean integrated stock 0-150m of  $3.90 \pm 0.04 \text{ mol m}^{-2}$ ).  
236 Finally, the lowest concentrations were measured in summer (mean integrated stock 0-150m  
237 of  $3.48 \text{ mol m}^{-2}$ ).

238 Vertical profiles of  $\text{PO}_4^{3-}$  present similar characteristics as  $\text{NO}_3^-$ , with the exception of the  
239 winter profile (Fig. 7b). The winter profile indicates that  $\text{PO}_4^{3-}$  concentrations are  
240 homogeneously mixed in the upper 150m. The concentrations seem overestimated at 150m and  
241 above. We do not think that the differences result from inter-annual variability because this  
242 would have also impacted  $\text{NO}_3^-$  concentrations. The high concentrations of  $\text{PO}_4^{3-}$  measured in  
243 winter 1995 lead to a  $\text{NO}_3^-:\text{PO}_4^{3-}$  ratio of 12.5 which is low. The overestimation of  $\text{PO}_4^{3-}$   
244 could result from methodological issues. The ANTARES3 samples were not analyzed  
245 aboard, but a few months later in a laboratory by a different analytical protocol. The lack of

246 certified international standards necessary for a strong quality control of the accuracy  
247 precludes rigorous comparison of sample collected in 1995 with more recent samples.

248 Similarly to  $\text{NO}_3^-$ , we consider the mean concentration of  $\text{PO}_4^{3-}$  at 150 m (excluding the  
249 ANTARES3  $\text{PO}_4^{3-}$  value) to estimate a mean winter  $\text{PO}_4^{3-}$  concentration in the surface layer of  
250  $1.93 \pm 0.09 \mu\text{mol L}^{-1}$ , that yields an integrated winter stock of  $0.30 \pm 0.02 \text{ mol m}^{-2}$ . The  
251 integrated stock for the group of stations E-1-2-3 ( $0.280 \pm 0.004 \text{ mol m}^{-2}$ ) was higher than for  
252 the group E-4-5 ( $0.274 \pm 0.005 \text{ mol m}^{-2}$ ). At the end of the season the integrated  $\text{PO}_4^{3-}$  stock  
253 was  $0.250 \text{ mol m}^{-2}$ .

### 254 3.3.2. The Kerguelen plateau station A3

255 ~~At Station A3, vertical profiles A similar seasonal change in of~~ changes of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$   
256 concentrations ~~was observed at Station A3 were observed between spring and summer~~ (Fig.  
257 8). ~~Albeit the stations were sampled in November 2011 and February 2013, we consider these~~  
258 ~~variations as seasonal changes~~. The profiles of both nutrients merge at 200 m in early spring  
259 and summer (A3-1 and A3-2). However, during the second visit at A3 (A3-2), we observed  
260 that the surface layer was mixed down to 170 m. We propose that the concentrations at 200 m  
261 are a good estimate of the winter concentrations of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  at this station. Thus, winter  
262 stocks (0-200m) were 6.27 and 0.43  $\text{mol m}^{-2}$  for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , respectively. At the first visit  
263 at station A3 the stocks have decreased to 5.96 and 0.41  $\text{mol m}^{-2}$ . Four weeks later (A3-2)  
264 they reached 5.29 and 0.36  $\text{mol m}^{-2}$ . Finally, in February the stocks were 4.77 and 0.35  $\text{mol m}^{-2}$ .  
265 <sup>2</sup>.

## 266 5. Discussion.

267 The distribution of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  in the world's oceans were extensively studied over the  
268 past decades. A major rationale for this research is the critical role of these major nutrients for  
269 phytoplankton growth and therefore marine primary production. Further, concentrations of

270  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  are used as tracers for biogeochemical processes in the ocean (Deutsch and  
271 Weber, 2012). In the Southern Ocean, south of the subantarctic front,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$   
272 concentrations are high. They are therefore considered as non-limiting and much less attention  
273 has been paid to their distribution if compared to other nutrients such as silicic acid or  
274 dissolved iron. However, the relief of iron limitation by natural or artificial fertilizations  
275 offers a different perspective because  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  should be consumed as the bloom  
276 develops. This has motivated the present detailed study of dissolved N and P in the naturally  
277 fertilized region of Kerguelen.

