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

by S. Blain et al.

Anonymous Referee #1

Received and published: 18 August 2014

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

Specific points:

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

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

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

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

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

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

We thank the referee for this suggestion which in principle could give additional support to our hypothesis of the age of the bloom. The comparison of the age of the bloom based on the nutrient drawdown would require a good estimate of the concentrations of nutrients before the bloom. At A3, we measured nutrient concentrations of NO3 and PO4 during the first visit which preceded the bloom, but for F-L the estimate is problematic because we did not visit this station before the bloom, and the location of F-L north of the polar front precludes to derive this value from the nutrient concentration at the depth of the winter water. Additionally, the occurrence of internal waves and episodic deepening of the mixed layer resupplied the mixed layer with nutrients, which lead to large uncertainties in the estimate of the drawdown due to biology. Thus, we prefer not to present this calculation in the manuscript.

Minor points:

Page 9950, Line 18: I believe you mean '…the occurrence of a subsurface minimum of N*…'

Correction done

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

The text was modified in the following way:

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

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

Done

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

We removed this sentence

Page 9953: Quéroué et al. 2014 didn't appear in the reference list.

Added

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

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

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

Yes, the legend was modified

"Figure 9: (a) Comparison of concentrations of NO_3^- versus PO_4^{3-}. Dots denote the samples and lines show different values of $N^* = NO_3^- - r_{N:P} PO_4^{3-}$ (b) Comparison of concentrations of TDN versus TDP. Dots denote the samples and lines show different values of $TNxs = TDN - r_{N:P} TDP$"

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

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

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

Anonymous Referee #2

Received and published: 10 September 2014

General comments:

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

Specific comments:

Abstract:

Please revise accordingly after revising the other sections.

C5050

Introduction:

Page 9951, L17: please use "air-to-sea flux of CO2".

done

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

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

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

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

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

We have added here the reference Wang et al. 2003

Materials and methods:

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

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

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

We have added a new paragraph in the analytical method section "For NO_3^-, NO_2^-, PO_4^{3-}, one sample was immediately analyzed aboard with a segmented flow analyzer (Skalar) equipped with colorimetric detection using methods described in Aminot, 2007. The accuracy of the methods was assessed using reference material (Certipur, Merck). The precision was in the range 1-4 %, and the limit of detection was 0.02 µM for $NO_3^-$and NO_2^-, 0.03 µM for PO_4^{3-}.

Results:

The first paragraph belongs to the M&M.

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

Please rephrase: page 9953, line 17;

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

page 9954, L17-19

It now reads: Above 150m, NO_2^- concentrations were clearly higher at the stations in the polar front zone (PFZ)(NO_2^- in the range 0.3-0.4 µM) than at those in the Antarctic Zone (AZ)(NO_2^- of 0.25 µM).

and L23-25;

At Stations TEW-1, concentrations of NH_4^+ increased from 0.19 µM (at 10m) to 1.45 µM (close to the bottom). The same trend was observed at TEW-2 (0.17 µM at 10m and 0.39 µM close to the bottom).

page 9955, L1-3

. It now reads:

DON concentrations above the Kerguelen plateau at Stations A3-1 and TNS-10 (6.0±1.0 µM) were similar DON concentrations in the meander of the PF 6.4±1.7 µM (stations TNS-3 to TNS-7). But higher values were detectable north of the PF (8.6±1.2 µM for stations TNS-1 and TNS-2)

