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Interactive comment on "Nitrogen cycling in the Southern Ocean Kerguelen Plateau area: evidence for significant surface nitrification from nitrate isotopic compositions" *by* F. Dehairs et al.

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bg-2014-443: Reply to Reviewer #2

Reviewer: 1/ DeHairs et al. argue that nitriïňĄcation above the Kerguelan Plateau (in the Southern Ocean) "could account for up to 80% of nitrate uptake" in the region (note to authors, I understand what you are trying to say, but this is awkward phrasing).

Reply: We changed the sentence in the abstract as follows: "A preliminarily mass balance calculation for the early bloom period points toward significant nitrification occurring in the mixed layer equivalent to some 80% of nitrate uptake above the Kerguelen Plateau".

Reviewer: 2/ They base this conclusion on a few lines of evidence: the d15N-NO3 and d18O-NO3, nitrate and silicate concentrations, and calculations incorporating all of their observations. First, the nitrate isotope evidence. The upper ocean d15N-NO3 and d18O-NO3 above the Kerguelan Plateau (in the Southern Ocean) has a much smaller difference than the putative source nitrate below, suggesting that nitriïňĄcation is altering the nitrate pool (see references in text). It is unfortunate that nitrite was not removed from their samples before being measured because (as the authors know and write) the inclusion of nitrite will produce the same lowering of d15N versus d18O that they are trying to understand. It is possible and perhaps likely that nitrite is only amplifying the lowering of d15N versus d18O, but there is no way to know without the removal of nitrite. I would be much happier if the study showed measurements with and without nitrite so that the readers can understand the impacts these might have on the conclusions. Can this be done? If not, the text should be changed to lower the signiïňĄcance of these results.

Reply: We acknowledge the fact that the isotopic values measured in this study concern the combined nitrate and nitrite pools. While we presently are conducting work on implementing the sulfamic acid method to eliminate nitrite prior to submitting the seawater samples to bacterial denitrification, we have not re-analysed our samples following sulfamic acid treatment. However, we argue that the possible effects (i.e., lowering the original nitrate δ15N and δ18O values by 0.4‰ and 0.2‰ in case of a 0.8% NO2 contribution to the combined NO2+NO3 pool, as reported in the suppl. mat. of Rafter et al., 2012) affects all surface samples alike, since nitrite concentrations in the upper ocean remain quite constant throughout time and space (Table 1). What will change of course is the vertical gradient of Δ(15-18), which will be less steep. As shown further below the calculations of nitrification rate are but minimally affected by this nitrite effect, since nitrate isotopic values t0 and tfinal of the observation period are affected similarly.

To acknowledge the effect of nitrite, we changed method section 2.2 (Lines 15 to 20)

as follows:

“Note that the method measures the isotopic composition of NO3- plus NO2- and that the presence even of small nitrite amounts would lower the δ15N and δ18O values of nitrate + nitrite relative to nitrate only (Casciotti et al., 2007). In the present study the effect of NO2- was neglected since overall nitrite concentrations were small, representing on average <0.5% of the nitrate + nitrite pool (see also DiFiore et al., 2009). However, Rafter et al., (2013; see their suppl. mat. section) report that slightly higher nitrite levels reaching some 0.8 % of the nitrite + nitrate pool, as is observed here for the surface waters, can result in a lowering of the ïĄď15N and ïĄď18O values by 0.4‰ and 0.2‰ on average. We have not corrected our surface water nitrate isotopic values for such nitrite effect, but have considered the impact of this when calculating nitrification rates (section 4.5).”

As stated above, our model calculations of the upper ocean nitrate evolution and nitrification rate over the one month study period would be affected minimally, since initial and final conditions for nitrate isotopic composition will be affected similarly by nitrite presence. Nevertheless, we recalculated the nitrification flux in the upper ocean, with all relevant δ15N and δ18O values increased by 0.4‰ and 0.2‰ respectively (see attached ’Review Table 1 showing data for the Plateau area). The nitrite effect would decrease nitrification rate from 17.4 to 16.2 mmol/m2/d in case upwelling is left variable and from 16.2 to 15.9 mmol/m2/d in case upwelling is kept constant.

