

Interactive comment on “Structure and functioning of the acid-base system in the Baltic Sea” by Karol Kuliński et al.

Anonymous Referee #2

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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

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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?

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?

Page 11, Line 9-12: This is an important issue. Couldn't such an evaluation of riverine AT data be a part of this study? Or at least add a table indicating the current knowledge/knowledge gaps concerning riverine AT 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 AT? 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 AT 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.

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 AT source from SGD, and further how large this source is compared to river loads along the Polish coast (where the authors have own data)?

Several more references should be included. Below I have indicated some that I think

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are important (see below).

There are numerous language issues (see below).

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

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 CaCO₃ 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)₃⁻]⁺⁺ [NH₃][]] – remove one of the plus signs

Line 25: “independent of temperature”

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Line 26: “behave conservatively”

Page 5

Line 3: “a functions” ...?

Line 14: 428 km³ is a long-term mean, right? – Large inter-annual variations. Do you have a reference for 428 km³?

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 CO₂^{*} concentration” or maybe just “Using again CO₂^{*}”

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

Page 8

Line 1: Earlier in the manuscript you write “HSO₄⁻” instead of “hydrogen sulphate ions”

Page 10

Line 22: Remove PSU.

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Page 12

Line 1: Rewrite: "At equilibrium with the atmospheric CO₂, 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/Ulfssbo parameterization for Aorg 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 pCO₂ decrease), right?

Line 29: "Baltic Sea surface water pCO₂"

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 CaCO₃ shells (e.g. blue mussels)?

Page 18

Line 16: "AT distribution depends"

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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 CO₂ exchange of a coastal sea-A sensitivity study on factors that influence the absorption and outgassing of CO₂ 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_x, NO_x, and NH_x 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

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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.

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