

We would like to thank the Reviewer for insightful and constructive comments. The Reviewer's comments are copied below (**bold**), followed by our replies.

**Anonymous Referee #2**

**Received and published: 11 May 2017**

#### **General comments**

**In this study the main objective is to collect and integrate the existing knowledge of the acid-base system in the Baltic Sea. The study aims to pinpoint the major research gaps/bottlenecks, and challenges for future research. The manuscript presents a review and synthesis of earlier studies focused on different issues related to the carbonate system and carbon cycling in the Baltic Sea. The manuscript includes a number of uncertainties and knowledge gaps of the carbonate system related to brackish waters and estuaries in particular (e.g. dissociation constants, riverine/terrestrial influence) as well as to coastal seas in general (changes in productivity, aerobic/anaerobic mineralization). I think this is a useful and even important contribution to the research on Baltic Sea carbonate system peculiarities, although the manuscript would benefit from a rather substantial revision. I have a few specific comments as well as numerous minor comments/suggestions listed below.**

#### **Specific comments**

**I think first of all that the various bottlenecks mentioned in the study need to be summarized a bit more clearly in a concluding paragraph, just to tie up the loose ends. If possible, I would further like to see some rough estimates of the relative importance of these bottlenecks and knowledge gaps. For example, is it possible to tell whether or not the borate issue is a problem comparable to the (large) issues with Aorg, or to uncertainties related to inaccessible river data, or the poorly known influence of SGD (see also next two points)? Is it possible to do some back-of-the-envelope estimates?**

The revised manuscript will end up with the Conclusion chapter that will summarize the identified bottlenecks, research gaps and thus also challenges for the Baltic Sea acid-base system studies. We would prefer to avoid giving in our manuscript verdicts on importance of different bottlenecks and knowledge gaps before detailed studies.

**Page 10, Line 18: Here you mention own data. Is this data published somewhere? If not, I think you should add a table indicating typical concentrations in these Polish rivers. How substantial is the mentioned AT decrease in western direction?**

No, this data is not published yet. We will add the values to the revised manuscript. We noticed the decrease of  $A_T$  in western direction from  $3300 \mu\text{mol kg}^{-1}$  in Vistula to  $2600 \mu\text{mol kg}^{-1}$  in

Odra. However, we do not want to give these values as the “typical ones” for those rivers/regions as they were taken during only one research cruise. We refer in our text only to our observations and give this information as an important aspect that potentially can shape the riverine  $A_T$  loads. However, more data on  $A_T$ , including its seasonality, are necessary to conclude more precisely on geographical patterns of  $A_T$  in Polish (but not only) rivers and to give the “typical concentrations” that can characterize the  $A_T$  loads.

**Page 11, Line 9-12: This is an important issue. Couldn't such an evaluation of riverine  $A_T$  data be a part of this study? Or at least add a table indicating the current knowledge/knowledge gaps concerning riverine  $A_T$  concentrations/loads. On page 18, line 8 you mention the river loads of terrestrial DOC (340 Gmol) referring to Kuliński and Pempkowiak (2011). What about river loads of DIC and  $A_T$ ? In the Kuliński and Pempkowiak (2011) study there is further a table indicating river loads of DOC and DIC; could something similar be done for  $A_T$  in this study? Or is the data restricted? I would say that one bottleneck in Baltic Sea carbonate system studies is restrictions in the use of monitoring data from the large continental rivers.**

We see quantifying riverine  $A_T$  loads to the Baltic Sea as a task for the separate study. This study would require definitely a better access to the monitoring data, especially for the continental rivers. In our present review manuscript we want to focus on the published data only. Nevertheless we see this gap in the present knowledge and identify the necessity of quantification of riverine  $A_T$  loads and improving the access to the monitoring data as the present-day challenges in the Baltic Sea acid-base system studies.

We fully agree with the Reviewer that restrictions in use of the monitoring data from large continental rivers are one of the biggest bottlenecks in the Baltic Sea acid-base systems studies. We do want to emphasize this fact in our manuscript hoping that such message can promote establishing an open access to the monitoring data.

**Page 11, Line 17-20: Ok, but how important do you think the SGD can be? Is it possible to use the Szymczycha data to at least do a rough estimate of the  $A_T$  source from SGD, and further how large this source is compared to river loads along the Polish coast (where the authors have own data)?**

We identify SGD as a potentially important source of  $A_T$  to the Baltic Sea based on the study by Szymczycha et al. (2014). This hypothesis must, however, first be verified. Szymczycha et al. (2014) did not focus directly on  $A_T$  in their study, but they noticed relatively high concentrations of  $C_T$  in SGD. High  $C_T$  may indicate high concentrations of carbonates and bicarbonates – components of  $A_T$ . It may also be related to the high content of  $CO_2$ , which contributes to  $C_T$  but not to  $A_T$ . Thus, any  $A_T$  estimations from this data without more details would be only a speculation. As far as we know there are no results published on direct  $A_T$  measurements in SGD

entering the Baltic Sea. This is why we do not want to speculate in our paper on how big the  $A_T$  load from SGD can be without more detailed studies on that issue, especially as also the estimations of water volume supplied by SGD to the Baltic are very unsure.

**Several more references should be included. Below I have indicated some that I think are important (see below).**

The suggested references will be included in the revised manuscript.

**There are numerous language issues (see below).**

All the linguistic corrections suggested by the Reviewer will be included in the revised manuscript.

**There are several occasions of repeated information in different sections of the manuscript.**

We will carefully revise the manuscript and avoid repetitions.