278 To explore the dynamics of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  we examined their stoichiometry in the  
279 study region. This is commonly done by establishing the ratio  $r_{\text{N:P}} = [\text{NO}_3^-] : [\text{PO}_4^{3-}]$  for  
280 comparison with the Redfield ratio of 16 (Redfield et al. 1963). However, the ~~use-interest~~ of  
281  $r_{\text{N:P}}$  is limited because this ratio is not conserved by mixing or biological processes such as  
282 uptake or remineralisation (Deutsch and Weber, 2012). We therefore calculated the linear  
283 combination  $\text{N}^* = [\text{NO}_3^-] - 16 [\text{PO}_4^{3-}]$ , similar to the parameter first introduced by (Michaels et  
284 al., 1996), but omitting the constant term required to obtain a global average of  $\text{N}^*$  equal to 0.  
285  $\text{N}^*$  traces the impact of processes that add or remove N and P with a stoichiometry different  
286 from the Redfield ratio of 16. At almost all stations and depths,  $\text{N}^*$  was close to  $-3 \mu\text{M}$  (Fig.  
287 9a). This value agrees well with the mean  $\text{N}^*$  computed for regions of the Southern Ocean  
288 close to the PF (Weber and Deutsch, 2010). A noticeable deviation from this value was  
289 observed for a set of data where  $\text{N}^*$  increased from  $\text{N}^* = -3 \mu\text{M}$  to  $\text{N}^* = 6 \mu\text{M}$ . All data with  
290  $\text{N}^* > 0$  are for samples collected in the mixed layer north of the PF, and located in ~~a large~~  
291 ~~diatom a~~ bloom where diatoms contributed to 70 % of the carbon biomass in the euphotic  
292 layer (Lasbleiz et al., 2014b).

293 Nutrient drawdown lower than the Redfield ratio was observed previously in the  
294 Southern Ocean. During the artificial iron fertilization experiment EIFEX, an apparent

295 differential consumption of  $\Delta(\text{NO}_3^-):\Delta(\text{PO}_4^{3-})$  of 6.4 was reported (Smetacek et al., 2012).  
296 Arrigo et al.(Arrigo, 1999) and (De Baar et al., 1997) determined a nutrient drawdown ratio in  
297 diatom blooms of 9.7 and 4.4-6.1, respectively. Near Crozet, the removal of  $\text{NO}_3^-$  versus  
298  $\text{PO}_4^{3-}$  measured in situ and during iron addition experiments revealed that the ratio was  
299 inversely related to the proportion of diatoms of the phytoplankton community (Moore et al.,  
300 2007). All these studies confirm the impact of diatom blooms on nutrient stoichiometry in the  
301 surface layer. However, the interpretations of these observations are diverse. (De Baar et al.,  
302 1997) suggested that the preferential drawdown of  $\text{PO}_4^{3-}$  during the bloom of *Fragiliaropsis*  
303 *kerguelensis* in the PF could be due to the reduction of nitrate reductase activity by iron  
304 limitation or due to the dominance of *Fragiliaropsis kerguelensis* with low N:P ratios  
305 considered as a specific physiological trait. These hypotheses could not explain our  
306 observations because the stations with a nutrient drawdown anomaly were located in an iron  
307 fertilized region and the diatom community was not dominated by *Fragiliaropsis kerguelensis*  
308 but rather by *Chaetoceros (Hylochaete) spp.*, *Pseudo-nitzschia spp* and *Centric sp.* (Lasbleiz  
309 ~~pers.-com-2014b~~).

