

## ***Interactive comment on “An assessment of the vertical diffusive flux of iron and other nutrients to the surface waters of the subpolar North Atlantic Ocean” by S. C. Painter et al.***

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Response to Reviewer 2

This manuscript reports diffusive flux of Fe, Al and macro-nutrients from below surface to surface layer in the North Atlantic Ocean. Authors conducted observational study and measured diffusivity by free-fall microstructure shear profiler, with measurement of dissolved Fe, dissolved Al and macro-nutrients profiles at 21 point in the sub-polar gyre in summer (July-August). Authors evaluate the fluxes quantitatively, with comparison to integrated mixed layer inventory, phytoplankton demand, winter convective nutrients supply, and Fe flux from the dust supply. They also discussed stoichiometry of diffusive

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supply and nutrient budgets in the surface layer. Authors concluded that diffusive nutrients fluxes in sub-polar gyre in summer (period of annual nutrient minima) are small magnitude, and not alleviate Fe limitation in this region. Over all, this topic “Quantitative evaluation of Fe and nutrients flux to surface” is extremely important issue for studying biogeochemistry in the Ocean. There are still many uncertainty in this topic. In this manuscript, authors adequately estimate and discuss about the diffusive Fe and nutrients fluxes in the North Atlantic sub-polar gyre based on their observed data set. Observation for Fe and nutrients profiles with physical turbulent mixing parameter are invaluable data set to understand nutrients fluxes from below surface. Comparison of the diffusive flux to other Fe supply processes and evaluate the budget in surface layer are important for understanding contribution of each Fe supply processes on biological responses, and authors clearly discuss this point in the manuscript. Their data is good quality and interpretations from the data are persuasive. Manuscript is well written. Therefore, this study contributes to understand the processes that control biogeochemical cycles in the North Atlantic Ocean. I recommend that this manuscript should be published in BG, after minor revision.

A: We thank the Reviewer for their time and critique of the paper.

General comments: The most valuable point in this study is evaluation of diffusive nutrients (Fe and macronutrients) fluxes, quantitatively, based on their observed data set. Readers will be able to understand calculated results for the fluxes by reading this manuscript. Diffusive fluxes were estimated by multiplication of diffusivity and vertical gradient of nutrients distributions. Authors clearly show the results of vertical profiles of physical parameters (especially K: turbulent diffusivity), however, vertical profiles of nutrients profiles are not shown in the manuscript. Therefore, it is not clear for readers that how did authors select the Fe and nutrient gradient from each profiles, which are very variable as authors indicated. This is very essential for evaluating the fluxes, therefore, authors should make clear this point to readers.

A: Nutrient and dFe concentrations were measured on the same CTD cast, though

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occasionally with differing vertical resolutions, and to account for this the data were handled in the same way. We extracted the gradients for the same depth in each profile (i.e. mixed layer depth) following the linear interpolation of data to a 1 m grid and the calculation of gradients between sequential depth bins. It was not clear in the original text that we had calculated gradients in this way so we have modified section 2.5 to include the sentences “Profiles of nutrient concentration were first linearly interpolated onto a regular 1 m grid to compensate for irregular sampling depths and nutrient gradients were then calculated between sequential depth bins. This approach made the extraction of nutrient gradients a slightly less subjective issue than trying to estimate mean gradients but also had the further benefit of allowing us to use a diffusivity value representative of a particular part of the water column.”

Authors describe in the manuscript that “Profiles of nutrients concentration were first linearly interpolated on to regular 1m : : : : : : : : : : .. and to allow for extraction of the nutrient gradients AT MIXED LAYER DEPTH (P18522, 19-21). ”. I do not understand the gradients “at the mixed layer depth” (or sometimes “base of the mixed layer” in the text). Were there nutrients gradient in the mixed layer depth even mixing occurred?

A: This is related to the comment above. To estimate nutrient fluxes we took the nutrient gradient at the mixed layer depth and combined this with a coincident measurement of the turbulent diffusivity. We think the confusion has arisen from the fact that the mixed layer depth can be precisely defined (e.g. 29 m) whereas the gradient is calculated over a broader depth range (e.g. 28-30 m). As described above we have modified section 2.5 to inform the reader how our gradients were defined.

Authors also report that there were subsurface maxima and minima in the Fe profiles, as showing in Fig. 3. I agree to author that this features were real (P18527, 11) and the subsequent calculation of the diffusive flux could be skewed by the sign of gradient (P18527, 8-9). However, I can't understand from the text and Fig.3 that how did authors select the gradient from these three types of the profiles? In my understanding,

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gradient from the bottom of mixed layer to below the mixed layer (nutrient increasing depth) is the most important gradient for estimating upward fluxes into surface layer. I understand that their Fe and nutrients profiles will be published elsewhere, however, evaluating the fluxes are the most important for discussion in this manuscript. Therefore, authors should explain more clearly in the manuscript that how did authors select Fe and nutrients gradient from each profiles.

