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Sopot, 2017-09-04

Dr. Marcus Reckermann,
Earth System Dynamics

Dear Dr. Marcus Reckermann,

Please find enclosed our responses to the reviews as well as revised version of our manuscript entitled „Structure and functioning of the acid-base system in the Baltic Sea" by Karol Kuliński, Bernd Schneider, Beata Szymczycha and Marcin Stokowski. We attach also the marked-up manuscript version, in which you can find all changes we made in the manuscript.

We hope that the content of the revised manuscript will meet the requirements of Earth System Dynamics.

Sincerely yours

Karol Kuliński

(on behalf of all co-authors)

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 present the general context of our manuscript in the "Summary and conclusions" 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.

"Summary and conclusion" section will be added to the revised manuscript. It wraps up the existing knowledge on the Baltic Sea acid-base system, including identification of the peculiarities. It also identifies 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 are summarized in the "Summary and 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 defined both these terms at the beginning of the revised manuscript.

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

We defined all the abbreviations in the revised version of the manuscript.

P2L20: Cite some works which demonstrate this belief.

We added 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_2, 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 CO2/carbonate system of seawater, not the complete acid-base system as illustrated later in the manuscript.

In the chapter 2 we present the CO2/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_2 components of the acid-base system. We conclude the chapter saying that that in the ocean studies the total concentrations of non-CO_2 acid-base components are either negligible or can be approximated by a functions of salinity. We say also that the influence of non-CO_2 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 added few more sentences here to clarify this aspect.

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

Indeed. We corrected 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 presented 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 rephrased that sentence to make it clearer in the revised manuscript.

P7L15-17: citations needed here.

The citation of the paper by Dickson (1984) was 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 was added to the revised version.

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

We corrected that part of the manuscript to make it clearer for the reader. In the revised manuscript we use the term $\Delta\log(K_1/K_2)$.

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?

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 interested 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.

We modified this part of the manuscript to make it clearer for the readers. We also replaced Fig. 2c and now it contains correctly described Y-axis. We explained in the revised manuscript our motivation for using the ratio K_1/K_2 and its logarithmic form. In that way we are able to compare the dissociation constants determined for different pH scales.

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

We deleted this sentence in the revised manuscript.

P11 Fig3: Is this all surface data? The alkalinity at salinity 35 still seems relatively low (below 2400 umol/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 the greatest challenges in the studies on the acid-base system in the Baltic Sea. This is 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?

We refer in this sentence to the equilibrium with the atmosphere. In this case the A_T controls the C_T and thus the pH.

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). Please note that we do not refer in that sentence to the observed pH range in the open ocean, but we interpret Fig. 4. According to it the pH of seawater at equilibrium with atmosphere CO_2 change in a narrow range due to the narrow A_T range (2170-2460 µmol kg^{-1} according to Riebesell et al., 2010).
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 added 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 corrected the text to avoid ambiguities.

P18L15-25: citations needed throughout this section.

The following citations were 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 Ulfsbo 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 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 “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” P11L11change 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 CO3 2-“ 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”

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

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 ends up with the Summary and conclusion chapter that summarizes 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 on that issues are published.

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 noticed the decrease of A_T in western direction from 3300 μmol kg^{-1} in Vistula to 2600 μmol 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. Taking into account these facts we decided to delete this sentence.

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.

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 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)?

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 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”
C3
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.

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/Ulfsbo 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”

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 Kreus et al. (2015)

References

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All the technical corrections and amendmendts as well as suggested citations have been included to the revised manuscript.

Structure and functioning of the acid-base system in the Baltic Sea.

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Key words: pH, total alkalinity, CO_2 system, borate alkalinity, organic alkalinity, dissociation constants, biomass production, mineralization

Abstract

The marine acid-base system is relatively well understood for oceanic waters. Its structure and functioning is less obvious for the coastal and shelf seas due to the number of regionally specific anomalies. In this review article we collect and integrate existing knowledge on the acid-base system in the Baltic Sea. Hydrographical and biogeochemical characteristics of the Baltic Sea, as manifested in horizontal and vertical salinity gradients, permanent stratification of the water column, eutrophication, high organic matter concentrations and high anthropogenic pressure, makes the acid-base system complex. We summarize in this study the general knowledge on the marine acid-base system as well as we describe the peculiarities identified and reported for the Baltic Sea specifically. In this context we discuss issues such as: dissociation constants in ~~the~~ brackish water, different chemical alkalinity models including contributions by organic acid-base systems, long term changes of total alkalinity, anomalies of borate alkalinity and thee acid-base effects of biomass production and mineralization. Finally, we identify research gaps and specify bottlenecks concerning the Baltic Sea acid-base system.

1. Introduction

The acid-base system controlling the seawater pH is formed by a number of chemical substances having acid-base properties (Dickson et al., 2007). The importance of each of these substances (structure of the acid-base system) depends on both concentrations of individual constituents and their dissociation constants. The control by physical conditions (temperature, salinity) and biogeochemical processes (e.g. biomass production and mineralization) as well as interrelationships between individual components determine the functioning of the acid-base system. ~~a complex net of interrelationships between chemical species and processes that control the seawater pH (Dickson et al., 2007).~~ The understanding of the ~~its~~ structure and functioning of the acid-base system is ~~a tool~~necessary to investigate important issues that shape the Baltic Sea ecosystem and that are of interest ~~for the~~in present-day chemical oceanography like: ocean acidification, calcium carbonate ($CaCO_3$) formation/dissolution and~~/or~~ carbon dioxide (CO_2) ~~gas~~ exchange through the air-sea interface.

The steady increase of the atmospheric CO_2 concentrations leads to enhanced dissolution of CO_2 in the ocean. Since CO_2 dissolved in seawater forms the diprotic carbonic acid, hydrogen ions are released. Although the major fraction of the hydrogen ions are taken up by carbonate ions (a buffering reaction), a significant fraction stays in the water column and thus causes a decrease ~~of the~~in pH. This phenomenon is known in the scientific literature as “ocean acidification” although seawater does not really become acidic but only moves from its alkaline character towards the acidic regime (Riebesell et al., 2010). Ocean acidification has been recognized as one of the greatest threats for marine ecosystems not only by the scientific community, but also in European Union (EU) legislation. EU Marine Strategy Framework Directive (MSFD, 2008) explicitly points out that the EU Member States should put more attention to ocean acidification, and emphasizes the necessity to include measurements of pH and of the CO_2 partial pressure (pCO_2) as descriptors for the environmental status of marine regions.

There is a general belief that the magnitude of ocean acidification can sufficiently be quantified from the atmospheric pCO_2 levels and the CO_2 exchange between seawater and the atmosphere (Zeebe, 2012; Riebesell et al., 2010; Caldeira and Wicket, 2003). This is approximately true for oceanic waters. However, it is not the case for coastal seas because several other processes ~~and mechanisms~~ are influencing the seawater pH such as: $CaCO_3$ formation and/or dissolution, euthrophication or oligotrophication, A_T consumption and/or production, weathering, contribution by organic substances etc. The general structure and functioning of the acid-base system in seawater are relatively well identified, however still some aspects contain a lot of gaps and/or shortcomings, which can lead to wrong conclusions and questionable predictions of the future pH development (Orr et al., 2015; Koeve and Oschlies, 2012; Hunt et al., 2011; Dickson et al., 2007; Cai et al; 1998).

Since the CO_2 system is an integral part of the ocean acid-base system, it is impossible to understand the CO_2 system and to assess processes such as the CO_2 gas exchange or $CaCO_3$ dissolution/formation, without a clear idea about the structure and functioning of the whole acid-base system. The ~~Saturation~~ saturation states of calcite and aragonite ~~is~~ are of crucial importance for organisms forming their exoskeletons from $CaCO_3$. Although pelagic calcifying organisms do not occur in the Baltic Sea this aspect is still relevant as some benthic organisms can also build $CaCO_3$ into their shells (Tyrrell et al., 2008). Moreover, calcifying processes not only depend on the acid-base system structure but in turn can modify it by decreasing the concentration of carbonate ions (CO_3^{2-}) and thus the alkalinity.

Carbon dioxide is a major ~~player in~~component of the global carbon cycle and transport of CO_2 links all Earth’s compartments. It is believed that the world oceans absorb about 25 % of ~~the~~ anthropogenic CO_2 emissions. However, there is still a debate on the role that the shelf seas play in this context (Le Quéré, 2016). The direction and magnitude of the CO_2 exchange through the air-sea interface depends largely on the pCO_2 difference between seawater and the atmosphere. The level of seawater pCO_2 is mainly controlled by the structure of the acid-base system that is influenced by the combined effect of biological activity (biomass production vs. mineralization), CO_2 exchange with the atmosphere and temperature (Emerson and Hedges, 2008).

