

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 #1**

**Review of Kulinski et al., "Structure and functioning of the acid-base system in the Baltic Sea" Summary**

**This manuscript synthesizes the accumulated studies of the acid-base chemistry of the Baltic Sea, a unique system which exhibits properties quite different from those of open ocean waters. This is a worthy topic of discussion, as increased attention is being paid to the acid-base chemistry of coastal waters in general, especially in the context of anthropogenically-driven ocean acidification. In that sense this paper may have broader applicability, as several of the processes discussed may be common to coastal and estuarine systems globally, although this possibility is not explicitly discussed in the manuscript.**

We will present the global context of our manuscript in the conclusion section.

**I do think the manuscript could stand a thorough revision. The structure of the manuscript consists of a short introduction, a section discussing open-ocean acid-base chemistry, then the bulk of the manuscript consists of a collection of specific Baltic Sea chemical traits, ending with a short section discussing the challenges of studying the Baltic acid-base system. The central section covers a number of disparate topics, but alkalinity seems to be a central thread in many of them (changing alkalinity, organic alkalinity, borate alkalinity, etc.). Perhaps these could be grouped together as their own section?**

We have the entire chapter 3.3. dedicated to the central role of alkalinity in the acid-base system. The specific aspects are, however, discussed in that chapter separately to avoid confusion.

**Additionally, English usage could be improved significantly- I have tried to include many specific edits to that end.**

We will correct English in our manuscript also by including Reviewer's suggestions.

**Several sections are really lacking in citations. While citations may not exist which are specific to the Baltic Sea, papers examining similar topics in others systems certainly exist. I will note specific sections where I noticed this below.**

Citations will be added to the revise manuscript. Some of them are already mentioned below, in the response to Reviewer's comments.

**I also think the final section needs more. A paragraph or two, or perhaps even a Conclusions section, detailing what the authors see are the next frontiers and obstacles to a comprehensive understanding of the Baltic acid-base system. What are the next steps needed? What are the implications of the unusual qualities of the Baltic acid-base system? What are the knowledge gaps that need to be filled in? A section like this may wrap up the overall paper in a very useful way.**

Conclusion section will be added to the revised manuscript. It will wrap up the existing knowledge on the Baltic Sea acid-base system, including identification of the peculiarities. It will also define bottlenecks and research gaps defining in that way challenges in acid-base system research in the Baltic Sea.

**Specific Comments Abstract- The last sentence mentions that the paper will “specify bottlenecks”, but these bottlenecks don’t come across clearly. Perhaps they can be assembled or summarized in their own section, similar to what I describe above? And what are the bottlenecks restricting, in other words, what are some of the larger goals they are blocking?**

As mentioned above, the bottlenecks will be summarized in the conclusion section that will be added to the revised manuscript.

**P2L3-4 and throughout: the terms “structure and functioning” is used often throughout the manuscript. But, the difference between these terms is not really clear to me in the context of this paper. By structure do you mean the collection of individual acid-base constituents, and by functioning do you mean changes brought about by long-term alkalinity changes, biomass production, and other processes? It would be informative to explicitly explain these terms at the beginning of the manuscript, to frame the work’s goals and purpose.**

Correct. By saying structure we have in mind collection of acid-base constituents (substances having acid-base properties), their concentrations and dissociation constants, while by saying functioning we have in mind changes in the structure caused by different processes occurring either on the short or the long time scale.

We will define both these terms at the beginning of the revised manuscript.

**Be sure to define terms before introducing their abbreviations, for example CO<sub>2</sub> P2L6, CaCO<sub>3</sub> P2L29, CO<sub>3</sub><sup>2-</sup> P3L4.**

We will define all the abbreviations in the revised version of the manuscript.

**P2L20: Cite some works which demonstrate this belief.**

We will add to that section the following citations:

Caldeira, K., Wickett, M. E., Anthropogenic carbon and ocean pH, *Nature*, 425, 365–365, 2003.

Riebesell, U., Fabry, V. J., Hansson, L. and Gattuso J.-P.: Guide to best practices for ocean acidification research and data reporting, 260, Luxembourg, Publications Office of the European Union, 2010.