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

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

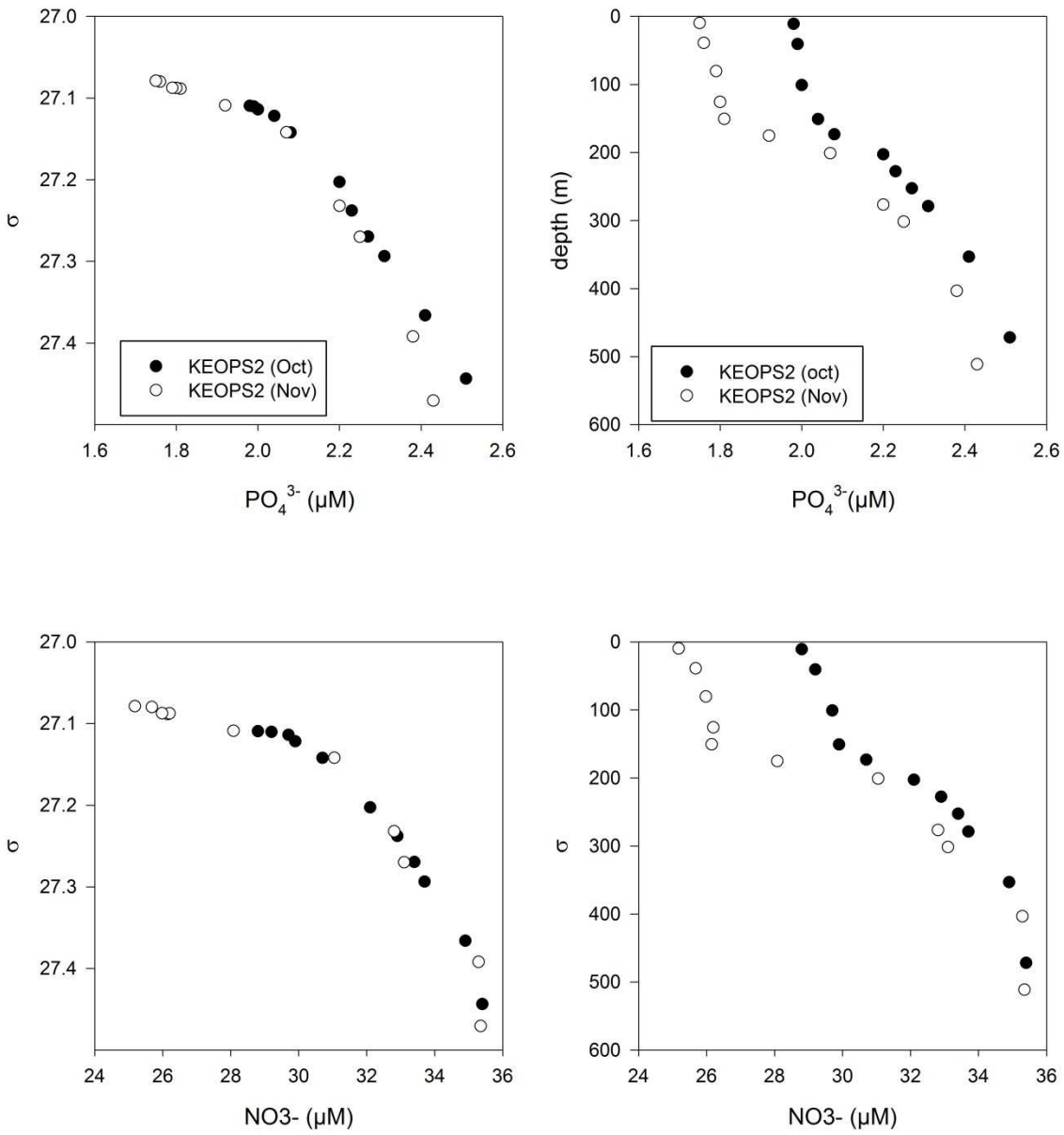
The vertical distribution of different chemical nitrogen species during the two visits at station A3 are detailed in figure 4. NO_3^- distributions are discussed in more detail in the section 3.3. Concentrations of NO_2^- were, during both visits, homogeneous in the mixed layer and revealed a small maximum below the mixed layer depth (MLD). NO_2^- increased from 0.27 µM at A3-1 to 0.33 µM at A3-2 (Fig. 4b). NH_4^+ concentrations roughly doubled between the two visits (0.1 µM at A3-1 to 0.2 µM at A3-2) and clear maxima were detectable at the base of the mixed layer. Concentrations of DON did not change between visits, however DON accounted for 20% of TDN in the mixed layer at A3-1, and this contribution increased to 25% in the upper 40 m water layer at A3-2. Both NO_3^- consumption and DON release during the 4 weeks that separated the two visits explained the increase in the percent DON of TDN. Below 200 m, TDN was higher at A3-1 than at A3-2. This was mainly driven by the differences in DON concentrations that were higher at A3-1 (4.7-6.7 µM) than at A3-2 (1.8-4 µM) in the 250-300 m layer (Fig. 4).