310 Thus, we interpret the positive values of  $\text{N}^*$  as a result of the preferential uptake of  
311  $\text{PO}_4^{3-}$  versus  $\text{NO}_3^-$  by fast growing diatoms. Diatoms have a mean elemental N:P  
312 stoichiometry of  $10 \pm 4$  (Sarhou et al., 2005) that differs from the Redfield value. Indeed, the  
313 elemental particulate matter composition determined at the stations with positive  $\text{N}^*$  during  
314 KEOPS2 (Lasbleiz et al. ~~this issue~~2014) exhibits a mean ratio of PON:POP of  $10.5 \pm 3.3$   
315 which is consistent with the observed nutrient drawdown  $\Delta(\text{NO}_3^-):\Delta(\text{PO}_4^{3-})$  of 8. We suggest  
316 that the preferential allocation of resources to the P-rich assembly of the cell machinery by  
317 exponentially growing cells is the most likely explanation for our observations (Klausmeier et  
318 al., 2004). The anomaly observed for the present data set is not linked to a particular species  
319 but to general traits of the diatom community responding to iron fertilization.

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320 As a variant of  $N^*$ , the tracer  $DIN_{xs}$ , takes into account  $NO_2^-$  and  $NH_4^+$  (Hansell et al.,  
321 2007), but none of those tracers consider the organic pools of N and P. (Landolfi et al., 2008)  
322 have defined the tracer  $TN_{xs} = [TDN] - 16[TDP]$  and have shown that the dissolved organic  
323 fraction significantly contributes to changes in  $TN_{xs}$ . For example, relying on  $N^*$  only, can  
324 lead to an underestimation of  $N_2$  fixation at the global scale (Landolfi et al., 2008). In the case  
325 of KEOPS2, the contribution of DON and DOP to TDN and TDP could reach 30-%. We have  
326 therefore ~~calculated-considered~~  $TN_{xs}$  and TDP at all KEOPS2 stations where ~~DON and DOP~~  
327 these measurements were available (Fig. 9b).  $TN_{xs} = f(TDP)$  reveals more dispersion of the  
328 data than  $NO_3^- = f(PO_4^{3-})$ , mainly due to the lower analytical precision for DOP and DON  
329 determinations. Still, clear trends are detectable.  $TN_{xs}$  were negative for most stations and  
330 depths, and relatively constant in the layer 0-500m. As for  $N^*$  the stations north of the PF had  
331 higher  $TN_{xs}$  in the layer 0-100m.

332 When a water parcel is considered,  $N^*$  is affected by the redistribution of N and P  
333 between the inorganic and the organic pools, whereas  $TN_{xs}$  is only affected by net non-  
334 redfieldien sources or sinks of N and P. Consequently, the positive anomaly observed for  
335  $TN_{xs}$  in surface waters north of the PF can be explained by three possible mechanisms:  
336 Deposition of N rich material from the atmosphere,  $N_2$  fixation and export of P rich material.  
337 The region of Kerguelen receives low quantities of atmospheric material (Heimbürger et al.,  
338 2012; Wagener et al., 2008) which is mainly from natural origin, such as desert dust, that  
339 contains little nitrogen compared to phosphorus (Zamora et al., 2013). This is confirmed by  
340 the low N deposition rate estimated around Crozet Island ( $2 \text{ nmol m}^{-2} \text{ d}^{-1}$ ; Planquette et al.,  
341 2007). We can therefore refute the deposition of N rich material as the cause of the  $TN_{xs}$   
342 anomaly. The second hypothesis involves  $N_2$  fixation. To date,  $N_2$  fixation was not reported to  
343 occur in the cold waters of the Southern Ocean. However, during KEOPS2 detectable  $N_2$   
344 fixation rates were measured at different stations with a few exceptionally high values ( $\sim 250$

