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Interactive comment on "Chemometric perspectives on plankton community responses to natural iron fertilization over and downstream of the Kerguelen Plateau in the Southern Ocean" *by* T. W. Trull et al.

Anonymous Referee #1

Received and published: 27 October 2014

This is overall a very interesting and informative manuscript (MS), as one of the many contributions from the KEOPS2 expedition. In the MS, the surveyed area over and downstream of the Kerguelen Plateau was clustered into 5 groups based on ocean circulation patterns and characteristics of natural iron fertilization. For each group, a wide range of original data, including POC, BSi/POC, d13C, and d15N, were measured for various plankton size groups. These measurements were further used as proxies to estimate size-specific biomass, fraction of diatoms, growth rate, and f-ratio, respectively. The authors also calculated the N and Si depletion in the water column and estimatedexport production based on these calculations. Setting these data in the context of the whole KEOPS2 study, the authors gave a detailed picture of the different responses of the plankton community to various types of natural iron fertilization, namely, the punc- tual and high level vs. the persistent yet relatively low iron supply, and came to several interesting points, e.g., the carbon export was decoupled from surface biomass, and the export could be higher in areas with low but lasting iron supply relative to areas with high but punctual supply.

The authors showed innovative utilization of several chemical proxies (although some of them have very large uncertainties), and discussed in great depth about the relationship between iron fertilization and carbon export. I would recommend this MS for publication on Biogeosciences, after the following comments are addressed, and a thorough proofreading is done.

Comments:

1. One interesting point the authors made is that the carbon export in the area with long-lasting but low iron supply may exceed that in area with episodic and strong iron supply. I would like to see a clearer definition of the time window of the carbon export the authors are examining and comparing. It seems that accumulation of biomass and export reported in the Polar Front Plume region represent an early phase of the iron-induced phytoplankton bloom, with a large standing stock of biomass in the mixed layer waiting to be exported, while the water in the recirculation feature has experience one or several full cycle(s) of phytoplankton growth and export. Considering the lag of export after the bloom, would export in the Polar Front region be much higher, and the conclusion be very different, if the experiment were extended for one more month?
   AUTHOR RESPONSE
   We agree with the reviewer that it is not possible to know the subsequent evolution of export over the seasonal cycle, but it is possible that this would change the perspectives that apply for our observed spring period. We added text to explicitly recognize this, in the Results section 3.5:
   MODIFIED TEXT
   Of course observation of these variations in spring does not mean that they would have persisted into summer, and it is possible that over the full season the extent of nutrient depletion was significantly different, either towards homogeneity across the region or towards larger variations.

   Is it possible to define a term T that is the days from the initiation of phytoplankton blooms to the day of sampling for each of the 5 groups, and compare the export in the unit of mmol m-2 day-1?
   AUTHOR RESPONSE We provided two time metrics in the text: "time since

fertilization" and "time since biomass accumulation" but both of these can only be estimated very approximately (at best two within a few weeks), and neither provides information on when export actually began, so we prefer to make the comparisons in the context of these approximate time frames in the text and not to provide false quantification. To make the times more clear we now list both of them in a revised version of Table 1:

2. The integration depth of the Group 5 (downstream PF plumes) stations based on the S-threshold method is overall significantly smaller than other stations. The choice of the S-threshold method over the T-min method thus accounts largely for the conclusion that the export in the Polar Front plume area was smaller than that in the recirculation area. It is possible that the authors are comparing water columns without much stratification since winter mixing to water columns that have recently being stratified and shoaled? A fuller description regarding the evolution of the hydrological structure would be very helpful.
   AUTHOR RESPONSE The reviewer is correct that the choice of depth for the nutrient depletion estimate has a very strong influence, in particular for these sites at the Polar Front which show salinity stratification above the depth of the winter-derived temperature minimum. And this is exactly why the Tmin depth should not be used, because stratification by horizontal mixing has re-defined the stratification and nutrient profiles between the two depths (Tmin and Sthreshold) more recently than the end of winter. Because the high biomass layer found in these Polar Frontal sites is in this shallow salinity-defined layer, and because the Fe fertilization of these waters is recent as shown by their short transit time since crossing the plateau (because the flow along the Polar Front is fast as determined from both altimetry and drifter releases (d'Ovidio et al., 2014; Park et al., 2014). We have added information on this to the text in section 3.5:

   MODIFIED TEX We believe the $S_{threshold}$ approach is the most appropriate given the observed salinity stratification, especially for the relatively weak subsurface thermal stratification observed in the Group 5 stations near the Polar Front, where it's choice makes the most significant difference from estimates based on the T_{min} approach. This is because the high biomass layer found in these Polar Frontal sites is in this shallow salinity-defined layer, and because the Fe fertilization of these waters is recent as shown by their short transit time of ~ 2 weeks since crossing the plateau as determined from both altimetry and drifter releases (d'Ovidio et al., 2014; Park et al., 2014). Thus attribution of nutrient depletion below the depth of the $S_{threshold}$ to iron fertilized biomass production is not warranted.

3. The authors talked at several points in the MS about the influence of lateral trans- ports on the calculated f-ratio and export production. Considering that the influence of lateral transport may be very different in the Polar Front Plume and the recirculation area, a more quantitative description about the lateral transports (e.g., timing, current in m/s) will be very helpful .
   AUTHOR RESPONSE We agree that this information is important, and we have summarized it in the context description in Methods Sections 2.1 and 2.2, provided an overview of the timing in Table 1, and included an animation of the biomass transport in the supplementary materials with a running calendar. Because the transport pathways are complex, time-varying, and their understanding requires detailed figures and discussion, it is best to refer readers to the sources of this information in the papers by Park et al., 2014 and d'Ovidio et al., 2014, as we have done in both these Methods sections and in the Results section 3.5. .
4. In the discussion (section 4.1), the authors reported that the growth rate calculated from the d13C measurements is higher in G4, then G3 and G5 and then G1 and G2. However, there does not seem to be significant difference between G1, G2, G3 and G5 on Figure 5. In addition, it seems that the model results, compared with the 13C uptake results, tend to over-estimate the growth rate by a factor of 2. Can the authors provided a little more discussion about the uncertainty of the d13C isotopic fractionation model method, e.g. , a sensitivity test on the growth rate derived from different assumptions about the cell shape and dimensions?
   AUTHOR RESPONSE We agree with the reviewer that this issue was insufficiently addressed and we have added several sections of new text that describe the large uncertainties in our calculated growth rates and emphasize that the overall conclusions do not rely upon them alone. For the full details, please see our extended response to Reviewer2 on this issue, which includes these new sections of text.

There are some minor issues the authors may need to consider:

1. It is probably more proper to move Section 2.2 and 2.3 to the Chapter 3 (Results)

s they are reporting actual data in great details;
AUTHOR RESPONSE Because this results come from other papers, as cited, we prefer to keep them in the Methods section along with all the other information on oceanographic context.

2. Line 27, pg. 13847: what is the difference between A3-1 and A3-2?
We added text to explain that these names reflect two visits to the same site.

3. Line 26, pg. 13850: do you mean "plateau <= Polar Front plume"?
AUTHOR RESPONSE Yes, thank you, and we corrected this typo as suggested.

5. Line 24, pg. 13857: Missing digit after "8."?
AUTHOR RESPONSE Yes, thank you, and we corrected this typo to show the full value of 8.0.

6. Line 18, pg 13861: what does the 13C-POCrs mean for the heterotrophic dominated size fractions?
AUTHOR RESPONSE Heterotrophs tend to have 13C-POC values similar to their prey, with additional contributions from low ^{13}C lipid reserves for organisms that form them. We added text as follows:
MODIFIED TEXT The presence of lipid-rich zooplankton in the two largest size fractions is another probable cause of their low ^{13}C-POC values, based on low ^{13}C-POC values for zooplankton collected with nets during KEOPS2 (Carlotti, 2014).

7. Figure 1. a) Latitude and Longitude on the left-bottom corner of the figure is not very readable. Could you put the numbers out of the box? b). Is it possible to show the location of the Station R on this figure?
AUTHOR RESPONSE We made both changes as requested.

8. Figure 2. Kerguelen and Heart Island on this map are not very distinguishable from the clouds. Is it possible to mark the islands using darker color?
AUTHOR RESPONSE We made this improvement as requested.

8. Figure 3. The x-axis in the middle panel is log(size), while on other figures it shows "filter size". It seems to be more straightforward to use "filter size".
AUTHOR RESPONSE We made this improvement as requested.

Interactive comment on Biogeosciences Discuss., 11, 13841, 2014.

Anonymous Referee #2

Received and published: 3 November 2014

In this manuscript results from the KEOPS2 survey in the vicinity of the Kerguelen Islands are presented. The purpose of the study is the understanding of the impact of natural iron fertilization on productivity and biogeochemistry of the Southern Ocean. These studies are highly relevant to our understanding of the impact of changes in the SO biological pump on past (Glacial/Interglacial) and future atmospheric pCO2. Here results on the size-fractionated composition of particulate organic matter (BSi, POC, PON, ∂13C and ∂15N) as well as estimates on nutrient utilization and, by comparison with standing stocks, export are presented. Further, ∂13C and ∂15N of particulate size fractionated organic matter is used to estimate growth rates and f-ratios of the different size classes in the community. Results are interpreted to infer the impact of different intensities in iron fertilization (based on hydrography and location) on community structure, and the impact of community structure on biogeochemistry.

I commend the authors on their effort to interpret the data, but must confess that I am not too convinced by the manuscript. Most of the data interpretation is based on indirect evidence itself based on assumptions that are possibly not valid (see also comments below).

AUTHOR RESPONSE

We consider that this statement is a fair assessment for one of our chemometric methods (growth rates estimated from ^{13}C, for which we provide further discussion below and have added a large section of new text regarding the associated caveats in the paper), but not for the others. Specifically, our measurements of the size distribution of POC, PN, and BSi do provide direct quantification of some of the most important characteristics of pelagic microbial ecosystems: i) size structure, which more than 50 years of measurements and models has placed at the centre of the understanding of ecosystem function, ii) the possibility of the presence of significant levels of detritus with higher C/N than autotrophs (not strongly present in this case), and iii) the extent of nitrogen recycling as estimated from the ^{15}N natural abundance contents of the community (this can be argued to be indirect, but neither reviewer raised any specific objections to this approach and in this paper and in previous work over the Kerguelen plateau (Trull et al., 2008) we have shown excellent correlation with the more time-consuming ^{15}N-tracer incubation approach to determining f-ratios). Nutrient depletion methods are also well tested to estimate export, especially in the Southern Ocean where the presence of the winter mixing derived temperature minimum provides a good guide to the initial water column inventory (see references in Sweeney et al., 2000). Yes, we also examined a salinity based estimate of the winter inventory, which is more uncertain (and we have added further discussion of this uncertainty in the revised paper), but we did not do this lightly and we do cite careful previous assessments of the scope of the probable biases from this approach (up to 2x, but more typically 30%, Wang et al., 2003).

Further, there are better and more direct methods to study both community composition and export.

AUTHOR RESPONSE

We agree that community composition is most directly and precisely studied by microscopy, and that other methods such as pigment analyses can also, in some cases, be more powerful than size-fractionated bulk chemical measurements (although we note with irony that the main use of pigment analyses from the KEOPS1 experiment was to estimate the size structure of the community, in keeping with the importance of size in assessing ecosystem function, Uitz et al.,2009). Microscopic study and pigment analyses were also pursued during KEOPS2, and we have cited the components of that work that are available (Lasbleiz et al, 2014 and L. Armand personal communication). But we don't agree that this knowledge necessarily makes it any easier to quantitatively connect community composition to export, because conversion of biovolumes to units of elemental concentrations for biomass quantification (and its subsequent comparison to dissolved nutrient fields) also has large uncertainties. Direct measures of export using free-drifting and gel-filled sediment traps were also carried out during KEOPS2, with this effort led by lead author Trull and published by his PhD student Laurenceau (Laurenceau et al., 2014). But this time consuming method could only be carried out at 6 sites (whereas our work examined 33) and has its own large uncertainties regarding trap collection efficiencies. In summary, and as is well known, evaluating ecosystem controls on export requires the application of multiple methods, (as many as possible!), and we have provided a large suite in this paper, and also cite and discuss many others from additional papers in this special volume, including the indirect method of ^{234Th} inventories.

Although I concur with the main conclusions of the study (i.e. high biomass and productivity does not necessarily lead to high export and is depen- dent on the community composition), this is already well known and the use of bulk parameters (as presented here) adds little to our understanding.

AUTHOR RESPONSE

In a broad sense we agree that this is well known, but we think that understanding this under the mesoscale varying conditions of iron fertilization in the Southern Ocean is far from resolved. For example, the high biomass over the Kerguelen plateau does correlate well with enhanced carbon export (both in autumn and for the full season, Blain et al, 2007; Jouandet et al., 2008; Ebersbach and Trull, 2008). But here we show that this does not necessarily extend to the downstream plume, and that this is not necessarily true in springtime. .

Finally, when study- ing export (highly dependent not only on whole community but possibly on behavior of individual species), there is a temporal component not taken into account (i.e. most of the export does generally not occur during the growth phase of a bloom) and is possibly masked by the large spatial variations in the area of study.

AUTHOR RESPONSE

Yes, we agree, and we addressed these temporal and spatial aspects in great detail by providing i) a full annual animation of the bloom development as seen by satellite surface Chla image, ii) 4 images detailing the stages of the bloom at the times of shipboard sampling, ii) two temporal metrics: time since Fe fertilization and time since onset of surface Chla accumulation. We suspect the reviewer means to imply that our assessment of spatial variations may not hold over the whole season, and of course that is true and we have added text to make this very explicit in the revised version in section 3.5:

MODIFIED TEXT

Of course observation of these variations in spring does not mean that they would have persisted into summer, and it is possible that over the full season the extent of nutrient depletion was significantly different, either towards homogeneity across the region or towards larger variations.

AUTHOR RESPONSE

[As an aside, we do not agree with the reviewers statement that "most of the export does generally not occur during the growth phase of a bloom". Our view is that most of the time ~90% of the production is removed by grazing (with a component of this sinking as fecal pellets each day) or aggregate sinking, and that even during the rapid build up of biomass at the start of a bloom this probably only drops to ~50% (indeed for our case this is the approximate value suggested by this reviewer in the last paragraph below) and thus at best the accumulation of biomass during the bloom might represent half the total seasonal export if it is all exported in autumn. This perspective of the autumn export being important but not dominant is consistent with results from the vast majority of deep ocean sediment trap time series (e.g. the reviews of Lampitt and Antia, 1997 and Lutz et al, 2007)]. .