A: Figure 3 was presented to summarise the difficulties we had in extracting Fe gradients in situations where the traditional “nutrient like” profile of increasing concentration with depth was not the case. As noted by the Reviewer, this can significantly complicate the derivation of Fe gradients from vertical profiles particularly when the depth of interest (such as the mixed layer) appears to be located at a point of inflection rather than cutting through a gradient. To account for the occasional difference in vertical sampling resolution between nutrient and Fe measurements we decided to interpolate the data to a regular 1 m grid and calculate gradients between sequential depth bins, which had the benefit of making the extraction of nutrient gradients a slightly less subjective issue. This also had the further benefit of allowing us to use a diffusivity value representative of a particular part of the water column. As a result and in all instances it became self evident from the data whether we had a situation where concentrations were decreasing as you crossed into the mixed layer (as was the case for the macronutrients) or increasing (as was often the case for Fe). We have modified section 2.5 to inform the reader how our gradients were defined.

Minor comments: P18520, 24: How long were the nutrients samples in the storage? Were nutrients samples measured onboard (or onshore)?

A: All nutrient samples were analysed onboard. Nutrient analysis usually started immediately after sample collection but when samples were collected overnight they were refrigerated for a few hours (<4 hrs) before analysis. We have added this information to the revised text as follows “Water samples for the determination of total nitrate (NO<sub>3</sub>- + NO<sub>2</sub>-, hereafter NO<sub>3</sub>-), phosphate (PO<sub>4</sub><sup>3-</sup>) and orthosilicic acid (Si(OH)<sub>4</sub>) concen-

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tration were drawn directly from CTD Niskin bottles and from the ship fitted non-toxic underway water system (5 m intake depth) into clear polystyrene vials and if not immediately analysed were stored (<4 hrs) in the dark at 4°C whilst awaiting analysis.”

P18521, 18-23: About Fe and Al measurement. Authors only inform to readers “Filtered water samples”. Which filter (type, pore size) did they use to measure dissolved fraction? Did authors measure international reference materials (SAFe or GEO-TRACES) for certify their obtained value? If authors measured these reference materials, they should report in the text.

A: All trace metal water samples were filtered using a Sartobran 300 MF 0.2 µm filter cartridge prior to analysis. We have added this additional information on filter brand/pore size to Section 2.3. All analyses were conducted against SAFe reference material D2 and S; details of this will appear in subsequent publications by Steigenberger et al (dFe) and Klar et al., (dAl).

P18524, 15-16: Need reference for determine Vd value (set to 1 and 0.1 cm/s).

A: Our choice of dry deposition velocities (Vd) derives from Duce et al., (1991). This reference has been added to the revised text.

P18524: In equation (3), atmospheric concentrations is represented by “Caero”. In equation (4) aerosol concentrations is represented by “CA”. Are those same? If those are same, the symbol should be unified. If those are difference value, please explain the differences between “atmospheric concentrations “Caero” and aerosol concentrations “CA”. In Table 6, “aerosol soluble Fe (Al) concentration” appear. This should be unified, too.

A: We thank the Reviewer for highlighting an inconsistency. Equation 4 has now been corrected to match equation 3. Caero is now used throughout to signify atmospheric concentrations. We have also added the symbols Caero and Fdry to the column headers of Table 6 to aid the reader.

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P18525, 20: Please indicate “East Greenland Current” in Fig. 1. This is helpful information for readers.

A: Although the Greenland Current is an important consideration for the interpretation of a very small subset of our data it is one of several major currents that can be found within the North Atlantic subpolar gyre. We have not added this current to Figure due to the small scale of the current relative to the area shown by Figure 1. For further details of the East Greenland Current we direct the Reviewer and interested readers to Wilkinson and Bacon (2005).

Wilkinson, D. and S. Bacon (2005). The spatial and temporal variability of the East Greenland Coastal Current from historic data. *Geophysical Research Letters* 32, L24618, doi: 24610.21029/22005GL023232.

P18525, 13-20: “Exceptions to this general pattern : : : : : : : : : : ..East Greenland Current (Bacon et al., 2005; Wilkinson and Bacon, 2005)”. This feature is difficult to identify in Fig.2 for readers. Fig. 2 is too small and low resolution to see the two stations.

A: We apologise to the Reviewer for the quality of the figure that was in the reviewed version of this manuscript but this was outside of our control. The data points can be seen in the pdf if the reader zooms in.

P18526, 14: Please indicate “Rockall Trough” in Fig.1. This is helpful information for readers.

A: We have added this identifier to Figure 1.

