

## Response to Reviewer #2

I have embedded specific responses to Reviewer #2's detailed and helpful comments below. Reviewer comments are in italicized text and my responses are in plain text. Excerpts from the revised text are in bold.

-Brendan and coauthors

### Reviewer 2:

*Carter et al. introduce a new composite tracer  $Alk^*$  in order to 'isolate the impact of acidification on biological calcification and remineralization' (abstract). Total alkalinity (AT) in the ocean changes due to several processes: (1) evaporation/precipitation, (2) formation of organic matter by phytoplankton, (3) remineralization of organic matter, (4) formation/dissolution of  $CaCO_3$ , (5) redox processes in marine sediments and in the water column, (6) riverine input of water with varying alkalinity (usually, however, not always smaller than mean seawater concentrations). Carter et al. are especially interested in (4) formation/dissolution of  $CaCO_3$ , which is difficult to quantify for the world oceans. They propose a new tracer ( $Alk^*$ ) that should ideally be a tracer of  $CaCO_3$  cycling alone.*

*The definition of  $Alk^*$  is a bit more tricky than for other \*-quantities:*

$$Alk^* = AT + 1.26 * [NO_3^-] - S * \text{mean}(AT + 1.26 * [NO_3^-]) / \text{mean}(S) \{Alk^*_{def}\}$$

*where the mean values are calculated over the 'top 50 meters of the ocean' (actually averaged vertically as well as horizontally yielding a value of  $66.4 \text{ mol kg}^{-1}$  for  $\text{mean}(AT + 1.26 * [NO_3^-]) / \text{mean}(S)$ , compare Eq. 5), AT is the total (or titration) alkalinity and S is the salinity. The term 1.26 times the nitrate concentration takes care of AT changes due to formation of organic matter by phytoplankton (uptake of nitrate, phosphate, sulphate) or the remineralization of organic matter. The value of the coefficient can be either taken from observations (1.26 based on Kanamori and Ikegami, 1982) or derived from the stoichiometry (N:P:S; Redfield & extensions; for details compare Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Körtzinger, A., and Dickson, A. G.: Total alkalinity: the explicit conservative expression and its application to biogeochemical processes, *Marine Chem.*, 106, 287–300, 2007.) of phytoplankton.*

*The sum of the first two terms on the rhs of  $\{Alk^*_{def}\}$  is called 'potential alkalinity'  $A_p$ :  $A_p = AT + 1.26 * [NO_3^-]$*

*$A_p$  is a conservative quantity with respect to organic matter production based on nitrate uptake (decrease of nitrate & increase of AT) and remineralization of organic matter (inclusively oxidation of reactive nitrogen to nitrate).*

*Please note that  $Alk^*$  can take on positive as well as negative values. The surface ocean mean (upper 50 m) of  $Alk^*$  is zero by definition. The depth of 50 m used for the definition of  $Alk^*$  is rather arbitrary and in my opinion a weakness of the proposed  $Alk^*$  concept.*

This is a fair and concise summary of the tracer.

*The discussion on regional variations of AT and Alk\* and the influence of riverine alkalinity input is quite insightful. Another interesting region with 'unusual' alkalinity values is the Mediterranean Sea (compare, for example, Schneider, Anke, Douglas WR Wallace, and Arne Körtzinger. "Alkalinity of the Mediterranean Sea." *Geophysical Research Letters* 34.15, 2007).*

Also true, we did little with this because we had little to add to it.

*I found it difficult to grasp the content of the section on process importance on saturation level (I had to read it several times). The case of atmospherically isolated water masses applies mainly to deeper layers (below the surface mixed layer, below the euphotic zone) and thus I suggest to use the terms remineralization of organic matter (instead of organic matter cycling) and carbonate dissolution (instead of carbonate cycling). The results are given in Table 1: the globally most important processes for changes in are cycling of (1) organic matter and (2) carbonate and (3) pressure changes (not really surprising) whereas temperature changes are of minor importance.*

This is a good point. However, other reviewers have noted that our "atmospherically isolated seawater" case applies also to surface seawater on short timescales. We therefore feel the more general terms (including organic matter formation and calcium carbonate precipitation) are more appropriate.