As the paper seems somewhat to be an attempt at synthesising results from the whole study, I would recommend the authors incorporate in their results and discussion other measurements (submitted in separate papers in this issue) in a more explicit manner.

AUTHOR RESPONSE

Our paper is focused on the chemometric results, which (as both reviewers have requested), requires detailed explanation of their uncertainties and their implications, and thus is not the right place for a broader synthesis (although we do cite and discuss comparisons to many other results from KEOPS2).

Additional comments:

Lines 311-318: In the description of the community how were non-diatom protists (including heterotrophs important in the $< 210\mu$m size fractions) assessed? These tend to be more delicate and probably damaged during filtration.

AUTHOR RESPONSE

We added text as follows:

MODIFIED TEXT

These microscopic assessments of the materials present on the filters are rather limited, and may well have missed significant contributions from autotrophs and heterotrophs without frustules or carapaces, but other studies during KEOPS2 of bacterial abundances (Christaki et al., 2014), phytoplankton (Georges et al., 2014; Lasbleiz et al., 2014), diatom species (L. Armand, personal communication), and zooplankton (Carlotti, 2014) are consistent with our chemometric interpretation that detritus, bacteria, and phytoplankton contributed to the 1 um fraction; phytoplankton and especially diatoms dominated the 5, 20, and 50 um fractions; a mix of large diatoms and copepods were present in the 210 um fraction and copepods, isopods, and occasionally krill were the primary contributions to the 300 um fraction.

Growth rates estimates from ∂13C of POC are based on the assumption that cells do not use bicarbonate. From previous laboratory studies, bicarbonate use is common and highly variable at a species-specific level (also dependent on light regime). I am not sure that any of the growth rates estimates given here are reliable. Also the authors failed to refer to the studies on this topic: Burkhardt et al. (1999) Geochimica et Cosmochimica Acta, 63: 3729-3741, Burkhardt et al. (1999) Marine Ecology Progress Series, 184: 31-41; Rost et al. (2002) Limnology and Oceanography, 47(1): 120-128. I also fail to see large differences in growth rate estimates for the different groups (Fig. 5).

AUTHOR RESPONSE

We share the reviewers' concerns regarding the fidelity of our transformation of the ^{13}C-POC values into growth rates (and not only because of the issue of CO_2 versus bicarbonate use), and we acknowledge that our introduction to the associated issues and uncertainties was too brief. We have completely rewritten the introduction to this section to cite these and many other works and to provide a clearer explanation of the influences of bicarbonate and CO2 uptake. In this regard, we note that while the Popp et al (1998) model fit to observed 13C dependencies on growth rate did assume uptake was solely of CO_2, this assumption is not necessary (as shown by the modeling work of Keller and Morel, 1999).

MODIFIED TEXT

Controls on the ^{13}C composition of phytoplankton are complex, and have been explored in hundreds of papers since an early survey of the variability in marine carbon isotopic compositions (Craig, 1953), with occasional significant advances and reviews, e .g. (Farquhar et al., 1982; Goericke et al., 1994; Laws et al., 1995; Laws et al., 2002; Rau et al., 1996; Schulz et al., 2007; Tortell et al., 2008). In brief, there are two main causes for ^{13}C variations of any given phytoplankton cell. Firstly, the cell ^{13}C content depends on the chemical form of DIC that is assimilated, because the less abundant aqueous molecular CO_2 form contains much less ^{13}C than the bicarbonate anion form which makes up more than 90% of the total DIC. At the temperatures pertaining during the KEOPS study, this equilibrium fractionation lowers the ^{13}C content of aqueous molecular CO_2 by ~11‰ (Rau et al., 1997):

$$^{13}C\text{-}CO_2 = {}^{13}C\text{-}DIC + 23.644 - 9701.5/T_{kelvin} \quad (1)$$

Secondly, the cell ^{13}C-POC content depends on the extent to which the enzymatic kinetic discrimination against ^{13}C during photosynthetic carbon fixation (of 20-30 ‰, varying with the specific metabolic pathways) is expressed. It is only fully expressed when inorganic carbon flow into and out of the cell (supply) is faster than fixation (demand).

Both these effects often lead to higher ^{13}C contents in faster growing cells, because faster growth favours use of the more abundant bicarbonate form of DIC and also leads to less expression of the kinetic fractionation. Thus the association of higher ^{13}C contents with faster growing cells is very strongly justified for any particular phytoplankton species, from both metabolic understanding and the plethora of batch and chemostat experimental studies. Despite this understanding, inferring growth rates for communities of phytoplankton from field measurements of ^{13}C-POC is fraught with difficulties. The magnitudes of these two main isotopic effects vary strongly among different phytoplankton (and with their conditions of growth including temperature, nutrient and trace metal availability, light levels, specific enzymatic pathways, etc. (Burkhardt et al., 1999b; Burkhardt et al., 1999c; Fontugne et al., 1991; Schulz et al., 2007)), and there is no universal quantitative relationship between growth rate and phytoplankton ^{13}C content. In particular, cell size is a key variable in the control of ^{13}C contents (Popp et al., 1999; Rau et al., 1996; Rau et al., 1997; Rau et al., 1990), and the global range of surface water ^{13}C-POC values can be observed within a single Southern Ocean sample, simply via its size fractionation (Trull and Armand, 2001). Good correlations between growth rates and ^{13}C contents when cell size is expressed in terms of the surface/volume ratio suggest this results from the balance of supply versus demand (Popp et al., 1998b), of either or both aqueous CO_2 and bicarbonate forms (Burkhardt et al., 1999a; Keller and Morel, 1999; Schulz et al., 2007), and with further

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modulation by other environmental controls such as the availability of light and other nutrients (Burkhardt et al., 1999c; Gervais and Riebesell, 2001; Schulz et al., 2004).

This complexity means that our observed ^{13}C-POC variations, even within a given size fraction, could arise by multiple mechanisms. Higher ^{13}C contents could reflect faster growth rates (via either greater use of bicarbonate or an increase of fixation of all DIC chemical forms relative to supply), or might instead reflect changes in species with inherently different uptake and assimilation metabolisms, or changes in metabolism driven by other controls such as light or iron availability. Our chemometric methods cannot distinguish among these possible causes, and thus our expression of the ^{13}C-POC variations in terms of growth rate variations can only be viewed as an indicative exercise. To pursue this, we chose a model fit to chemostat data (Popp et al., 1998b):

$$^{13}\text{C-POC} = (^{13}C_{source} - \varepsilon_f) + k \text{ demand-rate/supply-rate} \quad (2)$$

in which the first term expresses the lowest possible ^{13}C contents of the cell as growth rate approaches zero, and the second term describes the linear (constant k) dependence of isotopic composition on the relative rates of CO_2 supply into the cell and it's cellular fixation. Popp et al. (1998) assumed the chemical form was aqueous molecular CO_2, but further evaluation showed that the data could also be fit by a model allowing either or both CO_2 and bicarbonate uptake (Keller and Morel, 1999). Both models assume that the, supply rate depends linearly on its external concentration modulated by the surface area of the cell, and thus while the fitting constants we use here are from Popp et al (1998), the scaling to the surface/volume ratio (S/V) of the cell is independent of the chemical form of uptake):

$$^{13}\text{C-POC} = (^{13}\text{C-}CO_2 - 25) + 182\ \mu/([CO_2]\ S/V) \quad (3)$$

Rewriting this equation for growth rate, μ, and our measured ^{13}C-DIC and ^{13}C-POC values yields an indicative path to possible growth rates for our size fractions:

$$\mu = S/V\ [CO_2]\ [^{13}\text{C-POC} - (^{13}\text{C-}CO_2 - 25)]/182 \quad (4)$$

with ^{13}C-CO_2 calculated using equation (1), $[CO_2]$ obtained from underway pCO_2 observations (Lo Monaco et al., 2014) and Henry's Law (Weiss, 1974). In this expression, growth rate μ is in d^{-1}, S/V in μm^{-1}, and $[CO_2]$ in umol kg^{-1}.

This expression provides growth rates that we compare to other estimates. Of course, comparison of these rates is very sensitive to S/V estimates, as well as to all the other possible sources of variations in ^{13}C contents summarized above. For example, a 30% increase in the mean size of cells, such as could occur within a given size fraction, would yield a 69% increase in the model growth rate (for spherical cells). For this reason, our growth rate estimates must be viewed with great caution, not only in terms of their absolute magnitudes, but also in terms of their relative magnitudes across the different stations.

AUTHOR RESPONSE

In addition to this revised text regarding our growth rate estimates we have added caveats at several places in the Results and Discussion sections to emphasize that the growth rates are not quantitative and that our conclusions are not based solely upon them:
New text in Results Section 3.3:

MODIFIED TEXT

This provides a useful cautionary note that the apparent growth rate variations have no real quantitative validity; at best they provide indicative information on the relative intensities of CO_2 assimilation across the Groups. Indeed, it is possible that the variations among the Groups results from other issues such as species metabolic differences, or light and trace element availability (as discussed in detail in the Methods section). Thus it is important to emphasize that the overall view of ecosystem responses developed in the Discussion section does not depend only on these potential growth rate estimates from the ^{13}C-POC observations, but also draws on biomass accumulation rates from the POC concentrations, their distribution across size fractions, and other indicators as discussed below.

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AUTHOR RESPONSE

New text in Discussion Section 4.1.:

MODIFIED TEXT

Both of the more strongly iron fertilised offshore regions (the Group 3 central plateau and the Group 5 Polar Front bloom, Table 1.) exhibited increased ^{13}C model growth rates in comparison to HNLC waters (elevated by ~0.05 d^{-1}), but their community structures were quite different (emphasizing caution regarding the ^{13}C model growth rates, although the incubation results also indicated increased growth rates; (Cavagna et al., 2014)).

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I am not sure of the logic in separating some of the stations in 2 groups (groups 1 and

2) as they are in a similar location and could be used to infer temporal development.

AUTHOR RESPONSE

This was done largely for convenience to have a manageable number of stations in each of these two groups, and the temporal aspect is discussed in just the way the reviewer recommends – as an evolution from the status observed in Group 1 towards that observed in Group 2, and then with additional consideration of the temporal evolution within Group 2 which was specifically carried out as a time series.

Lines 685-690: I am not sure I agree with the authors on the method used: estimating nutrient consumption from nutrient profiles is valid under the assumption that there is no significant impact of lateral transport. If there is horizontal exchange (or mixing), especially in an area with strong horizontal gradients such as in this study, nutrient consumption estimates are highly uncertain. Using the Tmin as a criterion, helps to at least constrains the temporal scale of the estimate (i.e. from previous winter), while using other criteria does not. Hence robustness of the estimates given here can hardly be assessed and I doubt values for the different groups can be compared.

AUTHOR RESPONSE

Because all nutrient profiles do show surface depletions, they clearly contain information on export (from either local and recent export, or remote and prior export). Extracting the desired local and recent contribution information is difficult for just the reasons the reviewer mentions, and this is why we have pursued two criteria: the traditional temperature minimum based estimate of winter values, and a salinity threshold method designed to evaluate the possibility that this Tmin approach overestimates export when the surface depletion is associated with the overlaying of warm salty waters above the Tmin layer (via horizontal mixing). We have taken care to emphasize that this makes the depletion estimates uncertain, and to explain how this affects our conclusions, including adding new text:

MODIFIED TEXT

This analysis underlines the importance of appropriate winter nitrate (and silicic acid) surface nitrate concentration estimates to the assignment of export magnitudes. We believe the $S_{threshold}$ approach is the most appropriate given the observed salinity stratification, especially for the relatively weak subsurface thermal stratification observed in the Group 5 stations near the Polar Front.

Given the robustness of the different estimates and the variability (which might be related to both temporal and spatial patterns) I could also argue that there are no significant differences in organic matter (based on N) export between systems. When looking at figure 8 roughly half of the N uptake is lost (either through grazing or sinking). This is consistent with the fact that growth estimates are in the order of roughly one doubling every 3 days while biomass accumulation (from satellite Chla) indicates a doubling very week (between 28/10 and 6/11).

AUTHOR RESPONSE

We thank the reviewer for this insightful comment, and we have incorporated it in the revised text, in Results Section 3.5:

MODIFIED TEXT

Firstly, given the uncertainties regarding the estimation of nutrient depletions from the profiles, it could be argued that the most robust conclusion is that all the Groups exhibit similar depletions, with roughly half of the N uptake exported and half remaining as accumulated biomass. This is consistent with the growth estimates of roughly one doubling every 3 days and the satellite biomass observations indicating slower doubling approximately each week.

AUTHOR RESPONSE

Importantly, we also note that the Abstract emphasizes only this most robust conclusion, that all regions exported similarly:

MODIFIED TEXT

Comparison of these communities to surface water nitrate (and silicate) depletions as a proxy for export shows that the low biomass recirculation feature had exported similar amounts of nitrogen to the high biomass blooms over the plateau and north of the Polar Front.

Interactive comment on Biogeosciences Discuss., 11, 13841, 2014.

AUTHOR RESPONSE

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Chemometric perspectives on plankton community responses to natural iron fertilization over and downstream of the Kerguelen plateau in the Southern Ocean

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Abstract

We examined phytoplankton community responses to natural iron fertilisation at 32 sites over and downstream from the Kerguelen plateau in the Southern Ocean during the austral spring bloom in October-November 2011. Community structure was estimated from chemical and isotopic measurements (particulate organic carbon POC, ^{13}C-POC, particulate nitrogen PN, ^{15}N-PN, and biogenic silica BSi) on size-fractionated samples from surface waters (300, 210, 50, 20, 5, and 1 µm fractions). Higher values of ^{13}C-POC (vs. co-located ^{13}C values for dissolved inorganic carbon, ~~^{13}C~~ DIC ~~source values~~) were taken as indicative of faster growth rates, and higher values of ^{15}N-PN (vs. co-located ^{15}N-NO_3 source values) as indicative of greater nitrate use (rather than ammonium use, i.e. higher *f* ratios).

Community responses varied in relation to both regional circulation and the advance of the bloom. Iron fertilised waters over the plateau developed dominance by very large diatoms (50-210 µm) with high BSi/POC ratios, high growth rates, and significant ammonium recycling (lower *f* ratios) as biomass built up. In contrast, downstream Polar Frontal waters with similar or higher iron supply were dominated by smaller diatoms (20-50 µm) and exhibited greater ammonium recycling. Stations in a deep water bathymetrically trapped recirculation south of the Polar Front with lower iron levels showed the large cell dominance observed on the plateau, but much less biomass. Comparison of these communities to surface water nitrate (and silicate) depletions as a proxy for export shows that the low biomass recirculation feature had exported similar amounts of nitrogen to the high biomass blooms over the plateau and north of the Polar Front. This suggests that early spring trophodynamic and export responses differed between regions with persistent low levels vs. punctual high levels of iron fertilisation.

