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## ***Interactive comment on “Biogeochemical processes and buffering capacity concurrently affect acidification in a seasonally hypoxic coastal marine basin” by M. Hagens et al.***

**M. Hagens et al.**

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We thank all reviewers for their constructive feedback that have greatly improved our manuscript. In a previous Author Comment we responded to the comments given by the first reviewer. In this Author Comment we will reply to the comments given by the second and third reviewer (Wei-Jun Cai and Helmuth Thomas) and provide detailed notes on all changes made in the manuscript. Line numbers refer to the original BGD manuscript.

**Response to reviewer #2 (Wei-Jun Cai)**

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*(Major concern one) “The point is many people, like me, thought they know what the Hoffman approach is; but they probably don’t. Some text is needed earlier to say the advantage of the Hoffman approach rather than simply doing the traditional DIC/TA approach. I feel a paraphrase of what was said in Hoffman et al. (2010, section 3, p. 248) will help: “when multiple biogeochemical processes are acting concurrently, only the combined effect of all processes on pH can be calculated, one cannot quantify how strongly individual processes influence proton cycling.” ”*

We acknowledge that a full understanding of the advantages of the Hofmann approach is of utmost importance for the understanding of this paper. We thus agree that a better clarification of this method and its advantages is necessary in order to get our message across to as many people as possible. To this point, the following changes were made in the manuscript:

- p. 15831, line 18: after “on pH”, the following was added “using the method developed by Hofmann et al. (2010a), which uses DIC and  $[H^+]$ , rather than TA, to quantify the carbonate system.” This should make the reader aware of the use of this method as early as possible in the manuscript.
- p. 15842, line 1: after “Hofmann et al. (2010a).” the following was added: “Traditionally, the carbonate system is quantified using DIC and TA. Although this approach has many advantages, it can only determine the combined effect of several concomitantly acting processes on pH. In the method proposed by Hofmann et al. (2010a) pH is calculated explicitly in conjunction with DIC. As a result, the individual contribution of each individual process on pH can be extracted, even though several processes are acting simultaneously (Hagens et al., 2014). Therefore, this method is ideally suited for the analysis of proton cycling and constructing proton budgets.”

*(Major concern two) “The sum of  $dH/dt$  (total) of all measured processes was 1–2 orders of magnitude higher than  $dH/dt$  (obs). As a result, the budget closure term*

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*dominated the proton cycling intensity.” So I feel this point, plus the fact that  $H^+$  is turned over rapidly among various processes, would make it very hard to verify the model results. Some discussion of uncertainty will help.*

The point that the reviewer raises here is in line with the point raised by reviewer #1, who also asked for a more extensive discussion on the uncertainty of the budget related to the nitrification rates. As stated in the final part of the conclusions (p. 15862, lines 3-6), the main message we would like to get across by showing these proton budgets is: “that process rates, buffering capacity and ambient pH are all essential compartments when determining the vulnerability of a system to changes in pH. By constructing one of the first proton budgets originating from in situ measurements, this study shows the associated uncertainties and challenges for future studies”. So we acknowledge that there are many uncertainties underlying this budget, and we might not have discussed these uncertainties enough in section 4.3. In the revised manuscript, we now discuss these uncertainties in more detail by making the following changes to section 4.3:

- p. 15859, line 5: after “in 2012.” the following sentence was added: “One should realise that these proton budgets are one of the first of its kind based on measured data and contain many uncertainties.”
- p. 15860, line 7: after “ of the budget closure term.” we added the following: “The dominance of the closure term highlights the uncertainties underlying the current proton cycling budget. These uncertainties arise from spatial and temporal variability, measurement error and incomplete coverage of all processes affecting proton cycling. Taking the sediment fluxes (Fig. 6b) as an example, we see that the standard deviation of both the TA and DIC fluxes, which mostly results from small-scale spatial variability, ranges up to ~100% of the measured flux. As a result, this imposes a large uncertainty on the corresponding proton flux, which may severely impact the bottom-water proton budget. Similarly, by using an empirical nitrification rate expression based on  $[NH_4^+]$  and  $[O_2]$ , we ignore

temporal variability caused by, e.g., changes in the microbial community. As the nitrification rate, like the other process rates, linearly correlates with the amount of protons produced, changes therein may especially impact the proton budget in November.” (followed by a new section)