In this context the Baltic Sea can be considered as a very complex ecosystem.~~, in which o~~ On one hand the low buffer capacity makes the seawater vulnerable to acidification in most regions of the Baltic Sea, ~~and~~ on the other hand the sea is exposed to various anthropogenic influences which have the potential to change the acid-base system and thus also seawater pH and all pH-related processes. This makes the Baltic Sea different from the oceans for which the CO_2 system as part of the acid-base system has been well characterized during the last decades. Considerable research effort was also undertaken in recent years to investigate the Baltic Sea CO_2 system and its peculiarities. However, this was done from different perspectives and resulted in specific problem-oriented and divers knowledge. Therefore, the goal of this review article is to collect and integrate the existing knowledge on the structure and functioning of the acid-base system in the Baltic Sea, to point out the research gaps and thus also to address challenges for the future research in this field.

2. The standard acid-base model for ocean water

Four measurable variables exist to describe the acid-base system of seawater. These are: pCO_2, pH, total inorganic carbon concentration (C_T, known also as DIC) and total alkalinity (A_T). C_T is the total concentration of all inorganic carbon forms present in seawater (Eq. 1), where $[CO_2^*]$ represents the sum of molecular dissolved CO_2 and undissociated carbonic acid (H_2CO_3):

$$C_T = [CO_2{}^*] + [HCO_3^-] + [CO_3^{2-}] \qquad (1)$$

Measurements of C_T ~~usually base~~are usually based on acidification of the sample and coulometric or infrared detection of the extracted CO_2 (Dickson et al., 2007). A_T is defined as the excess of proton acceptors (bases formed from weak acids with a dissociation constant of $K \leq 10^{-4.5}$ at 25 °C) over proton donors (acids with $K > 10^{-4.5}$) and expressed as the hydrogen ion equivalent in one kilogram of sample (Dickson, 1981):

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + \cancel{+}[NH_3] + [HS^-] + [\text{minor bases}] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] - [\text{minor acids}] \qquad (2)$$

A_T can be determined by open- or closed-cell acidimetric titration. For both C_T and A_T certified reference materials are provided by the Andrew Dickson laboratory, UC San Diego, USA (Dickson et al., 2007). pH measurements in seawater are usually calibrated against TRIS buffer. Its characteristics is well known at salinities of 20-35 (Mosley et al., 2004; DelValls and Dickson, 1998). The efforts to improve the TRIS buffer characteristics for lower salinities are ongoing within the BONUS PINBAL project. The use of TRIS buffer helps to calibrate the systems for pH measurements but does not fully guarantee the quality of the pH results as ~~Reference~~ reference materials in seawater matrix still do not exist for pH measurements ~~in seawater~~. In many cases pH is still measured potentiometrically on the NBS scale although spectrophotometric measurements on the total scale (pH_{tot}), which takes into account also HSO_4^- ions, are currently state of the art in the field of chemical oceanography. The concentration of CO_2^* in seawater is obtained from the partial pressure of CO_2 in air in equilibrium with seawater. According to the standard operating procedure (Dickson et al., 2007), measurements of pCO_2 require continuous flow of water, which makes this parameter difficult to measure in discrete samples.

All four variables are interacting and control the pH by a set of equilibrium constants and mass balance equations. In general the interrelationships between these four parameters facilitate the calculation of any two variables, when the two others are known, e.g. through measurements, and when the dissociation constants of the involved acid-base reactions are known for the respective temperature and salinity. This fact is used in biogeochemical models ~~aiming at~~for the simulation of marine CO_2 system. All biogeochemical models are based on the transport and transformations of A_T and C_T, because these variables are independent ~~on~~ of temperature and pressure and behave conservatively with respect to mixing (mass conservation). Moreover, straightforward techniques for sampling and analysis for A_T and C_T exist and are supported by the availability of reference materials (Dickson et al., 2007). Hence, these two variables are very well suited for ~~studying the~~ CO_2 system studies. However, the use of A_T and C_T for the CO_2 system studies is not free from limitations. To obtain high accuracy for ~~the~~ calculation~~s~~ of pH and pCO_2 from measured or modelled A_T and C_T, all dissociation constants and total concentrations of all non-CO_2 components of the acid-base system must be known. This requirement is approximately fulfilled with regard to ocean studies where the total concentrations of non-CO_2 acid-base components are ~~there~~ either negligible or can be approximated ~~by~~ as a function~~s~~ of salinity (Riebesell et al., 2010). However, this issue is more critical for coastal and shelf regions, where the biogeochemical composition of seawater shows regional peculiarities (e.g. Kuliński 2014; ~~Hunt et al. 2011;~~ Hernandez-Ayon et al., 2007; Cai et al., 1998). This is the case for the Baltic Sea, which shows various unique biogeochemical characteristics.

3. Peculiarities of the Baltic Sea acid-base system

3.1. ~~Short introduction to relevant h~~Hydrographic setting~~s~~

The Baltic Sea is one of the largest brackish ecosystems in the world. This is caused by both limited inflows of saline oceanic water through the shallow and narrow Danish Straits and high river runoff. The drainage basin of the Baltic Sea is almost four times larger than the area of the sea itself, while the mean annual freshwater supply (428 km^3) constitutes about 2 % of the Baltic Sea water volume ($22 \cdot 10^3$ km^3). ~~This~~ The specific features of the Baltic Sea hydrology cause clear horizontal and vertical salinity gradients. Salinity in the surface layer fluctuate from 2 ~~PSU~~ in the northern Bothnian Bay to >20 ~~PSU~~ observed in the Kattegat. Dense and highly saline water, which irregularly enters the Baltic Sea, sinks and moves along the sea bottom.

This deep water is separated from the brackish surface water layer by a permanent halocline located at a depth of 60-70 m, which is at the same time the maximum mixed layer depth in the Baltic Sea (Lass and Matthäus, 2008; Winsor et al., 2001). The stratification limits ventilation of the deep water masses. Simultaneously, the deeper water layers are supplied with large amounts of particulate organic matter that ~~is~~ either ~~originating~~ originated from terrestrial sources or derived from the biomass production in the surface under the influence of high nutrient concentrations (eutrophication). Some fraction of the sedimentary organic matter mineralizes releasing CO_2 and consuming oxidants, ~~what~~ which leads to hypoxia or even anoxia in the bottom waters (HELCOM, 2009).

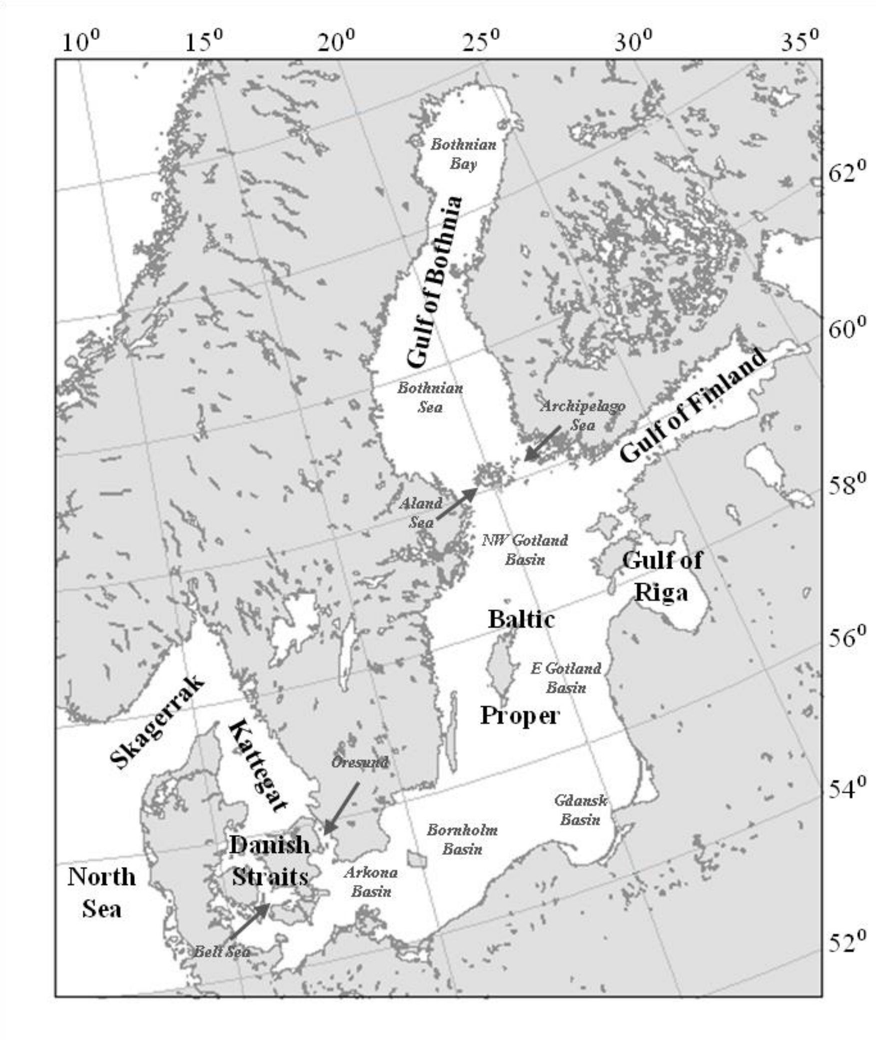


Fig. 1. Map of the Baltic Sea showing its division into natural basins and sub-basins (modified after Kuliński and Pempkowiak, 2011).