*When the water sample has the change to equilibrate with the atmosphere (i.e. in the surface ocean), production of organic material has a smaller impact on mainly via the associated change of AT by nitrate uptake. Freshwater cycling has a large input on AT and (for the Arctic Ocean compare, for example, Yamamoto-Kawai, Michiyo, et al. "Aragonite undersaturation in the Arctic Ocean: effects of ocean acidification and sea ice melt." *Science* 326.5956 (2009): 1098-1100.). I don't understand why you discuss pressure changes in this context (surface ocean!),*

Pressure changes (and the influence of pressure changes on calcite saturation) are indeed minimal in the surface ocean. We thought about not presenting these  $M$  and  $I$  values, though we feel it requires very little additional language/space to include it. Also, including this discussion will allow people concerned with the controls on calcium carbonate saturation in the euphotic zone to confidently ignore the pressure differences between the surface and whatever depth surface the calcifying organisms are found at. Finally, removing this term begs the reader to ask how we can compare  $I$  values for well-equilibrated waters to  $I$  values determined for atmospherically isolated seawater when we are dividing by the sum of a different number of  $M$  values.

*Process importance (Appendix A): I found it difficult to read Appendix A. If I understand it right the authors calculate the propagation of standard deviations for single processes similar to the standard method known as 'combination of errors' where products of variances and squared partial derivatives are added for various independent variables.*

This is not quite accurate.

*The problem here is the complicated dependency of the saturation level on various quantities and processes. In a single process various quantities can co-vary and impact via different 'routes'. The authors try to take these complications into account by summing over seven products of partial derivatives (Eqs. A3 and A5; products stemming from chain*

*rule). In total five different equations are given for the metric  $M_i$ . Finally, the authors apply Monte Carlo simulations to estimate variability and uncertainty of the metric (which of the five versions given?).*

We decided that additional clarity was required. We have reduced the number of equations for  $M$ , and now explicitly state which equation is used to calculate  $M$ .

The comment about the different ‘routes’ is certainly also correct. This was the motivation for our Monte Carlo analysis where we allowed the initial state of the seawater to vary to reflect the range of possible seawater states and compositions that would result through the action of the processes we consider. As noted, we found that the impact of a process varied strongly with the initial state and composition of the water considered. However, the impact of the processes relative to other processes did not. This distinction is why we present different uncertainties/variabilities for our  $M$  and  $I$  metrics.

*Throughout the manuscript, the authors talk about ‘carbonate cycling’ and it remains ambiguous whether they refer to carbonate ions ( $\text{CO}_3^{2-}$ ) or calcium carbonate minerals ( $\text{CaCO}_3$ ). Also ‘carbonate saturation’: replace by carbonate saturation state, introduce which is used later on and give equation.*

We followed this recommendation.

***Further points:***

*The authors fail to give a thorough introduction into the topic.*

We reorganized our background material in light of this and the following comments.

*p. 11140, L. 20: The tracer  $\text{Alk}^*$  should not be introduced in the introduction, but in the next section "The tracer  $\text{Alk}^*$ ".*

We now only mention  $\text{Alk}^*$  at the end of the introduction (formerly it was at the start), in the paragraph in which we give an overview of the paper.

*11140, L. 20:*

*... to isolate the influences carbonate cycling ... ->*

*... to isolate the **influence of** carbonate cycling ...*

Changed

*p.11141, L. 20: operational definition gives  $A_T$  ->*

*operational definition gives  $A_T$  (measured in  $\text{mol kg}^{-1}$ , gravimetric units)*

We now state “ $A_T$  (expressed in  $\text{mol kg}^{-1}$ )”

*p. 11141, L. 6-8: This is summary and outlook and is misplaced in the introduction. A proper introduction could include an introduction to the carbonate system, calcium carbonate minerals, the concept of alkalinity (parts of section 2 could go here), sources of alkalinity*

(parts of section 3 could go here, p. 11145, lines 8-17) including the role of rivers, and then at the end the main questions posed for this paper.

We now indicate that rivers are a major alkalinity source in the introduction.

p.1142 L. 5-6:

... while still mixing and responding to calcium carbonate cycling linearly. ->

... while still mixing **linearly** and responding to calcium carbonate cycling.

Changed.

p. 11142, L. 17-19: This sentence is unclear. What is the link between export of organic matter and release of OH<sup>-</sup>? Also, you say a '1:1 release of proton acceptors' - this is a ratio, so 1:1 release per what?