#### **Technical corrections**

##### **Page 1**

**Line 24: “the acid-base”, not “thee acid-base”**

**Line 25: “bottlenecks concerning the Baltic Sea”**

##### **Page 2**

**Line 15: “by the scientific”**

**Line 23: “...several other processes are influencing the seawater pH”**

**Such as CaCO<sub>3</sub> formation/dissolution, eutrophication/oligotrophication, AT consumption/production, weathering, organic alkalinity...**

##### **Page 3**

**Line 15: “low buffer capacity” ! in some sub-basins but not all (e.g. large differences between the Gulf of Riga and Bothnian Bay)**

**Line 29: “total dissolved inorganic carbon”**

##### **Page 4**

**Line 2-3: Strange sentence.**

**Line 7-8: Maybe use italic font here?**

**Line 7: [SiO(OH)<sub>3</sub>-] ++ [NH<sub>3</sub>] – remove one of the plus signs**

**Line 25: “independent of temperature”**

##### **C3**

**Line 26: “behave conservatively”**

##### **Page 5**

**Line 3: “a functions”...?**

**Line 14: 428 km<sup>3</sup> is a long-term mean, right? – Large inter-annual variations. Do you have a reference for 428 km<sup>3</sup>?**

**Line 15: “This specific feature” or “These specific features”?**

**Line 16: “Salinity in the surface”**

**Line 16-17: Remove PSU, salinity has no unit nowadays**

**Line 16-17: Maybe add a reference (e.g. Winsor et al., 2001) as well for people not familiar with Baltic Sea salinity gradients?**

**Line 24-25: “fraction of the sedimentary”**

**Line 25: “oxidants, which leads”**

**Page 6**

**Line 12: “basis of other”**

**Page 7**

**Line 12: “Using again the CO<sub>2</sub>\* concentration” or maybe just “Using again CO<sub>2</sub>\*”**

**Line 16-17: Repetition, this is already mentioned on page 4, line 13-14.**

**Page 8**

**Line 1: Earlier in the manuscript you write “HSO<sub>4</sub>-“ instead of “hydrogen sulphate ions”**

**Page 10**

**Line 22: Remove PSU.**

**Page 12**

**Line 1: Rewrite: “At equilibrium with the atmospheric CO<sub>2</sub>, AT controls CT and thus pH. Hence, pH may be depicted: : :”**

**Page 13**

**Line 30: Ok, and what are the typical DOC concentrations for Baltic Sea and ocean waters respectively?**

**Page 14**

**Line 27-28: Repetition from page 4, line 25-26**

**Line 29-31: The Kuliński/Ulfsbo parameterization for A<sub>org</sub> is actually included in at least two different Baltic Sea models (Gustafsson et al., 2015; Omstedt et al., 2015)**

**Page 15**

**Line 29: Remove PSU**

**Page 16**

**Line 24: “dampens the pH increase” (or pCO<sub>2</sub> decrease), right?**

**Line 29: “Baltic Sea surface water pCO<sub>2</sub>”**

**Page 17**

**Line 2: also phosphate consumption, although the effect is small. Maybe add Wolf-Gladrow et al. (2007) as reference?**

**Line 7-13: Are there any estimates of the influence on AT of other organisms that produce CaCO<sub>3</sub> shells (e.g. blue mussels)?**

**Page 18**

**Line 16: “AT distribution depends”**

**Line 33: “after also the sulphate concentration has”**

**Page 20**

**Line 11-12: Pyrite and vivianite can be buried permanently and thus contribute to AT generation (Reed et al., 2016)**

**Line 30: “the BONUS PINBAL”**

**Page 21**

**Line 2-3: How about the WEGAS system (cf. Thornton et al., 2016)?**

**Page 22**

**Line 23-25: Here you should also mention the modelling efforts by Kreuz et al. (2015)**

**References**

**Gustafsson, E., Omstedt, A., Gustafsson, B.G., 2015. The air-water CO<sub>2</sub> exchange of a coastal sea-A sensitivity study on factors that influence the absorption and outgassing of CO<sub>2</sub> in the Baltic Sea. *Journal of Geophysical Research: Oceans* 120, 5342–5357.**

**Kreuz, M., Schartau, M., Engel, A., Nausch, M., Voss, M., 2015. Variations in the elemental ratio of organic matter in the central Baltic Sea: Part I-Linking primary production to remineralization. *Continental Shelf Research* 100, 25–45.**

**Omstedt, A., Edman, M., Claremar, B., Rutgersson, A., 2015. Modelling the contributions to marine acidification from deposited SO<sub>x</sub>, NO<sub>x</sub>, and NH<sub>x</sub> in the Baltic Sea: Past and present situations. *Continental Shelf Research* 111, 234–249.**

**Reed, D.C., Gustafsson, B.G., Slomp, C.P., 2016. Shelf-to-basin iron shuttling enhances vivianite formation in deep Baltic Sea sediments. *Earth and Planetary Science Letters* 434, 241–251.**

**Thornton, B.F., Geibel, M.C., Crill, P.M., Humborg, C., Mörth, C.-M., 2016. Methane fluxes from the sea to the atmosphere across the Siberian shelf seas. *Geophys. Res. Lett.* 2016GL068977.**

**Winsor, P., Rodhe, J., Omstedt, A., 2001. Baltic Sea ocean climate: an analysis of 100 yr of hydrographic data with focus on the freshwater budget. *Climate Research* 18, 5–15.**

**Wolf-Gladrow, D.A., Zeebe, R.E., Klaas, C., Körtzinger, A., Dickson, A.G., 2007. Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. *Marine Chemistry* 106, 287–300.**