*The rest of notes are all very minor and it is up to the authors to take or ignore them.*

*I do not feel figure 1 to be very informative. It gives a general picture but not much details about the sample sites. For example, one cannot tell where is the connection to the North Sea and where are the two sills at the landward and seaward. And where are S1, S2, and S3? What exactly is a sluice? From fig. 2, it appears it can be closed or open to variable depths. (I see it is explained later in section 3.1)*

We agree that Fig. 1 is most useful when seen concurrently with Fig. 2. However, we do feel it is helpful to show Fig. 1, since it helps getting a general picture of the sampling location and because of the very specific bathymetry of the lake. What might help the reader getting the right information at the right time is to change the figure references in the text. So, on line p. 15831, line 26, we changed “Fig. 1a” into “Fig. 1”, and on p. 15832, we changed “Fig. 1b” into “Fig. 2”.

As written on p. 15832, line 9, the sluice extends between 3 and 11 m water depth. We have adapted Fig. 2 by adding this range more clearly. Additionally, we added the location of the sluice to Fig. 1b. To this point, we have adapted the figure caption on p. 15878 by adding at the end: “Red bar indicates sluice location.”

*p.15830, line 22-23, I believe the first part of the sentence is correct (an effect that is most pronounced in eutrophied waters), but the last part is incorrect (at relatively high temperatures and salinities) I assume you do not mean that the effect is most pronounced “in high temp and high salinity waters” (which is incorrect and is not what Sunda and Cai’s paper says), and that you simply mean the example Sunda & Cai give is “at relatively high temperatures and salinities.” So please modify the sentence.*

To avoid confusion and to keep the statement general, we removed the second part from p. 15830, lines 22-23. The modified sentence now reads: “an effect that is most pronounced in eutrophied waters”.

*p.15841, line 1. Since your samples dates have lower wind speed than average, the calculated air-sea CO<sub>2</sub> flux could be lower than real. I suggest you use monthly averaged wind speed plus a non-linear coefficient (Jiang et al. 2008 JGR-Ocean). In the context of examining monthly evolving of CO<sub>2</sub> system parameters, I feel this most appropriate. But it probably won't make too big a difference; so up to you. –Jiang, L.-Q., Cai, W.-J., Wanninkhof, R., Wang, Y. and Lüger, H., 2008. Air-sea CO<sub>2</sub> fluxes on the U.S. South Atlantic Bight: Spatial and seasonal variability. J. Geophys. Res., 113(C7): C07019.*

We have taken the wind speed at the day of sampling to be consistent with the other rate measurements. Since we have daily wind speed measurements available we do know the diurnal variation of the air-sea CO<sub>2</sub> flux, assuming that a linear interpolation of the air-sea CO<sub>2</sub> gradient is a valid approach. This information is therefore presented in Fig. 6a. However, we cannot say anything on the diurnal variation in, e.g., primary production or sediment fluxes. Another reason to present the daily rates is that for the proton budget calculations it would be inappropriate to take the monthly average, especially given the fast H<sup>+</sup> cycling relative to the net H<sup>+</sup> change. The annual fluxes presented on p. 15853, lines 16-17 are, however, based on the daily wind speed measurements. Therefore we have not included the non-linearity coefficients presented in Jiang et al. (2008). In an earlier stage we have, however, already calculated the air-sea CO<sub>2</sub> flux using two other parameterisations: Wanninkhof (1992, equation given in Figure 4, for lakes only) and Cole and Caraco (1998, equation 5). Both parameterisations are specifically fitted for lakes and might therefore be not suitable for Lake Grevelingen given its proximity to the coast. They lead to lower air-sea fluxes, with annual integrated fluxes that are 74% and 66% of the currently used parameterisation, respectively.

*p.15848, line 21, the word “strongly” probably should be replaced with “greatly.” It is*

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*better to put the description of DIC variation in the context of salinity unless some kind of normalization is applied (nDIC). Otherwise, we have no idea how much change is due to mixing (or lateral transport).*

We have replaced 'strongly' with 'greatly'. For the reply to the second part of the comment, see the next response.