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

New version : "At Station A3, vertical profiles of changes of NO_3^- and PO_4^{3-} concentrations were observed between spring and summer (Fig. 8). Albeit the stations were sampled in November 2011 and February 2013, we consider these variations as seasonal changes".

I would think that this section could be moved to the discussion section because (1) there may be uncertainties in your estimates of stocks given that there is a considerable difference in PO4 concentration below 200 m between Oct and Nov, 2011;

We agree that there is some variability in the vertical profiles of PO_4^{3-} and NO_3^-, but the reasons for the variation below 200m between October and November 2011 are related to internal waves. This is demonstrated by the plot below where the two profiles are very similar if sigma is considered in place of depth.



(2) the authors may calculate the ratio of depleted NO3 and PO4, which is relevant (see page 9959, line 20-28).

We have calculated the ratio of integrated N/integrated P for the three time points. They are quite similar: 14.6 in winter, 14.5 at the first visit, 14. 5 at the second visit and 13.6 in February. However, as mentioned in the manuscript it is better to consider N* or TNxs to address the decoupling between N and P. This approach is presented in Fig 8 and discussed at the end of the discussion section.

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

done

Discussion:

Page 9959, L7-10: please reword.

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

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

Nitrate to phosphate ratio is often <16 in the Southern Ocean, and there has been evidence of subsurface minimum of NO3:PO4 ratio (e.g., in AU9309 and AU9706), which would lead to minimum N* in the subsurface.

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

Figures:

Please use the same orders for labels and sub-plots. For example, in Fig 4, both A3-1 and A3-2 may have an order of NO3, DON, TDN, andin labels; Figs 5 and 6 have similar problems; Figs 7 and 8 should use the same order, e.g., (a) nitrate and (b) phosphate.

Done and legend of figures modified accordingly.

Blain et al. Biogeosciences

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

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

by S. Blain et al.

Anonymous Referee #3

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

1. Materials and Methods.

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

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

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

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

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

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

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

done, see response to comment c.

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

Modified according to the recommendations of the referee :

In the method section

"This provides the concentrations of Total Dissolved Nitrogen (TDN) and Total Dissolved Phosphorus (TDP). The concentrations of DON and DOP were calculated as follows; DON=TDN-[NO_3^-]-[NO_2^-] and DOP = TDP-[PO_4^{3-}]"

in the discussion section

"In the case of KEOPS2, the contribution of DON and DOP to TDN and TDP could reach 30%. We have therefore considered TDN and TDP at all KEOPS2 stations where these measurements were available (Fig. 9b)."
see also response to comment 2.e.

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

Done

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

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

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

2. Results

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

done: "(~0.3 mg m^{-3}) (Lasbleiz et al. 2014)"

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

Yes

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

Done

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

Done

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

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

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

The sentence was modified as follows :

"Below 200 m, TDN was higher at A3-1 than at A3-2. This was mainly driven by the differences in DON concentrations that were higher at A3-1 (4.7-6.7 µM) than at A3-2 (1.8-4 µM) in the 250-300 m layer (Fig. 4)."
See also other changes already mentioned in response to comments 1.e.

f. Section 3.2.2, 2nd line. Is 0.39 uM significantly different from 0.22 uM NO2?

The precision of measurement of NO_2^- is around 4%. Thus we think these values are significantly different.

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

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

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

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

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

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

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

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

j. Section 3.3.1.The authors should explain why the NO3 concentrations from ANTARESS 3 are acceptable/intercomparable with the present study. They mention only why PO4 is not.

NO3 concentration in the deep water, including in the winter water, were very similar for ANTARES3 and KEOPS2. There was no systematic shift observed for nitrate as observed for phosphate. Therefore, NO3 concentrations of ANTARES were considered as "oceanographically" consistent.

3. Discussion.

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

Done

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

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

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

Done

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

Done

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

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

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

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

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

Done