3.2. Dissociation constants in the brackish water

If any variables of the marine CO_2 system~~s~~ are to be used for biogeochemical studies, it is advisable to measure these directly and not to derive it from the measurements of other variables of the CO_2 system. However, sometimes direct measurements may be prevented by technical reasons or routine analytical methods do not exist. The latter refers for example to the determination CO_3^{2-} ion concentrations which are important for the assessment of the state of the $CaCO_3$ saturation and thus for the dissolution or formation of $CaCO_3$ shells. In this case, calculations on the basis of other known variables such as C_T, A_T, pCO_2 or pH are indispensable and require knowledge about the equilibrium constants of the CO_2 system. Here we examine the availability of the necessary constants for low salinity brackish water. Three fundamental equations characterize the equilibria of the marine CO_2 system. The first refers to the solubility of gaseous CO_2 in seawater:

$$[CO_2{}^*] = k_0 * fCO_2 \tag{3}$$

The solubility constant, k_0, relates the concentration of CO_2^* in seawater to the CO_2 fugacity, fCO_2. In contrast to the CO_2 partial pressure, pCO_2, the fugacity accounts for the non-ideal behaviour of CO_2 at atmospheric conditions. It differs only slightly from the pCO_2 and in many cases can be replaced by the pCO_2. The solubility and thus k_0 decreases with increasing temperature and salinity and vice versa. Studies by Weiss (1974) that describe k_0 as a function of temperature and salinity~~,~~ have received widespread acceptance and are almost exclusively used in chemical oceanography. The situation is somewhat more complicated for the determination of the dissociation constants for carbonic acid because it is a diprotic acid. Using again ~~the~~ CO_2^* as variable, the two dissociation equilibria are given by:

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \tag{4}$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \tag{5}$$

In these formulas the terms for the hydrogen ions are given in concentration units which include HSO_4^- ion concentration~~. This convention is called “total” hydrogen ion scale and its use is currently state of the art~~ (Dickson, 1984).

Systematic studies concerning the dissociation constants of carbonic acid in seawater were already performed during the twenties and thirties of the last century. One of the leading scientists in this field was Kurt Buch from the former Finnish Institute for Marine Research, whose research was mainly related to the Baltic Sea, and ~~consequently also his~~whose laboratory studies on the CO_2 system focused on brackish water with salinities down to zero. The results of his lab work and of field studies performed during 1927 to 1936 are summarized in Buch (1945). The presented dissociation constants must be considered as “hybrid” constants because the hydrogen ions are represented by the hydrogen ion activity whereas the CO_2 constituents refer to concentrations.

With the ~~upcoming~~ increasing awareness of the importance of the oceans for the uptake of anthropogenic CO_2 and thus for climate change scenarios, large-scale measurement programmes concerning the state of the marine CO_2 system on an oceanic scale were performed. These efforts were accompanied by numerous laboratory studies ~~that~~ aimed at the determination of improved dissociation constants. All these constants referred to the total hydrogen concentration scale that includes the contribution by HSO_4^- ~~hydrogen sulphate ions~~ (Dickson, 1984). However, the validity of most of the constants was confined to salinities that are encountered in ocean water. An exception are the constants suggested by Roy et al. (1993), which were determined for salinities down to values of 5 and could be used accordingly for brackish water. However, with regard to research in the Baltic Sea where large areas, e.g. in the Gulf of Bothnia, have surface water salinities less than 5, the situation was unsatisfactory. It took until 2006 when Millero et al. (2006) published dissociation constants that covered the salinity range from 0 to 50 and that were consistent with the constants for fresh water. An update of these constants was performed in 2010 (Millero, 2010) and since then this set of dissociation constants is state of the art for CO_2 research in brackish waters. The salinity and the temperature dependency of K_1 and K_2 are presented in Fig. 2a and 2b, respectively.

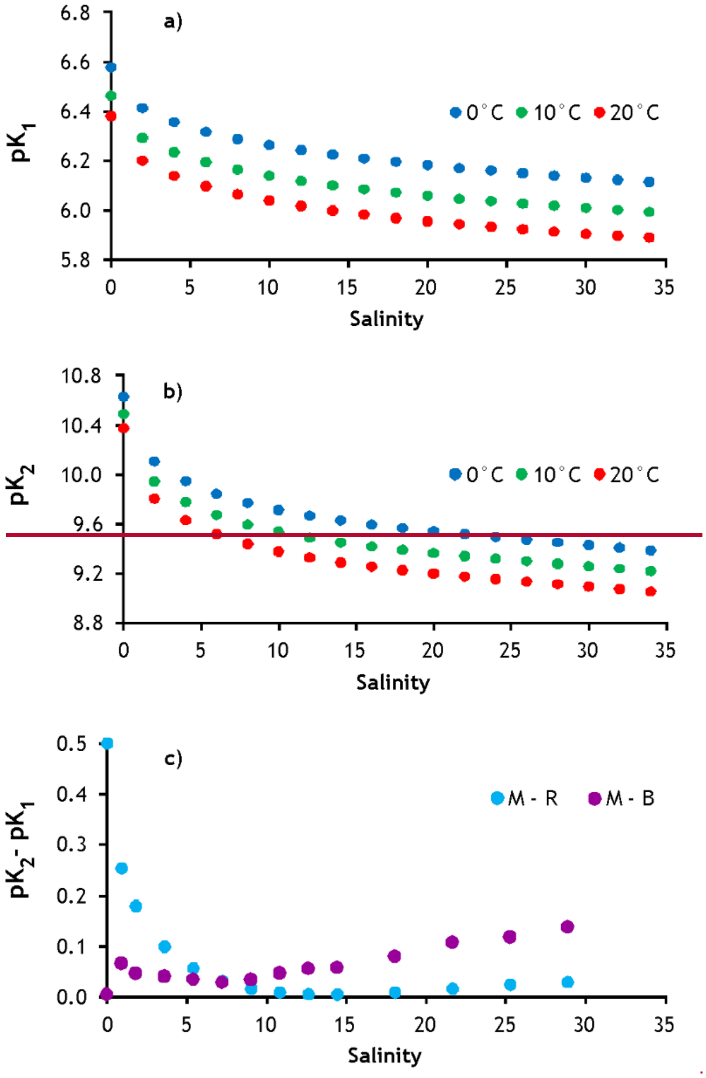
A direct comparison between the dissociation constants that were used in the past for brackish water is difficult because the constants by Buch (1945) are based on a pH scale that is based on the hydrogen ion activity. Since it is difficult to convert the activities to total hydrogen ion concentrations, we use the ratio K_1/K_2 ~~(pK_1-pK_2) that does not include the hydrogen ion activities or concentrations,~~ for a comparison. This ratio is obtained by dividing the equilibrium equations for the first dissociation step (Eq. 4) through that of the second dissociation step (Eq. 5):

$$\frac{K_1}{K_2} = \frac{[HCO_3^-]^2}{[CO_2^*]*[CO_3^{2-}]} \qquad (6)$$

Eq. 6 shows that K_1/K_2 is not connected to the hydrogen ion concentration and is thus not affected by the choice of the pH scale. Hence it is suited as an indicator for the quality of the early dissociation constants determined by Buch (1945). We used the logarithmic notation, $\log(K_1/K_2)$ which is equivalent to $pK_1 - pK_2$, for a comparison of the dissociation constants suggested by Buch (1945), Millero (2010) and Roy et al. (1993). The differences $\Delta\log(K_1/K_2)$

referring to Millero (2010) and Buch (1945), and Millero (2010) and Roy et al. (1993) indicated as M-B and M-R, respectively, are shown as a function of salinity in Fig. 2c.

~~The deviations of the (pK_1-pK_2) obtained from Buch (1945) and Roy et al. (1993) from the (pK_1-pK_2) according to Millero (2010), indicated as M-B and M-R, respectively, are shown in Fig. 2c.~~ At salinities >7, M-R is less than 0.03, but the differences increase rapidly at lower salinities and amount to 0.06 and 0.10 already at S = 5.4 and S = 3.6, respectively. Such differences in $\log(K_1/K_2)$~~pK_1-pK_2 (K_1/K_2)~~ are equivalent to a temperature change of 1 °C. The deviations of the Buch (1945) data from those of Millero (2010) (M-B in Fig. 2c) ranged below 0.10 at salinities below 20. This is a surprisingly small difference in view of the limited technical possibilities that were available to ~~Kurt~~ Buch and his co-workers in the twenties and thirties of the last century.