*p.15848 and p.15849, same. a description of TA distribution (in particular the surface bottom difference) without in the context of salinity doesn't provide much meaning information. Thus, I feel this part can be shortened.*

We have concerns about using salinity normalisation to present the DIC and TA data. Several studies (Friis et al., GRL, 2003; Jiang et al., GBC, 2014) have shown that a normalisation of the form  $nX = X / S * S_{ref}$  cannot be used when the freshwater end-member deviates from zero. For TA, this may especially be the case in coastal regions where processes other than evaporation and precipitation control TA at zero salinity. In addition, it is questionable if the effect of salinity on DIC and TA is significant. Combining all 2012 data for Lake Grevelingen, we found no statistically significant linear correlations between either TA and salinity ( $r^2 = 0.02$ ,  $P = 0.113$ ), or DIC and salinity ( $r^2 = 0.04$ ,  $P = 0.0513$ ).

Finally, rather than normalising DIC and TA to salinity, we have explicitly addressed the effect of changing salinity on pH as described in Hofmann et al. (2009). Basically this involves applying equation (7) on p. 15842, where  $R_x$  represents the change in salinity over time (dS/dt) and  $\nu_{H^+}^x$  is a salinity-dependent coefficient similar to the stoichiometric coefficient for the proton. This latter coefficient describes the changes in equilibrium constants due to salinity changes and is calculated numerically as described in Hofmann et al. (2009) (equation A29). Over the year, its value ranges from 2.91-8.26  $\mu\text{mol kg}^{-1}$ . Note that, in contrast to the coefficients in Table 1 (p. 15876), these values are not dimensionless and are thus not directly comparable. From this calculation, which was part of the proton budget presented in Fig. 8 (p. 15885), it was found that changes

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in salinity did not significantly affect the proton budget on this time scale. For a detailed discussion of the time scale to which the proton budget applies, please refer to the response to the first comment of reviewer #3.

*In p.15849, line 21, the word “drawdown” is a misuse (it is simply a shift of equilibrium of CO<sub>2</sub>, which is converted to HCO<sub>3</sub><sup>-</sup>; thus simply say low T led to a low pCO<sub>2</sub> would be better. Why pCO<sub>2</sub> build-up had a time delay (is behind) of DIC build-up? Hope you will explain this in the Discussion.*

We were slightly confused by this comment. On p. 15849, lines 21-22, we write that: “a substantial drawdown in surface-water CO<sub>2</sub> was observed coinciding with an increase in [O<sub>2</sub>], which is indicative of high autotrophic activity.” Thus, we believe that there was an actual drawdown in CO<sub>2</sub> caused by phytoplankton growth. In addition, surface-water temperature increased between June and August.

*In p. 15850, line 8, can’t you just say “as expected, TA had no significant correlation with...”? Isn’t that something we would expect?*

We acknowledge that for oceanic environments, this was indeed to be expected. We therefore changed p. 15850, line 8 from “Finally, TA could not statistically...” to “Finally, as expected TA could not statistically...”

*p.15861, while the conclusion derived here is correction, do we really need the lengthy discussion in p.15861 (lines 7 to bottom) to derive the conclusion? I would say this is true for any natural water. We know pH in seawater is controlled (buffered) by weak acid-base (mainly the carbonate system) thus proton production/consumption is rapidly supplied and taken away by the various acid-base equilibrium reactions. We simply know this. (maybe I am wrong)*

We agree that part of this section may be somewhat trivial. The discussion from p. 15861, line 21 to p. 15862, line 3, which stresses the general importance of the buffering capacity on proton turnover, was therefore shortened. However, in lines 7-21 we

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would like to stress that variations in proton turnover time cannot be explained by variations in buffering capacity only. Or, in other words, proton turnover time cannot be predicted based on buffering capacity alone. The section from p. 15861, line 21 to p. 15862, line 3, now reads: “When the proton turnover time is divided by  $\beta$ , one calculates the gross proton turnover time, i.e., the turnover time without buffering (Hofmann et al., 2010a). Given that the average  $\beta$  in the Den Osse Basin is  $\sim 30\,000$  and  $\tau_{H^+}$  varies between 14.4 – 35.9 days in the four months studied, the gross proton turnover time is in the order of minutes. This exemplifies that buffering reactions in active natural systems are extremely important in modulating the net change in  $[H^+]$ , and again highlights that pH dynamics in these settings cannot be studied by measuring process rates alone.”

