

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

Anonymous Referee #1

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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.

I do think the manuscript could stand a thorough revision. The structure of the

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

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.

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?

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

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goals and purpose.

Be sure to define terms before introducing their abbreviations, for example CO₂ P2L6, CaCO₃ P2L29, CO₃ 2- P3L4.

P2L20: Cite some works which demonstrate this belief.

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

P3L28: The four parameters discussed in this section really describe the CO₂/carbonate system of seawater, not the complete acid-base system as illustrated later in the manuscript.

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

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

P5L14-18: this information probably needs a citation.

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

P5L22: Are there multiple deep water layers?

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?

P7L15-17: citations needed here.

P8L1: citations needed here.

P8L16-18: this information might be better presented as a pair of equations: $\Delta = (pK1M - R - pK2M - R)$

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P9: should the y-axis of Fig 2c be $pK1 - pK2$? 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 $pK1 - pK2$. . . what does that difference tell us?

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

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

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.

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

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

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

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

P14L26-27: cite some examples here.

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?

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

P18L15-25: citations needed throughout this section.

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

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they really interfere with the measurement of overall total alkalinity, especially by a method like the Gran titration?

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

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

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.

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 CO₂” 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 [NH₃] P4L23 change to “models for the simulation” P4L25 change to “independent of temperature” P4L26 change to “conservatively” P4L29 change to “for CO₂ 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 CO₂” 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

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“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 CO₂ 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 H₂CO₃ and pCO₂? 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 CO₃²⁻” P17L8 change to “pCO₂ 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 CO₂, 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 (pCO₂, . . .” 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 CO₂ 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 CO₂ subscript P22L1 change to “mainly control”

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