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1 Introduction

Natural iron fertilisation from islands, shelves, and plateaus in the Southern ocean produces local and downstream elevations of phytoplankton biomass, ~10-fold higher than in surrounding high nutrient low chlorophyll (HNLC) waters, e.g. (de Baar et al., 1995). In some of these systems, carbon export has been observed to be elevated ~2-3 fold, e.g over the Kerguelen Plateau (Blain et al., 2008;Savoye et al., 2008) and to the north of Crozet Island (Pollard et al., 2007). But these studies produced order of magnitude variations in estimates of the amount of carbon export per unit iron supply, as have deliberate iron fertilisation studies (Boyd et al., 2007). These variations appear to reflect both observational limitations and system complexity, including the possibility of variations in initial communities prior to fertilisation (as a result of north-south oceanographic variations or the extent of connection to coastal habitats).

General principles for expected phytoplankton responses to iron fertilisation have been elucidated, though they remain to be fully tested. These include increased growth rates for all size classes and elevated new production, i.e. increased nitrate use (e.g. (Armstrong, 1999;Maldonado et al., 2001)). A prevailing view of the overall community response is that it depends on the interaction of these changes with the response of zooplankton grazers, which are thought to be more able to keep up with small cell growth and thus to favour accumulation of larger phytoplankton (Assmy et al., 2013;Morel et al., 1991). This, in turn, may favour export via either direct sinking or aggregation (Smetacek, 1985;Smetack, 1998). Variations in diatom life cycles and strategies add seasonal complexity to this picture (Queguiner, 2013), and the translation of increases in new production into enhancements in export can be relatively weak, for example, as a result of strong N recycling (Mosseri et al., 2008).

The KEOPS2 expedition sought to examine these and other aspects of community responses to natural iron fertilisation over and downstream of the Kerguelen plateau, in austral spring, October-November 2011, as detailed in the multiple papers in this volume. In this paper, we examine a suite of chemical and isotopic indicators of phytoplankton community structure and function (chemometrics) and relate them to nitrate (and silicate) depletion in surface waters as a proxy for carbon export. The following paragraphs provide an overview of the approach and the structure of the paper.

~~We first~~First, we describe the complex regional circulation, and use it to cluster the stations into 5 groups (coastal, plateau, waters well downstream near the Polar Front, and waters in a recirculation close to the plateau - separated into ~~an~~ a broad early survey and a later focused, quasi-Lagrangian time series). For these groups we briefly summarize the relative levels of iron fertilisation from dissolved and particulate standing stocks (Quéroué et al., 2014;van der Merwe et al., 2014) and Fe supply estimates (Bowie et al., 2014;d'Ovidio et al., 2014). We also assess the elapsed time since iron fertilisation and its persistence, from seasonal perspectives on vertical mixing (Bowie et al., 2014) and Lagrangian perspectives on water mass trajectories around the Kerguelen plateau (d'Ovidio et al., 2014). We also consider two other overarching perspectives on ecosystem responses: the elapsed time since the beginning of phytoplankton accumulation (from an animation of satellite ocean colour images; Supplementary Materials), and the level of biomass enrichment at the time of sampling. Our subsequent chemometric analysis is undertaken at the level of these 5 Groups, against this framework of relative intensities and timings of Fe fertilisation and biomass accumulation.

Next, we describe ~~the~~ our chemometric approach. In brief, ~~i.e.~~we relied on total particulate organic carbon (POC) as an indication of eutrophy, size distribution as a indicator of ~~diversity~~community structure, biogenic silica /particulate organic carbon

(BSi/POC) ratios as a measure of diatom dominance, ^{13}C as a qualitative metric for growth rates, and ^{15}N as a metric for ammonium recycling. For our ^{13}C and ^{15}N chemometrics, which present methods to estimate rates from standing stocks, we provide a comparison to shipboard incubation results for growth rates and *f*-ratios (from ^{13}C and ^{15}N tracer uptake experiments, Cavagna et al., 2014this volume). To determine nitrate (and silicic acid) depletion by the biological pump, we explored both temperature and salinity based approaches to estimate initial winter surface water concentrations, and also evaluated the fraction of the observed depletion that still remains remained in the water column for potential future export using particulate nitrogen and biogenic silica stocks from CTD casts (Blain et al., 2014;Lasbleiz et al., 2014).

These chemometric approaches are not as direct as other methods (such as microscopy for community structure, incubation experiments for growth rates and *f*-ratios, and sediment trap collections for export), but offer some advantages in terms of quantitative connections to dissolved nutrient budgets and the ability to examine more sites. To address these shortcomings, we compared our ^{13}C growth rate and ^{15}N *f*-ratio estimates to shipboard incubation results from ^{13}C and ^{15}N tracer uptake experiments, (Cavagna et al., 2014), and discuss our more extensive results with respect to information on community composition from pigment and microscopic analyses (Lasbleiz et al., 2014), and carbon export from ^{234}Th depletions (Planchon et al., 2014) and sediment trap collections (Laurenceau et al., 2014). , we arrive at anIn summary, this provides an overview of the relative importance of Fe inputs and temporal evolution in the control of community structure and carbon export in springtime, for the phytoplankton bloom that forms over and downstream of the Kerguelen plateau.

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2 Methods

2.1 Site description

The KEOPS2 campaign was carried out in October - November 2011 over and downstream of the Kerguelen plateau in the Southern Ocean, under conditions of complex circulation and rapidly changing phytoplankton biomass, as summarized in Fig. s. 1 and 2, and further showcased in the full annual satellite chlorophyll animation (Supplement).

The Kerguelen plateau is a northwest-southeast oriented seafloor feature which rises to ~500m below the surface over much of its extent. It also hosts several volcanic islands, in particular the large Kerguelen Island archipelago in the north and the smaller Heard Island at the southern edge of the central Kerguelen plateau. The plateau blocks the eastward flowing Antarctic Circumpolar Current (ACC). Much of the ACC flow goes to the south of the plateau and through the Fawn Trough (to the south of Heard Island), with a smaller portion associated with the Subantarctic Front flowing around the northern edge of Kerguelen island. A narrow jet of ACC water also flows across the plateau in the narrow, mid-depth (~1000m) channel just to the south of Kerguelen Island (Fig. 1). This feature corresponds with the northernmost presence of a subsurface temperature minimum formed by winter cooling (near 200m depth), and thus defines the northernmost branch of the Polar Front (Park et al., 2014a;Park et al., 2008). This jet was a particularly important feature of the area sampled during KEOPS2, because it separated the central plateau and downstream offshore stations to the south of the Polar Front (PF), from those to the north of the PF, where the coastal stations were also located. As discussed in section 2.2, the modes of supply of Fe to the waters north and south of this jet may also differ, with some downstream Polar Front stations potentially influenced by Fe inputs from coastal waters associated with Kerguelen Island or its shallow northern shelf (d'Ovidio et al., 2014).

From a dynamical perspective, the full ocean depth branch of the Polar Front lies to the south of Heard Island, where the ACC flow transits the Fawn Trough (Sokolov and

Rintoul, 2009). As this flow passes to the east of the pleateau it follows the bathymetric contours to the north where it enters a bathymetrically-trapped recirculation region to the south of the Polar Front, before eventually exiting downstream (d'Ovidio et al., 2014;Park et al., 2014a). This recirculation feature and the flow along the PF jet are fixed in space by the bathymetry close to the plateau, but at their eastern edge over the abyssal plain (where the strong ACC flows passing south and north of the plateau re-join) meandering is strong and varies with time. For example, the animation of ocean colour (Supplement) suggests the PF moved southward in this region over the course of the KEOPS2 observations.

As shown in Fig. 1, the initial sampling was carried out along a deep water transect (stations TNS 1-10) run northwards from the central plateau (TNS-10) across the recirculation feature and Polar Front and into Subantarctic waters (TNS-1). This was followed by a west to east transect (stations TEW 1-8) running offshore from the Kerguelen Island coast, across the middle of the recirculation, and reaching the southward meandering Polar Front in the far east of the study region. This initial survey was followed by multiple "time-series" visits to the recirculation feature, (designated as stations E1- E5, with two stations at the E4 time step - to the western side, E4-W, and eastern side, E4-E, of this recirculation). In addition several other features at the margins of the survey region were also sampled, with rather complicated nomenclature based on locations, links to other programs, durations, and purposes:

- ~~reference~~ Reference HNLC waters to the west of the plateau (stations R and R2)
- A central plateau station that had served as the bloom reference site in the previous KEOPS campaign in late summer/autumn 2005 (station A3, sampled twice as A3-1 and A3-2).

– High biomass waters in the extreme northeast of the study region, near the downstream location of the Polar Front (Stations F-L and F-S; L for long, S for short)

– Two stations carried out to compare geochemical tracer concentrations in waters over the plateau (G1) with Kerguelen coastal waters (G2).

All of these stations (except TNS-4 and TNS-7) on the initial survey transect were sampled for our size-fractionated chemometric analyses (with some stations also sampled both at night and day).

The five colour-coded Groups mapped in Fig. 1 cluster the KEOPS2 stations based largely on the interactions of the circulation with the bathymetry (with some additional regard for temporal evolution and the timing and extent of iron supply and biomass accumulation, as discussed below). The properties of these Groups are summarized in Table 1. In brief, Groups 1 and 2 cluster stations from the recirculation feature. Group 1 consists of stations in this region occupied during the initial transects when biomass was low, and also ~~for convenience~~ includes the upstream HNLC reference site R2 (which was also sampled early in the voyage). Group 2 holds the stations subsequently occupied as a pseudo-Lagrangian time series within the recirculation. Group 3 holds the central plateau stations, including waters that flow northward to leave the plateau along the south side of the Polar Front jet. Group 4 ~~has~~ holds the coastal stations~~; although the inclusion~~, including ~~of~~ TEW-3 ~~is debateable given its location~~ at the plateau edge (which displayed a mix of coastal, plateau, and recirculation properties). Group 5 has the downstream stations near and north of the Polar Front. Two stations in this Group, at the northern Subantarctic end of the initial survey, TNS-1 and TNS-2, were included to keep the number of Groups low, but stand out as quite distinct in having lower biomass with greater proportions of non-diatom taxa (Lasbleiz et al., 2014), and are marked by distinct colouring in the figures.

Additional discussion of stations near the boundaries of these Groups is provided below, and other clusterings are possible, especially for stations at the boundaries among the Groups (for further discussion see Lasbleiz et al., 2014). The majority of the analysis presented in this paper is based on comparisons across these Groups rather than individual stations (although variations within the Groups do occur and sometimes provide additional insights, and for this reason the figures display the individual stations in each group in chronological order (e.g. see Fig. 3).

2.2 Intensity and timing of Fe fertilisation

Iron sampling and analysis was carried out at a much-reduced subset of the stations discussed here, albeit with greater vertical resolution (Bowie et al., 2014;Quéroué et al., 2014;van der Merwe et al., 2014). Thus, comparisons to our results are only possible at the level of our station Groups, and only in a relative sense. The lowest Fe levels were observed at the HNLC reference station upstream to the west of the Kerguelen Plateau (slightly less than 0.1 nM at station R2). The recirculation region (Groups 1 and 2) had low to moderate dissolved Fe (0.06-0.38 nM at stations E2, E3 and E5). Slightly higher minimum concentrations were observed over the plateau (0.18- 0.21 nM at the Group 3 stations A3-1 and G1). Moderate enrichments were also observed in the Group 5 downstream waters near the Polar Front (~0.26 nM at station F-L). The highest dissolved Fe levels were in the Group 4 Kerguelen Island coastal waters (surface concentrations of 2.17 nM for TEW 1 and 1.26 nM for TEW 2).

Particulate Fe levels were not measured in coastal waters, but generally exceeded dissolved Fe levels in the Group 3 stations over the plateau (by factors of 13 - 20) and offshore in the Group 1 and 2 stations in the recirculation feature and the single Group 5 station in the downstream plume (by factors of 2 - 34). The bio-availability of this

particulate Fe is unknown, but assuming a conservative fraction of 1% (for discussion see van der Merwe et al., 2014) leads to a 20% increase over the plateau of available iron and 4-34 % increase offshore.

Estimating Fe supply is more difficult. It appears possible that downstream waters north of the Polar Front (Group 5 stations F-S, F-L, TEW-7, and TEW-8, but not the Subantarctic influenced stations TNS-1 and TNS-2) receive~~s~~ more iron than the plateau (Group 3) especially in summer when stratification reduces vertical supply over the plateau, but advection continues to sweep iron-rich coastal waters from the northern Kerguelen shelf along the northern side of the Polar Front jet (Bowie et al., 2014;d'Ovidio et al., 2014;Park et al., 2014a).

The nature of Fe fertilisation also varies among the regions, in terms of both its timing relative to our sampling, and its persistence. Recent and brief iron fertilisation appears likely to characterize the Polar Front (Group 3 region). Water parcel trajectories calculated from drifter trajectories and altimetry based geostrophic currents (d'Ovidio et al., 2014) suggest times of less than 0.5 to 1 month for the downstream Polar Front stations (Group 5 stations F-S, F-L, TEW-7, TEW-8), with rapid dispersal and thus low persistence. In comparison, it appears to take longer for northern Kerguelen shelf waters to reach the recirculation region (Group1and 2 stations), where the water is then retained for a relatively long time (30 to 60 days), but is also diluted by approximately equal volumes of waters derived from the south (d'Ovidio et al., 2014;Park et al., 2014a). These supply paths are also indicated by Ra isotope distributions (Sanial et al., 2014). Thus fertilisation of the recirculation feature appears to be less recent and intense than that of the Polar Frontal region, but probably more persistent. For the Kerguelen coastal stations (Group 4), where water columns were well mixed to the bottom, fertilisation is both recent and persistent. Fertilisation over the plateau is also relatively recent in a seasonal context,

having presumably reached a maximum at the time of deepest winter mixing (i.e ~ 2 months from maximum cooling winter mixing in August-September to sampling in Oct-Nov. Its persistence may be similar or somewhat larger than that of the recirculation region given estimates of water parcel residence times over the plateau of order 2-3 months (Park et al., 2008).

In summary, this evaluation of iron inputs yields rank orders as follows:

Intensity of Fe fertilisation (lowest to highest):

recirculation feature < *plateau* <≈ *Polar Front plume* << *coastal stations*

Elapsed time since Fe fertilisation and its persistence (most recent to oldest):

Polar Front plume < *recirculation feature* <≈ *plateau* < *coastal stations*

For easy reference these properties are summarized for the station Groups in Table 1.