*p.15863, “neither does it not show a clear pattern with TA”? (is this correct?) The conclusion drawn at the end of A2 is puzzling. calculated  $pCO_2$  is higher than measured. If there is additional base inside the TA (DOM for example) and our acidbase model doesn't include it, then we would expect a lower calculated  $pCO_2$  (the TA used in the calculation is too high). Now since the calculated  $pCO_2$  is too high, I can only conclude that your TA is too low, assuming your DIC has no problem. You also mentioned that this happened to samples below the pycnocline. Okay, I think I have an answer—your waters have high  $NH_4$  concentrations.  $NH_4$  was then oxidized during sample storage or titration, thus leading to a lower TA. But what I don't understand is those samples with highest  $pCO_2$  values (they should be from bottom waters) have lower calculated  $pCO_2$ . Why?*

We replaced “neither” on p.15863, line 22 with “nor”. Furthermore, we would like to stress that for most of the samples, calculated  $pCO_2$  was lower than measured  $pCO_2$ . Only in the range of higher measured  $pCO_2$  ( $> ca. 1000$  ppmv), calculated  $pCO_2$  exceeded measured  $pCO_2$ . In addition,  $[NH_4^+]$  only exceeded  $20\ \mu mol\ kg^{-1}$  below 20 m depth in June and July, so we do not think it can explain the required TA decrease. Interestingly, in the Godthåbsfjord system in Greenland, where DIC, TA, pH and  $pCO_2$



were measured concurrently, calculated  $p\text{CO}_2$  was consistently lower than measured  $p\text{CO}_2$  (L. Meire, personal communication, 2014). This is in line with our observation in this range of  $p\text{CO}_2$  values ( $\sim 100\text{--}400$  ppmv). Our results are contradictory, however, to a recent paper on freshwaters published by Abril et al. (2015) where  $p\text{CO}_2$  calculated from TA and pH was found to be higher than measured  $p\text{CO}_2$ , which was partly attributed to the contribution of organic matter. Combining all these results, we agree with the reviewer that they are puzzling. We do not have a satisfactory explanation for them and this is exactly one of the reasons why we present this comparison. We feel it falls beyond the scope of this work but is definitely worth a further examination

### Response to reviewer #3 (Helmuth Thomas)

*Major point: I might have overlooked this point, but I do miss the discussion of the role of temperature and its seasonality in regulating the pH and the buffer capacity. Both pH and buffer capacity depend strongly on the ambient temperature, with the pH decreasing and the buffer-capacity increasing with increasing temperature. This can be seen by simple thermodynamic computations using available software, and is one of the reasons for the low buffer-capacity of polar waters as compared to tropical waters (e.g. Thomas et al., 2007, GBC), or in other terms, for the positive temperature coefficient of the anthropogenic  $\text{CO}_2$  uptake (e.g. Thomas et al., 2001 GRL). Also from the seasonal perspective this has been discussed for example by Shadwick et al., 2011 (L&O) and 2013 (Nature Science reports), many other examples could be given here, as well. With a little bit of guess work from my side, the temperature role could be evident in the discussion in section 3.2.2, and figures 3-5, when comparing the seasonalities of temperature (Fig 3), then pH or the buffer-capacity (Fig. 4), and GPP/CR (Fig. 5). However, I do not see an explicit discussion here. Also this aspect has been ignored, as far as I can see, entirely throughout the paper. While the proper assessment of the role of temperature is crucial under many aspects, it appears to be key to the closing term estimation of the lateral proton fluxes with seasonal resolution as discussed toward the end of the paper. I think this problem can be easily addressed,*

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*since it is inherent to the computations anyway.*

The reviewer is correct in his statement that the effect of temperature on both pH and the acid-base buffering capacity was only implicitly included in the manuscript, and should (and can easily be) discussed in more detail.

We addressed the effect of T on  $\beta$  and pH (in the form of  $[\text{H}^+]$  because of the logarithmic nature of pH) by calculating both parameters for each month and depth isothermally, i.e., by keeping the temperature at its annual average, which is 10.8°C for 2012. From this, we have calculated their anomalies as  $[\text{H}^+]$  (in situ T) –  $[\text{H}^+]$  (annual average T) and  $\beta$  (in situ T) –  $\beta$  (annual average T), respectively. If variations in  $[\text{H}^+]$  and  $\beta$  were not at all driven by temperature, the anomaly would be zero. Thus, the larger the anomaly, the more important the effect of temperature. The  $[\text{H}^+]$  and  $\beta$  anomalies were then plotted versus the temperature anomaly (in situ T – annual average T) (Fig. 1).