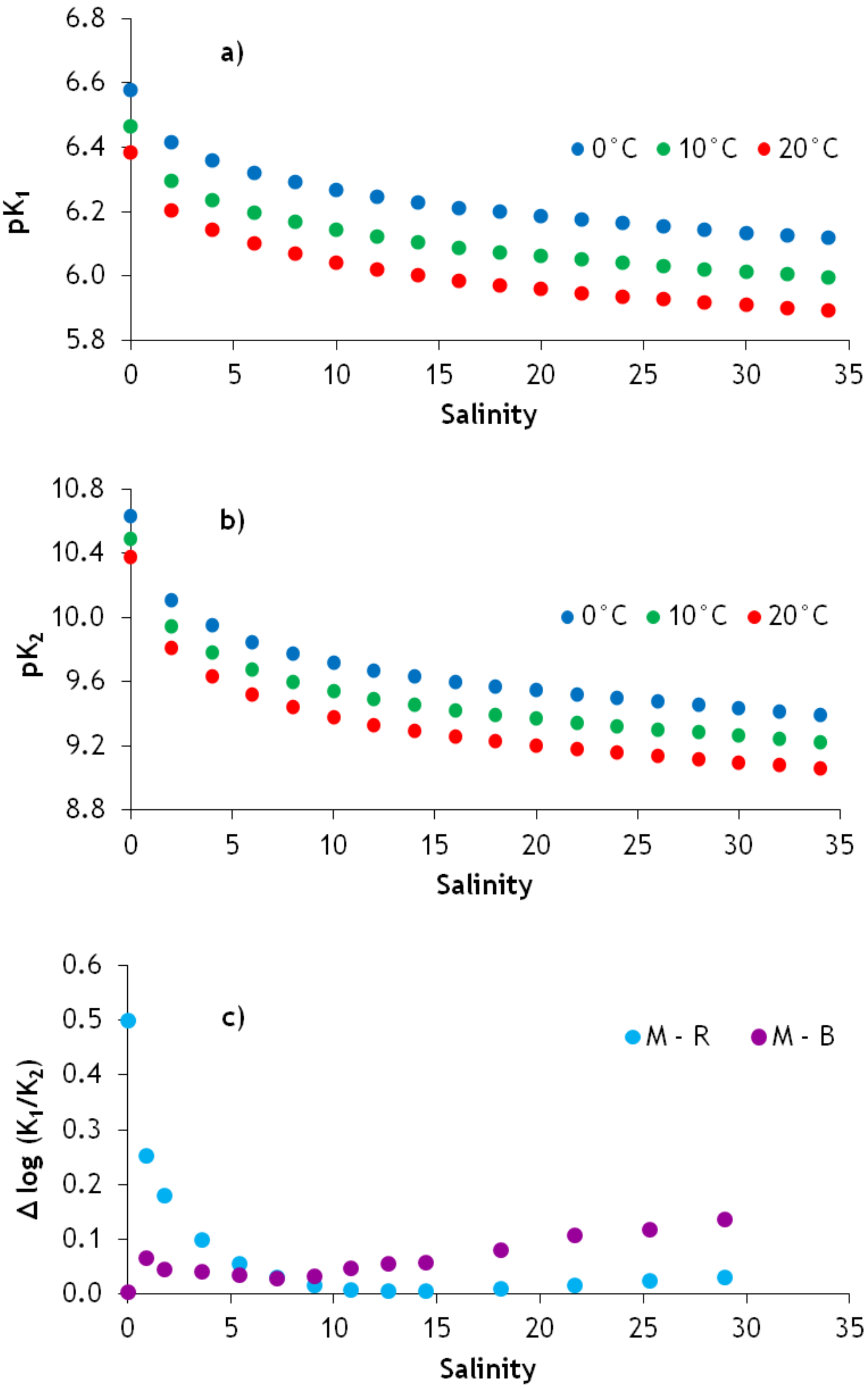


Fig. 2. Dissociation constants (a) pK$_1$ and (b) pK$_2$ as a function of salinity calculated according to Millero (2010) for three different temperatures: 0, 10 and 20 ºC; (c) differences in log(K$_1$/K$_2$) between the dissociation constants ~~deviations of (pK$_1$ – pK$_2$)~~ obtained from Millero (2010) and Roy et al. (1993) (M-R, blue dots) and between Millero (2010) and ~~from~~ Buch (1945) (M-B,

purple dots) ~~with regard to the (pK_1 – pK_2) obtained from by Millero (2010)~~ at different salinities.

~~In case that also~~When alkalinity is also used for the calculation of any variables of the CO_2 system, the contributions of non-CO_2 acid-base components to A_T (Eq. 2), which are generally low, must be taken into account. This requires knowledge about the concentration of the individual acid-base pairs and about the corresponding dissociation constants. In the deep basins of the central Baltic Sea, ammonia and sulphide anions are released during organic matter mineralization at anoxic conditions (see ~~Chapter~~ Section 3.4.2). Both these constituents are strong proton acceptors forming mainly HS^- and NH_4^+. Since their concentrations may be ~~in~~ on the order of several tens and up to a few hundred µmol L^{-1} (Nausch et al., 2008), respectively, they have a strong effect on alkalinity and pH. Therefore, any calculations concerning the CO_2 system at anoxic conditions must account for the dissociation equilibria of H_2S-HS^- (Millero et al., 1988) and NH_4^+-NH_3 (Clegg and Whitfield, 1995; Johansson and Wedborg, 1980). The concentrations of S^{2-} at the pH of anoxic water are extremely small and can be neglected.

3.3. The central role of alkalinity

3.3.1. Regional A_T vs. S distribution, consequences for pH distribution pattern

There are several different A_T vs. S regimes in the Baltic Sea (Fig. 3, Beldowski et al., 2010). They reflect different A_T concentrations in the respective rivers, which can be deduced from extrapolation of regional A_T vs. S relationships to zero salinity. Low alkalinities are observed in rivers entering the Gulf of Bothnia whereas rivers from south-eastern part of the Baltic catchment, as shown by the A_T vs. S plot for the Gulf of Riga (Fig. 3), are rich in alkalinity. These differences are a consequence of the geological conditions and weathering processes in the respective catchment areas. As a result lower alkalinities (low buffer capacity) and lower mean pH are observed in the Gulf of Bothnia and Finland, whereas higher mean alkalinities and thus somewhat higher pH are found in the Gulf of Riga and also in the Gdansk Bay (Kulinski et al., 2014; Beldowski et al., 2010; Hjalmarsson et al., 2008). ~~First investigations made in the Polish rivers (own data) suggest additionally that A_T concentrations in river water decrease substantially in western direction.~~

The central Baltic Sea acts as a mixing chamber for the different water masses, including water originating from the North Sea. This causes that ~~, resulting in an~~ alkalinity in the surface water of the Baltic Proper (salinity around 7~~ PSU~~) is of about 1600-1700 µmol kg^{-1}. ~~However, the river A_T characteristics in the Baltic Proper are not well defined because several A_T vs. S regimes are superimposing each other.~~

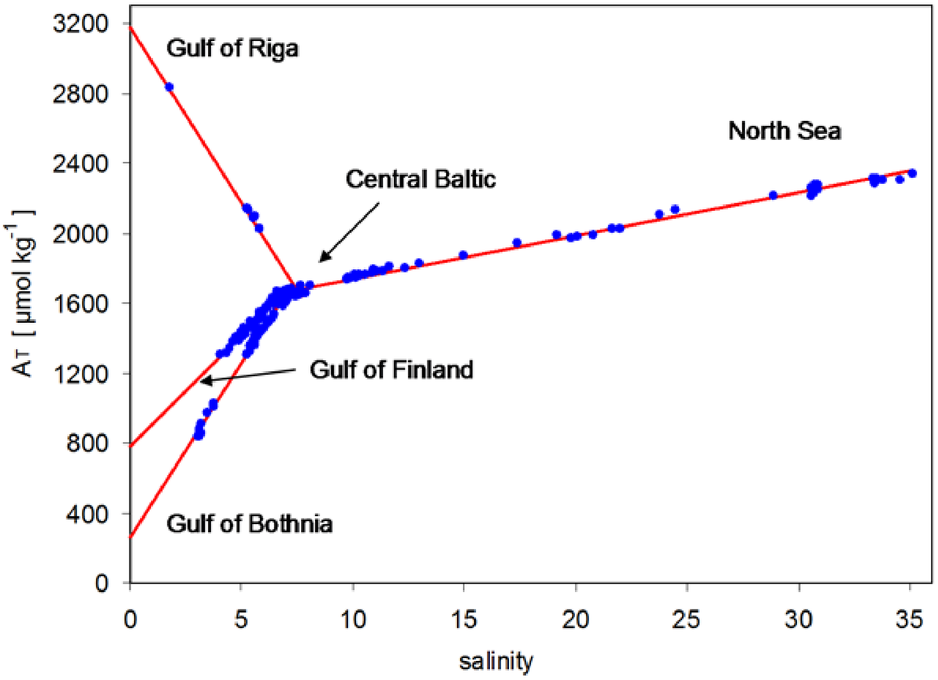


Fig. 3. Different A_T vs. S regimes observed in the Baltic Sea (modified after Beldowski et al., 2010)

An important, but still not well investigated, aspect of the A_T supply to the Baltic Sea is the A_T seasonality in river water. As A_T is one of the variables used in biogeochemical models to study the CO_2 system, well described spatial and temporal variability of A_T loads could improve the characterization the A_T distribution in the Baltic Sea and thus increase the accuracy of the modelled pH and pCO_2. This could be achieved by evaluation of the ~~monitoring~~ A_T monitoring data which are regularly collected by some Baltic Sea states within the framework of the HELCOM monitoring program. In some countries ~~like~~ such as Sweden the monitoring data are ~~publically~~ publicly accessible, in others still some limitations exist.