2.3 Intensity and timing of phytoplankton biomass accumulation

The KEOPS2 sampling was carried out in spring, spanning the period when phytoplankton biomass was rapidly increasing both over and downstream of the plateau, forming rather complex patterns in satellite chlorophyll images (Fig. 2). Thus the time of sampling relative to the development of surface biomass enrichment varied strongly among the stations. The sequence of ocean colour images in Fig. 2. (see also the Supplement) suggests that this chlorophyll increase occurred first in coastal Kerguelen island waters (starting in mid-September very close to the island and extending northwards by mid October; but reaching only moderate Chl-a levels near 1 μg L^{-1}), followed by the downstream plume north of the Polar Front (near Group 5 stations F-S, F-L, TEW-7, TEW-8) where chlorophyll biomass jumped very rapidly from below 0.5 to above 2 μg L^{-1} early in the first week of November.

At this time (as shown in the animation in the Supplement), the central plateau and the recirculation feature still had only minor biomass development, with concentrations near 0.5 μg L^{-1}. But, within a few days, by 9 November, all strongly Fe enriched regions (coastal, central plateau, and the downstream waters near the Polar Front) had Chl-a levels above 2.5 μg L^{-1}. Yet, the recirculation region still had low levels of ~0.5 μg $L^{-1}$for another week, and only reached levels of 1-1.5 μg L^{-1} by end November. Only in early December, after the end of field sampling, did the recirculation feature reach levels of 2.5-3 μg L^{-1}. Interestingly, the downstream waters near the Polar Front maintained high levels throughout most of this period, but the central plateau bloom faded (as sampled by station A3-2) before being replaced by a second bloom somewhat further east, though still over the plateau. The animation of these satellite chlorophyll images provides further detail of the structure and sequence of biomass accumulation, both during and after the voyage (Supplement).

In summary, satellite biomass accumulation yields rank orders as follows:

Magnitude of biomass accumulation (lowest to highest, at end of voyage):

recirculation feature < *coastal stations* < *plateau* <≈ *Polar Front plume*

Elapsed time since initiation of biomass accumulation (most recent to oldest):

recirculation feature < *Polar Front plume* <≈ *plateau* << *coastal stations*

For easy reference these properties are summarized for the station Groups in Table 1.

2.4 Samples

This study is based primarily on chemical and isotopic compositions of dissolved nutrients and size-fractionated particles sampled from surface waters using the ship's clean seawater supply. Full details of the sample collection and analytical methods are provided in Appendix A. In brief, particles were analysed for 6 size fractions collected by large

volume sequential filtration through a pre-screen (1000μm) and 6 filters (300, 210, 50, 20, 5 and 1 μm pore sizes). These samples were analysed for POC, PN, BSi, ^{13}C-POC and ^{15}N-PN (although BSi could not be analysed on the 1μm fraction, as it was collected with a quartz filter). Seawater samples collected from the same supply, and also from Niskin bottles on the CTD system, were analysed for nitrate and dissolved inorganic carbon concentrations and isotopic compositions (DIC, ^{13}C-DIC, NO_3^-, ^{15}N-NO_3^-, and ^{18}O-NO_3^-). In addition, approximately ~~small volume~~one litre ~~-~~samples ~~(1L)~~ were filtered for bulk POC and PN concentrations and these are reported along with ~~a~~ the total POC ~~that is the~~determined from the sum of the size fractions. Surface water nitrate concentrations were continuously mapped using an ultra-violet nitrate sensor.

Speaking broadly for all stations, the largest size fractions (300-1000 μm) for the suspended particles were dominated by zooplankton, primarily copepods. Intact faecal pellets and phytoplankton aggregates did not contribute significantly to these fractions (presumably they were disaggregated by the pumping system, because both particle types were observed in sediment traps equipped with polyacrylamide gels (Laurenceau et al., 2014); although the presence of intact needles of *Thallasiothrix antarctica* and chains of *Fragilariopsis kerguelensis* diatoms suggests individual cells were largely undamaged). The smaller size-fractions were dominated by diatom frustules, with small centric diatoms abundant on the 5 μm filter, a mix of centric and pennate diatoms on the 20 and 50 μm filters, and large diatoms and chains of pennate diatoms and small copepods on the 210 μm filter. The particles on the 1 μm quartz filter were too small to examine in any detail using stereo microscopy. The light beige colour of these filters, in comparison to the greener shades of the intermediate sizes suggests important contributions from detritus and/or bacteria (and absorption of dissolved organic matter onto the 1 μm quartz filters may have also occurred, but was not assessed). These microscopic assessments of the

materials present on the filters are rather limited, and may well have missed significant contributions from autotrophs and heterotrophs without frustules or carapaces, ~~Absorption of dissolved organic matter onto these filters may have also occurred, but was not quantified.~~

~~More detailed information on the organisms present on our filters is not available,~~ but other studies during KEOPS2 of bacterial abundances (Christaki et al., 2014), phytoplankton (Georges et al., 2014;Lasbleiz et al., 2014), diatom species (L. Armand, personal communication), and zooplankton (Carlotti et al., 2014) are consistent with our chemometric interpretation that detritus, bacteria, and phytoplankton contributed to the 1 µm fraction; phytoplankton and especially diatoms dominated the 5, 20, and 50 µm fractions; a mix of large diatoms and copepods were present in the 210 µm fraction and copepods, isopods, and occasionally krill were the primary contributions to the 300 µm fraction.

2.5 Chemometric methods for community structure and function

Evaluation of community structure and function is ideally done via detailed taxonomy and physiology, but the plethora of organisms makes this very difficult. Chemical methods offer an easier path with the added advantages of quantitative connections to dissolved chemical concentrations and budgets. Size fractionation adds value to this approach, firstly because it provides some separation of phytoplankton (which dominated the 1, 5, 20, and 50 µm fractions) from heterotrophs (210 and 300 µm fractions), and secondly because differing sizes of phytoplankton often occupy different biogeochemical niches (e.g. greater reliance on ammonium by small phytoplankton; less contribution to direct export owing to smaller sinking rates) and experience differing ecological couplings

(e.g. tighter coupling to grazing control in smaller sizes, because smaller zooplankton have shorter life cycles).

Thus our primary chemometric tool is to simply examine variations in the distribution of POC across the size fractions as an indicator of community structure. (To remove the influence of our particular choice of filter sizes, we express the POC concentration variations as spectra, i.e. we divide the concentrations by the width of each filtration interval, yielding units of µM µm^{-1}). Secondarily we use high BSi/POC ratios as an indication of community dominance by diatoms. ~~(T of course t~~his is simplistic given the presence of silicoflagellates at some stations (Lasbleiz et al., 2014) and the occurrence of a wide range of BSi/POC ratios in diatoms ~~(Ragueneau et al., 2006),~~ (Ragueneau et al., 2006). ~~and~~ We use low POC /PN ratios as an indication of contributions from heterotrophic biomass (below the values of ~6-7 that characterise most phytoplankton~~; e.g.~~ (Anderson and Sarmiento, 1994;Redfield et al., 1963).

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2.5.1 Isotopic chemometric principles – ^{13}C

The isotopic chemometric tools are not as common and require greater explanation. Variations in ^{13}C-POC and ^{15}N-PN values derive from both primary photosynthetic production and the overlay of secondary heterotrophic imprints, especially in the smallest size fraction (1-5 µm) in which bacterial processing was important, and the two largest size fractions (210-300 and 300-1000 µm) which contained significant contributions from zooplankton. For the middle size fractions (5-20, 20-50 and 50-210 µm), biomass was dominated by phytoplankton and thus these fractions can be used to examine the impacts of iron fertilisation and other controls on primary production. This is our focus for the use of these tools. In particular we interpret ^{13}C enrichment as potentially indicative of higher growth rates and ^{15}N enrichment as indicative of higher *f* ~~-~~ratios (i.e. greater use of nitrate

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in comparison to reduced forms of nitrogen). In the following paragraphs we introduce quantitative expressions for these relationships, but also acknowledge that they rest on many assumptions, ~~which we evaluate further in light of our results~~and are thus indicative rather than definitive. After ~~this~~ discussion of these autotrophic expressions, we also briefly describe the scale of heterotrophic effects.

Controls on the ^{13}C composition of phytoplankton are complex, and have been explored in hundreds of papers since an early survey of the variability in marine carbon isotopic compositions (Craig, 1953), with occasional significant advances and reviews, e .g. (Farquhar et al., 1982;Goericke et al., 1994;Laws et al., 1995;Laws et al., 2002;Rau et al., 1996;Schulz et al., 2007;Tortell et al., 2008). In brief, there are two main causes for ^{13}C variations of any given phytoplankton cell. Firstly, the cell ^{13}C content depends on the chemical form of DIC that is assimilated, because the less abundant aqueous molecular CO_2 form contains much less ^{13}C than the bicarbonate anion form which makes up more than 90% of the total DIC. At the temperatures pertaining during the KEOPS study, this equilibrium fractionation lowers the ^{13}C content of aqueous molecular CO_2 by ~11‰ (Rau et al., 1997):

$$^{13}C\text{-}CO_2 = {}^{13}C\text{-DIC} + 23.644 - 9701.5/T_{kelvin} \quad (1)$$

Secondly, the cell ^{13}C-POC content depends on the extent to which the enzymatic kinetic discrimination against ^{13}C during photosynthetic carbon fixation (of 20-30 ‰, varying with the specific metabolic pathways) is expressed. It is only fully expressed when inorganic carbon flow into and out of the cell (supply) is faster than fixation (demand). Both these effects often lead to higher ^{13}C contents in faster growing cells, because faster growth favours use of the more abundant bicarbonate form of DIC and also leads to less expression of the kinetic fractionation.

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Thus the association of higher ^{13}C contents with faster growing cells is very strongly justified for any particular phytoplankton species, from both metabolic understanding and the plethora of batch and chemostat experimental studies. Despite this understanding, inferring growth rates for communities of phytoplankton from field measurements of ^{13}C-POC is fraught with difficulties. The magnitudes of these two main isotopic effects vary strongly among different phytoplankton (and with their conditions of growth including temperature, nutrient and trace metal availability, light levels, specific enzymatic pathways, etc. (Burkhardt et al., 1999b;Burkhardt et al., 1999c;Fontugne et al., 1991;Schulz et al., 2007)), and there is no universal quantitative relationship between growth rate and phytoplankton ^{13}C content. In particular, cell size is a key variable in the control of ^{13}C contents (Popp et al., 1999;Rau et al., 1996;Rau et al., 1997;Rau et al., 1990). This effect is so important that the global range of surface water bulk ^{13}C-POC values can be observed across different size fractions within a single Southern Ocean sample (Trull and Armand, 2001). Good correlations between growth rates and ^{13}C contents when cell size is expressed in terms of the surface/volume ratio suggest this results from the balance of supply versus demand (Popp et al., 1998b), of either or both aqueous CO_2 and bicarbonate forms (Burkhardt et al., 1999a;Keller and Morel, 1999;Schulz et al., 2007), and with further modulation by other environmental controls such as the availability of light and other nutrients (Burkhardt et al., 1999c;Gervais and Riebesell, 2001;Schulz et al., 2004).

This complexity means that our observed ^{13}C-POC variations, even within a given size fraction, could arise by multiple mechanisms. Higher ^{13}C contents could reflect faster growth rates (via either greater use of bicarbonate or an increase of fixation of all DIC chemical forms relative to supply), or might instead reflect changes in species with inherently different uptake and assimilation metabolisms, or changes in metabolism driven by other controls such as light or iron availability. Our chemometric methods cannot

distinguish among these possible causes, and thus our expression of the ^{13}C-POC variations in terms of growth rate variations can only be viewed as an indicative exercise. To pursue this, we chose a model fit to chemostat data (Popp et al., 1998b):

$$^{13}\text{C-POC} = (^{13}C_{source} - \varepsilon_f) + k \text{ demand-rate/supply-rate} \quad (2)$$

in which the first term expresses the lowest possible ^{13}C contents of the cell as growth rate approaches zero, and the second term describes the linear (constant k) dependence of isotopic composition on the relative rates of CO_2 supply into the cell and it's cellular fixation. Popp et al. (1998) assumed the chemical form was aqueous molecular CO_2, but further evaluation showed that the data could also be fit by a model allowing either or both CO_2 and bicarbonate uptake (Keller and Morel, 1999). Both models assume that the supply rate depends linearly on its external concentration modulated by the surface area of the cell, and thus while the fitting constants we use here are from Popp et al (1998), the scaling to the surface/volume ratio (S/V) of the cell is independent of the chemical form of uptake):

$$^{13}\text{C-POC} = (^{13}\text{C-}CO_2 - 25) + 182\ \mu/([CO_2]\ S/V) \quad (3)$$

Rewriting this equation for growth rate, μ, and our measured ^{13}C-DIC and ^{13}C-POC values yields an indicative path to possible growth rates for our size fractions:

$$\mu = S/V\ [CO_2]\ [^{13}\text{C-POC} - (^{13}\text{C-}CO_2 - 25)]/182 \quad (4)$$

with ^{13}C-CO_2 calculated using equation (1), $[CO_2]$ obtained from underway pCO_2 observations (Lo Monaco et al., 2014) and Henry's Law (Weiss, 1974). In this expression, growth rate μ is in d^{-1}, S/V in μm^{-1}, and $[CO_2]$ in $\mu mol\ kg^{-1}$.

This expression provides growth rates that we compare to other estimates. Of course, comparison of these rates is very sensitive to *S/V* estimates, as well as to all the other possible sources of variations in ^{13}C contents summarized above. For example, a 30% increase in the mean size of cells, such as could occur within a given size fraction, would

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yield a 69% increase in the model growth rate (for spherical cells). For this reason, our growth rate estimates must be viewed with great caution, not only in terms of their absolute magnitudes, but also in terms of their relative magnitudes across the different stations.

In comparison to these fractionation effects accompanying primary production, trophic ^{13}C enrichment is thought to be relatively small within a given class of compounds for carbon (~ 1‰ per trophic level; (Michener and Schell, 1994)). However, accumulation of lipids, which are ^{13}C depleted owing to their multi-step synthesis pathways, causes many zooplankton to have lower ^{13}C contents than their diet (Michener and Schell, 1994;Syvaranta and Rautio, 2010). This is a probable contributor to the ^{13}C-POC values of the two largest size fractions, as discussed in the results section.