As expected, the  $[\text{H}^+]$  anomaly is positively correlated with the T anomaly, i.e., an increase in temperature leads to a decrease in pH, while the  $\beta$  anomaly is negatively correlated with the T anomaly, i.e., an increase in temperature leads to a decrease in the acid-base buffering capacity. The variability of data points at the highest T anomalies, however, as well as some other irregularities, indicate that temperature only partly explains the variability in both  $\beta$  and  $[\text{H}^+]$ . This can also be seen by the range covered by these anomaly plots. The buffering capacity changed by at most  $\sim 30000$  as a result of the temperature variations Lake Grevelingen experienced in 2012, while the actual seasonal variation exceeds 60000. Similarly, the maximum  $[\text{H}^+]$  change induced by temperature was  $0.0064 \mu\text{mol kg}^{-1}$ , while over the year surface-water  $\text{pH}_T$  varied by 0.46 units, corresponding to a  $[\text{H}^+]$  change of  $0.0072 \mu\text{mol kg}^{-1}$ , and bottom-water  $\text{pH}_T$  variation was 0.60 units, matching a  $[\text{H}^+]$  change of  $0.016 \mu\text{mol kg}^{-1}$ . Thus, although temperature appears to exert an important control on pH fluctuations on the seasonal scale, especially in the surface water, it can also be seen that temperature effects on  $\beta$  cannot fully explain pH anomalies. In the revised version of the manuscript,

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a shortened version of this discussion was included.

Even more complexity arises because of the different time scales that are considered in the manuscript. Over the seasons, temperature varies by about 20°C in the surface water and ~15°C in the bottom water. As discussed above, this influences both equilibrium constants and the acid-base buffering capacity, leading to a distinct effect on the seasonal signal in pH. This general trend is depicted in Figs. 3-4. In addition, as the reviewer mentions, temperature is well known to affect process rates. This has already been briefly mentioned in the manuscript, e.g., on p. 15844, lines 8-10 in the case of nitrification, where T dependency is included by adding  $q_{10}$ , and on p. 15855, lines 14-16 in the case of community respiration. Fig. 8, however, shows seasonal variability of processes influencing the cycling of protons on a much shorter time scale, i.e., on the day of sampling. Therefore, the temperature dependency of both the process rates and the acid-base buffering capacity is included in the proton budgets, as these are measured / calculated at the in situ temperature on the day of sampling.

For the construction of Fig. 8, which now includes the effect of temperature on the proton cycling, equation (7) is applied in a similar fashion as for biogeochemical processes and salinity changes in order to calculate  $dH/dt$  as a result of a change in temperature. In this case,  $\beta$  represents the buffering capacity, which dependency on temperature is discussed in detail above.  $\nu_{H^+}^x$  is a coefficient describing the changes in equilibrium constants due to temperature changes. This coefficient is calculated numerically as described in Hofmann et al. (2009) (equation A30) and over the year 2012, its value ranges from 3.86-10.9  $\mu\text{mol kg}^{-1} \text{ } ^\circ\text{C}^{-1}$ . Similar as for  $\nu_{H^+}^x$  related to salinity changes, these values are not dimensionless and are thus not directly comparable to the coefficients presented in Table 1 (p. 15876). Finally,  $R_x$  represents the change in temperature over time ( $dT/dt$ ). The temperature change from one day to the next is much smaller than the seasonal change in temperature. Therefore, it makes sense that temperature does not have such a dominant effect on pH on this time scale. However, we shared the suspicion of the reviewer that the temperature effect must be larger than

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what was presented in the original manuscript. Thus, we recalculated our budgets and found indeed a more significant temperature effect than previously. We thank the reviewer for pointing out this important factor. We would like to stress that the closure term in Fig. 8 includes processes acting on a daily scale that could not be included in the calculation, such as lateral transport. It thus does not represent the difference between the seasonal budgets.