The effect of NO2 presence on the calculated nitrification rates appears to be minimal. Therefore we kept to the calculations based on uncorrected (for NO2 presence) nitrate isotopic compositions, and changed the text Page 13925, Lines 7 to 18 as follows:

“The best fit calculations yield nitrification rates of 1.7 $\pm$ 2.3 and 17.4 $\pm$ 4.1 mmol m-2 d-1 for Meander and Plateau, respectively (Table 3). Best fit values are 0 and 5.5 mmol m-2 d-1 for NO2- uptake and 4.0 and 6.1 mmol m-2 d-1 for NO3- upwelling, for Meander and Plateau sites respectively (Table 3). We note that the values for nitrate upwelling

are quite similar to the value of 7.4 mmol m-2 d-1 we calculate, as based on an Ekman pumping velocity of 3 x 10-6 m s-1 for the studied KEOPS 2 area, reported by Gille et al. (2014), and an average subsurface (150m) NO3- concentration of 28.5 μM. In case the NO3- upwelling rate is fixed and set equal to the calculated value of 7.4 mmol m-2 d-1 based on the Ekman pumping velocity, the best fit nitrification rates are slightly smaller but more constrained with values of 1.3 $\pm$ 1.2 and 16.2 $\pm$ 2.4 mmol m-2 d-1, for Meander and Plateau, respectively. It appears for the Meander site that nitrification rates are low and poorly constrained, in agreement with the fact that surface water Δ(15-18) values are large and similar to those for the HNLC R-2 reference station. We also verified the effect of nitrite presence on these calculations. Indeed, Rafter et al. (2012) report a lowering of the true nitrate δ15N and δ18O compositions by 0.4‰ and 0.2‰ respectively, in case nitrite contents amount to some 0.8% of the nitrate content, what is the case here (see also methods section 2.2). It appears that nitrification rate would be reduced by at most 7% due to unaccounted for nitrite.”

3/ Reviewer: As for the nutrient concentration evidence, the nitrate and silicate concentration data in Table 1 does not clearly show a depletion of silicate relative to nitrate except for the 3 stations at the Polar Front. The difference between mixed layer silicate (about 15 μM) and nitrate (about 26 μM) at the 15 other stations should not be described as silicate “depleted,” even if the uptake does not appear to be 1:1 with nitrate.

Reply: In fact we compared average nutrient utilization in the mixed layer vs. the value in the Tmin waters, taken as the winter condition. The apparent utilization is systematically larger for silicic acid than for nitrate.

We clarified this by changing the text at page 13921, Line 21 as follows: “We also note that the average deficit of silicic acid and nitrate in the mixed layer vs. the winter values in underlying Tmin waters are systematically » 1 (up to 4) for the whole area, while Si(OH)4/NO3- uptake ratios are generally close to 1 (0.74 to 1.51) for the Plateau and Meander areas, consistent with iron replete conditions there (Closset et al., 2014; Cavagna et al., 2014). The larger deficit of silicic acid compared to nitrate could thus

partly result from shallow recycling of nitrogen. The replenishment of nitrate in the mixed layer . . ."

4/ Reviewer: It is confusing that the manuscript never proposes a reason to explain such high nitriïňĄcation. One possible explanation that is not explored in the manuscript is that the sediments are playing a role. Shallow sediments can be an important source of ammonia / ammonium, nitrite, and nitrate (as Granger et al. 2011 showed in Bering Sea shelf sediments). In fact, the ammonium and nitrite concentrations are highest just above the Kerguelan Plateau sediments (see Figure 6a). It may be that sedimentary nitriïňĄcation has a negligible inïňĆuence on open ocean waters off the Kerguelan Plateau, but this is not discussed or quantiïňĄed. As it is, sedimentary ammoniïňĄcation/nitriïňĄcation is only mentioned as a potential inïňĆuence from the slope sediments on the deep waters (>2000 m).