I assume you refer to an increase of alkalinity by 1 mole when 1 mole of N from nitrate or nitrite is assimilated (Wolf-Gladrow et al., 2007), but please take the time to make the explicit link (from export) to nitrate.

We clarified this statement:

**Nitrate uptake for anaerobic denitrification and the production of amino acids occurs in an ~1:1 mole ratio with the release of molecules that increase A<sub>T</sub> (Chen 2002).**

p. 11143, L. 1-5, you're too fast: switch sentences, first introduce empirical value by Kanamori and Ikegami, give equation, then the sentence with the comparison to theoretical value by Wolf-Gladrow et al (give number here, too).

We followed this recommendation:

**We thus use the ratio found by Kanamori and Ikegami (1982) to define potential alkalinity ( A<sub>p</sub> ).**

$$A_p = A_T + 1.26 * [NO_3^-] \quad (1)$$

**While the empirical ratio of 1.26 may be specific to the elemental ratios of the North Pacific, Wolf-Gladrow et al. (2007) provide a theoretical derivation from Redfield ratios and obtain a similar value of 1.36.**

p. 11143, salinity normalization of Robbins (2001). This is a very important part of your Alk\* calculation and therefore needs some more explanation besides referring to Robbins. Go step by step, don't mention the subtraction in line 14 yet, that is not relevant here for the definition of what you call 'passive conservative potential alkalinity'. Also give the number for averaged A<sub>p</sub> (line 19/20).

We also followed this recommendation.

p. 11143, L. 20: this is a typical sentence that was written without due diligence: "The mean surface values are chosen to capture the impact of freshwater cycling where precipitation and evaporation occur." After reading the sentence three times, I realized it should read:

*"The mean surface values were chosen because \*we assume that they\* capture the impact of freshwater cycling where precipitation and evaporation occur." Sentences like this one are manifold throughout the manuscript.*

We mostly followed this recommendation:

**The mean surface values are chosen in an effort to best capture the impact of freshwater cycling where precipitation and evaporation occur.**

This phrasing seems preferable to suggesting that we assume our approach captures this influence perfectly, which we do not. Instead, we aim to do the best we can with a single value.

*p. 11144, after eq. 5 add eq. 6 where you give the full equation:  $Alk^* = AT + 1.26 NO_3^- - 66.4 S$ . Don't add the unit in eq.5 but give it below as: "where  $Alk^*$  has same units as  $AT$  ( $\mu mol kg$ )."*

Done.

*p.11144 L.8: Mean global surface  $Alk^*$  is zero by definition, and negative  $Alk^*$  is possible when potential alkalinity is less than expected from salinity. ->*

*Mean global surface  $Alk^*$  is zero by definition, and thus  $Alk^*$  can take on positive as well as negative values.*

Done (we switched "negative" and "positive" in R2's recommendation since we think negative will be more alarming to first time readers).

*p. 11144, l. 14-23: this paragraph comes as a surprise, it is unclear why this is discussed here. This is because the Robbins paper was not thoroughly introduced (see comment above). Maybe it should be in an extra paragraph or section "Evaluation of the tracer  $Alk^*$ ". It definitely needs more explanation of why this is important.*

Due to this and other reviewer comments, we moved this discussion to supplementary materials (see other response to reviewers).

*p. 11145, l. 1-17:  $AT$  and  $Alk^*$  seem to be used intermittently. Do you want to talk about  $AT$  or about  $Alk^*$ . The part of introducing sources for  $AT$  should be moved to the introduction.*

We followed this recommendation.

*Line 14-17: this is disconnected to the previous paragraph, convert to alkalinity units.*

Done.

*p.11146 L.2: The  $Alk^*$  distribution has a broadly similar explanation to the phosphate distribution. **MAY NEED MORE EXPLANATION***

We rewrote this section, and this sentence is now missing (see responses to R4 for more).

*p. 11146 L.6: Several **qualitative** differences between  $Alk^*$  and phosphate are visible in Figs. 2, 4, and 5. ->*

Several differences between Alk\* and phosphate *patterns* are visible in Figs. 2, 4, and 5.