Summarising, we made the following changes in the manuscript:

- p. 15843, line 22: after “(Hofmann et al., 2008, 2009)” the following sentence was added to highlight the time scale considered in the budget: “These budgets thus represent the processes influencing the cycling of protons on the day of sampling.”
- p. 15850, line 24: a new paragraph was added after “bottom-water  $\beta$ ” discussing the effect of temperature on  $\beta$ : “To assess the effect of temperature on the acid-base buffering capacity, we calculated  $\beta$  for each month and depth using the annual average temperature at Den Osse, which was 10.8°C for 2012. From this, we calculated the anomaly in  $\beta$  as the difference between the actual and isothermally calculated value for  $\beta$ . This analysis shows that the  $\beta$  anomaly is negatively correlated with the T anomaly, i.e., an increase in temperature leads to a decrease in the acid-base buffering capacity. However,  $\beta$  changed by at most  $\sim 30000$  as a result of the range of temperatures the Den Osse Basin experienced in 2012, while the actual seasonal variation in the acid-base buffering capacity exceeds 60000. Temperature thus only partly explains the variation in  $\beta$  over the year.”
- p. 15857, line 13: after “the surface water” the following was added: “In line with previous studies focussing on the CO<sub>2</sub> buffering capacity (e.g., Thomas et al., 2007; Shadwick et al., 2013), temperature was found to exert an important

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control on the seasonal variability of the acid-base buffering capacity of the Den Osse Basin.”

- Fig.8 (p. 15885) and Fig. S1 (supplementary information) have been adapted by including the effect of temperature changes on proton cycling, and changing the colouring for clarity. Accordingly, the percentages, rates and proton turnover times mentioned in section 4.3 were adapted to account for these new budgets. These changes are as follows:

- p. 15859, line 10: “38.1 – 100%” was replaced with “34.8 – 99.2%”
- p. 15859, line 12: “2.8 – 34.1%” was replaced with “2.7 – 30.3%”
- p. 15859, line 14: “62%” was replaced with “56.6%”
- p. 15859, line 16: “15.4%” was replaced with “14.2%”
- p. 15859, line 18: “0.05 – 14.4%” was replaced with “0.04 – 12.7%”
- p. 15859, line 21: “72.6” was replaced with “62.3” and “2.9” was changed to “2.6”
- p. 15859, line 22: “27.1%” was replaced with “24.0%”
- p. 15859, line 26: after “dH(nitr)/dt” we added “and dH(temp)/dt”
- p. 15860, line 27: “-1.68” was replaced with “-1.85”
- p. 15861, line 8: “42.2” was replaced with “32.8” and “36.1” was changed to “35.9”
- p. 15861, line 9: “18.5” was replaced with “17.7” and “14.6” was changed to “14.4”

- A discussion of the importance of dH/dt due to both nitrification and temperature changes over the year was added on p. 15859, lines 16-17, after “less than 6%”: “Nitrification accounted for 0.00 – 34.4% of the total proton production and was mostly a significant proton cycling process in November and in May below 17.5

m depth. The change in temperature from one day to the next contributed 0.2 – 30.7% to the proton cycling intensity and was generally a more important factor in the proton budget in March and November than in May and August.”

*Minor points:*

*abstract, line 6: maybe replace “of the hypoxic” by “in any hypoxic”?*

This was changed in the revised version of the manuscript.

*introduction, page 15830, l26. Please delete the word “counteract”. The only proper term here is “buffer”! Beside the fact that buffer and counteract mean different processes, strong acids/bases can counteract each other, but cannot buffer.*

In the revised version of the manuscript ‘counteract’ was replaced by ‘buffer’.

*Page 15841, line 24 see above, please replace “counteract” by ”buffer”. If the authors do not like buffer, another option might be resilience toward a perturbation?*

In this case, we have changed the sentence in line 23-24 such that it reads: “the resilience of the coupled ocean-atmosphere system toward a perturbation in atmospheric CO<sub>2</sub>.”

*Page 15848, 2nd and 3rd paragraphs. Please (re-)consider the use of the term gradient. In this section only concentrations (!) are given, but NOT gradients. A gradient is a concentration change over a certain distance, and a gradient thus carries a corresponding unit (concentration change per distance). In this section only concentrations differences between two compartments are reported.*

We agree that gradient may not be the best term to use here. Therefore, we have made the following adaptations to p. 15848 and some other pages where the term gradient was incorrectly used:

- p. 15845, lines 14-15: “This gradient persisted, albeit with decreasing magnitude,  
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- until August.” was replaced with: “This surface-to-bottom difference in temperature decreased but persisted until August.”
- p. 15848, lines 12-13: “The gradient between surface and deeper water intensified until ca.  $70 \mu\text{mol kg}^{-1}$  in April” was replaced with: “The difference between surface and deeper water increased until ca.  $70 \mu\text{mol kg}^{-1}$  in April”
  - p. 15848, line 15: “gradient” was replaced with “difference”.
  - p. 15848, line 16: “gradient” was replaced with “transition”.
  - p. 15848, line 20: “DIC gradient” was replaced with “surface-to-bottom difference in DIC” and “gradient” was replaced with “difference”
  - p. 15849, line 5: “gradient” was replaced with “difference”
  - p. 15849, lines 5-6: “This gradient was strongest” was replaced with “This difference was highest”
  - p. 15849, line 23: “gradient” was replaced with “difference”

*Page 15855, last paragraph. This paragraph is entirely unclear to me. If needed, please explain the meanings of: depth-weighted, volumetric annually averaged, volume-weighted mean value. If these are the same please use only one term.*

We understand the confusion that may arise from this terminology. In case of depth-weighted, annually averaged CR (line 21) we first linearly interpolated the measured CR rates with depth for each month, divided these into a part above and a part below the LPD, and averaged them. Then, we linearly interpolated these average values over the year, and averaged those again. A similar approach, and the same terminology, was used for GPP (p. 15852, lines 17-23). To be consistent with this, we keep this terminology throughout the manuscript.

We have therefore carefully reconsidered the terms ‘volumetric annually averaged’ and ‘volume-weighted mean value’. Volumetric on p. 15855, line 23 was used here as opposed to depth-integrated, which numbers were presented in an earlier version of the manuscript. It can therefore safely be removed. Thus, we have changed “volumetric annually averaged CR” into “annually averaged CR”. Volume-weighted on p. 15855, line 24 refers to the fact that the range of measured CR values in the Western Scheldt estuary can only be averaged properly if the change in volume with distance from the coast is taken into account. In the scope of this discussion, however, it can be removed as the calculation details can be found in Gazeau et al. (2005b). Thus, we have replaced “volume-weighted mean value” with “mean value”. We hope that this clarifies our approach.

### Other changes)

- p. 15837, line 3: “( $\mu\text{g chl a}$ )<sup>-1</sup>” was replaced with “( $\text{mg chl a}$ )<sup>-1</sup>”
- p. 15837, line 4: “( $\mu\text{g chl a}$ )<sup>-1</sup>” was replaced with “( $\text{mg chl a}$ )<sup>-1</sup>”
- p. 15837, line 5: “ $\mu\text{E m}^{-2} \text{ s}^{-1}$ ” was replaced with “ $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$ ”
- p. 15841, line 23: “which” was replaced with “that”
- p. 15854, line 10. “2014a” was replaced with “2015a”
- p. 15855, line 20. “2014b” was replaced with “2015b”
- p. 15855, line 28: “2014” was replaced with “2015”
- p. 15863, lines 5-6: “By calculating one of the first proton budgets originating from measurements, this study shows the certainties and uncertainties therein.” was replaced with: “By constructing one of the first proton budgets originating



from in situ measurements, this study shows the associated uncertainties and challenges for future studies.”

- p. 15871, lines 15-18: This reference was updated: issue and page numbers were added and “2014” was replaced with “2015”
- p. 15874, lines 1-3. This reference was updated, it now reads:
  - Seitaj, D., Schauer, R., Sulu-Gambari, F., Malkin, S. Y., Martinez Hidalgo, S., Slomp, C. P., and Meysman, F. J. R.: Temporal succession of cryptic sulphur cycling in a seasonally hypoxic basin, in preparation, 2015a.
- p. 15874, lines 4-6. This reference was updated, it now reads:
  - Seitaj, D., Sulu-Gambari, F., Malkin, S. Y., Burdorf, L., Slomp, C. P., and Meysman, F. J. R.: Sediment mineralization and benthic oxygen dynamics in a seasonally hypoxic basin, in preparation, 2015b.
- p. 15874, line 7: the following reference was added:

Shadwick, E. H., Trull, T. W., Thomas, H., and Gibson, J. A. E.: Vulnerability of polar oceans to anthropogenic acidification: comparison of Arctic and Antarctic seasonal cycles., Sci. Rep., 3, 2339, doi:10.1038/srep02339, 2013.
- p. 15875, line 1: the following reference was added:
  - Thomas, H., Prowe, A. E. F., van Heuven, S., Bozec, Y., de Baar, H. J. W., Schiettecatte, L.-S., Suykens, K., Koné, M., Borges, A. V., Lima, I. D. and Doney, S. C.: Rapid decline of the CO<sub>2</sub> buffering capacity in the North Sea and implications for the North Atlantic Ocean, Global Biogeochem. Cycles, 21(4), GB4001, doi:10.1029/2006GB002825, 2007.