Finally, because our focus is on extracting information about growth conditions for the communities at the time of sampling, we remove the influence of source inorganic carbon isotopic composition spatial variations on the 13C-POC variations, by examining their offset relative to the source: $^{13}C\text{-}POC_{rs} = {}^{13}C\text{-}POC - {}^{13}C\text{-}DIC$.

~~Controls on the ^{13}C composition of phytoplankton are complex (Goericke et al., 1994), but in general, within a phytoplankton size class (and relative to source compositions) ^{13}C enrichment is a sign of faster growth~~ (Popp et al., 1998b;Popp et al., 1999;Rau et al., 1997;Trull et al., 2008)~~. In other words, discrimination against ^{13}C assimilation is less strong in rapidly growing cells. We briefly review the processes involved in this discrimination to inform our use of ^{13}C-POC variations to estimate approximate growth rates, and return to this issue again in the results section in light of the specifics of the KEOPS2 observations.~~

~~One possible control is a change from use of the scarce molecular CO_2 form of DIC to greater use of the ~100-fold more abundant bicarbonate form (although this form is~~

~~electrically charged and thus likely to be more energetically costly to assimilate).~~ ~~Assimilation of bicarbonate raises ^{13}C POC, because it has much higher ^{13}C contents than dissolved molecular CO_2 (~11‰ higher at KEOPS2 temperatures, as expressed by the approximate equilibrium fractionation expression (Rau et al., 1997):~~

~~$^{13}C\ CO_2 = {}^{13}C\ DIC + 23.644 - 9701.5/T_{kelvin}$ (1)~~

~~There is presently no understanding of how a possible switch from CO_2 to HCO_3^- assimilation might depend on growth rate, but some aspect of the relative availability of CO_2 supply versusvs. biological demand is likely to be involved. This balance also affects the extent of fractionation that occurs if only one external species (e.g. molecular CO_2) is assimilated, and models of supply versusvs. demand have been shown to reproduce ^{13}C variations well for many phytoplankton (e.g. Rau et al., 1997; Popp et al., 1998), and we rely on this approach to re-express our field ^{13}C variations in terms of (relative) growth rates.~~

~~The discrimination against ^{13}C that accompanies intra-cellular enzymatic fixation of CO_2 (ϵ_f ~25-28‰ for the most common enzymes but less for other forms) exceeds the isotopic offset between the external DIC species, and thus has been a focus for the likely control on fractionation during carbon assimilation. The extent to which this enzymatic discrimination is expressed in the ^{13}C POC depends on the balance of supply into the cell versusvs. demand from growth. If all supply is assimilated ^{13}C POC equals the supply value, but if little is assimilated (with the rest re-exported), the full enzymatic fractionation occurs (i.e. ^{13}C POC approaches the supply value minus ϵ_f). Laboratory experiments have confirmed the general validity of the supply versusvs. demand model and shown (for a limited set of phytoplankton) that ^{13}C POC increases linearly with growth rate~~ (Popp et al., 1998b)~~. Specifically, Popp et al. (1998) applied the model that:~~

~~$^{13}C\ POC = ({}^{13}C_{source} - \epsilon_f) + k\ demand\ rate/supply\ rate$ (2)~~

in which the first term expresses the lowest possible ^{13}C contents of the cell as growth rate approaches zero, and the second term describes the linear (constant k) dependence of isotopic composition on the relative rates of CO_2 supply into the cell and it's cellular fixation. They found an excellent fit to data by assuming the chemical form is aqueous molecular CO_2 and that supply rate depends linearly on its external concentration modulated by the surface to volume ratio (*S/V*) of the cell:

$$^{13}C\ POC = (^{13}C\ CO_2 - 25) + 182\ \mu/([CO_2]\ S/V) \quad (3)$$

Rewriting this equation for growth rate, μ, and our measured ^{13}C DIC and ^{13}C POC values yields a possible path to quantitative growth rates for our size fractions:

$$\mu = S/V\ [CO_2]\ [^{13}C\ POC - (^{13}C\ CO_2 - 25)]/182 \quad (4)$$

with $^{13}C\ CO_2$ calculated using Eq.equation (1), $[CO_2]$ obtained from underway pCO_2 observations (Lo Monoco et al., this volume2014) and Henry's Law (Weiss, 1974). In this expression, growth rate μ is in d^{-1}, *S/V* in μm^{-1}, and $[CO_2]$ in $\mu mol\ kg^{-1}$.

As discussed further in the results section, this expression predicts two useful things. Firstly, it predicts growth rates that we compare to other estimates. Secondly it shows that a given ^{13}C POC increase predicts a larger increase in growth rate for small cells than for large cells, because smaller cells have higher *S/V* (and this sensitivity to *S/V* is large). Of course, comparison of these rates is sensitive to *S/V* estimates and to the assumption that transport into and out of the cell scales with this parameter. For this reason, our growth rate estimates must be viewed with great caution.

Trophic ^{13}C enrichment is thought to be relatively small within a given class of compounds for carbon (~ 1‰ per trophic level; (Michener and Schell, 1994)). However, accumulation of lipids, which are ^{13}C depleted owing to their multi-step synthesis pathways, causes many zooplankton to have lower ^{13}C contents than their diet (Michener

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and Schell, 1994;Syvaranta and Rautio, 2010). This is a probable contributor to the ^{13}C POC values of the two largest size fractions, as discussed in the results section.

Finally, because our focus is on extracting information about growth conditions for the communities at the time of sampling, we remove the influence of source inorganic carbon isotopic composition spatial variations on the 13C POC variations, by considering only their offset relative to the source rs: $^{13}C\ POC_{rs} = {}^{13}C\ POC - {}^{13}C\ DIC$.

2.5.2 Isotopic chemometric principles – ^{15}N

Phytoplankton ^{15}N-PN variations result primarily from the relative use of reduced nitrogen (mainly ammonium) which has low ^{15}N contents vs. the more abundant nitrate pool which has higher ^{15}N contents, and secondarily from variations in the isotopic fractionation accompanying nitrate assimilation (Goericke et al., 1994;Karsh et al., 2003;2014;Trull et al., 2008). As with the carbon isotopes, we discuss the ^{15}N-PN variations relative to co-located ^{15}N-NO_3 source values (^{15}N-PN_{rs} = ^{15}N-PN - ^{15}N-NO_3), to separate source composition effects (that have accumulated from the history of nitrogen metabolism in a given parcel of water) from the fractionation associated with current PN production. This source composition effect was larger for nitrogen than for carbon, because variation in ^{15}N-NO_3 values was larger (6.1 to 8.0‰), and ^{15}N-PN variations were smaller (6‰).

By estimating expected values for ^{15}N-PN_{rs} formation from nitrate and from ammonium, estimates of new vs. recycled production (i.e. *f* ratios) can be obtained for each size fraction by mass balance. The observed range of fractionation factors for nitrate assimilation during KEOPS2, namely ε_{na} of -4 to -4.5 ‰, as estimated from ^{15}N-NO_3 variations in the water column (Dehairs et al., 2014), provides an upper limit for growth on nitrate of ^{15}N-PN_{rs} (-4‰). For ammonium, the simplest approximation is to use a value

just below the lowest observed ^{15}N-PN$_{rs}$, i.e. to assume that these cells grew on ammonium alone (Trull et al., 2008). Using these end members (^{15}N-PN$_{Nrs}$ = -4 ‰ for growth on nitrate; ^{15}N-PN$_{Ars}$ = -8 ‰ for growth on ammonium), yields *f* ratio estimates for each size-fraction, from:

$$f = (^{15}\text{N-PN}_{rs} - {}^{15}\text{N-PN}_{Ars})/(^{15}\text{N-PN}_{Nrs} - {}^{15}\text{N-PN}_{Ars}) \quad (5)$$

In comparison to carbon, trophic enrichment of ^{15}N is relatively large (~3‰ vs ~1‰; (Michener and Schell, 1994;Wada and Hattori, 1978), which provides a cautionary note on the interpretation of the *f* ratio estimates. The largest zoo-plankton containing size fractions (210-300 µm, 300-1000 µm) have higher ^{15}N-PN$_{rs}$ values than are achievable by primary production and derive from this process.

3 Results

3.1 Total biomass variations

POC biomass concentrations in surface waters varied from ~ 3 to 25 µM (Table 2), reported as the "total" sum of fractions as filtered from as much as 2600 L of underway supply water, and are in agreement with our 1 L single filter "bulk" filtrations (Appendix A). Although there ~~are~~ were some differences in POC results across the multiple sample methodologies of the entire ~~mission~~ KEOPS2 program e.g. from underway supply, Niskin bottles, and in-situ pumps (Dehairs et al., 2014;Lasbleiz et al., 2014;Tremblay, 2014), these remain to be fully assessed and ~~hence~~ here we focus on our own internally consistent results.

There were significant variations of POC concentrations within the Groups as well as among them (Fig. 3). The ~~Group 1~~ upstream Fe-poor HNLC reference station R2 and the early sampled furthest south and coldest Group 3 plateau station A3-1 had the lowest values. The recirculation initial survey stations in Group 1 had somewhat higher values

(5-10 µM; with a single higher value of 15 µM at TEW-4, attributable to a high heterotropic contribution to its largest size fractions), with little increase over time as represented by the Group 2 recirculation time series (again with a single outlier at E4-E). The Group 5 downstream Polar Front bloom stations had the highest biomasses, exceeding all but 1 of the Group 3 Plateau stations as well as all Group 4 coastal stations. Note that the Group 5 stations from warmer waters north of and near the Subantarctic front (TNS 1 and 2), where the upstream flow may not cross the Kerguelen shelf, stand out from the other Group 5 stations as having much lower biomass, similar to the upstream HNLC reference station (R2). This distribution of POC among the Groups provides important results: (i) waters that have not crossed the plateau have low biomass, presumably reflecting a lack of Fe fertilisation, and (ii) downstream blooms achieve higher concentrations of biomass than coastal blooms. Given that Fe concentrations were highest in the coastal waters (Table 1; section 2.2), this means that ecosystem dynamics must also contribute importantly to the control of biomass.

Distributions of POC with particle size also varied significantly (Fig. 3). All stations exhibited the highest concentrations in the smallest size fraction (1-5 µm) *when normalized to the width of this fraction interval* (Fig. 3), but these concentrations were relatively constant across the Groups. In contrast the concentrations in the three phytoplankton dominated intermediate size fractions (5, 20, 50 µm filters) varied among the groups, and drove the total POC biomass changes described above. There were significant variations within these 3 size fractions as well. Abundance decreased monotonically with size at the HNLC reference station. The Group 1, and even more so the Group 2, stations exhibited greater increases (as total biomass increased either among stations in Group 1 or with time in the Group 2 time series; note that Table 2 lists all stations in chronological order) in the 20 µm fraction than the 5 µm fraction, but still low

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values in the 50 µm fraction. The Group 3 plateau stations started with this slightly "humped" ~~(i.e. 5< 20 >50 µm)~~ POC distribution (i.e. POC higher in the 20 µm fraction than in both the 5 and 50 µm fractions), but as biomass increased with time the 50 µm fraction came to dominate. Interestingly, this never occurred in the Group 4 coastal or Group 5 Polar Frontal biomass rich stations, which remained dominated by the 20 µm size fraction.

Heterotrophic biomass (as represented by the two largest size filters, 210 and 300 µm) was generally an order of magnitude lower than autotrophic biomass (as represented by the 3 intermediate fractions), and more than 2 orders of magnitude lower if the smallest fraction is also included as an autotroph fraction. ~~It~~ Heterotrophic biomass generally increased with total biomass in all the Groups, except the Group 4 coastal waters. As mentioned earlier, ~~Station~~ station TEW-4 in Group 1 had unusually high heterotrophic biomass, which explains its outlier status of exceptionally high total POC for this Group.

3.2 Variations in BSi concentrations and associated contributions to biomass

BSi estimates were not possible for the smallest size fraction (owing to use of a quartz 1 µm filter). Thus total BSi is underestimated, and comparisons to total POC must be done cautiously. As shown in Fig. 3 (top row), the highest BSi levels were observed in the Plateau stations late in the voyage, with these exceeding those of the Group 5 Polar Frontal bloom stations as well as all the other Groups. The lowest levels were in the Polar Frontal Zone and Subantarctic stations (Group5, stations TNS1 and 2). More detailed evaluation is possible on a size-fractionated basis. The initial survey of Group 1 low biomass waters found a wide range of BSi/POC ratios that covered most of the variability seen across the entire KEOPS2 study (Fig. 3; bottom row). Among the other groups, the Group 3 plateau stations stands out for having high BSi/POC ratios in all the autotrophic

fractions (5, 20, 50 μm filters), in contrast to uniformly low ratios for the Group 5 stations. The presence of non-zero BSi/POC ratios in many of the largest, zooplankton dominated size fractions (210 and 300 μm filters) reflects the presence of chain-forming diatoms, although their POC biomass was insignificant in comparison to that of the autotrophic intermediate fractions.

Much of the range in BSi/POC ratios for the intermediate size fractions overlaps with that expected for diatoms under iron-impoverished (BSi/POC ~0.6) to iron-replete (BSi/POC ~0.15) conditions (Hoffman et al., 2007;Hutchins and Bruland, 1998;Takeda, 1998), but note that this is a simplistic view of diatom BSi/POC variations in response to Fe inputs which ignores variations across taxa and across life cycle stages (Leynaert et al., 2004;Marchetti and Cassar, 2009;Ragueneau et al., 2006) . There was no clear correspondence across the groups between BSi/POC values and Fe fertilisation levels, in that the Group 4 Fe-rich coastal waters had intermediate BSi/POC ratios in comparison to the moderately Fe-rich Group 3 plateau and Group 5 downstream Polar Front waters. Community variations in the ratio of diatom to non-diatom taxa thus appear to overprint any dependence of diatom BSi/POC ratios on Fe ~~for~~levels ~~diatom BSi/POC ratios~~.

3.3 ^{13}C variations

We first note that the $^{13}C\text{-}POC_{rs}$ values of the HNLC reference station (R-2) were the lowest of all stations, and we take them as an indication of expectations for slowly growing offshore polar phytoplankton (Fig. 4). In comparison, Group-1 and Group-2 stations (which had indistinguishable $^{13}C\text{-}POC_{rs}$ values), were elevated by ~2‰ (ranging from 1 to 4‰) in comparison to the R-2 HNLC reference level. These stations also displayed an increase in $^{13}C\text{-}POC_{rs}$ values from the smallest (1-5 μm) towards larger size fractions (5-20, 20-50 μm) before decreasing again in the largest autotrophic size fraction

(50-210 µm) and generally also in the heterotrophic dominated- size fractions (210-300 and 300-1000 µm). This hump-shaped pattern was also present at the Group-3 plateau stations, where $^{13}C\text{-}POC_{rs}$ values were elevated further. The Group-4 coastal stations had the highest $^{13}C\text{-}POC_{rs}$ values, with values as high as -20‰.