Added “distributions” in place of patterns for consistency with our terminology in the rest of the manuscript.

p.11146 L.10: *a maxima* -> *a maximum*

Changed

p.11147, L1: *The nearly-zero mean surface Pacific Alk\* indicates that Alk\* supply from upwelling and a small riverine source very nearly balances carbonate precipitation.*

***THE FACT THAT THE MEAN SURFACE ALK\* OF THE PACIFIC MIGHT IN PART BE DUE TO THE LARGE SURFACE AREA AND THE BY DEFINITION ZERO GLOBAL MEAN OF SURFACE ALK\*.***

We removed this sentence.

p.11148, L.21: *I suggest to drop ‘The higher Alk\* found for May through July is consistent with Moore et al. (1986)’s radium isotope based finding that 20–34% of the surface waters in this region are derived from Amazon during July vs. 5–9% during December. However, if we assume the Atlantic seawater mixing with the Amazon outflow had an Alk\* of 25–35  $\mu\text{mol kg}^{-1}$ , these Amazon River water fractions would result in Alk\* of  $-15$  to  $0 \mu\text{mol kg}^{-1}$  in December and 45 to  $100 \mu\text{mol kg}^{-1}$  in July. We see lower Alk\* values in our distribution and a smaller disparity between winter and summer Alk\*, suggesting a smaller average Amazon influence for the ocean’s surface during both seasons than found by Moore et al. (1986). However, our estimate does not account for any changes in calcium carbonate export induced by nutrient-rich Amazon outflow.’ because it leads to nowhere.*

We dropped everything after an altered version of the first sentence (see responses to R3).

p. 11149, l. 4: *"intermediate to high": give numbers*

This paragraph was removed.

p. 11150, L.3: *This bay has two high AT rivers that join and flow into it, the Brahmaputra ( $1114 \text{ mol kg}^{-1}$ ) and the Ganges ( $1966 \text{ mol kg}^{-1}$ ) (Cai et al., 2008).*

->

*This bay has two high AT rivers that join and flow into it, the Brahmaputra ( $AT = 1114 \text{ mol kg}^{-1}$ ) and the Ganges ( $AT = 1966 \text{ mol kg}^{-1}$ ) (Cai et al., 2008).*

*or (???)*

*This bay has two high AT rivers that join and flow into it, the Brahmaputra ( $Alk^* = 1114 \text{ mol kg}^{-1}$ ) and the Ganges ( $Alk^* = 1966 \text{ mol kg}^{-1}$ ) (Cai et al., 2008).*

This paragraph was removed.

*Section 3.3: Riverine Alk\* regionally: what information is added by this discussion to the study of Cai et al (2008) on alkalinity contribution from rivers? Why is Alk\* needed for that discussion?*

We removed most of this, but we still think Alk\* is useful for discussing the (smaller than expected) role of the Amazon, and the (larger than expected) Red Sea Alk\* deficit.

*p. 11153, l. 7-8: what is the outcome of testing this assumption?*

We expanded on this discussion:

**We test the validity of this assumption by also estimating  $M$  for the observed global  $p\text{CO}_2$  variability in the Takahashi et al. (2009) global data product. This test reveals transient air-sea disequilibria are indeed important for surface ocean calcite saturation, but only as a secondary factor when considered globally. Despite this, it is important to recognize that air-sea equilibration following a process is not instantaneous, and that the  $S_R$  value estimates in section 4.1 will be better for estimating short term changes following fast acting processes such as spring blooms (e.g. Tynan et al., 2014) or upwelling events (e.g. Feely et al. 1988).**

*p. 11154, l. 2-6: it would be more informative to plot temperature versus surface calcite saturation in a x,y-plot or at least calculate a correlation and give that number.*

Added a correlation coefficient.

*section 5: Conclusions: not all that is written here is a conclusion by definition, e.g: p. 11154, L. 17-18: "A plot of Alk\* against salinity reveals the large AT input from the Amazon River". That is a sentence for the results section. The conclusion section should be considerably shortened and be reduced to main conclusions. It should include a paragraph on: what are advantages of the Alk\* method, why is it needed, what can we use it for that cannot be achieved by AT alone?*

We truncated this section considerably.

*Figures:*

*The choice of figures seems arbitrary. They are randomly introduced but not discussed at the same time. Page 11145, L. 19-21: First sentence introduces Figure 2. Second sentence introduces Figure 3. There is no discussion of Figure 2.*

We have rewritten our text to better explain why we chose the figures we did, and to better guide the reader from figure to figure (see below for text).