Zeebe, R.E., History of Seawater Carbonate Chemistry, Atmospheric CO<sub>2</sub>, and Ocean Acidification, *Annual Review of Earth and Planetary Sciences*, 40, 141–165, 2012.

**P3L5-13. This is a good paragraph, and it might make sense to move it to be the third paragraph of the Introduction.**

Indeed this paragraph could be easily moved to be the third one in the Introduction. Nevertheless we would like to leave it in the place it is now as the narration included in this paragraph is closely linked with the next paragraph – the last one in the Introduction.

**P3L28: The four parameters discussed in this section really describe the CO<sub>2</sub>/carbonate system of seawater, not the complete acid-base system as illustrated later in the manuscript.**

In the chapter 2 we present the CO<sub>2</sub>/carbonate system as the core of the acid-base system for all seawater bodies. We do also present here  $A_T$  equation (and discuss it briefly), which includes non-CO<sub>2</sub> components of the acid-base system. We conclude the chapter saying that that in the ocean studies the total concentrations of non-CO<sub>2</sub> acid-base components are either negligible or can be approximated by a functions of salinity. We say also that the influence of non-CO<sub>2</sub> components is more critical for coastal and shelf regions what is the core of the chapter 3.

**P4L11: Dr. Andrew Dickson's lab provides certified Tris buffer for the calibration of pH- do these not qualify?**

Right. We will correct this in the revised version of the manuscript.

**P5L5 Note that the Hunt reference discusses river water, not seawater.**

Indeed. We will correct this in the revised version of the manuscript.

**P5L14-18: this information probably needs a citation.**

The citation (Lass and Matthäus, 2008) is given after the next sentence. This citation refers to all the information given before in the chapter 3.1.

**P5L16-17: using PSU might require justifying your units, as the convention is for unit-less salinity. Or you may need to consider citing which salinity scale you are presenting.**

We will present salinity in unit-less convention in the revised version of the manuscript.

**P5L22: Are there multiple deep water layers?**

We used plural to stress out high vertical variability of the seawater properties under the halocline. Sometimes, especially after the new inflow of the dense water from the North Sea there are some clearly separated sub-layers under the halocline.

**P5L23: if surface and deep waters are separated by a halocline, how does the terrestrial organic matter make its way to the deep layers? Unless the terrestrial matter is particulate, and you are talking about a sinking process?**

Indeed, our intention was to say here about the sinking of particulate organic matter – both terrestrial and marine. We will rephrase that sentence to make it clearer in the revised manuscript.

**P7L15-17: citations needed here.**

The citation of the paper by Dickson (1984) will be added to the revised manuscript.

Dickson, A. G. (1984). pH scales and proton-transfer reactions in saline media such as sea water. *Geochim. Cosmochim. Acta* 48 (11): 2299–2308.

**P8L1: citations needed here.**

Similar as for the previous comment we suggest that the citation of the paper by Dickson (1984) is the most adequate here. It will be added to the revised version.

**P8L16-18: this information might be better presented as a pair of equations:**

$\Delta = (\text{pK1M-R} - \text{pK2M-R})$

We will follow the Reviewer's suggestion in the revised manuscript.

**P9: should the y-axis of Fig 2c be  $pK_1 - pK_2$ ? Fig 2c is the most interesting part of this Figure- do you need panels A and B? Some more explanation of Fig 2c is probably needed. What does it mean to subtract  $pK_1-pK_2$ ... what does that difference tell us?**

Yes, the y-axis should be  $pK_1 - pK_2$ . This will be corrected in the revised manuscript.

The figures Fig. 2 a and b give clear impression how the dissociation constants of carbonic acid change along with salinity and temperature. This information can be interesting for readers as it is not very obvious for people not working deeply with  $CO_2$  system. Thus, we see meaningful to keep both these figures in the manuscript.

$pK_1$  is a negative logarithm from  $K_1$ . Thus  $pK_1-pK_2$  (difference of logarithms) means the same as  $K_1/K_2$ . We present the comparison between dissociation constants obtained by different authors for brackish waters as  $pK_1-pK_2$  (or  $K_1/K_2$ ) because they cannot be compared directly. The reason for that is the fact that the constants given by Buch (1945) refer to the hydrogen ion activity, while those by Millero (2010) and Roy (1993) to total hydrogen ion concentration. However, comparison of the constants ratios ( $K_1/K_2$  or  $pK_1-pK_2$ ) is free from this limitation. Thus, we used an indirect way allowing for comparison dissociation constants obtained by different techniques and using different pH scales.