Reply: In response to the above criticism that the original text does not discuss the possible mechanism leading to high surface nitrification, we have added the following text at Page 13926, Line 3:

"The conditions leading to the high upper ocean nitrification above the Plateau are believed to be related with the depth range of the euphotic layer and the mixed layer. Above the Plateau the euphotic layer (0.1% PAR level) is consistently shallower than the mixed layer and any nitrate produced from nitrification, a process which is supposedly inhibited by light (references), at the bottom of the euphotic layer therefore becomes retained in the surface mixed layer. This aspect is discussed in more detail in a paper by Fripiat et al. (submitted)."

Role of sediments: We have now changed the text to discuss a possible advective origin (from shallow plateau sediments) of the nitrification signal. Conditions reflecting possibly nitrification at the sediment water column boundary are present above the shallow shelf (70m) at station of TEW1, north of the Polar Front. The following paragraph was added page 13922 at the end of section 4.4: "The question can be raised

to what extent this is a local or imported condition from an upstream area. Nitrification may occur at the shelf sediment water column interface as reported for the Bering Sea shelf by Granger et al. (2011). For instance, at the shallow (< 100m) TEW1 shelf station (see Figure 6A) ammonium contents are enhanced (up to 1.1 μM) close to the seafloor and Δ(15-18) values are low (<2‰ over the whole 70 m water column (Figure 6A), which are conditions suggestive of nitrification. However, except for this station we do not see evidence for nitrification at the sediment water column boundary layer elsewhere above the Kerguelen Plateau. Furthermore the shallow TEW1 station is located north of the Polar Front, and surface waters advected from this shallow shelf area flow north, north-east, staying north of the PF (see flow lines in Figure 1). Therefore, it appears unlikely that sediment boundary layer nitrification is a source of nitrate to the mixed layer above the main Kerguelen Plateau area south of the Polar Front."

5/ Reviewer: Another confusing aspect of the manuscript is the reference station, which shows the same isotopic feature (lower d15N relative to d18O) even though this station is "upstream" of the Plateau. Does this say that there is nitriïňĄcation occurring on and off the Plateau? Or is this a case of including nitrite in the measurements? These are outstanding questions that need to be addressed.

Reply: Recently we re-analysed a series of samples including the reference R-2 and the A3-1, A3-2 profiles (CTD's 17, 4 and 111, resp.) using the same analytical conditions as applied originally. The median s.d. for the repeat analyses is 0.11‰ and 0.26‰ and the maximum s.d. value is 0.5‰ and 1.1‰ for δ15N and δ18O, respectively. Some samples have been analysed 4 times. The isotope values in the different tables and figures have been adjusted taking the average values of the repeat analyses into account. For the R-2 profile (see the attached Review Figure 1) the original elevated δ18O value (4.32‰ at 201m is not reproduced, with the repeat δ18O value now being 3.14‰.The elevated original value at 100m (4.71‰, however, is repeated (4.80‰ $seeboxedvalueinthefigure).However, sincenosuchoffsetisobservedforthe\delta$15N profile, we suspect that the integrity of that particular sample has been affected leading

to an erroneous result. Therefore we do not consider the δ18O value at 100m at R-2.

The corrected Δ(15-18) profile at HNLC R-2 station indeed shows decreased values in the upper 200m, but the deep to surface gradient is less than for the Kerguelen Plateau stations, indicating that whatever nitrification would be ongoing at the HNLC site, it is certainly less than above the Plateau.

The following text was added at the end of section 4.4 (page 13922, Line 3): "The question can be raised to what extent this is a local or imported condition from an upstream area. At the HNLC reference station, located upstream of the Kerguelen Plateau and Meander areas the upper mixed layer values of δ15N and δ18O are increased by about 1.2‰ and 2‰ respectively, relative to local deep waters (Figure 2). This results in decreased Δ(15-18) values (average value upper 100m = 2.25‰, which are similar to values for the Meander (Δ(15-18) = 2.20 $\pm$ 0.42‰, PF (Δ(15-18) = 2.39 $\pm$ 0.28‰ and also Plateau sites sampled during the earlier part of the study period (A3-1; E4W-1; TNS8; TEW4; E4W1; Δ(15-18) = 2.47 $\pm$ 0.26‰. Such values, however, are larger than those for Plateau sites sampled toward the end of the study period (E4W2 and A3-2; average Δ(15-18) = 1.79 $\pm$ 0.25‰, adding evidence for ongoing nitrification during this early bloom phase, at least above the Plateau. Meander and Polar Front sites on the contrary do not show such evidence as their upper ocean Δ(15-18) values do not differentiate from the value at the HNLC reference station. Nitrification could possibly occur at the shelf sediment water column interface as reported for the Bering Sea shelf by Granger et al. (2011). For instance, at the shallow (< 100m) TEW1 shelf station (see Figure 6A) ammonium contents are enhanced (up to 1.1 μM) close to the seafloor and Δ(15-18) values are low (<2‰ over the whole70 m water column (Figure 6A), which are conditions suggestive of nitrification. However, except for this station we do not see evidence for nitrification at the sediment water column boundary layer elsewhere above the Kerguelen Plateau. Furthermore the shallow TEW1 station is located north of the Polar Front, and surface waters advected from this shallow shelf area flow north, north-east, staying north of the PF (see surface water flow lines in Figure 1). Therefore,