345  $\mu\text{mol m}^{-2} \text{d}^{-1}$ ) in the mixed layer of station F-L (~~Fernandez personal communication~~[González](#)  
346 [et al. 2014](#)). Such high fixation rates could contribute to an enrichment of about 1% of TDN  
347 that is not enough to create the observed anomaly. If  $\text{N}_2$  fixation was a dominant process  
348 driving the N:P stoichiometry at this station, POM elemental composition should be also  
349 affected. Generally,  $\text{N}_2$  fixing microorganisms have a high N:P ratio (Laroche, J. and  
350 Breitbarth, E., 2005). Such high ratios are at odds with the low N:P measured in the POM at  
351 station F-L (Lasbleiz et al., 2014). The third hypothesis for explaining the anomaly relies on  
352 the export of P rich material from the mixed layer. We do not have direct measurements of  
353 N:P in the exported material, but we already mentioned above that the elemental composition  
354 of particulate matter at station F-L yielded the lowest N:P ratio in POM (Lasbleiz et al.,  
355 2014). This provides support that the export of P rich material could result in high  $\text{TN}_{\text{xs}}$  values  
356 north of the PF. We propose that the anomaly of  $\text{TN}_{\text{xs}}$  results from the imprint on  
357 stoichiometry of the diatom bloom which consumed and exported phosphorus in a ratio below  
358 the Redfield value.

359 During KEOPS2 rapidly growing diatom blooms were also sampled at other stations  
360 located south of the PF, but anomalies similar to those at F-L were not observed. We  
361 discussed here the case of stations A3 and E-4W, which had similar chlorophyll  
362 concentrations as F-L. ~~Station A3 had also similar a contribution of diatoms to carbon~~  
363 ~~biomass -and dominant diatoms species similar to F-L (these features are not available for E4-~~  
364 ~~W) (Lasbleiz 2014b)~~. There is no reason that the physiological features of exponentially  
365 growing diatoms ~~mentioned as revealed for station at~~ F-L do not apply to the diatoms growing  
366 at stations A3 and E4-W. It is, however, possible that ~~the resulting is~~ effect is not large enough  
367 to translate into  $\text{N}^*$  or  $\text{TN}_{\text{xs}}$  anomalies. A possible explanation could be the differences in the  
368 age of the blooms. ~~The stoichiometry would be less affected in a~~ younger bloom ~~would have~~  
369 ~~less affected the stoichiometry~~ as compared to a bloom of longer duration. This hypothesis

370 cannot be fully verified due to the poor temporal resolution of the satellite ocean color images  
371 available. Another or complementary explanation is the difference in [the](#) mixed layer depths  
372 that were 50 m and 150 m at stations F-L and A3-2, respectively. Such a deep mixed layer as  
373 observed at station A3-2 resulted likely from a deep episodic mixing event generated by  
374 strong wind prevailing during the day preceding our visit. The deepening could have  
375 dampened the anomaly by diluting and mixing the affected water parcel with underlying  
376 water having a typical stoichiometry (e.g.  $N^*$  or  $TN_{xs}$  around -3).

377 In February 2013, two years after the KEOPS2 cruise, we had the possibility to return to two  
378 sites visited during KEOPS2 (stations A3 and TNS-6), and obtain measurements for the  
379 concentrations of  $NO_3^-$  and  $PO_4^{3-}$ . These data, in combination with KEOPS2 data allowed us  
380 to compare  $N^*$  during two different seasons (Fig. 10). In the mixed layer, little changes of  $N^*$   
381 were observed between spring and summer. However, in summer,  $N^*$  exhibited a clear  
382 subsurface minimum between 100-200 m, at both stations. Denitrification is a process that  
383 could produce this subsurface feature. But denitrification would require low oxygen  
384 concentrations that are not observed at these stations. ~~We propose that highly negative values~~  
385 ~~of  $N^*$  result from preferential remineralisation of P versus N.~~ In a general manner,  
386 preferential remineralisation of P versus N in the water column is supported by an increase of  
387 N:P in high molecular dissolved organic matter (Clark, L. L. et al., 1998) in particulate matter  
388 (Copin-Montegut and Copin-Montegut, 1978) and in supernatant of sediment trap material  
389 (Lourey et al., 2003). The observation of the  $N^*$  subsurface minimum at the end of the season,  
390 but not at the beginning implies a temporal cumulative effect. The minimum is located just  
391 below the mixed layer in the region of the pycnocline that presents the highest density  
392 gradient. This could represent a zone with a higher residence time for sinking particles  
393 resulting in an accumulation of biomass. Consequently, the remineralization would also be  
394 increased in this layer compared to the rest of the water column resulting in a higher