A_T can also enter the Baltic Sea by submarine groundwater discharge (SGD). The chemical composition of groundwater, ~~similar as it is for~~as in river water, depend to some extent on the geological structure of the catchment through which the water flows. Thus, SGD entering the

Baltic Sea along the continental part of the coast~~, similar as rivers entering here,~~ can be rich in A_T. Szymczycha et al. (2014) noticed significant C_T concentrations (5400 µmol kg^{-1} on average) in SGD seeping to the southern Baltic along the Polish coast. This indicates that SGD can play, at least locally, an important role for the A_T budget. However, direct measurements of A_T concentrations and loads in SGD have ~~never~~ not been reported in the Baltic Sea so far.

At equilibrium with the atmospheric CO_2, ~~the~~ A_T controls ~~the~~ C_T and thus ~~the~~ pH. Hence, ~~the~~ pH may be depicted as a function of A_T and pCO_2. A sensitivity study performed by Omstedt et al., (2010) indicates that the pH of the Baltic Sea surface water that is at equilibrium with the atmosphere (pCO_2 of ca. 400 µatm at 0 °C) can vary between 7.7 and 8.3 depending on the A_T (Fig. 4). This range is significantly higher than that observed in the open ocean, where A_T oscillates only in a narrow range: 2170-2460 µmol kg^{-1} (Riebesell et al., 2010). The reason for that is the high spatial variability of A_T in the surface Baltic Sea waters, from low A_T (below 1000 µmol kg^{-1}) observed in the Bothnian Bay to the A_T-rich (more than 3000 µmol kg^{-1}) estuaries of the large continental rivers. The diagram presented in Fig. 4 also shows ~~also~~ that higher A_T reduces ~~vulnerability of the~~shifts in seawater pH ~~upon~~ caused by changes in pCO_2.

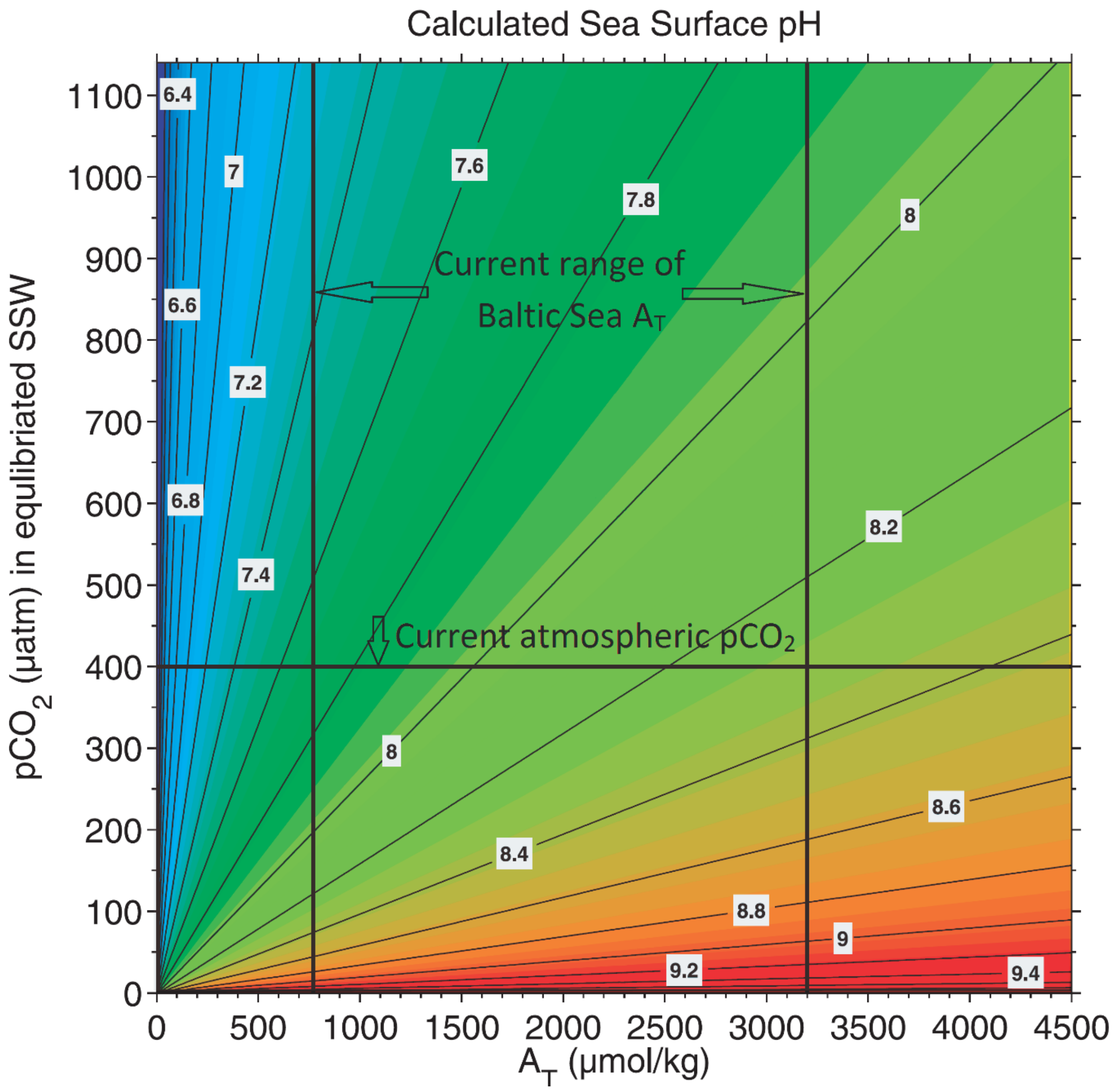


Fig. 4. Distribution of pH_{tot} as a function of A_T and pCO_2 at salinity of 7.5 and temperature of 0 °C (modified after Omstedt et al., 2010). The A_T range represents findings by Beldowski et al. (2010). SSW is an abbreviation ~~of~~ for surface sea~~-~~water.

3.3.2. Long-term A_T changes, consequences for ocean acidification

Long-term high resolution pH measurements at station BATS (Bermuda Atlantic Time Series) in the sub-tropical North Atlantic have shown that ocean acidification occurs at a rate that is thermodynamically consistent with the increase of the atmospheric CO_2 (Bates, 2014). This ~~gave~~ gives reason to expect that the ~~future development~~progression of ocean acidification can be assessed on the basis of CO_2 emission scenarios and the modelling of the effect on the atmospheric CO_2. It implies that changes in alkalinity will not occur in the future. On time scales of decades this may be a reasonable assumption for the oceans which react very slowly ~~upon~~ to internal or external changes. However, the situation is different for the Baltic Sea that is under the immediate influence of natural ~~or~~ and anthropogenic processes on land. ~~First~~ The first hints ~~for~~ of increasing alkalinity in the surface water of the central Baltic Sea were reported by Schneider et al. (2015) who argued that this may have considerably mitigated ~~considerably~~ the acidification ~~by~~ due to increasing atmospheric CO_2. Müller et al. (2016) took up this idea and performed a thorough and comprehensive statistical analysis of all alkalinity data that were available since the ~~very beginning~~start of ~~the~~ CO_2 research in the Baltic Sea at the beginning of the last century. The authors focused on high-quality data measured after 1995 and ~~they~~ detected a distinct A_T trend that showed a clear regional gradient. The highest trend was found in the Gulf of Bothnia (7.0 µmol kg^{-1} yr^{-1}), followed by 3.4 µmol kg^{-1} yr^{-1} in the central Baltic, whereas no trend could be detected in the Kattegat. Müller et al. (2016) estimated that the changes in A_T have reduced the acidification effect in the central Baltic Sea by about 50 % and that the Gulf of Bothnia was not subjected at all to acidification during the last 20 years. 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.

3.3.3. Effect of organic alkalinity

The Baltic Sea water contains 3-5 times more organic matter than open ocean waters. In the surface water of the open Baltic Sea, concentrations of dissolved organic carbon (DOC) range from about 260 to about 480 µmol C L^{-1}, while those in the surface water (top 100 m) of the Atlantic Ocean are much lower and range between 50 and 80 µmol C L^{-1} (Hoikkala et al., 2015; Carlson et al., 2010). This is a result of both high inputs of terrestrial organic matter and eutrophication driven by nutrient supply from land (Hoikkala et al., 2015; Kuliński and Pempkowiak, 2011; Kuliński et al., 2011). Organic substances contain functional groups~~. Some of them~~, some of which (carboxylic, phenolic, amines) have acidic character and can dissociate in seawater releasing protons (H^+). This contributes to pH decrease. However, as most of these groups are believed to act as weak acids (pK_a>4.5), their dissociation releases also an equivalent of organic anions being strong bases. This, according to Eq. 2, causes no change in A_T concentration since an equivalent amount of protons have been released. It affects the internal structure of A_T by changing the contributions of different A_T components according to their individual dissociation constants (Cai et al., 1998; Hunt et al., 2011; Kuliński et al., 2014). The lower the pK_a of an organic acid added to the system~~ is~~, the greater are the shifts in the internal A_T distribution. As a consequence bases forming the acid-base system are partially protonated and their concentration decreases while the concentration of the corresponding undissociated acid is increasing. In case of the carbonate alkalinity this means a reduction of CO_3^{2-} and an increase of H_2CO_3 and thus of the pCO_2.