P18526, 20- P18527, 14: Additional drawing of gradient line on the three types of profiles in Fig. 3 is helpful to understand the gradient in the profiles. Please add each data points on each profiles in Fig. 3.

A: Data points on each profile have been resized for clarity. The addition of lines to indicate the approximate gradient are not needed as this is adequately described in

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the text.

P18528, 15: Please indicate “Hatton Bank” in Fig. 1. This is helpful information for readers.

A: Hatton Bank is labeled in Figure 1

P18530, 24-25: Authors estimated annual diffusive flux of Fe,  $0.64 \text{ umolFe m}^{-2} \text{ yr}^{-1}$  and  $0.46 \text{ umolFe m}^{-2} \text{ yr}^{-1}$ , in the Iceland basin and the Irminger basin. In this calculation, they multiplied 365 days to daily diffusive flux value. However, active convection period should not count for this calculation (convection reach down several hundred meter, and mixed well in the water column, then profile of nutrients do not have gradient in the several hundred meter).

A: Given the inherent uncertainty in our subbasin estimates of median dFe and dAl fluxes due to the considerable variability in flux magnitude and even flux direction between stations our annual diffusive flux calculation can only be considered as an approximation. The Reviewer is correct that we have assumed the median flux can be extrapolated across a full year and that we have not taken into account seasonal changes to subsurface gradients of dFe and dAl. However, whilst we acknowledge this to be a relatively important consideration it is ultimately a minor factor. Our reasoning is that the magnitude of the diffusivity term is unlikely to change significantly on seasonal timescales and any change to the vertical gradients of dFe and dAl may very well be similar to the wide range of subsurface gradient estimates we obtained in this study and subsequently used to calculate the median flux. It is possible that at certain times of the year the vertical gradients all result in positive upward diffusive fluxes when the water column is mixed and subsurface maxima and minima are removed but it is not clear if the gradient itself will exceed the range of values reported here as we would expect the gradient to decrease to zero in a homogenous water column. It is possible therefore that some of the largest gradients were observed during this study. We do make clear in the text that there is significant variability in the data and conse-

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quently some uncertainty over the annual diffusive flux supply even though our results are comparable to previous studies. The deepening of the mixed layer and the annual convective supply are distinct processes that are addressed in section 3.8.

P18531, 22-26: In the text, authors discuss integrated primary production rate using a unit of “gC m<sup>-2</sup> d<sup>-1</sup>”. In the Table 1, authors use the unit of “mmolC m<sup>-3</sup> d<sup>-1</sup>” for uptake rate. These should be unified.

A: The data in Table and 1 and the text of page 18531 are not exactly equivalent. Table 1 presents averaged volumetric estimates of surface primary production for several subsectors of the North Atlantic subpolar gyre typically based on 1 sampled depth (and not a series of measurements that we could integrate). In the text however we report integrated rates of new production based on NO<sub>3</sub>- uptake, which we then compare to annual estimates of new production from the literature. The difference in units is appropriate for the presentation of the data.

P18532, 8: I could not find supplement Fig. 2 in the BGD web site.

A: This was outside our control and having looked we could not find it either. We will discuss this with the Editor.

P18537, 5-7: “Thus, we can only conclude that: : : : : : : : : : :the seasonal productivity in this region”. Is this true? I think summer diffusive flux from below is important for supporting summer phytoplankton production, although surface nutrients concentration apparently depleted or low.

A: We are puzzled by this comment as our statement is supported by the data presented in this manuscript. Although surface nutrient concentrations could be low (e.g. surface NO<sub>3</sub> varied from <0.1 to 6.47 umol litre) on an integrated basis the availability of NO<sub>3</sub> (17-310 mmol m<sup>2</sup>) within the mixed layer was far larger than the diffusive fluxes into the mixed (20-391 umol m<sup>-2</sup> d<sup>-1</sup>). We could not link these minor diffusive fluxes to the seasonal productivity of the region in a significant manner and maintain that the

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diffusive nutrient fluxes are of minor significance for the seasonal productivity of the region.

P18539, 15-17: Between 20 and 40 m : : : : : : : : : : ..Fe cycle of the subpolar North Atlantic.” I could not identify this feature (dFe:N ratios increased lending) in Fig. 7.

A: This comment relates to the change in gradient in dFe:NO<sub>3</sub> that can be seen in many of the vertical profiles presented in Figure 7.

P18540-18541, section 4.3.1: I am interested in dFe:N ratio in the period of convection (in mixing water column). This ratio is very important to determine limiting nutrients at the end of spring bloom. Authors can compare the ratio between convective mixing supply and diffusive supply. (Compare the dFe:N concentration ratio of bottom depth of winter convective mixing to the dFe:N ratio which is obtained from vertical dFe gradient/ N gradient).