it appears unlikely that sediment boundary layer nitrification is a source of nitrate to the mixed layer above the main Kerguelen Plateau area south of the Polar Front. In the next section we evaluate the strength of a possible nitrification in the surface layers."

6/ Reviewer: Page 13909 Line 15: "bound to the south" is confusing. I don't know what you mean by this. Line 20: "till the sill" Don't understand.

Reply: Sentence was changed as follows: This basin was delimited to the south by the Kerguelen Plateau and to the north by a sill (Gallieni Spur).

7/ Reviewer: Page 13910 Second paragraph. I cannot understand this paragraph and it is composed of a run-on sentence.

Reply: We changed the paragraph as follows: "The T-S diagram (Figure 1) highlights the hydrodynamic environment of the Kerguelen area, with profiles characteristic of the Open Ocean Zone. Most salient features are: highest temperatures in surface waters; presence of subsurface temperature minimum Winter Water; increased temperatures in Upper Circumpolar Deep Water; increased salinities in Lower Circumpolar Deep Water; a broad salinity maximum reflecting the remnant North Atlantic Deep Water; slightly less saline and cold Bottom Waters.

8/ Line 14: should read "superimposed" Corrected

9/ Page 13912 Line 7: remove "are" Done

10/ Page 13915 First paragraph. The idea behind identifying the isotope effect of nitrate uptake / utilization using a Rayleigh model needs to be introduced.

Reply: We have changed the text at Page 13915 beginning Line 3 till Line 8 as follows: "The clear 15N, 18O enrichments of nitrate in the upper ocean (Figure 2) suggest a strong effect of isotopic discrimination during nitrate uptake by the phytoplankton (Sigman et al., 1999; DiFiore et al., 2010). This isotope discrimination effect is visualized by plotting δ15NNO3 and δ18ONO3 values vs. the natural logarithm of nitrate concentration (Figure 4). The degree of linearity of these relationships is indicative of the

degree by which isotopic discrimination approaches a closed system Rayleigh fractionation. The slope values of these regressions are equivalent to apparent discrimination factors (ε). Whole water column values are -4.08 $\pm$ 0.17 ($\pm$se), -4.18 $\pm$ 0.20 and -4.54$\pm$0.21, for Meander, Polar Front and Plateau areas, respectively (Figure 4).

11/ Page 13916 Line 23: should be “which is not the case here” Done

12/ Line 18: deïňĄne LADCP Has been defined in the text (Lowered Acoustic Doppler Current Profiler)

13/ Page 13924 The equations (and what they mean) would be signiïňĄcantly improved if there were an equal sign and designation of what they equal!

14/ Line 11: “weighted” instead of “weighed” Done

15/ Page 13925 Line 19: Sensitivity tests are good. No comment

16/ Page 13925, Last sentence: does this sentence say that nitriïňĄcation produces 52% of the nitrate consumed? Or is the nitriïňĄcation rate 52% of the nitrate uptake rate? Confusing sentence.

To clarify the message we changed the sentence as follows: “From this we conclude for the Plateau site that significant surface layer nitrification needs to be invoked to explain the observed nitrate isotopic compositions which could be equivalent to 47% of the nitrate uptake flux.”