395 accumulation of  $\text{PO}_4^{3-}$  relative to  $\text{NO}_3^-$ . This effect might be amplified by the occurrence of  
396 particulate organic matter with low N:P ratio resulting from ~~diatom~~ diatom accumulation at the  
397 pycnocline. The subsurface minimum being located above 200 m depth, it is erased when the  
398 winter mixing occurs.

399 To our knowledge such a subsurface minimum has not been reported in the Southern Ocean.  
400 This could be due to the limited studies that investigate concurrently dissolved N and P  
401 biogeochemistry, and due to the lack of samples collected at the appropriate vertical and  
402 temporal time scale. Our finding raises several further questions. Is the subsurface minimum  
403 of  $\text{N}^*$  a particular feature of iron fertilized regions? What is the link between its occurrence  
404 and the strength of stratification of the water column? And what is the role of this layer in the  
405 remineralisation of carbon? These questions argue for future detailed investigations of the  
406 cycling of both elements in the upper layer of the Southern Ocean.

407

408

409 **Figure captions**

410  
411 **Figure 1:** Map of the KEOPS2 study area. The locations of the stations are marked by color  
412 dots. Blue indicates the stations of the North-South transect (TNS), green indicates the  
413 stations of the East-West transect (TEW), orange indicates the stations E located in the  
414 meander of the polar front (zoom panel). Red stands for other stations located in the fertilized  
415 region and black stands for the station located in the HNLC region.

416

417 **Figure 2:** ~~Two dimensional distribution~~ Vertical sections of dissolved nitrogen and  
418 phosphorus species along the East-West transect (TEW). (a) Nitrate, (b) Ammonium, (c)  
419 Phosphate, (d), Nitrite, (e) Dissolved organic nitrogen, (f) Dissolved organic phosphorus. The  
420 isolines for sigma are plotted on each panel.

421

422 **Figure 3:** ~~Two dimensional distribution~~ Vertical sections of dissolved nitrogen and  
423 phosphorus species along the North-South transect (TNS). (a) Nitrate, (b) Ammonium), (c)  
424 Phosphate, (d), Nitrite, (e) Dissolved organic nitrogen, (f) Dissolved organic phosphorus. The  
425 isolines for sigma are plotted on each panel.

426

427

428 **Figure 4:** Dissolved nitrogen speciation at station A3-1 (a, b) and at station A3-2 (c, d) during  
429 KEOPS2. Depth profiles of temperature and sigma are plotted on each panel.

430

431 **Figure 5:** Dissolved nitrogen speciation at stations F-L and F-S during KEOPS2.

432

433 **Figure 6:** Dissolved nitrogen speciation at station R-2.

434

435 **Figure 7** : Temporal variability of the vertical profiles of concentrations of  $\text{NO}_3^-$  (a) and  
436  $\text{PO}_4^{3-}$  (b) for stations located in the meander of the Polar Front. Details for profiles of  
437 KEOPSMOOR (February 2013) and ANTARES3 (October 1995) are provided in the text.

438

439 **Figure 8**: Temporal variability of the vertical profiles of concentrations of  $\text{NO}_3^-$  (a) and  
440  $\text{PO}_4^{3-}$  (b) at the station A3.