This pattern has been found before in Antarctic polar waters, with the initial increase in $^{13}C\text{-}POC_{rs}$ with size attributed to the effect of decreasing surface/volume on CO_2 uptake (Popp et al., 1998a;Popp et al., 1999), and the subsequent decrease in larger fractions attributed to the presence of needle-shaped diatoms with high surface/volume (*S/V*) ratios similar to small cells (Trull and Armand, 2001). Detailed *S/V* estimates for our samples are not yet available to assess this explanation or the influence of the presence of chains of *Fragillariopsis kerguelensis*, *Eucampia antarctica*, and *Chaetoceros hyalochaeta* diatoms which contribute strongly to the larger autotrophic size fractions at many stations (Armand et al., personal communication, 2014). The presence of lipid-rich zooplankton in the two largest size fractions is another probable cause of their low ^{13}C-POC values, based on low ^{13}C-POC values for zooplankton collected with nets during KEOPS2 (Carlotti et al., 2014).~~but one that we are unable to explore further.~~

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To translate our observed ^{13}C-POC variations (in the autotrophic size classes) to growth rates using the relationships described in the Methods (section 2.5.1), we must make some assumptions about the size and shapes of the phytoplankton in the different filter fractions. This choice is difficult in the absence of detailed observations, and we took a very simple approach of representing the phytoplankton as rectangular prisms with square cross-sections, with the dimensions given in Table 3 for the 1, 5, 20, and 50 µm filter fractions. For the two larger fractions, we assumed diatoms were predominantly present as chains (based on microscopy; Armand et al., personal communication, 2014), and that the surface for CO_2 exchange was accordingly reduced (the details accompany

669 Table 3). These assumptions are of course tenuous because diatom chains vary in their
670 morphology, and of course the relationship between *S/V* and uptake is itself a large
671 assumption, in that it presupposes that both diffusive and active inorganic carbon uptake
672 scale with cell surface area (see Methods for additional discussion of the uncertainties in
673 estimating growth rates from ^{13}C-POC contents). Nevertheless, on this basis, we obtained
674 ^{13}C model growth rate variations for each of the autotrophic size fractions (Table 2) and
675 total community growth rates (Fig. 5) for each station by summing results for the four
676 smallest size fractions (1, 5, 20, 50 μm). Similar variations across the stations were
677 obtained by limiting the sum to the 5, 20, and 50 μm fraction results (data not shown).
678 The ^{13}C model growth rates decreased with size across the size fractions (from the 1 to the
679 50 μm filter) by factors of 10 to 15, in excellent agreement with allometric relationships
680 assembled for a much broader range of phytoplankton, although the high growth rates of 2
681 to 3 d^{-1} in the smallest fraction are greater than expected for polar waters (Chisholm,
682 1992;Cózar and Echevarría, 2005). This could reflect significant contributions from
683 detritus from larger autotrophs and bacteria in this fraction, or other errors in the model
684 (see the Methods section for discussion of the low fidelity of the ^{13}C model growth rates).
685 Our community (sum of fractions) ^{13}C model growth rates compare reasonably
686 well with a limited set of incubation results, calculated by integrating results from
687 different light level deck onboard incubations (Cavagna et al., 2014) over the depth of the
688 surface mixed layers as shown in Table 4 (Park et al., 2014b;Park et al., 2014a).
689 The overall dynamic range of the incubation and model growth rates was identical
690 (0.18 d^{-1}). For the model this ranged from 0.08 d^{-1} at the coldest early-sampled low
691 biomass station over the plateau (A3-1) to 0.27 d^{-1} at coastal station TEW-2. The
692 incubations ranged from a low value of 0.065 d^{-1} at the HNLC reference station (A3-1 was
693 not studied) to a high of 0.24 d^{-1} at the Group 5 Polar Front station F-L (coastal stations

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694 were not studied). Overall correlation between the 8 pairs of results from the same stations
695 (though not sampled at identical times) was very poor (r^2<0.1) but this was driven by
696 strong disagreement at the single Group 5 downstream Polar Front station where the
697 incubations found their highest depth integrated growth rate (0.24 d^{-1} at F-L) but our ^{13}C-
698 based estimates were much lower, and without this pair, the correlation was reasonably
699 strong (r^2=0.67).

700 Given the importance of *S/V* variations to the ^{13}C model growth rate estimates (see
701 the Methods section), variations between Groups with similar size distributions and
702 phytoplankton flora (the Group 1, 2 recirculation and Group 3 plateau stations) are
703 probably more reliably assessed than variations between Groups with more distinct flora
704 (coastal Group 4 stations and downstream Polar Front Group 5 stations). The Group 2
705 recirculation time series showed quite constant and moderate growth rates (0.17 – 0.19 d^{-1}).
706 Interestingly, values during the earlier Group 1 initial survey were somewhat higher in this
707 region (0.19 – 0.21 d^{-1}), and reached 0.23 d^{-1} at the southern end of the north-south transect
708 over the plateau (TNS 9, 10). Later sampled Group 3 plateau stations (A3-2, G1, E4W,
709 E4W2) also had high ^{13}C model growth rates (0.19 - 0.24 d^{-1}).

710 These growth rate variations are in broad agreement with the development of
711 blooms in these regions – in that the lowest biomass accumulation over the study period
712 occurred in the recirculation, with higher values over the plateau. In contrast, the model
713 suggests that the highest growth rates occurred in Group 4 coastal waters, where biomass
714 accumulation was only moderate, and found only moderate growth rates for the Group 5
715 Polar Front stations where a strong bloom was already underway at the time of sampling
716 (Fig. 2). Unfortunately, it is not currently possible to determine ~~why this misfit occurred,~~
717 ~~and it is not really surprising given~~whether this reflects the simplicity of the model ~~and~~ or
718 the complexity of the ecosystem dynamics. This provides a useful cautionary note that the

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apparent growth rate variations have no real quantitative validity; at best they provide indicative information on the relative intensities of CO_2 assimilation across the Groups. Indeed, it is possible that the variations among the Groups results from other issues such as species metabolic differences, or light and trace element availability (as discussed in detail in the Methods section). Thus it is important to emphasize that the overall view of ecosystem responses developed in the Discussion section below does not depend only on these potential growth rate estimates from the ^{13}C-POC observations, but also draws on biomass accumulation rates from the POC concentrations, their distribution across size fractions, and other indicators as discussed below.

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3.4 ^{15}N variations

Similarly to the carbon isotopes, we discuss the ^{15}N-PN variations relative to co-located ^{15}N-NO_3 values (^{15}N-PN_{rs} = ^{15}N-PN - ^{15}N-NO_3), for the reasons outlined in the Methods (section 2.5.2). As shown in Fig. 4, almost all the phytoplankton dominated size fractions (5-20, 20-50, 50-210 μm) had ^{15}N-PN_{rs} values that fall between the upper bound of production from nitrate (^{15}N-PN_{rs} = -4) and the lower bound of production from ammonium (^{15}N-PN_{rs} = -8). There was also a tendency across all Groups towards lower ^{15}N-PN_{rs} in the smaller phytoplankton fractions; consistent with greater use of ammonium by smaller phytoplankton (Armstrong, 1999;Karsh et al., 2003). The largest zoo-plankton containing size fractions (210-300, 300-1000 μm) had higher ^{15}N-PN_{rs} values, which presumably result from the relatively large (~3 ‰) trophic enrichment that occurs in many marine organisms (Michener and Schell, 1994;Wada and Hattori, 1978). While these general variations with size held for all Groups, there were significant differences. In particular, the Group 3 plateau stations had the lowest ^{15}N-PN_{rs}values for the larger autotrophic size classes (20-50 and 50-210 μm).

Using the end-member mixing model (Methods section 2.5.2), we obtained the estimated community *f* ratios as shown in Fig. 5. The Group 3 plateau stations tended to have somewhat higher values (~0.7 vs. ~0.6) than the Group 5 downstream Polar Front bloom stations (TEW-7, TEW-8, and F-S); although this was not true for the highest biomass station (F-L). As with the ^{13}C model growth rates, the Group 1 recirculation stations sampled early on the TNS transit were somewhat surprising in having relatively high values, though these were not observed on the later TEW transit or during the Group 2 time series. Finally, the coastal stations had high *apparent f* ratios, including values that exceed 1 (pointing to limitations of the model). Importantly, these high values are driven by the relatively low ^{15}N-NO_3 values in these coastal waters, rather than by higher ^{15}N contents in their PON. The low ^{15}N-NO_3 values are a surprise given the relatively low nitrate concentrations in these coastal waters (Fig. 6), suggesting other processes are at work. Our observations are insufficient to explain this. One possibility is delivery of low ^{15}N nitrate from sedimentary nitrification, but this still leaves open the question of why recently formed PN does not track the overall nitrate pool isotopic composition. Reliance on the *f* ratios from these coastal stations is thus not advisable. In contrast, comparison of our offshore *f* ratios to incubation results (Fig. 5) shows similar values and excellent correlation (r^2=0.90; provided the one very low incubation based *f* ratio at the HNLC station R2 is discounted).

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3.5 Nutrient depletion estimates

Surface water nutrient concentrations provide an initial perspective on the efficiency of the biological pump. ~~Overall, t~~The surface nitrate concentrations ~~indicate~~ were lower ~~values~~ north than south of the Polar Front, but of course this may reflect longer term, ~~larger region~~basin scale, controls on nitrate. Determination of the role of local recent

769 biological activity in nitrate depletion requires a much closer examination. Fig. 6 shows
770 high spatial resolution maps of nitrate, temperature, and salinity obtained with the sensors
771 operated continuously underway. Waters upstream from the plateau and south of the Polar
772 Front were cold and saline with high nitrate concentrations, with these parameters
773 reaching their highest values over the central plateau early in the voyage (near the Group 3
774 KEOPS bloom reference station A3-1), with temperature less than 2ºC, salinity greater
775 than 33.9, and nitrate above 30 μM. At the other extreme, Group 4 coastal waters had the
776 lowest surface nitrates (below 10 μM), in association with very fresh (salinity <33.6) and
777 relatively warm (>3.5ºC) waters. The Group 5 waters downstream in the bloom that
778 formed north of the Polar Front well to the east (near 74-75ºE and the Group 5 stations
779 TEW-7, -8, F-L and F-S), also had relatively low surface nitrates (15-20 μM) and low
780 salinities (33.7-33.8), and were quite warm (>4 ºC). In comparison, The Group 2
781 recirculation feature had intermediate nitrate concentrations between the plateau, coastal,
782 and downstream Polar Front plume conditions.
783 These conditions evolved over the course of the study, with decreases in surface
784 nitrate values being particularly strong (reaching 6-8 μM from winter conditions; Table 4)
785 in regions of rapid biomass accumulation over the central plateau (especially along the
786 plateau edge to the north of the A3 station) and in the bloom north of the Polar Front (near
787 stations TEW-8, F-L, F-S). Low nitrate concentrations were also found in association with
788 relatively low salinities to the southeast of the recirculation region, where the ship
789 transited without station sampling. This appears to represent southward supply of waters
790 from north of the Polar Front in association with its meandering (as also suggested by the
791 satellite chlorophyll image sequences (Fig. 2 and animation in the Supplement, and by
792 water parcel trajectories estimated from drifters and satellite altimetry; d'Ovidio et al.,
793 2014). This process also appears to have driven warming and freshening in the

recirculation over time. Thus nitrate budgets require partitioning of temporal changes driven by both hydrology and biology.

To separate local biological nitrate depletion from hydrological controls, we examined nitrate depletions in surface waters relative to estimates of initial winter nitrate concentrations for each station, as estimated from CTD profiles. We considered integrations to two different depths: (a) the frequently used choice ~~(e.g.~~ (e.g. Arrigo et al., 1999;Sweeney et al., 2000) of the depth of the remnant winter water temperature minimum (T_{min}-depth), and (b) shallower depths based on a threshold increase in salinity of 0.05 ($S_{threshold}$-depth). This second choice was motivated by the presence of significant salinity gradients above the T_{min}-depth (examples are shown in Fig. 7), particularly in waters near and north of the Polar Front, suggesting either that the most recent winter mixing was not as deep as previous years, or that horizontal mixing had brought fresher waters over the top of the T_{min}, and thus in either case that nitrate depletion between the T_{min}-depth and $S_{threshold}$-depth was not attributable to ~~recent consumption~~local biological processes~~. Note that each of these nitrate depletion metrics reflects the sum of export since stratification and the current standing stock, which may make a contribution to future export (at some unknown discounted rate owing to heterotrophic loss).~~

The two nitrate depletion metrics give differing views of the contributions to export from the different community Groups (as summarized in Fig. 8). Estimates based on the T_{min} approach were much higher than those from the $S_{threshold}$ approach, because the T_{min}-depth and was generally deeper and had higher nitrate than the $S_{threshold}$-depth (Table ~~2~~4). ~~The T_{min} approach also yielded more widely varying results within a Group~~, The T_{min} approach ~~and~~ suggested that the greatest depletion occurred ~~for~~ in the downstream plume ~~of Kerguelen island coastal waters that formed the bloom~~ to the north of the Polar Front. In contrast, the $S_{threshold}$ approach identified the highest seasonal nitrate depletion as

occurring over the central plateau, with somewhat lower values in the recirculation feature, followed by the Polar Frontal bloom and the reference station. These methodological differences were even larger for the silicic acid depletions (Fig. 8). This analysis underlines the importance of appropriate winter nitrate (and silicic acid) surface nitrate concentration estimates to the assignment of export magnitudes.

We believe the $S_{threshold}$ approach is the most appropriate given the observed salinity stratification, especially for the relatively weak subsurface thermal stratification observed in the Group 5 stations near the Polar Front, where its choice makes the most significant difference from estimates based on the T_{min} approach. This is because the high biomass layer found in these Polar Frontal sites is in this shallow salinity-defined layer, and because the Fe fertilization of these waters is recent as shown by their short transit time of ~ 2 weeks since crossing the plateau as determined from both altimetry and drifter releases (d'Ovidio et al., 2014; Park et al., 2014). Thus attribution of nutrient depletion below the depth of the $S_{threshold}$ to local iron fertilized biomass production is not warranted. ~~We believe the $S_{threshold}$ approach is the most appropriate given the observed salinity stratification, especially for the relatively weak subsurface thermal stratification observed in the Group 5 stations near the Polar Front.~~ ~~Both~~ For all the Groups, both the T_{min} and $S_{threshold}$ based nitrate depletions are relatively small as percentages of the initial upper water column inventories (2-18%; Table 4). This reflects the early seasonal sampling, as well as a significant extent of recycling via nitrification (Dehairs et al., 2014;Lasbleiz et al., 2014). Fractional depletions of silicate were higher (3-53%; ~~data but not values shown in~~ Table 4b), consistent with the results of the autumn KEOPS expedition which revealed low nitrate removal but near complete Si depletion (Mosseri et al., 2008). ~~(~~Finally, ~~Note~~ we note that we could not estimate export for the Group 4

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Kerguelen Island coastal stations because neither the T_{min} nor the $S_{threshold}$ approaches were compatible with their shallow water columns~~)~~.