Kuliński et al. (2014) estimated the organic alkalinity (A_{org}) in the Baltic Sea as an excess alkalinity calculated from the difference between measured A_T and that calculated from C_T and pH or pCO_2. They found A_{org} of 25-35 µmol kg^{-1} in the surface Baltic Sea water (from the Arkona Basin to the Bothnian Bay) without any clear spatial distribution pattern. This Aorg contribution amounted from 1.5 % to 3.5 % of the measured A_T values. Even higher values of more than 50 µmol kg^{-1} were found by Hammer et al. (2017) in the Baltic Sea surface mixed layer during the spring phytoplankton bloom. They reported also that A_{org} decreases with depth and approaches zero below the permanent halocline due to pH decrease.

In sensitivity studies Kuliński et al. (2014) showed for the Baltic Sea that calculations concerning the CO_2 system that are using measured A_T~~,~~ may lead to significant errors if A_{org} is ignored. Highest deviations between calculated and observed values were found when A_T was used together with C_T for computations of pCO_2 and pH. The pCO_2 values obtained in that way were by 27-56 % lower than the measured ones, while pH was overestimated by more than 0.4 units. These results are especially important as this combination (A_T and C_T) is used in biogeochemical models because they are conservative variables (Edman and Omstedt, 2013; Kuznetsov and Neumann, 2013; Omstedt et al., 2012 and 2009). This means that they are independent ~~on~~ of pressure and temperature and follow the law of conservation of mass during mixing, which are prerequisites for variables transported in models. The first attempts to include A_{org} parametrisation in biogeochemical models have been made by Gustafsson et al., (2015) and Omstedt et al. (2015). However, ~~The~~ the sensitivity of ~~biogeochemical~~ the models with regard to the inclusion/negligence of A_{org}~~, however,~~ has not yet been reported.

The source of the calculation errors related to ignoring A_{org} is due to the fact that measurements catch also A_{org} while subsequent calculations using the standard chemical A_T model and respective software, interpret the measured A_T only as inorganic alkalinity. Including organic substances into the A_T model is, however, challenging as there are number of organic substances having acidic functional groups and, according to the A_T definition, for each of them the information on concentration and dissociation constant must be available. Accounting for A_{org} in the chemical A_T model is less important for oceanic research because the low concentrations of dissolved organic matter (DOM) in the oceans cause only minor effects. As a first approximation of the acid-base properties of DOM for the Baltic Sea water, Kuliński et al. (2014) proposed to use one single bulk dissociation constant, pK_{DOM} and relate A_{org} to the concentration of dissolved organic carbon (DOC), a commonly measured parameter. According to their studies, slightly corrected by Ulfsbo et al. (2015), pK_{DOM} in the Baltic Sea amounts to 7.34. They estimated also experimentally that 12 % of DOC acts as a carrier for acidic functional groups in the Baltic Sea DOM. The model studies by Ulfsbo et al. (2015) showed that this experimentally derived share fits to the hypothetical structure of the fulvic acids. They suggested also that method proposed by Kuliński et al. (2014) is the best available approach for representing organic alkalinity in biogeochemical models at the current state of knowledge. They showed also that organic matter (as represented by the fulvic acids) contains also a lot of acidic functional groups having pK_a already below 4.5. According to the definition (Dickson, 1981) they should be considered as strong acids. In experimental studies Hammer et al. (2017) found also that humic and/or fulvic substances are more acidic than the bulk DOM naturally occurring in the Baltic Sea. This may also be a source of uncertainty in the A_T measurements as the determination of the titration end-point requires to titrate the samples through this pH region.

3.3.4. Role of borate alkalinity

The carbonate system plays a central role in the marine acid-base system. Thus, studies on seawater pH and buffering capacity focus usually on the carbon species. Less attention is paid to boron, though borates are, after bicarbonates and carbonates, the third most abundant constituent of seawater A_T (Eq. 2). Boron exists in seawater in form of weak boric acid, $B(OH)_3$, and their anions, $B(OH)_4^-$. The high pK_a (8.60 at salinity 35 ~~PSU~~ and temperature 25 °C) causes that at seawater pH of about 8 the undissociated boric acid predominates. The boron concentration, B_T, in seawater is approximated as a function of salinity or, for the historical data, as a function of chlorinity ($S = 1.80655 * Cl$). First measurements of boron concentrations in the Baltic Sea were reported by Buch (1945), who found that B_T [mg kg^{-1}] = 0.133 * S. This finding was confirmed recently by Lee et al. (2010) for the oceanic waters. Another relationship linking B_T and S and often used in acid-base system studies~~,~~ is that by Uppström~~,~~ (1974), who reported that B_T [mg kg^{-1}] = 0.128 * S. All these formulas suggest a fixed B_T/S ratio which is only the case if the river water that enters the Baltic Sea contains no boron. However, the studies by Kremling (1970, 1972) indicated that this is not the case and that a B_T concentration anomaly exists in the Baltic Sea. He found that the experimentally determined T_B vs. S relationship yielded a river water B_T (anomaly term) of 0.15 – 0.20 mg kg^{-1} at S = 0. This anomaly is not included in the chemical A_T model commonly used for numerical simulations of the CO_2 system and, similar to the effects ~~similarly to the effect~~ of ignoring A_{org}, may lead to wrong conclusions., This can be especially critical at low salinities, where the effect of anomaly is the largest.

3.4. Modulation of the acid-base system by organic matter production/mineralization (concurrent A_T and C_T changes)

3.4.1. Biomass production

~~As pointed out before, i~~In case that pH changes ~~are discussed that~~ refer to equilibrium with the atmosphere, it may be meaningful to consider the pH at a given alkalinity as a function of pCO_2 because the atmospheric pCO_2 is then the driver for any pH changes. However, when assessing pH changes as the consequence of internal biogeochemical transformations, it is more appropriate to consider A_T and C_T as the controls for the pH and the pCO_2. Biomass production primarily alters ~~primarily~~ C_T because phytoplankton (but also other plants) consume CO_2 in the course of photosynthesis (Fig. 5). As a consequence it increases the pH and lowers the pCO_2 in the upper water layers and causes a pCO_2 disequilibrium between seawater and the atmosphere. This leads to CO_2 uptake by the seawater and thus counteracts the effect of biomass production and dampens the pH ~~decrease~~increase. However, the CO_2 exchange through the air~~/~~-sea interface is much slower than the effects of biological processes. Therefore, the Baltic Sea water is in almost permanent pCO_2 disequilibrium with the atmosphere throughout the year. In spring and summer seawater is undersaturated with respect to atmospheric CO_2 with two characteristic pCO_2 minima and two pH maxima (Fig. 5) which reflect the spring bloom and the mid-summer nitrogen fixation period. In autumn and winter the Baltic Sea surface water pCO_2 increases over the atmospheric values as a consequence of less active production in the upper water column and transport of deeper CO_2-enriched water to the surface by mixing (Fig. 5; Schneider, 2011).

Another way in which biomass production influences seawater pH and pCO_2 is related to nitrate consumption. ~~Since~~ As phytoplankton assimilate~~s~~ nitrate~~s~~ for ~~its~~ growth an equivalent of H^+ is also transported to the cells to keep the charge balance neutral. According to Eq. 2 this increases the seawater A_T and thus enhances the pH during biomass production (Brewer and Goldman, 1976). At the same time it decreases the pCO_2 and therefore reinforces the drop in

pCO_2 by biomass production. Some small A_T changes can be also induced by phosphate consumption. However, due to low phosphate concentration the effect is negligible (Wolf-Gladrow et al., 2007).

Biological production also may consume ~~also~~ CO_3^{2-} ions in the calcification processes. This causes A_T reduction and in consequence pCO_2 increase and thus also pH decrease. However, this mechanism has been recognized as less important in the Baltic Sea. According to studies by Tyrrell et al. (2008) the Baltic Sea surface water is undersaturated in winter with respect to both aragonite and calcite which are biogenic modifications of $CaCO_3$. This possibly prevents ~~possibly~~ the growth of calcifying plankton and is the reason for the absence of coccolithophores in the Baltic Sea.