441

442 **Figure 9**: (a) Comparison of concentrations of  $\text{NO}_3^-$  versus  $\text{PO}_4^{3-}$ . (Dots denote the samples  
443 and lines show different values of  $N^* = \text{NO}_3^- - r_{\text{N:P}} \text{PO}_4^{3-}$  (lines) calculated for different  
444 values of  $r_{\text{N:P}}$ . (b) Comparison of concentrations of TDN versus TDP. Dots denote the  
445 samples and lines show different values of  $\text{TN}_{\text{xs}} = \text{TDN} - r_{\text{N:P}} \text{TDP}$  (lines)  
446 calculated for different values of  $r_{\text{N:P}}$ . For both panels the black line correspond to  $r_{\text{N:P}} = 16$   
447 ( $N^*$  or  $\text{TN}_{\text{xs}} = 0$ ).

448

449 **Figure 10**: Depth profiles of  $N^*$  at stations A3 (a) and TNS-6 (b) for the month of November  
450 (in red) and February (in blue). Vertical profiles of sigma are shown with the same color code.

451

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460

#### 461 **Bibliography**

462 Aminot, A.: Dosage automatique des nutriments dans les eaux marines: méthodes en flux  
463 continu, Ifremer, France., 2007.

464 Arrigo, K. R.: Phytoplankton Community Structure and the Drawdown of Nutrients and CO<sub>2</sub>  
465 in the Southern Ocean, *Science*, 283(5400), 365–367, doi:10.1126/science.283.5400.365,  
466 1999.

467 De Baar, H. J. W., Van Leeuwe, M. A., Scharek, R., Goeyens, L., Bakker, K. M. J. and  
468 Fritsche, P.: Nutrient anomalies in *Fragilariopsis kerguelensis* blooms, iron deficiency and the  
469 nitrate/phosphate ratio (A. C. Redfield) of the Antarctic Ocean, *Deep Sea Res. Part II Top.*  
470 *Stud. Oceanogr.*, 44(1-2), 229, 1997.

471 Blain, S., Quéguiner, B., Armand, L., Belviso, S., Bombled, B., Bopp, L., Bowie, A., Brunet,  
472 C., Brussaard, K., Carlotti, F., Christaki, U., Corbière, A., Durand, I., Ebersbach, F., Fuda, J.  
473 L., Garcia, N., Gerringa, L. J. A., Griffiths, F. B., Guigue, C., Guillerm, C., Jacquet, S.,  
474 Jeandel, C., Laan, P., Lefèvre, D., Lomonaco, C., Malits, A., Mosseri, J., Obernosterer, I.,  
475 Park, Y. H., Picheral, M., Pondaven, P., Remenyi, T., Sandroni, V., Sarthou, G., Savoye, N.,  
476 Scouarnec, L., Souhault, M., Thuillers, D., Timmermans, K. R., Trull, T., Uitz, J., Van-Beek,  
477 P., Veldhuis, M. J. W., Vincent, D., Viollier, E., Vong, L. and Wagener, T.: Effect of natural  
478 iron fertilisation on carbon sequestration in the Southern Ocean, *Nature*, 446(7139), 1070–  
479 1075, doi:doi:10.1038/nature05700, 2007.

480 Boyd, P. W., Jickells, T., Law, C., Blain, S., Boyle, E. A., Buesseler, K. O., Coale, K. H.,  
481 Cullen, J. J., De Baar, H. J. W., Follows, M., Harvey, M., Lancelot, C., Levasseur, M.,  
482 Owens, N. J. P., Pollard, D. A., Rivkin, R. B., Sarmiento, J. L., Schoemann, V., Smetacek, V.,  
483 Takeda, S., Tsuda, A., Turner, D. R. and Watson, A.: Mesoscale iron enrichment experiments  
484 1993-2005: Synthesis and future directions, *Science*, 315, 612–617, doi:DOI:  
485 10.1126/science.1131669, 2007.

486 Clark, L. L., Ingall, E. and Benner, R.: Marine phosphorus isselectively remineralized, *Nature*,  
487 393, 426, 1998.

488 Copin-Montegut, C. and Copin-Montegut, G.: the chemistry of particulate matter from the  
489 south indien and antarctic ocean, *Deep Sea Res.*, 25, 911–931, 1978.