Our preferred $S_{threshold}$ nitrate depletion estimate can be further refined by removal of the standing stock of other nitrogen forms produced by the ecosystem (ammonium, urea, dissolved organic nitrogen, particulate nitrogen) to give a better estimate of N export from surface waters. PN dominated these stocks, with concentrations up to 5 μM (Lasbleiz et al., 2014)), in contrast to ammonium, nitrite, and surface enhancements of DON (i.e. the fresh component) with concentrations below 1 μM (Blain et al., 2014;Dehairs et al., 2014). Subtracting PN stocks (integrated to 200m depth (Lasbleiz et al., 2014) suggests that for many stations about half of the consumed nitrate has been exported and about half remains in the water column (Table 4).

A few stations exhibited negative N export estimates, because of higher PN stocks than their nitrate depletion estimates (Table 4). This could arise from either underestimation of nitrate depletions owing to entrainment of subsurface waters (an effect that can halve nutrient depletion estimates under conditions of weak water column stratification and strong winds; (Wang et al., 2003)), or horizontal interleaving of relatively undepleted water parcels with relatively PN rich waters. Notably the largest excesses of PN stock over nitrate depletions occurred at stations located close to fronts (TEW-3 and F-S).

Viewed at the Group level, the nitrate depletions and N export estimates (Fig. 8) provide very useful insights. Firstly, given the uncertainties regarding the estimation of nutrient depletions from the profiles, it could be argued that the most robust conclusion is that all the Groups exhibit similar depletions, with roughly half of the N uptake exported and half remaining as accumulated biomass. This is consistent with the growth estimates of roughly one doubling every 3 days and the satellite biomass observations indicating

slower doubling approximately each week. Looking into more detail, and ~~Focusing~~ focusing on the salinity threshold approach, ~~we see~~suggests that the highest nitrate depletions occurred for the Group 3 plateau stations, with significantly lower values in the Group 1 and Group 2 recirculation stations (Fig. 8 middle panel). However, the larger standing stock of PN biomass over the plateau means that the export up to the time of sampling was only slighter higher than in the Group 1 and 2 recirculation stations. This aspect is even stronger for the Si budgets, with the export of Si higher for Groups 1 and 2 than over the plateau in Group 3, emphasizing the retention of N in comparison to Si during export.

Another interesting insight is that, in comparison to the Group 3 plateau stations, nitrate depletion and export are much lower in the Group 5 Polar Frontal bloom stations. Considering the $S_{threshold}$-depths (Table 4), and the associated Si depletion and export results (Fig. 8), helps understand why the Polar Frontal bloom ~~produces~~ produced less nitrogen depletion and export than the plateau bloom. Firstly, the Polar Frontal bloom depletion is a shallow feature compared to that over the plateau (Fig. 7), secondly a much greater proportion of the assimilated nitrogen is still present as standing stock (Fig. 8 bottom panel), and thirdly, there is some suggestion that more nitrogen than silicon is retained as standing stock (as a portion of depletion; compare the Fig. 8 middle and bottom panels). Of course observation of these variations in spring does not mean that they would have persisted into summer, and it is possible that over the full season the extent of nutrient depletion was significantly different then observed during the KEOPS2 shipboard campaign, either towards homogeneity across the region or towards larger variations.

4. Discussion

Our overall interest is to understand community responses to iron fertilisation, with a particular focus on ecosystem control of nutrient depletion and carbon export. We expect this response to vary as a function of iron inputs, but also possibly with time since fertilisation and its persistence (as a result of cascading trophic effects), and time of year (as a result of strong seasonality of the physical and biological background). Specific probable seasonal modulators of the response to iron include insolation, stratification, and the abundance of organisms with life cycles that resonate at the seasonal scale, e.g. larger zooplankton. In the following sections, we summarize the structure and function variations, relate them to temporal settings (as developed in the Methods section), and compare them to our estimates of nitrate (and silicic acid) depletion from surface waters as a proxy for carbon export.

4.1 Overview of community structure and function variations

Our size-fractionated chemometric parameters for microbial ecosystem structure and function identified significant differences among the various environments sampled by the KEOPS2 program. The upstream HNLC reference station (R2) displayed low phytoplankton abundance, relatively high BSi/POC ratios, slow growth rates (as indicated by both strong discrimination against ^{13}C uptake (this work) and slow growth rates measured in deckboard incubations (Cavagna et al., 2014)). , ~~and~~ Its ^{15}N-PN values ~~suggesting~~ suggested that growth was predominantly on nitrate, ~~(~~although this result must be viewed with caution since it differs from the surprisingly low *f* ratio obtained by incubation ~~-~~(Cavagna et al., 2014). These characteristics are consistent with its selection as a HNLC reference, but the total integrated biomass was higher than the lowest values seen in Southern Ocean HNLC waters and mesopelagic Ba levels indicated POC remineralization, possibly indicating a low-level early production event (Jacquet et al.,

2014;Lasbleiz et al., 2014) as a result of a small degree of Fe fertilisation, possibly from particulate Fe inputs from the nearby Leclaire Rise (van der Merwe et al., 2014).

The moderate iron fertilisation of the recirculation feature downstream from the plateau (stations in Groups 1 and 2) increased ^{13}C model growth rates (relative to the HNLC reference station R2) by ~0.02 to 0.04 d^{-1} (Fig. 5) and biomass ~2-fold (increasing from ~50% to 4-fold over time; Fig. 3), particularly in the larger phytoplankton size fractions (20-50 and 50-210 μm). There was no systematic change in BSi/POC ratios, with some stations showing lower values consistent with relief of iron limitation, but others showing higher values. Whether this resulted primarily from changes in species or the presence of empty frustules is unclear, although the analysis of depletions and standing stocks suggests loss of empty frustules (as did earlier work during KEOPS; (Mosseri et al., 2008)). This may reflect varying levels of low production (Cavagna et al., 2014) coupled closely to export, as well as the possibility that production was in part limited by variations in mixed layer depth (Lasbleiz et al., 2014). The ^{15}N-PN observations indicated growth primarily on nitrate (as at the HNLC reference station).

Both of the more strongly iron fertilised offshore regions (the Group 3 central plateau and the Group 5 Polar Front bloom, Table 1.) exhibited increased ^{13}C model growth rates in comparison to HNLC waters (elevated by ~0.05 d^{-1}), but their community structures were quite different (emphasizing caution regarding the ^{13}C model growth rates, although the incubation results also indicated increased growth rates; (Cavagna et al., 2014)). The plateau stations exhibited most of their enhanced biomass in the largest phytoplankton size fraction (50-210 μm); whereas Polar Frontal biomass increases were dominated by the next smaller size (20-50 μm). This was also true for the very strongly Fe fertilized Group 4 coastal stations where ^{13}C model growth rates were even more elevated (by 0.1 to 0.19 d^{-1} above the HNLC reference). Use of ammonium vs. nitrate (as

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942 estimated from both natural abundance 15N values in this work and tracer 15N uptake
943 incubations by Cavagna et al., 2014), was also different between the plateau and
944 downstream Polar Frontal blooms, with the plateau stations using a greater proportion of
945 nitrate.
946
947 **4.2 Links between community structure and export**
948 Overall, one of the most important outcomes of our results regarding export (presented
949 in section 3.5 and Fig. 8) is that surface biomass is not a good guide to the history of
950 export, i.e. the low biomass recirculation feature exhibited as much export as from the
951 higher biomass Polar Front or Plateau blooms. This same conclusion was reached on the
952 basis of sparse sediment trap deployments at 200 m depth (Laurenceau et al., 2014) and
953 ^{234}Th depletions in surface waters, which identified the recirculation feature as having the
954 highest C exports of all regions (Planchon et al., 2014).
955 The cause of the low export, at 200m depth, from the Polar Front bloom (Group 5
956 downstream stations) may in part be the shallowness of its high biomass surface layer
957 (only ~ half that of the recirculation feature and plateau; (Lasbleiz et al., 2014;Laurenceau
958 et al., 2014)), allowing for more remineralisation before export through the 200m depth
959 horizon.
960 The cause of the high export from the low biomass recirculation feature is less easy to
961 understand – it suggests that production (also found to be moderately high in these waters
962 compared to the other regions; (Cavagna et al., 2014)) and export have been in close
963 balance in these waters. This is a phenomenon often found in association with small
964 phytoplankton dominated communities, and attributed to tight coupling with small grazers
965 (Boyd and Newton, 1999;Cullen, 1995). Our observations show that this tight coupling
966 also persisted as very large, moderately to heavily silicified diatoms (Fig. 3) became

dominant. This suggests that tight coupling may have also been achieved for the larger phytoplankton. Notably there were abundant large~~r~~ herbivorous zooplankton in the recirculation region (Carlotti et al., 2014), and large fecal pellets as well as diatom aggregates were important contributors to export, based on observations in polyacrylamide gel filled sediment traps (Laurenceau et al., 2014). In making these comparisons among the station Groups, it is of course important to remember that our observations of nutrient depletion and export apply only at the this early spring observation time, and the subsequent evolution of the different water parcels may lead to different outcomes when averaged over the full annual cycle.

4.3 Influence of fertilisation time and persistence on ecosystem responses

As developed in the Methods section, we consider four possible relative indices for the nature of the Fe fertilization and the overall ecosystem responses:

i. Intensity of Fe fertilisation (lowest to highest):
recirculation feature < *plateau* <≈ *Polar Front plume* << *coastal stations*

ii. Elapsed time since Fe fertilisation and its persistence (most recent to oldest):
Polar Front plume < *recirculation feature* ~~<~~≈ *plateau* < *coastal stations*

iii. Magnitude of biomass accumulation (lowest to highest, at end of voyage):
recirculation feature < *coastal stations* < *plateau* <≈ *Polar Front plume*

iv. Elapsed time since initiation of biomass accumulation (most recent to oldest):
recirculation feature < *Polar Front plume* <≈ *plateau* << *coastal stations*

If we put aside the coastal stations, where depletion and export could not be estimated, we can ask which of these might explain why the recirculation feature achieved high export in comparison to its low to moderate biomass and low to moderate intensity of iron fertilisation. Index (ii) emerges as the most likely candidate – the recirculation feature

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receives low intensity ongoing iron fertilisation as a result of the recirculation of waters along the Polar Front and into it from the northeast (d'Ovidio et al., 2014), with possible augmentations from shallow Ekman transport from the nearby Kerguelen shelf (d'Ovidio et al., 2014;Sanial et al., 2014). This is a fascinating possibility, because it suggests ecosystems are modulated differently by persistent as opposed to punctual inputs of Fe.

~~Index~~ Indices (i) and (iv) also list~~s~~ the recirculation as an end-member, but it seems unlikely that low Fe levels or low~~er~~ biomass ~~is of itself a~~are driver~~s~~ of ~~low~~ high export, given that many studies of export have found positive correlations with biomass, though with significant modulation by community structure, e.g. (Boyd and Newton, 1995;Boyd and Newton, 1999;Boyd and Trull, 2007;Buesseler, 1998;Buesseler et al., 2001;Buesseler et al., 2007).

Do any of these indices also provide insight on why the community differs between the two strongly iron fertilised regions (the central plateau vs. the downstream Polar Front)? For size structure, none of the time perspectives (indices ii-iv) appears to help – the plateau and recirculation features with their dominance by very large diatoms (vs. the more balanced size structure of the coastal and downstream Polar Front bloom) do not fall appropriately along any of the time spectrums of these three 'clocks'. To the extent that the intensity of iron fertilisation (index i) may have been higher in both coastal and Polar Front waters than over the plateau, despite similar current Fe levels (see the Methods section for discussion), this could provide an explanation, but it would imply that more Fe produces communities with smaller cells and thus be counter to the results of artificial iron experiments (Boyd et al., 1999;Boyd et al., 2007). This leaves us with the strong possibility that the community structure differences between the plateau and Polar Front regions derive in part from other factors beyond levels, timing, or persistence of iron fertilisation.

5. Conclusions

A complex mosaic of phytoplankton blooms forms in response to natural iron fertilisation from the Kerguelen plateau. Community structure variations in the downstream waters appear to have multiple influences, including the intensity and persistence of iron fertilisation, the progress of biomass accumulation, and possibly whether they were sourced from plateau vs. coastal waters. These differences developed even though phytoplankton growth rates appeared to increase more directly with the level of iron availability, pointing to additional influences from trophodynamics. These community effects strongly decoupled levels of surface biomass from levels of particle export to the ocean interior over the timescales of spring bloom development studied here.

Tables

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Figure Captions

Figure -1. Map of KEOPS-2 station locations. The Kerguelen and Heard islands mark the northern and southern end of the central plateau (bathymetry in meters). The Polar Front jet that passes through the mid-depth channel south of Kerguelen Island is shown as a bold line. Full ocean depth flows of the Antarctic Circumpolar Current pass to the north of Kerguelen Island in association with the Subantarctic Front and to the south of Heard Island in the Fawn Trough. This latter flow follows the eastern slope of the plateau northwards to bring cold waters into a bathymetrically trapped quasi-stationary recirculation feature (d'Ovidio et al., 2014;Park et al., 2014a). Waters over the central plateau are also carried into this region. During the initial survey, the TNS transect was sampled first (south to north) and then the TEW transect (west to east). The E stations were designed to provide a Lagrangian temporal sequence in the recirculation region (including some to the east and west of its centre), with interspersed visits to the HNLC reference station (R2); the region of high biomass near and north of the Polar Front (F-L and F-S), and the central plateau bloom station (A3) previously studied in autumn 2005 by the KEOPS project. Two additional stations (G1, G2) carried out for high volume geochemical tracer studies and provided additional plateau and coastal samples, respectively. The stations are colour coded into 5 Groups as shown on the map (QGIS) and detailed in Table 1.