We will modify this section of the manuscript to make it clearer for the readers.

**P10L22-24: What is this sentence trying to convey?**

We will rephrase this sentence in the revised manuscript. Our intention here was to say that it is impossible to define one  $A_T$  end-member value for the rivers entering the Baltic Proper as different rivers have often very different  $A_T$ .

**P11 Fig3: Is this all surface data? The alkalinity at salinity 35 still seems relatively low (below 2400  $\mu\text{mol/kg}$ ).**

Yes, this is surface data. All the results (blue dots) on the picture were experimentally obtained. For details please see the paper by Beldowski et al. (2010), from where the picture has been taken. Please note that data you refer to describe the mixing between the Baltic Sea water and the North Sea water – the latter may be slightly different in terms of  $A_T$  from the open ocean water.

**P11L5-12: Why doesn't this study attempt to synthesize these data, as discussed? This could be an important addition to the study. At the very least this could be included in a discussion at the end of future needs.**

We do see synthesizing data on the riverine  $A_T$  in the Baltic Sea an important task. However, due to the limitations in the access to the data, it is impossible to do it in the present manuscript.

Definitely we identify this as one of the greatest challenges in the studies on the acid-base system in the Baltic Sea. This will be underlined in the discussion/conclusion part of the revised version of the manuscript.

**P11L1: alkalinity controls the DIC speciation (and thus the pH), but not the overall DIC, right?**

Yes. The sentence will be rephrased.

**P11L5: give the open ocean pH range, and give citations as well.**

The open ocean pH range is 7.9-8.7 according to Riebesell et al. (2010). This information will be given in the revised manuscript.

Riebesell, U., Fabry, V. J., Hansson, L. and Gattuso J.-P.: Guide to best practices for ocean acidification research and data reporting, 260, Luxembourg, Publications Office of the European Union, 2010.

**P13L21-22: these alkalinity increases are quite large! What are some of the proposed mechanisms that might produce this increase?**

Indeed, these increases are high. As it is already said in the manuscript: “Several reasons for the increasing  $A_T$  are discussed by Müller et al. (2016), but a major player could not be identified and, hence, it remains unclear whether the trend will continue in the future.” The authors (Müller et al. 2016) identified some potential mechanisms for  $A_T$  increase:

- increasing  $A_T$  loads from rivers as a result of enhanced weathering of limestone in the catchment
- liming activities in Scandinavia aiming at counteracting the acidification in freshwater systems
- internal alkalinity generation: primary production, denitrification, sulphate reduction

**P13L30: when using the term organic matter, do you mean dissolved, particulate, or both?**

We have in mind in this sentence both particulate and dissolved organic matter. That is why we use the general term “organic matter”. However, one should keep in mind that concentration of the particulate organic matter is usually several times lower than the dissolved one.

**P14L26-27: cite some examples here.**

In the revised manuscript we will enrich this sentence with the citations of the following papers: Edman and Omstedt, 2013; Kuznetsov and Neumann, 2013; Omstedt et al., 2009, 2012. All of them nicely illustrate the use of  $C_T$  and  $A_T$  in the biogeochemical models.

**P16L19-21. This figure makes some significant assumptions, such as that the produced biomass is not remineralized (discussed in the next section). What is gained by presenting biomass production and remineralization separately?**

We do not agree with the Reviewer at this point. Fig. 5 does not make any assumptions as it presents the measured  $pCO_2$  values. This is a typical seasonality observed (not assumed) in the surface waters of the open Baltic Sea. In spring seawater  $pCO_2$  goes significantly down as photosynthesis predominates over mineralization and produced particulate organic matter (POM) is exported below the mixed layer depth, which is at the same time significantly decreasing. This gives an impression that POM is not mineralized. In fact it is mineralized but in the deep water separated from the upper productive zone by thermocline or halocline or both. The mineralization signal starts to predominate in autumn, when mixed layer depth is deepening, what brings to the surface  $CO_2$  accumulated in the deeper water layers.