17/ Page 13927 Line 4: typo? “, and (Mosseri et al., 2008)” Corrected

18/ Table 1 Listed stations don’t match stations in Figure 1 All stations sampled for nitrate isotopic composition are shown on Figure 1, but they are not all labeled to keep the figure readable.

19/ Table 2 Asterisk should refer to an asterisk within the table text, which there is none. This comment should probably be integrated into the Table summary. There is an asterisk in the table text ..

20/ Table 3 Look over text. Too many plural forms of nouns (e.g., should just read “concentration”). We corrected the plural forms.

21/ Figure 1: text is too small and no description of the yellow dots. Figure 1 now shows the yellow dots.

22/ Figure 3: should include plot of Δ(15,18) Done

23/ Figure 5: the Polar Front stations look green to my eye (not blue). Not sure these ïňĄgures are necessary. The legend of Figure 5 has been corrected. We prefer to keep this figure.

24/ Figure 6: should include plot of Δ(15,18) Done

25/ Figure 8: X and Y axes should be equal length. DifïňĄcult to interpret the ïňĄgures when the X axis is so much longer than the Y. The X and Y scales in Figure 8 have been put to equal length.

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mmol/m2/d	NO3 + NO2	NO3 + NO2 (fixed upwelling)	NO3 – NO2	NO3 – NO2 (fixed upwelling)
Nitrification	17.4	16.2	16.2	15.9
NO2 uptake	5.5	4.7	5.4	5.2
Upwelling	6.1	7.4	7.3	7.4

Review Table 1: Recalculated the nitrification flux in the upper ocean, with all relevant $\delta^{15}N$ and $\delta^{18}O$ values increased by 0.4‰ and 0.2‰, respectively (table shows data for the Plateau area).

Review Figure 1: Recently we re-analysed a series of samples including the reference R-2 and the A3-1, A3-2 profiles (CTD's 17, 4 and 111, resp.) using the same analytical conditions as applied originally. The median s.d. for the repeat analyses is 0.11‰ and 0.26‰, and the maximum s.d. value is 0.5‰ and 1.1‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively. Some samples have been analysed 4 times. The isotope values in the different tables and figures have been adjusted taking the average values of the repeat analyses into account. For the R-2 profile (see the figure below here) the original elevated $\delta^{18}O$ value (4.32‰) at 201m is not reproduced, with the repeat $\delta^{18}O$ value now being 3.14‰. The elevated original value at 100m (4.71‰), however, is repeated (4.80‰; see boxed value in the figure). However, since no such offset is observed for the $\delta^{15}N$ profile, we suspect that the integrity of that particular sample has been affected leading to an erroneous result. Therefore we do not consider the $\delta^{18}O$ value at 100m at R-2.

The corrected Δ(15-18) profile at HNLC R-2 station indeed shows decreased values in the upper 200m, but the deep to surface gradient is less than for the Kerguelen Plateau stations, indicating that whatever nitrification would be ongoing at the HNLC site, it is certainly less than above the Plateau.

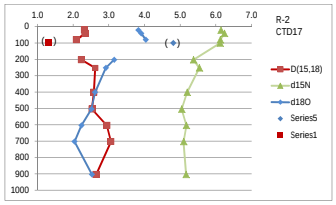

Fig. 1.

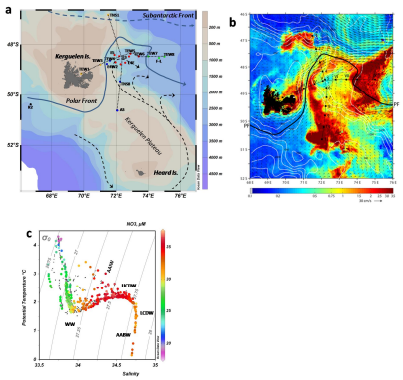

Figure 1: "(a) Kerguelen area with KEOPS 2 sampling grid. Blue dots = 'Plateau' stations; Red dots = 'Meander' stations; Green dots = stations at the Polar Front and north of the PF; black dot = 'Reference' station; Orange dots = stations outside the Plateau and Meander areas. The black line marks the position of the Polar Front; (b) MODIS Chlorophyll distribution (colour bar: mg m^{-3}); arrows represent the current speed, with scale marked by the small black arrow under the colour scale bar; (courtesy F. d'Ovidio); (c) T-S diagram (all stations) with [NO_3^-] superimposed. (ODV-AWI, R. Schlitzer).