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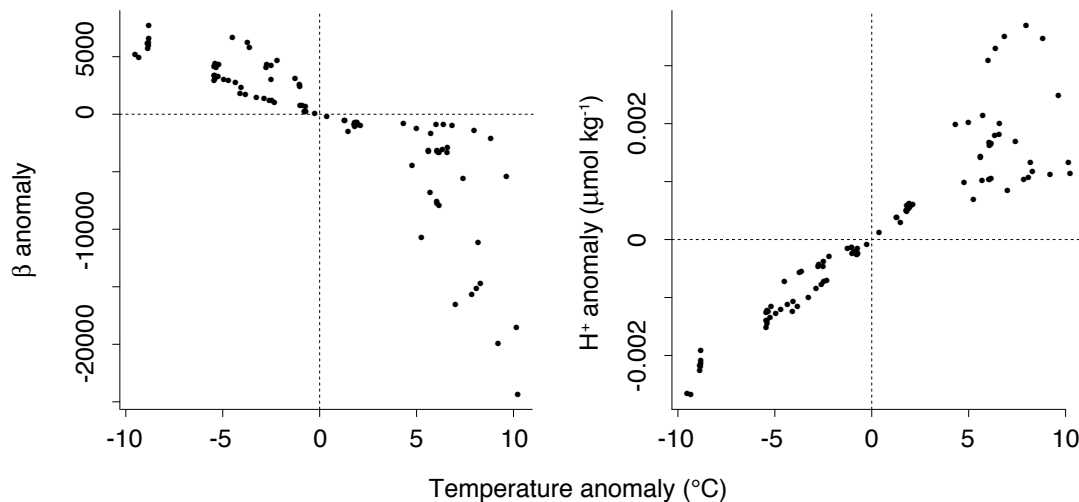
- p. 15880, fig. 3: marginal changes in the lay-out were made
- p. 15881, fig. 4: marginal changes in the lay-out were made
- p. 15883, fig. 6: we reconsidered the lay-out of Fig. 6b, which was a suggestion of reviewer #1. To be consistent with Fig. 6a, we like to keep the seasons on the x-axis. We also considered grouping together the DIC fluxes and the TA fluxes, so change the order of presenting from left to right to S1-DIC, S2-DIC, S3-DIC, S1-TA, S2-TA, S3-TA. This, however, makes it more difficult to compare the DIC and TA fluxes visually and thus determine which of the two dominates the net proton flux at a given moment in time and space. Thus, we decided to keep the figure as it is.
- p. 15886, fig. A1: marginal changes in the lay-out were made

## References

- Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tammooh, F., Ochieng Omengo, F., Geeraert, N., Deirmendjian, L., Polsenaere, P., and Borges, A. V.: Technical Note: Large overestimation of  $p\text{CO}_2$  calculated from pH and alkalinity in acidic, organic-rich freshwaters, *Biogeosciences*, 12, 67–78, doi:10.5194/bg-12-67-2015, 2015.
- Friis, K., Körtzinger, A., and Wallace, D. W. R.: The salinity normalization of marine inorganic carbon chemistry data, *Geophys. Res. Lett.*, 30(2), 1085, doi:10.1029/2002GL015898, 2003.
- Jiang, Z., Tyrrell, T., Hydes, D. J., Dai, M., and Hartman, S. E.: Variability of alkalinity and the alkalinity-salinity relationship in the tropical and subtropical surface ocean, *Global Biogeochem. Cycles*, 28(7), 729–742, doi:10.1002/2013GB004678, 2014.

Interactive comment on *Biogeosciences Discuss.*, 11, 15827, 2014.

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**Fig. 1.** Anomalies of acid-base buffering capacity (left) and proton concentration (right) versus temperature anomaly for the Den Osse Basin in 2012

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