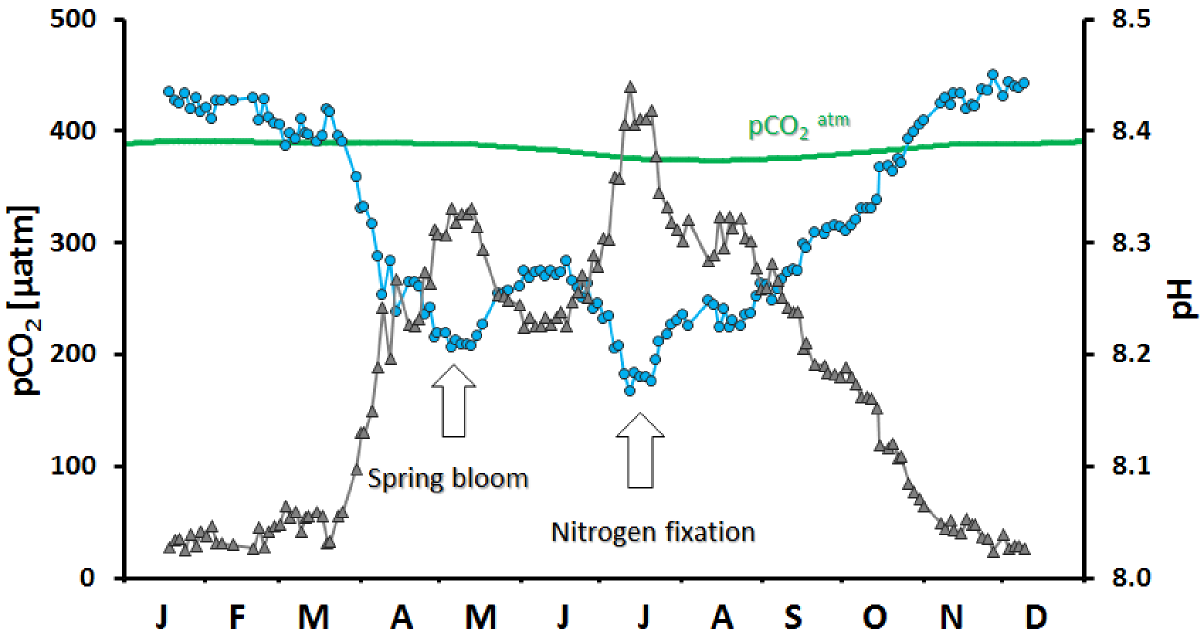


Fig. 5. Typical seasonality of pCO_2 in surface water (blue line) and the atmosphere (green line) in the Eastern Gotland Sea modified after Schneider (2011) and presented together with pH calculated from the shown pCO_2 data and the mean A_T value.

3.4.2. Remineralization

In contrast to biomass production, CO_2 is released during the remineralization processes and causes an increase in C_T. Consequently, this leads to a pH decrease and pCO_2 increase. Some fraction of organic matter produced in situ undergoes remineralization ~~already~~ in the upper water layers. Particulate organic matter (POM) may be mineralized directly or via prior release of dissolved organic matter (DOM). In the Baltic Sea terrigenous organic matter entering the sea from rivers constitutes an important part of the organic matter. Kuliński and Pempkowiak (2011) reported that the Baltic Sea receives annually 340 Gmol of ~~terrestrial~~ organic carbon from land ~~(tDOC)~~. The model studies by Gustafsson et al. (2014a) suggested that as much as 39.5% of ~~tDOC~~ terrigenous organic carbon that enters~~in~~ the Baltic Sea undergoes mineralization without distinguishing between mineralization pathways. The incubation experiments performed by Kuliński et al. (2016) indicated that ca. 20 % of ~~tDOC~~ terrestrial dissolved organic carbon and 34 % of DOC present in the Baltic Sea is bioavailable. ~~Important~~ It is important to mention here is that the latter result refers likely to the mixture of terrestrial and marine DOC.

Whereas the A_T in surface water is mainly controlled by mixing of different water masses, the deep water A_T distribution depends additionally on the organic matter transformations by various redox processes (Brenner et al., 2016; Krumins et al., 2013; Thomas et al., 2009; Schulz and Zabel, 2006). A certain fraction of the organic matter produced in the euphotic zone is exported to deeper water layers and to surface sediments, where it undergoes mineralization, and produces CO_2, and ~~at the same time~~ changes the alkalinity. The change in ~~alkalinity~~ A_T depends on the oxidant that is required for the mineralization and may cover a wide range. Therefore, it is not possible to predict the change of pH or pCO_2 during the mineralization process without knowledge of the oxidant. In the presence of oxygen, mineralization takes place according to Eq. ~~6~~ 7 which is reversing the bulk photosynthesis reaction. However, in sediments and in deep water layers of some basins of the central Baltic, where longer periods (years) of stagnation occur, oxygen may be entirely depleted. Organic matter can then be mineralized in a certain thermodynamically controlled sequence by other oxidants (Schulz and Zabel, 2006). First, manganese dioxide takes over the role of oxygen (Eq.~~7~~8), followed by denitrification where nitrate acts as oxidant (Eq. ~~8~~9). After ~~also~~ nitrate is consumed, the mineralization process may be continued by iron (III) oxide (Eq. ~~9~~10) before sulphate ~~is oxidizing~~oxidizes the organic matter and ~~generating~~ generates hydrogen sulphide (Eq. ~~10~~11). In the Baltic Sea these processes may take place in the water column where a pelagic redoxcline (an interface between oxic and anoxic conditions) can develop during longer periods of stagnation. Only the final mineralization, that is an internal oxidation and generates methane (methanogenesis, Eq. ~~11~~12) after ~~also~~ the sulphate concentration ~~have~~ has approached zero, is confined to deeper sediment layers only. Except oxic mineralization, all other processes are connected with a simultaneous A_T increase caused either by release of strong bases (S^{2-}) or by consumption of H^+ (see Eq. 2) (Ulfsbo et al., 2011; Schneider et al., 2015; Lukawska-Matuszewska, 2016). The change in A_T (ΔA_T) for different mineralization pathways is given in moles A_T per 106 moles of released CO_2 (Eqs. ~~6~~ 7 – ~~11~~12). It shows large differences and is highest when the insoluble oxides of iron (III) and manganese (IV) are reduced during the mineralization process. As a consequence of the higher A_T level, the pCO_2 increase and pH decrease by increasing C_T during the mineralization is mitigated or may even be reversed. In the eastern Gotland Sea ~~this~~ these mechanisms stabilize the pH in the deep, anoxic water layers at level of about 7 (Hammer et al., 2017).

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow 106CO_2 + 16H^+ + 16NO_3^- + 122H_2O + H_3PO_4$$ (~~6~~7)

$\Delta A_T = -16$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236MnO_2 + 472H^+ \rightarrow$$

$$236Mn^{2+} + 106CO_2 + 8N_2 + 366H_2O + H_3PO_4$$ (~~7~~8)

$\Delta A_T = +472$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8H^+ + 84.8NO_3^- \rightarrow$$

$$106CO_2 + 42.4N_2 + 16NH_3 + 148.4H_2O + H_3PO_4$$ (~~8~~9)

$\Delta A_T = +100.8$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212Fe_2O_3 + 848H^+ \rightarrow$$

$$424Fe^{2+} + 106CO_2 + 16NH_3 + 530H_2O + H_3PO_4$$

(~~9~~10)

$\Delta A_T = +864$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow$$

$$106CO_2 + 16NH_3 + 53S^{2-} + 106H_2O + H_3PO_4$$

(~~10~~11)

$\Delta A_T = +122$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$$

(~~11~~12)

$\Delta A_T = +16$

Generally, benthic processes linked to early diagenesis of organic matter can be an important source for A_T to the water column (Brenner et al., 2016). This corresponds to the findings by Gustafsson et al. (2014b), who found ~~by~~ in a model study that external sinks and sources of A_T in the Baltic Sea are imbalanced and cannot reproduce the observed A_T inventory ~~of the Baltic Sea~~, and that an internal A_T source must exist in the Baltic Sea. However, it must be taken into account that alkalinity released from sediments as sulphide and/or ammonia, influence the acid-base system only locally. Upon contact with oxic water most of the A_T generating processes – except denitrification - are reversed and do not constitute a permanent A_T source. Some minor increase of A_T can be also expected due to the burial of iron (II) minerals like pyrite or vivianite (Reed et al., 2016).

4. Challenges for the research on the acid-base system in the Baltic Sea.

The general knowledge on the marine acid-base system was gained mainly from the oceanic research. It has been integrated and documented in the form of a guide (Dickson et al., 2007) and included in different software packages (Orr et al., 2015), that allow for computations of two out of the four acid-base system parameters (pCO_2, pH, A_T, C_T) ~~the acid-base system parameters~~, when the other two are known (e.g. by measurements). Although this works nicely for the open ocean waters, problems appear when that knowledge is used for ~~the studies of~~studying the acid-base system related processes in coastal and shelf seas. This uncovers research gaps and bottlenecks but also define challenges for marine biogeochemists working in these regions.