490 Deutsch, C. and Weber, T.: Nutrient Ratios as a Tracer and Driver of Ocean Biogeochemistry,  
491 *Annu. Rev. Mar. Sci.*, 4(1), 113–141, doi:10.1146/annurev-marine-120709-142821, 2012.

492 Gnanadesikan, A., Sarmiento, J. L. and Slater, R. D.: Effects of patchy ocean fertilization on  
493 atmospheric carbon dioxide and biological production, *Glob. Biogeochem. Cycles*, 17(2), doi:  
494 10.1029/2002GB001940, 2003.

495 Hansell, D. A., Olson, D. B., Dentener, F. and Zamora, L. M.: Assessment of excess nitrate  
496 development in the subtropical North Atlantic, *Maine Chem.*, 206, 562–579, 2007.

497 Hart, T. J.: Phytoplankton periodicity in Antarctic surface water, *Discov. Rep.*, VIII, 1–268,  
498 1942.

499 Heimburger, A., Losno, R., Triquet, S., Dulac, F. and Mahowald, N.: Direct measurements of  
500 atmospheric iron, cobalt, and aluminum-derived dust deposition at Kerguelen Islands, *Glob.*  
501 *Biogeochem. Cycles*, 26(4), n/a–n/a, doi:10.1029/2012GB004301, 2012.

502 Holmes, R. M., Aminot, A., K erouel, R., Hooker, B. and Peterson, B.: a simple and precise  
503 method for measuring ammonium in marine and freshwater ecosystem, *Mar. Chem.*, 56(10), 1801–1808,  
504 1999.

505 Klausmeier, C. A., Litchman, E., Daufresne, T. and Levin, S. A.: Optimal nitrogen-to-  
506 phosphorus stoichiometry of phytoplankton, *Nature*, 429(6988), 171–174,  
507 doi:10.1038/nature02454, 2004.

508 Landolfi, A., Oschlies, A. and Sanders, R.: Organic nutrients and excess nitrogen in the North  
509 Atlantic subtropical gyre, *Biogeosciences*, 5(5), 1199–1213, doi:10.5194/bg-5-1199-2008,  
510 2008.

511 Laroche, J. and Breitbarth, E.: Importance of the diazotrophs as a source of new nitrogen in  
512 the ocean, *J. Sea Res.*, 53(1-2), 67–91, 2005.

513 Lasbleiz, M., Leblanc, K., Blain, S., Ras, J., Cornet-Barthaux, V., H elia Nunige, S. and  
514 Qu eguiner, B.: Pigments, elemental composition (C, N, P, Si) and stoichiometry of particulate  
515 matter, in the naturally iron fertilized region of Kerguelen in the Southern Ocean,  
516 *Biogeosciences Discuss.*, submitted, 2014.

517 Lourey, M. J., Trull, T. W. and Sigman, D. M.: Sensitivity of  $\delta^{15}\text{N}$  of nitrate, surface  
518 suspended and deep sinking particulate nitrogen to seasonal nitrate depletion in the Southern  
519 Ocean, *Glob. Biogeochem. Cycles*, 17(3), doi:10.1029/2002GB001973, 2003.

520 Marshall, J. and Speer, K.: Closure of the meridional overturning circulation through  
521 Southern Ocean upwelling, *Nat. Geosci.*, 5(3), 171–180, doi:10.1038/ngeo1391, 2012.

522 Martin, J. M. and Fitzwater, S. E.: Iron deficiency limits phytoplankton growth in the north-  
523 east Pacific subarctic, *Nature*, 331, 341–343, 1988.

524 Martinez-Garcia, A., Sigman, D. M., Ren, H., Anderson, R. F., Straub, M., Hodell, D. A.,  
525 Jaccard, S. L., Eglinton, T. I. and Haug, G. H.: Iron Fertilization of the Subantarctic Ocean  
526 During the Last Ice Age, *Science*, 343(6177), 1347–1350, doi:10.1126/science.1246848,  
527 2014.