*What is the added value of showing the top 50 m mean right after showing the surface values? I can't see any.*

We now explain why we have Figure 1 (was Fig. 2):

**Figure 1 maps surface Alk\* (top 50 m) at the measurement stations. We provide this figure to show where we have viable Alk\* estimates and to demonstrate that our gridded data product adequately captures the measured Alk\* distribution. Figure 2**

maps gridded global surface  $A_T$ , salinity,  $Alk^*$ , and phosphate distributions and mask the regions that are lacking data in Fig. 1.

*In line 26 it becomes even clearer: "The subtropical gyres have the lowest open ocean  $Alk^*$  in Figs. 2, 3 and 4." First, this is badly formulated, but then if you can see the same thing in three figures, two of them are not needed, right?*

We rewrote this section generally to make it more clear how we are using each figure:

The similarity of the  $A_T$  (Fig. 2a) and salinity (Fig. 2b) distributions demonstrates the strong influence of freshwater cycling on the surface marine  $A_T$  distribution (see also: Millero et al. 1998, Jiang et al., 2014). The dissimilarity between  $Alk^*$  (Fig. 2c) and salinity (Fig. 2b) suggests  $Alk^*$  removes the majority of this influence. The phosphate (Fig. 2d) and  $Alk^*$  (Fig. 2c) distributions are similar at the surface. They are also similar at depth. Figures 3 and 4 show zonally-averaged gridded depth sections of  $Alk^*$  and phosphate.  $Alk^*$  and phosphate concentrations are low in the deep Arctic Ocean (Figs. 3d, and 4d), intermediate in the deep Atlantic Ocean (Figs. 3a and 4a), and high in the deep North Pacific (Figs. 3b and 4b) and deep North Indian (Figs. 3c and 4c) Oceans.  $Alk^*$  and phosphate distributions are similar because similar processes shape them: the hard and soft tissue pumps transport  $A_T$  and phosphate from the surface to depth, respectively. The "oldest" water therefore has the highest net phosphate and  $Alk^*$  accumulation. High surface phosphate and  $Alk^*$  in the Southern Ocean and North Pacific in Figs. 2, 3, and 4 are due to upwelled old deep waters.

Several qualitative differences between  $Alk^*$  and phosphate distributions are visible in Figs. 2c, 2d, 3, and 4. Surface phosphate is low in the Bay of Bengal and high in the Arabian Sea (Fig. 2d), while the opposite is true for  $Alk^*$  (Fig. 2c). Also,  $Alk^*$  reaches its highest surface concentration in the Arctic (Figs. 2c and 3d) where phosphate is not greatly elevated (Figs. 2d and 4d). These surface differences are due to regional riverine  $Alk^*$  inputs (Section 3.3). Another difference is that  $Alk^*$  reaches a maximum below 2000 m in all ocean basins except the Arctic, while phosphate maxima are above 2000 m. We attribute the deeper  $Alk^*$  maxima to deeper dissolution of calcium carbonates than organic matter remineralization. Finally,  $Alk^*$  values are higher in the deep Indian Ocean than in the deep Pacific. This is likely due to elevated biogenic carbonate export along the coast of Africa and in the Arabian Sea (Sarmiento et al., 2002; Honjo et al., 2008).