In this context the Baltic Sea can be considered as a perfect experimental field, where strong horizontal and vertical salinity gradients, permanent stratification of the water column, eutrophication, high organic matter concentrations and high anthropogenic pressure make the acid-base system even more tangled. The challenges are related to analytical methods, interpretation of the data and parametrization of the acid-base system related processes for the use in numerical models. Great effort has recently been made to adapt ~~pH~~ spectrophotometric pH measurements based on m-cresol purple to the Baltic Sea conditions. This was done by Hammer et al. (2014) and was recently improved within a framework of the BONUS PINBAL project. Further progress can be expected if pH reference materials for brackish water will be available in the future. For the pCO_2 measurements the state-of-the-art method that is based on measuring the CO_2 content in ~~the~~ air equilibrated with the seawater is commonly used (e.g. Schneider et al., 2014). Due to a relatively long response time, this method may, however, not be ~~not~~ fast enough to resolve steep horizontal pCO_2 gradients in the vicinities of river mouths. The development of accurate and precise sensors for pCO_2, like optodes, could improve our understanding of the CO_2 system in the transition area from the coast to the open sea. Additionally, it would facilitate pCO_2 measurements in ~~the~~ discrete samples, which is highly desired for investigations of the organic matter mineralization processes in the water column, but difficult to obtain with common underway measurement techniques. The determination of A_T by titration with an acid (HCl) allows a high accuracy (+/-2 µmol kg^{-1}) for ~~the~~ ocean water. This is difficult to achieve for Baltic Sea water because the detection of the endpoint of the A_T titration is more difficult due to the influence of ~~the~~ organic acid-base constituents. The studies by Ulfsbo et al. (2015) showed that fulvic and humic acids, substances widely spread in the Baltic Sea, have relatively high concentrations of acid-base constituents, which have pK_a values close to the pK_a of carbonic acid and may thus impede the correct detection of the titration endpoint. C_T measurements are less critical since reference materials exist and the analytical procedure is relatively straightforward. However, development of high accuracy underway methods for C_T (but also A_T) would improve the horizontal coverage of the data.

Interpretations of the acid-base system data require~~s~~ appropriate parameterization of the ~~acid-base system~~ related processes and chemical reactions. With regard to the Baltic Sea some peculiarities of the composition of the acid-base system must be taken into account which are neglectable in ocean waters. An example is the influence of DOM on the acid-base system. In the oceans it is ignored due to ~~the~~ low DOM concentrations but in the Baltic Sea organic alkalinity, A_{org}, becomes a noticeable component of A_T (Kuliński et al., 2014). The challenge remains to include the contribution by DOM to the chemical A_T model. The approach suggested by Kuliński et al. (2014) to use the so called bulk dissociation constant, K_{DOM}, is only a first approximation, as K_{DOM} has no real thermodynamic meaning. It also does not allow for distinguishing the influence of individual substances. Respective improvements would require, however, also a progress in analytical methods as the characterization of the structure and composition of DOM is still far from being ~~satisfactorily~~ satisfactory (Nebbioso and Piccolo, 2013). Problems arise also due to the ion anomalies observed in the Baltic Sea (Kremling 1970, 1972) that are not taken into account in the A_T model. An example is boron, whose concentration is usually approximated by the assumption of a constant boron/salinity ratio. However, the function linking both these parameters does not account for river water as a source of boron. Furthermore, common software for CO_2 system calculation~~s~~ also omits ~~also~~ seawater constituents that are generated at anoxic conditions. These are mainly the acid-base systems: H_2S-HS^--S^{2-} and NH_4^+-NH_3 which require ~~hence~~ consideration in computational models. All these shortcomings may cause uncertainties in any calculations of the CO_2 system including those in biogeochemical models when A_T is used as a controlling variable. It is also recommended to perform sensitivity studies in order to estimate the quantitative importance of potentially missing or inadequate chemical characterization of A_T.

Furthermore, we promote the implementation of the acid-base system (or marine CO_2 system) into biogeochemical models. This includes the simulation~~s~~ of ~~the~~ surface water CO_2 partial pressure, pCO_2. The pCO_2 is an ideal validation variable because on the one hand it can easily be measured with high spatiotemporal resolution (e.g. on Voluntary Observation Ships, VOS), and on the other hand it reflects the biogeochemical transformations such as biomass production. Hence, the agreement between simulated and measured pCO_2 data give an indication for the quality of the biogeochemical process parameterization. Or, vice versa, unsatisfactory agreement gives reason to rethink the description of the respective processes in the model.

The latter aspect was in the focus of several model studies which initially failed to reproduce the observed pCO_2 draw down during spring and summer (Fig. 5). This indicated that the traditional parameterization of the biomass production that is based on the Redfield (1963) C/N/P ratios and on nutrient concentrations at the start of the productive period, does not reflect the reality. Omstedt et al. (2009) solved the problem by including a fractional nutrient release into their model. This means that nutrients that have been used for production, are partly released from the POM and reused for new production. In another study Kuznetsov et al. (2011) introduced an additional cyanobacteria group and flexible C/N/P ratios into their model in order to achieve approximate agreement between the simulated and measured pCO_2. A further study by Gustafsson et al. (2014a) investigated the changes in the simulated CO_2 air-sea flux upon including organic alkalinity and changes in external inputs of carbon, alkalinity and nutrients. Modelling the CO_2 system was also used to simulate the vertical distribution of total CO_2 and alkalinity in stagnant waters of the deep basins (Edman and Omstedt, 2013) and to assess the importance of internal alkalinity generation (Gustafsson et al., 2014b). Finally, model calculations were used to estimate future changes in the Baltic Sea CO_2 system and in particular in the development of the ocean acidification effect (Omstedt et al., 2012; Kuznetzov and Neumann, 2013). Both simulations indicated that the increasing atmospheric CO_2 will mainly control ~~mainly~~ long-term changes in pH, of course, not taking into account the recently reported current increase in alkalinity (see Chapter 3.3.2; Müller et al., 2016).

5. Summary and conclusions

With our review we have shown that the Baltic Sea acid-base system cannot be confined to dissolved CO_2 and a minor contribution of boric acid. Whereas acid-base components other than CO_2 and borate may be ignored in ocean waters, this is not the case in the Baltic Sea and other marginal and semi-enclosed seas, which in a similar way are strongly impacted by high biomass production and natural and anthropogenic processes in the connected catchments area as well. The complexity of the Baltic Sea acid-base system is displayed in the formulation of the alkalinity (Eq. 2), which is the central variable for the characterization of the acid-base properties of seawater. The peculiarities of the Baltic Sea alkalinity system are either caused by specific internal processes related to intense production/mineralization of organic matter, or to immediate effect of riverine input of substances with acid acid-base properties. The latter. This refers mostly to dissolved organic matter which may strongly affect the composition of the alkalinity in the Baltic Sea surface water (Kuliński et al., 2014). But it refers also to boric acid (borate) which in ocean water is linked to salinity by a constant ratio, but may show distinct deviations from this ratio in some of the Baltic Sea estuaries because of boron input by river water (ion anomaly).

Internal biogeochemical processes such as organic matter production or mineralization have also the potential to affect the acid-base system in the Baltic Sea. Alkalinity changes by organic matter production caused by the removal of H^+ during the uptake of nitrate, are of minor importance. This may be different if the production is associated with calcification that reduces the alkalinity. But the abundance of calcifying plankton in the Baltic Sea is restricted to the high-salinity Kattegat region. Although the effect of organic matter production on alkalinity is minor, it is the major control for the seasonal modulation of the acid-base properties such as pH and pCO_2 which however is nothing specific for the Baltic Sea.

In contrast, organic matter mineralization taking place at anoxic conditions in the Baltic Sea deep basins, causes changes in the acid base system which are specific for marine systems with a pelagic redoxcline. Mineralization of organic matter on the basis of sulphate reduction generates large amounts of alkalinity by the formation of sulphide ions and the release of ammonia. This reduces the increase of the pCO_2 in the deep water and stabilizes the pH at a value close to 7. Although these processes are reversed upon re-oxidation during a deep water renewal event and are do not affecting the acid-base system of the Baltic Sea as a whole, they are influencing influence the deep water redox chemistry which is partly controlled by the pH. But On the other hand the existence of a pelagic redoxcline has another more far-reaching importance. It is the medium for intense denitrification, which increases the alkalinity not only locally, but may affect the alkalinity budget of the entire Baltic Sea proper (Gustafsson et al., 2014).

Our compilation of the major features of the Baltic Sea acid-base system indicates that an exact quantitative treatment of its properties is difficult to achieve. This refers to both the biogeochemical modelling and the interpretation of measured alkalinity in terms of the calculation of individual alkalinity contributions. An example is the calculation of the carbonate alkalinity that is necessary for the full characterization of the CO_2 system based on measurements of alkalinity and together with another variable. It requires knowledge of the dissociation constants and the determination of the total concentrations of the individual compounds with acid-base properties. Regarding inorganic alkalinity contributions, it may be realistic to get these information. But in view of our limited knowledge concerning the composition of the dissolved organic matter, it is currently hopeless to specify and characterize the contributions of individual organic acid-base compounds to the alkalinity. Hence we conclude that this is one of the greatest challenges for more adequate comprehensive physico-chemical characterization of the acid-base system in the Baltic Sea and likely in the other coastal seas. Another important bottleneck, especially for the biogeochemical modelling, is also an insufficient knowledge on short and long term development of alkalinity loads from land caused by processes occurring in the catchment.

~~5.~~6. Acknowledgements

The study was completed thanks to funding provided by the National Science Centre, Poland, grants no. 2015/19/B/ST10/02120 and 2014/13/D/ST10/01885. Significant financial support was provided also by BONUS and the Polish National Centre for Research and Development – sponsors of BONUS PINBAL project. The contribution of B. Schneider to this study was supported by the Foundation for Polish Science within the Alexander von Humboldt Polish Honorary Research Scholarship. This study comprises a part of the Baltic Earth — Earth System Science for the Baltic Sea Region.

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