Our motivation to present the effects of biomass production and remineralization separately is the fact that both these processes influence the acid-base system differently but also that the bulk effects of both these processes appear in the different parts of the water column – production in the upper productive zone, while mineralization in the deeper water layers and on sediments surface. The latter may include also number of redox reactions depending on what is an oxidant. Having in mind this motivation and to make the text clearer we decided to separate the description of both these processes in the manuscript.

**P18L12: does tDOC include POC? Could you specify the contributors to total DOC?**

No, tDOC refers only to terrestrial dissolved organic carbon and does not include POC. We will correct the text to avoid ambiguities.

**P18L15-25: citations needed throughout this section.**

The following citations will be added to the section:

Brenner, H., Braeckman, U., Le Guitton, M. and Meysman, F.J.R.: The impact of sedimentary alkalinity release on the water column  $CO_2$  system in the North Sea., *Biogeosciences*, 13, 841-863, 2016.

Krumins V., Gehlen M., Arndt S., Van Cappellen P. and Regnier P.: Dissolved inorganic carbon and alkalinity fluxes from coastal marine sediments: model estimates for different shelf environments and sensitivity to global change. *Biogeosciences*, 10, 371-398, 2013.

Schulz, H.D. and Zabel, M., Marine geochemistry, Springer-Verlag Berlin Heidelberg, 574, 2006.

Thomas H., Schiettecatte L.-S., Suykens K., Koné Y. J. M., Shadwick E. H., Prowe A. E. F., Bozec Y., de Baar H. J. W. and Borges A. V.: Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments, Biogeosciences, 6, 267–274, 2009.

**P21L15: But reference materials exist for alkalinity too. While fulvics and humics may compromise components of the alkalinity system not found in the alkalinity CRM, will they really interfere with the measurement of overall total alkalinity, especially by a method like the Gran titration?**

Indeed, CRMs exist also for total alkalinity measurements. They definitely increase the quality of  $A_T$  measurements. What we wanted to point out in this section is that  $A_T$  measurements are not trivial in the Baltic Sea water. This is due to the presence of humics and fulvics. From the study by Ulfso et al. (2015) we know that fulvic or humic acids have  $pK_a$  values close to the  $pK_a$  of carbonic acid and may thus impede the correct detection of the titration endpoint. However, at the moment we do not know how big this effect can be.

**P21L18-23: this section seems repeated from the previous paragraph.**

We will rephrase this section in the revised manuscript.

**P21L31-33: this section also seems repeated from previous discussion.**

We will delete this section from the revised manuscript.

**P22L17-P23L2: this is an excellent paragraph, and I think it belongs in the Introduction or very early on in Section 3, as it really synthesizes a number of interesting studies.**

We consciously put this paragraph at the end. We see that experimental studies should support development of the biogeochemical models. Thus, we see the structure of the text, in which the description of the achievements and limitations of the acid-base system (or marine  $CO_2$  system) modelling is at the end as a natural one. We hope the Reviewer does not object when the place of that section will remain unchanged.

**Suggested Technical and Language Changes Abstract L22 change to “constants in brackish water” Abstract L24 change to “alkalinity, and the acid-base” P2 “The understanding of its structure and functioning is a tool” awkward phrase. P2L5 change to “interest in present-day” P2L6 change to “dissolution and  $CO_2$ ” P2L11 change to “(a buffering reaction) P2L12 change to “decrease in pH” P2L15 change to “the scientific”**