A: This calculation has proven to be rather interesting and as a result we have added the following paragraph to Section 4.2. We thank the Reviewer for this suggestion. “Based on the concentrations of NO<sub>3</sub> and dFe found at the maximum depth of convective winter mixing for 2010 we estimate that the dFe:NO<sub>3</sub>- ratio of the convective supply to have been 0.019 and 0.039 umol:mmol m<sup>-3</sup> for the Irminger and Iceland Basins respectively. These estimates are comparable to the mean dFe:NO<sub>3</sub>- ratio in the diffusive supply of 0.03:1 umol:mmol m<sup>-3</sup>, and suggests that there may only have been small differences in the supply ratio of dFe:NO<sub>3</sub>- during the convective period compared to what is supplied during the rest of the year via diffusion. However, it is worth noting that from the profile data shown in Figure 7 a slightly higher mean dFe:NO<sub>3</sub>- ratio of 0.06 umol:mmol m<sup>-3</sup> can be calculated for the upper 100 m of the water column. This ratio is heavily influenced by the input of Fe at the sea surface, and if the upper 30 m of observations are excluded (i.e. the mixed layer where the mean dFe:NO<sub>3</sub>- ratio is 0.13 umol:mmol m<sup>-3</sup> but also highly variable) the ratio reduces to 0.028 umol:mmol

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m<sup>-3</sup>, similar to the deep water values and comparable to the diffusive supply ratio. This near surface elevation in dFe:NO<sub>3</sub>- ratios suggests that input of Fe to the mixed layer, presumably from the atmosphere, can have an important role in increasing dFe:NO<sub>3</sub>- ratios and hence in increasing the likelihood of nutrient drawdown and in the alleviation of Fe limitation. The significance of the convective supply for summer productivity may therefore be rather small but this conclusion requires further investigation.”

What is NO<sub>3</sub>- in the Table 1. Need explanation in caption. Additional information on N;P, N:Si and Fe:N ratio in Table 1 is helpful information for readers.

A: Table 1 represents the mean surface conditions/ nutrient concentrations based on data collected during this study. We have now corrected the table legend to read as follows “Table 1: Mean ( $\pm$  1 S.D.) surface conditions, productivity rates (where sampled) and nutrient concentrations in various subsectors of the subpolar gyre as measured in July-August 2010. All state measurements are based on samples collected from the ship’s non-toxic underway water supply (nominal depth 5m). The surface productivity rate measurements are based on water samples collected via CTD cast (<10 m depth).” We do not think it appropriate to include mean nutrient ratios in this table as there is a detailed discussion of these in the text (Section 3.3) and they can be easily calculated from the data in Table 1 should they be required.

Throughout the manuscript, authors estimate diffusive supply relative to surface nutrient pool (integrated nutrient standing stocks value in mixed layer). However, the unit of diffusive nutrients fluxes are “mol m<sup>-2</sup> d<sup>-1</sup>” and the unit of integrated nutrient standing stocks are “mol m<sup>-2</sup>”. In fact, diffusive flux should be multiply “day number” for this comparison (“one day” in this comparison in the manuscript). Therefore, to compare these number, authors should use a word of “daily diffusive flux”. In abstract, they clearly use “daily macronutrient flux into surface layer”, but some place in the text, they did not use. Table 4 also should change to “daily diffusive supply relative to pool (%)”.

A: We thank the Reviewer for highlighting this detail. Throughout the manuscript we are

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indeed referring to daily diffusive fluxes, though at times we may use the simpler phrase “diffusive flux”. We have now clarified this at several points throughout the manuscript. Column headers in Table 4 have been relabeled as suggested.

Fig. 3: Add data point on the profiles. Explain “Zmld”, “Zeu” in the caption.

A: We have now defined Zmld (mixed layer depth) and Zeu (euphotic depth) in the legend to Figure 3. Data points were indicated in the original version of this figure but were too small to see clearly. We have resized them.

Fig. 6: Add data point on the profiles of Fe.

A: We have added data points to the Fe profiles in Figure 6.

Ideally, this manuscript should be published with a report of Fe and Al and nutrients profiles. In the manuscript, authors indicate these profiles are published in elsewhere (P18521, 12). If it is possible, please add the information on the other publication, which include profiles, on the reference list.

A: At the time of writing we are unable to provide further details on where the full dFe and dAl dataset will be published as there has been a delay in the completion of these related manuscripts. This is something that we are attempting to resolve with some haste due to the significance of the formal description of the iron field for a number of other papers. It is anticipated that a submission will occur during 2014. Although this is far from satisfactory we have tried to provide as much explanation as possible in the present paper without compromising these evolving papers. All being well Steigenberger et al (dFe) and Klar et al., (dAl) will be available soon. We apologise to the Reviewer and to interested readers for this situation.

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Interactive comment on Biogeosciences Discuss., 10, 18515, 2013.