528 Michaels, A. F., Olson, D., Sarmiento, J., Ammerman, J. W., Fanning, K. A., Jahnke, R. A.,  
529 Knap, A. H., Lipschultz, F. and Prospero, J.M.: Inputs, losses and transformations of nitrogen  
530 and phosphorus in the pelagic North Atlantic Ocean, *Biogeochemistry*, 35, 181–226, 1996.

531 Moore, C. M., Hickman, A. E., Poulton, A. J., Seeyave, S. and Lucas, M. I.: Iron–light  
532 interactions during the CROZet natural iron bloom and EXport experiment (CROZEX): II—  
533 Taxonomic responses and elemental stoichiometry, *Deep Sea Res. Part II Top. Stud.*  
534 *Oceanogr.*, 54(18-20), 2066–2084, doi:10.1016/j.dsr2.2007.06.015, 2007.

535 Planquette, H., Statham, P. J., Fones, G., Charette, M. A., Moore, C. M., Salter, I., Nédélec, F.  
536 H., Taylor, S. L., French, M., Baker, A. R., Mahowald, N. and Jickells, T. D.: Dissolved iron  
537 in the vicinity of the Crozet islands, Southern Ocean, *Deep-Sea Res. II*, 54, 1999–2019, 2007.

538 Sarmiento, J. L., Gruber, N., Brzezinsky, M. A. and Dunne, J. P.: High-latitude controls of  
539 thermocline nutrients and low latitude biological productivity, *Nature*, 427, 2004.

540 Sarthou, G., Timmermans, K. R., Blain, S. and Treguer, P.: Growth physiology and fate of  
541 diatoms in the ocean: a review, *J. Sea Res.*, 53(1-2), 25, 2005.

542 Sigman, D. M. and Boyle, E. A.: Glacial/interglacial variations in atmospheric carbon  
543 dioxide, *Science*, 407, 859–869, 2000.

544 Smetacek, V., Klaas, C., Strass, V. H., Assmy, P., Montresor, M., Cisewski, B., Savoye, N.,  
545 Webb, A., d’ Ovidio, F., Arrieta, J. M., Bathmann, U., Bellerby, R., Berg, G. M., Croot, P.,  
546 Gonzalez, S., Henjes, J., Herndl, G. J., Hoffmann, L. J., Leach, H., Losch, M., Mills, M. M.,  
547 Neill, C., Peeken, I., Röttgers, R., Sachs, O., Sauter, E., Schmidt, M. M., Schwarz, J.,  
548 Terbrüggen, A. and Wolf-Gladrow, D.: Deep carbon export from a Southern Ocean iron-  
549 fertilized diatom bloom, *Nature*, 487(7407), 313–319, doi:10.1038/nature11229, 2012.

550 Wagener, T., Guieu, C., Losno, R., Bonnet, S. and Mahowald, N.: Revisiting atmospheric  
551 dust export to the southern hemisphere ocean: biogeochemical implication, *Glob.*  
552 *Biogeochem. Cycles*, 22(GB2006), doi:10.1029/2007GB002984., 2008.

553 Weber, T. S. and Deutsch, C.: Ocean nutrient ratios governed by plankton biogeography,  
554 *Nature*, 467(7315), 550–554, doi:10.1038/nature09403, 2010.

555 Zamora, L. M., Prospero, J. M., Hansell, D. A. and Trapp, J. M.: Atmospheric P deposition to  
556 the subtropical North Atlantic: sources, properties, and relationship to N deposition, *J.*  
557 *Geophys. Res. Atmospheres*, 118(3), 1546–1562, doi:10.1002/jgrd.50187, 2013.

558 Zhou, M., Zhu, Y., d’ Ovidio, F., Park, Y.-H., Durand, I., Kestenare, E., Sanial, V., Van-  
559 Beek, P., Queguiner, B., Carlotti, F. and Blain, S.: Surface currents and upwelling in  
560 Kerguelen Plateau regions, *Biogeosciences Discuss.*, 11(5), 6845–6876, doi:10.5194/bgd-11-  
561 6845-2014, 2014.

562