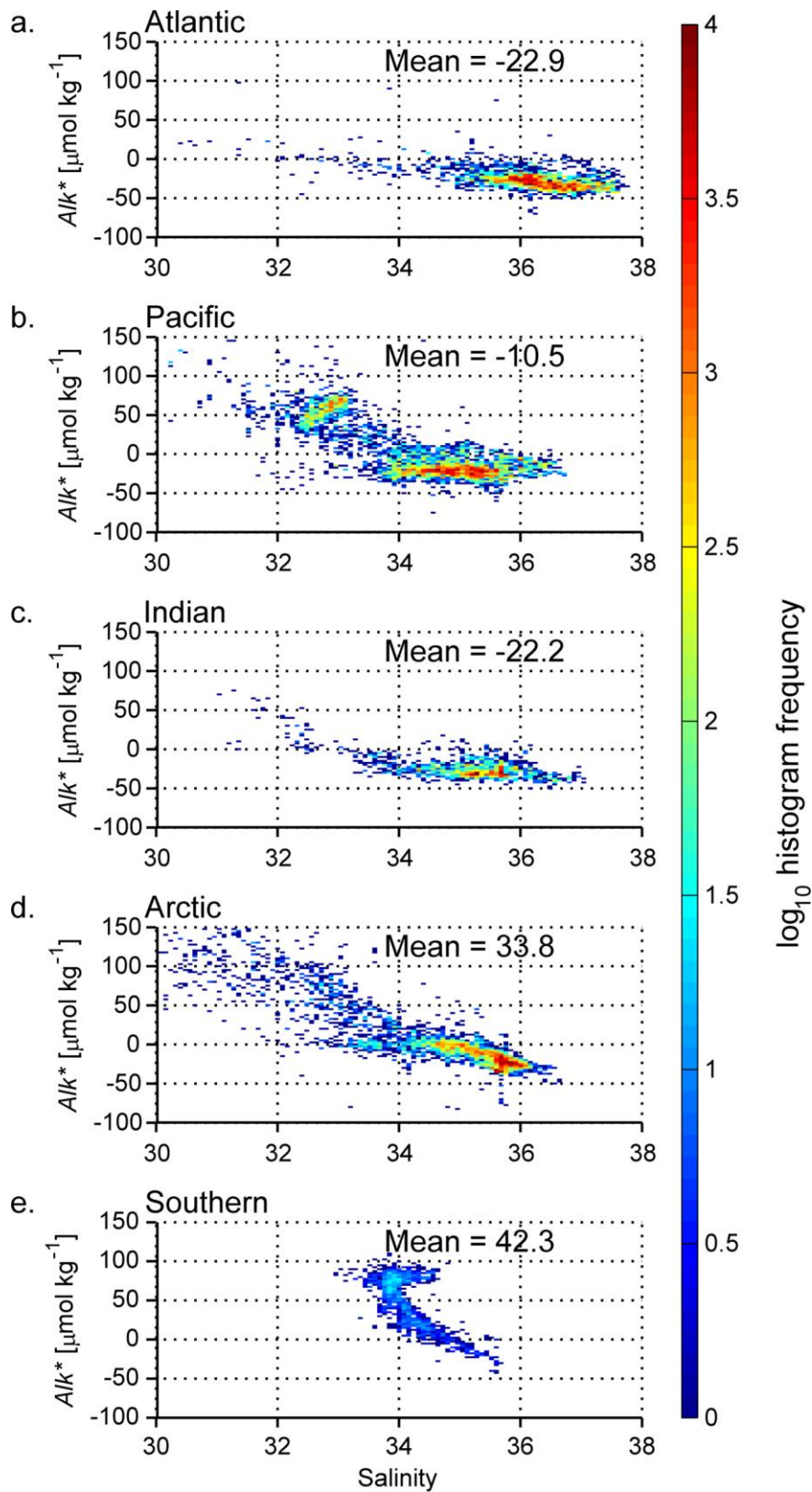
*I suggest to: introduce one figure. Then discuss it. Then introduce the next figure. Then discuss it. Take out the figures where there is no extra information to be discussed.*

We followed this suggestion in the text above.

*Same in Figure 6, p. 11146, line 18: In the "2D color histograms" the colors and number of data points for certain bins are not further discussed, so the graph could be more simple without colors.*

We feel it important to note that the majority of the data fall within specific bins. For example, without the color histogram, the rare measurements near river mouths in the Arctic would have nearly the same visual impact as the elevated North Pacific  $Alk^*$ . We did remove un-discussed detail by eliminating an entire panel of  $A_T$  vs.  $S$  histograms, however:

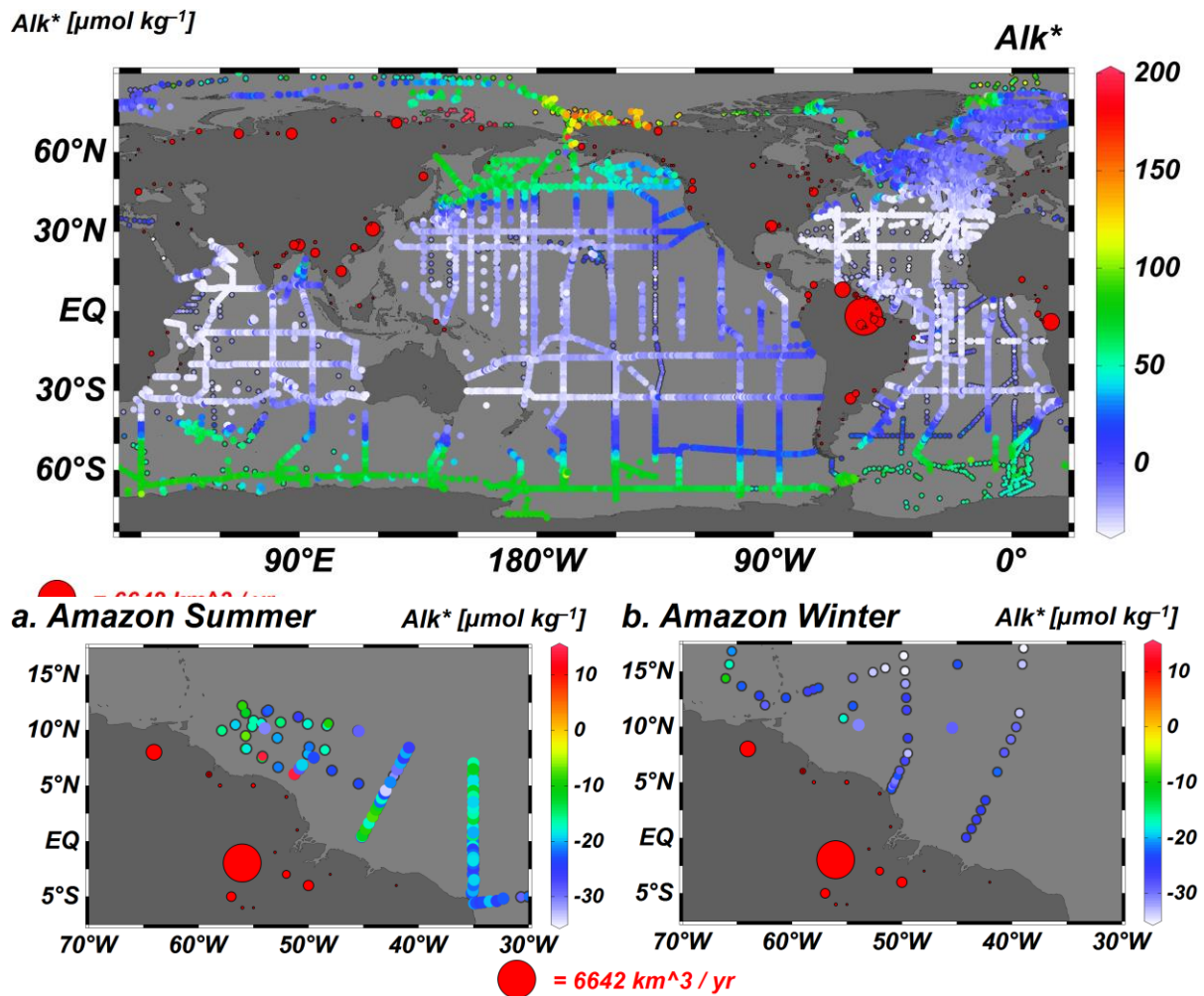




All figures need a revision, just some examples:

\* Figure 3: legend for size of dots missing

We have added a legend to this figure and Figure 6 (was Figure 7).



\* Figure 4: the figures look like prepared with ODV. One very helpful feature of ODV is that one can have dots to indicate where samples were taken. This illustrates the density of measurements and gives a feeling of how much one can trust the interpolation. This should be applied here.

This figure is a zonal average plot of gridded data. Showing where our gridded data was located would just be revealing what we chose for our grid. As a zonal average, showing all measurements within a given basin (measurements we used to determine our gridded data) would both clutter the figure with a tremendous number of dots and mislead the reader into assigning the wrong weights to isolated points. For instance, a measurement that appears in the middle of a clump of other measurements may actually have a large influence on the plot if it is separated from other points longitudinally.

\* Figure 7: Dots for river outflow are plotted on land.

With the exception of one suspected typo (an Alaskan river in the central Pacific) we had no choice but to plot these points where Dai and Trenberth located them. If we moved them, we'd be guessing at the true river mouths, and, I believe, we'd be indicating the incorrect location at which the flow is estimated.

*p. 11156 Eq. (A2) one '∂' missing in eq.*

Fixed.

*p.11166/7 Tables A1 & A2: Units missing for the partial derivatives (some are dimensionless, however, others possess units).*

Fixed.