P2L16 define EU P2L28 specify “ocean acid-base system” P2L30 change to “dissolution without” P2L31 change to “system. The saturation states of calcite and aragonite are of...” P3L5 change to “major component of” P3L6 change to “25% of anthropogenic” P3L14 change to “ecosystem. On one hand” P3L15 change to “acidification, on the other...” P4L2 change to “CT are usually based on...” P4L7 remove second + before [NH<sub>3</sub>] P4L23 change to “models for the simulation” P4L25 change to “independent of temperature” P4L26 change to “conservatively” P4L29 change to “for CO<sub>2</sub> system studies” P4L30 change to “calculation of pH” P5L2 change to “are either” P5L3 change to “approximated as a function of salinity” P5L4 change to “where the biogeochemical” P5L10 change heading to just “Hydrographic Setting” P5L12 add reference to Fig 1 P5L15 change to “The specific” P5L23 change to “that either originated” P5L25 change to “which leads” P6L6 change to “system” P6L12 change to “of other known” P7L9 remove comma P7L12 change to “again CO<sub>2</sub>” P7L21 change to “Baltic Sea, and whose laboratory” P7L27 change “upcoming” to “increasing” P7L30 change to “studies aimed at” P8L23 just use the last name, Buch P9L7 change to “When alkalinity is also used...” P9L12 change to “Section 3.4.2” P9L13 change to “on the order of” P10L11 does this also apply to the Gulf of Finland? P10L12 change to “shown by the” P10L17-19 rephrase this sentence P10L22-24 rephrase this sentence as well P11L9 change to “At monitoring data” P11L10 change to “framework of the HELCOM” P11L11 change to “countries such as Sweden” P11L11 change to “publicly” P11L14 change to groundwater, as in river water, depends...” P11L16 change to “part of the coast can be rich...” P11L20 change to “have not been reported” P12L1 change to “with atmospheric” P12L8 change to “Fig. 4 also shows” P12L9 rephrase this line P13L3 “an abbreviation for surface seawater” P13L9 change to “gives reason” and “progression of ocean acidification” P13L12 change “upon” to “to” P13L14 change to “natural and anthropogenic” P13L14 change to “The first hints of increasing” P13L15 change to “the central Baltic” P13L16 change to “have considerably mitigated the acidification due to” P13L18-19 change to “since the start of CO<sub>2</sub> research” P13L20 remove “they” P13L21 is this regional gradient increasing? P14L1 change to “functional groups, some of which” P14L9 change to “system, the greater” P14L12 doesn’t this also mean an increase in bicarbonate as well as H<sub>2</sub>CO<sub>3</sub> and pCO<sub>2</sub>? P14L22 change to “using measured AT may lead” P14L28 change to “independent of pressure” P16L2 change to “studies is that by Uppstrom (1974)” P16L9 change to “and, similar to the effects” P16L15-16 rephrase this P16L19 change to “as the controls” P16L20 change to “primarily alters CT” P16L24 change to “through the air-sea interface” P17L2 change to “As phytoplankton assimilate nitrate for growth an equal...” P17L7 change to “also may consume CO<sub>3</sub><sup>2-</sup>” P17L8 change to “pCO<sub>2</sub> increases and pH decreases” P17L11 change to “This possibly prevents” P18L4 change to “undergoes remineralization in the” P18L9 change to “suggested” P18L13 change to “It is important to mention...” P18L16 change to “depends” P18L19 change to “, produces CO<sub>2</sub>, and changes the alkalinity. The change in AT depends..” P18L27 change were to where P18L28 change to “After nitrate”

**P18L29 change to “, before sulphate oxidizes the organic matter and generates” P18L31 can you define a redoxcline? P18L33 change to “after the sulphate concentration has” P19L8 change to “Gotland Sea these” P20L7 change to “in a model study” P20L8 remove “of the Baltic Sea” P20L18 change to “two out of the four acid-base system parameters (pCO<sub>2</sub>, ...” P20L19 change to “known (e.g. by measurements).” P20L20 change “studies” to “study” P20L28 change to “spectrophotometric pH” P20L30 change to “the Bonus PINBAL” P20L31 change to “reference materials” P21L1 change to “measuring the CO<sub>2</sub> concent in air” P21L2 change to “not be fast enough” P21L6 change to “in discrete samples” P21L9 is this +/- 2 umol? P21L9 change to “for ocean water” P21L11 change to “influence of organic” P21L13 change to “concentrations” P21L18 change to “require” P21L18 change to “parameterization of the related processes” P21L22 change to “due to low DOM” P21L29 change to “satisfactory” P22L1 change to “calculation also omits” P22L3 remove “hence” P22L9 change to “simulation of surface water” P22L31 CO<sub>2</sub> subscript P22L1 change to “mainly control”**

All the technical and linguistic improvements suggested by the reviewer will be included in the revised version of the manuscript.