Fig. 2.

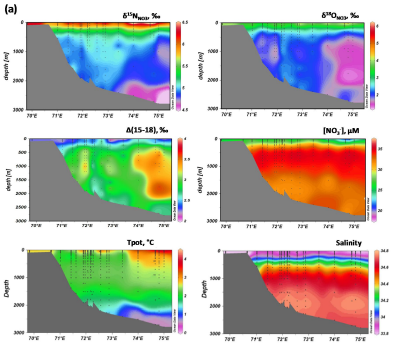

Figure 3: Whole water column distributions of $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, Δ(15-18), NO_3^-, Tpot and Salinity; (a) West to east section starting on the Kerguelen Plateau and crossing the Polar Front Meander; the Polar Front loop is crossed at about 71.3°E and at 74°E; (b) South to North section along about 72°E. (ODV-AWI, R. Schlitzer)

Fig. 3.

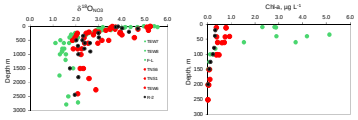

Figure 5: Profiles of $\delta^{18}O_{NO3}$ and Chl-a (µg l^{-1}) profile for stations underlying the high Chlorophyll plume in the vicinity of the Polar Front (green circles; stations TEW7, TEW8, F-L) and in the central part of the Polar Front Meander (red circles; stations TNS6, TNS1, TEW6) and the Reference station (black circles; station R-2).

Fig. 4.

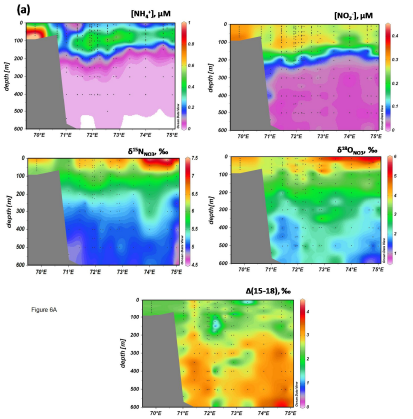

Figure 6: Sections of NH_4^+, NO_2^-, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ and Δ(15-18) in the upper 600m of water column; (a) West to East section; (b) South to north section. NH_4^+ and NO_2^- data are from Blain et al. (2014). (ODV-AWI, R. Schlitzer).

Fig. 5.

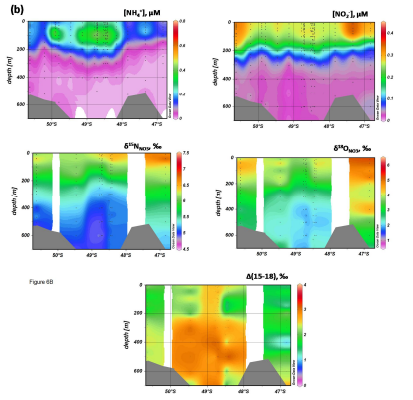

Figure 6b:

Fig. 6.

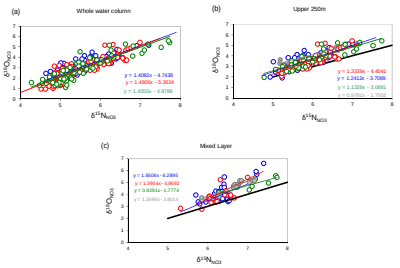

Figure 8: $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$; Blue = Plateau; Red = Meander; Green = Polar Front and north of PF; (a) whole water column; (b) Upper 250 m; (c) Mixed Layer; Grey circles in (B) and (C) represent the late season Plateau values recorded during KEOPS 1 (Trull et al., 2008); the black line with slope = 1 represents the evolution of reference deep water nitrate with $\delta^{15}N_{NO3}$ = 5‰ and $\delta^{18}O_{NO3}$ = 2‰ in case the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ fractionation factors are similar.

Fig. 7.