Figure 2. Temporal development of the Kerguelen bloom. Successive images of surface chlorophyll distributions (NASA MODIS-Aqua; SSALTO/DUACS 1 km daily product) show the bloom development. Image date 28 October: most stations of the initial survey downstream of Kerguelen Island (TNS 1-10, TEW 1-6), the HNLC reference station (R2, upstream) and the first visit to the KEOSP1 plateau reference station (A3-1 at the southern

1067 end of the TNS transect) were sampled before any significant biomass accumulation had
1068 occurred. Image date 06 November: The developing downstream Polar Front bloom (TEW
1069 7, TEW 8, F-L, F-S) was sampled early in its development, and the recirculation visited a
1070 second time (E2). Image date 11 November: the now well developed central plateau
1071 bloom was sampled (G1; E4-W) along with also blooming coastal waters (G2). Two more
1072 visits to the still low biomass recirculation were also completed (E3 and E4-E). Image
1073 date 18 November: the plateau bloom was re-sampled as it began to fade (A3-2 and E4-
1074 W2), along with the final recirculation station (E5). Bathymetry is shown by contours at
1075 1000, 2000, and 3000 m depths. A full annual animation of the phytoplankton bloom
1076 evolution is available in the ~~supplement~~Supplement.
1077
1078 Figure 3. Surface water total and size-fractionated POC and BSi concentrations.
1079 Top row: total POC and BSi concentrations for the identified station Groups (see Table 1);
1080 individual stations in each group are in chronological order from left to right. Middle row:
1081 POC size distribution spectra, i.e. concentrations normalised by dividing by the width of
1082 the size fraction (i.e. division by 4 for the 1-5 μm fraction); dotted lines provide visual
1083 guides and reveal little variation among groups for the smallest particles, and largest
1084 variations in the intermediate size fractions. Bottom row: BSi/POC ratios; grey band
1085 indicates approximate range of values for extant diatoms, with higher values possibly
1086 indicative of higher iron stress.
1087
1088 Figure 4. Isotopic variations in the size-fractionated particles.
1089 Top row: ^{13}C-POC values relative to ^{13}C-DIC values; dotted line shows the lowest values
1090 for the intermediate, autotrophic, size fractions samples as observed at upstream Fe poor
1091 reference station (R2). Bottom row: ^{15}N-PON values relative to co-located $^{15}N\text{-}NO_3^-$

values; grey band indicates values expected for phytoplankton that grow exclusively on nitrate.

Figure 5. Isotopic chemometric estimates of growth rates and f-ratios
Top row: Growth rates based on the supply vs. demand ^{13}C isotopic fractionation model (summed across the 4 smallest particle size fractions). Estimates from a limited set of ^{13}C tracer uptake incubations are shown as darker bars (measured at varying light levels and integrated to the mixed layer depth light level; (Cavagna et al., 2014)). Bottom row: *f* ratios, i.e. the fraction of total nitrogen nutrition provided by nitrate, based on the ^{15}N ammonium and ^{15}N nitrate end-member mixing model (summed across 4 smallest particle size fractions). Estimates from a limited set of ^{15}N tracer uptake incubations are shown as darker bars (Cavagna et al., 2014).

Figure 6. High resolution distributions of surface water properties from continuous sensor measurements.
Top to bottom: ship trajectory as revealed by dates of sampling; nitrate concentrations (from ISUS ~~UV~~ ultra-violet spectrometry), temperature, and salinity~~, ISUS)~~. Stations at the ends of the trajectories are indicated to aid in co-location with the lower resolution station sampling map (Fig. 1).

Figure 7. Example profiles of temperature, salinity, nitrate concentrations, and nitrate isotopic compositions. Top row: Group 3 central plateau station A3-2. Middle row: Group 5 downstream Polar Front station F-L. Bottom row: Group 5 Subantarctic station TNS-1. Depths of the remnant winter water T_{min} mixed layer depth (T_{min}-depth; solid line) and salinity stratification mixed layer depth ($S_{threshold}$-depth; dotted lines) are shown. These

depths define our two approaches for the calculation of depth integrated nitrate and silicate depletions (Table 4; Fig. 8).

Figure 8. Nitrogen and silicon depletion and export estimates

Top row: nitrate (light bars) and silicate (dark bars) depletions from the T_{min} winter concentration method. Middle row: nitrate (light bars) and silicate (dark bars) depletions from the $S_{threshold}$ winter concentration method. Bottom row: N (light bars) and Si (dark bars) export, as estimated from the $S_{threshold}$ depletion method, after accounting for the PN and BSi standing stocks integrated to 200m (Table 4; (Lasbleiz et al., 2014)). Group 4 coastal stations are not shown because CTD casts could not define winter values. Negative export values are not plotted (see Table 4 and text). Groups 1, 2, 3 and 4 are coloured as in Fig. 1 and are ranked from left to right with temporal order within each group.

Appendix A: Chemical and isotopic analyses

A1 Particle collection

The ship supply collected water from ~7m depth via a 10 cm diameter plastic hose extended through a vertical stainless-steel stand-pipe protruding ~1 m below the ship's forward hull. A sealed rotary propeller pump drew the supply through a 1000 μm nylon cylindrical pre-filter and distributed it via a manifold at more than 50 L min^{-1}, with most water returned over the side. This pre-filter was cleaned before each sample, and then a manifold valve was opened to supply a smaller flow of 8-10 L min^{-1} through our small volume bulk particle and large volume sequential filtration systems. The large volume size fractionation system passes the water through a 47 mm diameter 1000 μm screen (to remove any large particles that managed to pass through the pump pre-filter at higher flow rates), followed by 142 mm diameter Nitex nylon screens (300, 210, 50, 20, and 5 μm mesh sizes) and a final 142 mm diameter QMA quartz fibre filter (1 μm nominal pore size, Sartorius). The small volume bulk enclosed sample system rapidly fills a precisely known ~1 L volume and low pressure filters it through a QMA quartz filter (muffled and pre-loaded under clean conditions into in-line filter holders). Quartz filters were used in preference to glass to minimize ^{234}Th backgrounds and to give better combustion characteristics during elemental and isotopic analysis. The flow path allowed a larger flow rate through the larger meshes (Table 2). The very minor amounts of material on the 1000 μm screen were not analysed. Particles on the other nylon screens were immediately resuspended (1 μm filtered seawater from the sampling location) and refiltered onto 25 mm diameter, 1.2 micron pore size silver membrane filters (Sterlitech) and, along with the QMA filter (Sartorius T293), were dried at 60ºC. Following drying, the particles were examined under stereo-microscopy onboard the ship at magnification up to 50x, and then

1155 analysed non-destructively onboard for ^{234}Th activities (Planchon et al., 2014). All other
1156 analyses were carried out in the Hobart laboratories.
1157
1158 **A2 Particle analyses**
1159 Biogenic silica (BSi), Particulate organic carbon (POC), and particulate nitrogen (PN),
1160 δ^{13}C-POC, and δ^{15}N-PN analyses were carried out in Hobart. For BSi, a single 5mm
1161 diameter punch of the silver filters was analysed using an approach used previously for
1162 Southern Ocean samples (Queguiner, 2001). The biogenic silica was dissolved by adding
1163 4mL of 0.2M NaOH and incubating at 95°C for 90 minutes. Samples were then rapidly
1164 cooled to 4°C and 1mL of 1M HCl was added. Thereafter samples were centrifuged at
1165 1880 x *g* for 10 minutes and the supernatant was transferred to a new tube and diluted with
1166 artificial seawater (36 g L^{-1} NaCl). Biogenic silica concentrations were determined by
1167 spectrophotometry using an Alpkem model 3590 segmented flow analyser and following
1168 USGS Method I-2700-85 with these modifications: ammonium molybdate solution
1169 contained 10g L^{-1} $(NH_4)_6Mo_7O_{24}$, 800µl of 10% sodium dodecyl sulphate detergent
1170 replaced Levor IV solution, acetone was omitted from the ascorbic acid solution, and
1171 artificial seawater was used as the carrier solution. Biogenic silica standard concentrations
1172 were 0 µM, 28 µM, 56 µM, 84 µM,112 µM and 140 µM. Standard curves across all runs
1173 had an average slope of 48 438 ± 454 (1 s.d. *n*=4). The mean concentration of repeated
1174 check standards (140 µM) was 139.85± 0.31 µM (n=68). The average blank value was
1175 0.009 ± 0.006 µmoles $punch^{-1}$ (1 s.d. *n*=5), equating to 0.08% of the mean of 50 µm
1176 fraction samples (highest concentrations) and 1.22% of the mean of 300 µm fractions
1177 (lowest concentrations).
1178 For the POC and PN analyses, 3 x 5mm punched sub-samples of the 25 mm diameter
1179 silver membrane filters were placed in acid-resistant silver capsules (Sercon SC0037),

1180 treated with two 10 µL aliquots of 2N HCl (and 2 x 20 µL for the bulkier QMA filter sub-
1181 samples, 5 x 5mm punches) to remove carbonates (King et al., 1998), and dried at 60 ºC.
1182 A first set of sub-samples was analysed for POC and PN concentrations by combustion of
1183 the encapsulated samples in a Thermo-Finnigan Flash 1112 elemental analyser with
1184 reference to sulphanilamide standards in the Central Sciences Laboratory of the University
1185 of Tasmania. Precision of the analyses was ~1 %, but the overall precision was limited to
1186 5-10 % by the sub-sampling of the filters that often had patchy or uneven coverage. Based
1187 on the POC and PN results, a third set of sub-samples was punched for isotopic analyses
1188 with the number of punches adjusted to ensure similar voltages within the dynamic range
1189 of the spectrometer.

1190 δ^{13}C-POC and δ^{15}N-PN on the silver filters were analysed separately using a Fisons
1191 NA1500 Elemental Analyser coupled via a Con-flow IV interface to a Finnigan Delta
1192 V^{PLUS} isotope ratio mass spectrometer at CSIRO Marine and Atmospheric Research with
1193 separate oxidation and reduction columns installed. For the QMA filters, a Flash 2000
1194 EA1112 HT Thermoscientific was fitted with a single combined oxidation/reduction
1195 column with dead spaces minimised for improved precision at <20µg N. During all ^{15}N
1196 analyses, CO_2 was removed using a sodium hydroxide scrubber (self-indicating Ascarite 2,
1197 Thomas Scientific) to avoid CO^+ interference at m/z 29 and 28 (Brooks et al., 2003). The
1198 δ^{15}N and δ^{13}C isotopic compositions are expressed in delta notation vs. atmospheric N_2
1199 and the VPDB standard, respectively. Standardization was by reference to CO_2 and N_2
1200 working gases injected before and after each sample, with normalization to solid reference
1201 materials inserted (along with blank cups) after each 6 samples. For δ^{13}C, the solid
1202 standards were NBS-22 oil (RM8539, -29.73 ‰) and NBS-19 (limestone, RM8544,
1203 +1.95 ‰), and casein (Protein Standard OAS B2155 batch 114859, Elemental
1204 Microanalysis, δ^{13}C +5.94 and δ^{15}N -26.98). For δ^{15}N, the solid standards were IAEA-N1

(ammonium sulphate, RM8547, +0.43‰) and IAEA-N3 (potassium nitrate, RM8549, +4.72 ‰) and casein (as above). Based on replicate analyses of these standards the estimated precisions were typically 0.1‰ or 1 standard deviation for both $\delta^{13}C$ (n=15) and $\delta^{15}N$ (n=20).

Sample replicates generally had comparable precisions to the reference materials, but filters with patchy coverage had lower precision (0.3‰ in the worst cases, presumably reflecting isotopic heterogeneity within the size fractions). In addition, a small correction of ~~(~~<+0.4‰ was made to the QMA filter results after indirect ~~measurement~~ estimation of the blank ~~(Avak and Fry, 1999)~~ $\delta^{13}C$ ~~=~~ to be -29.6 (Avak and Fry, 1999), at ~10% of the sample signal strength~~(Avak and Fry, 1999)~~. Procedural blanks were measured by passing 1 litre of seawater through the onboard pumping system and subsequent processing in parallel to the samples, and yielded negligible amounts of POC and PN (<1% of typical samples), and with ratios close to those of the samples, and no correction was applied.

A3 Dissolved component analyses

Underway nitrate concentrations were mapped using an ultra-violet nitrate sensor (ISUS V3, Satlantic), calibrated 3 times during the voyage against sea water nitrate standards (~15, 20, 25, 30 μM) , with additional comparisons to nitrate samples collected from the underway supply at every station sampled for particle analyses, yielding precision of ~1.5 μM. Nitrate concentrations for these samples and the CTD-Niskin bottles were measured onboard using a segmented flow spectrometric autoanalyser, with precision of ~0.1 μM. The N and O isotopic compositions of dissolved nitrate were measured via its bacterial conversion to nitrate to nitrous oxide followed by isotope ratio mass spectrometry at the Vrije Universitait Bruxelles, with precision of approximately 0.2‰

for $^{15}N\text{-}NO_3$ and of 0.4‰ for $^{18}O\text{-}NO_3$ (further analytical details are provided in Dehairs et al., 2014).

Samples for measurement of the carbon isotopic composition of dissolved inorganic carbon were collected in 10mL Exetainer vials, with airtight septa, by filling the tubes from QMA filtered (~0.8 μm) underway supply and preserving them by addition of 20μL of saturated mercuric chloride. 1mL aliquots were withdrawn and injected into acid washed, helium flushed Exetainer tubes. 100μL of ortho-phosphoric acid (99%, Fluka) was injected and the headspace equilibrated at 25°C for 18 hours (modification of Assayag et al., 2006). Solid NBS19 $CaCO_3$ (200 to 230ug, $\delta^{13}C$=+1.98, *n*=10 standard deviation 0.02), and bulk quality assurance sediment trap material (1200μg, 12.9%CaCO3, $\delta^{13}C$=+2.9), was weighed into smooth wall tin capsules (5x5.5mm SC1190, Sercon) and lowered into the Exetainer tubes, purged, then 1mL of DIC free sea water added before proceeding as for the samples. Blank, standard and sample headspaces (one standard after each 5 samples) were sampled using a Finnigan GasBench2 (Thermoscientific) fitted with a 100μL sample loop. The headspace gases from the Gas Bench were analysed (continuous flow) by the DeltaV^{Plus} isotope ratio mass spectrometer and Isodat 3 software at CSIRO Marine and Atmospheric Research.

The Supplement related to this article is available online at doi:10.5194/bgd-11-13841-2014 supplement.

File: Animation_keops2bloom2011_2012.mp4

The animation shows a full annual cycle of phytoplankton bloom development over and downstream of the Kerguelen plateau from daily 8km resolution NASA MODIS Aqua chlorophyll images. The images were provided by SSALTO/DUACS at CLS with support from the Centre Nationale des Etudes Spatiales, Toulouse, France.

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