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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.

Reviewer#1
Review of Kulinski et al. "Structure and functioning of the acid-base system in the Baltic Sea" (revised re-submission)
The authors have prepared a substantially revised manuscript, which addresses the issues raised by myself and another previous reviewer. This revision improves the readability and presentation greatly over the first version, and I commend the authors for their work. I still think some sections are light on citations, and I will try to indicate those places below. I also have a couple significant comments which I think should be addressed before publication, as well as a number of technical language suggestions which the authors may choose to implement or not.
Overall Comments
P2L2-11: This section describing the difference between structure and functioning is a nice addition.
P6L10-11: why is this advisable? What are the limitations of derivation? Discuss error propagation, uncertainties in K values, alkalinity contributors.
We do not see the need to discuss here these limitations, and especially error propagation. This could confuse the reader as it would not be linked with the following text. Instead we added a citation, where the discussion of the analytical techniques is given.

P7L21-28, P8L1-13: Other Ks are available for brackish water in addition to those of Buch, for example those of Cai and Wang 1998.
We are aware of that. Our intention writing this paragraph was to appreciate the work by Kurt Buch as it was the very first in the field. The effects of his work are even more spectacular as the limited technical capabilities that were available in 20' and 30' of the XX century are taken into account.

P8L14-27. This explanation is a good addition. What temperature is used for the calculations in Figure 2c?
Thank you. 0°C

P12L4-13: This paragraph discusses pH changes mostly in terms of pCO2 in equilibrium with atmospheric pCO2, and mentions that at equilibrium AT drives pH changes. The opposite of course is also true, that at constant AT pCO2 disequilibrium drives pH change, as in Figure 5. Indeed from Figure 5 we see that pCO2 is rarely at equilibrium with atmospheric levels in the Baltic, and that the observed pH range at constant AT (about 8.1-8.5) is narrower and lower than that cited in this paragraph (7.7-8.3). So I suppose my question is, why frame this paragraph in terms of pCO2 conditions that rarely occur in the Baltic, and by the same token why present the data in Figure 5 in terms of constant AT? Figure 3 indicates that there is a fair amount of in situ AT data in the Baltic (and that AT is really variable!).
We would like to keep the structure of this paragraph as it is now. Both pCO_2 and A_T are highly variable in the Baltic Sea. We present the case for the constant pCO_2 to emphasize how big effect on pH has A_T. Variable A_T is something specific for the Baltic Sea. In the open ocean A_T is constant or at least much less variable. Thus, our intention was to show how big effect variable A_T can have on pH.

Figure 4: the text for "Current Range of Baltic AT" and "Current Atmospheric pCO2" is really hard to read. I'd suggest putting a white background behind this text, similar to the pH labels, to improve readability.
Done.

P16L5-11: pKDOM is cited as 7.34, while the pKa of "organic matter (as represented as fulvics)" is below 4.5. This is a big difference! Is this <4.5 pKa only for some fulvic groups, and not for the overall DOM? Some explanation for this discrepancy should be added.
pKDOM is a bulk dissociation constant for DOM. It can be considered as a "mean" dissociation constant for all the acidic functional groups. This means that in DOM there might be very different acidic functional groups including strong (pK_a <4.5) but also very weak (pK_a >8) groups. We do not argue in the text that pK_a for fulvics is <4.5 but say only that some functional groups in fulvics (not the entire molecules) have pK_a <4.5. Thus, in our opinion there is no discrepancy in our text. We have modified the text slightly in the revised version to make it clearer.

Figure 5. Temperature has a big effect on pCO2 and pH. Can some discussion of temperature influence vs. other biogeochemical factors be added?
Fig. 5 present the data at *in situ* temperature.

P19L3-4: "without distinguishing between mineralization pathways". This could be an important point: the mineralization pathway affects the relative production of CT vs. AT, right? Some more discussion of this might be useful.
We fully agree with the reviewer statement that the mineralization pathway affects the relative production of CT vs. AT. The phrase cited by the reviewer refers to the model study by Gustafsson et al. (2014a). The study was rather focused on the mass transport within the Baltic Sea carbon budget and not on the consequences different processes have for the acid-bases system. Thus, we said in the manuscript that this estimation was done "without distinguishing between mineralization pathways" to emphasize that the use of this data may be limited for the interpretation of the acid-base system functioning. We have added the sentence to the text that clarifies this.

P21L22: This phrase "permanent stratification" seems to contradict the assertion made in P17L25 where 'deeper CO2-enriched water" is transported to the surface via mixing in autumn and winter. How can both be true?
The permanent stratification of the water column with a halocline at approx. 60-70m is very well phenomenon in the Baltic Sea – see for instance Lass and Matthäus (2008). In summer there is additionally a thermocline that separates upper approx. 20m of the water column. When mixing increases in autumn and winter it destroys the thermocline and transports CO_2 from the deeper layers, but not from below the halocline. The depth of halocline is at the same time the maximum mixed layer depth in the Baltic Sea.

P23L5-13: a citation here would be good- perhaps the SOCAT project?
This is our own conclusion and we will not give citation here. In fact modelled and measured pCO_2 is sometimes compared to each other but the reason for that is usually a quantification of the uncertainty in the modelled CO_2 exchange. We promote here to do this for biogeochemical process parameterization. Having this in mind it is difficult to find a suitable citation.

P24L27: Is sulphate reduction the dominant anerobic process in the Baltic? From the previous discussion this is not clear, as other processes (Mn reduction, denitrification, etc) are presented as more energetically favorable.
We corrected that sentence. Now it refers to all anoxic mineralization pathway of organic matter and not only to sulphate reduction.

Technical/Language Comments
P1L14: Change to "a number"
Done

P1L20: remove "we"
Done

P2L12: change to "of atmospheric CO2"
Done

P2L19: "by the scientific community"- this seems like it needs some citation
Done

P2L29: AT not defined
Corrected

P2L30-31: try to avoid shorthands like "etc" or "and/or"
Corrected

P2L28-30: should terrestrial inputs be included in this list of processes?
Added

P2L31: what are the specific gaps and shortcomings?
All of them are given later in the text. There is no need to define them here.

P3L22-23: "low buffer capacity", "various anthropogenic influences"-citations needed. Specify the anthropogenic influences.
Done

P3L26: "well characterized during the last decades"- citation(s) needed
Done

P3L28-29: remove the sentence beginning "However, this was done…", not really sure what it is saying.
We suggest to leave that sentence as it is now.

P4L21: "BONUS PINBAL", most readers will not be familiar with this project
We added to the text the address of the project web page.

P4L30: change to "the pH as described by a set…"
Done

P5L3: change to "of the marine CO2 system. Many biogeochemical models…". Also citations of these models are needed.
Done

P5L9: change to "for the calculation"
Done

P5L8-17: another limitation is that current sensor technology is mostly focused on pH and pCO2 observations
We agree, but this has no direct influence. We do not see the necessity to add this information here. It could confuse the reader.

P5L21-26: citations needed

The suitable citation (Lass and Matthäus, 2008) is given few lines later.

P6L9: change to "in brackish water"
Done

P6L14: change to "determination of CO32-…". Also, I don't think CO32- has been previously defined.
Done. The ion defined on P3L11.

P9L1: change "possibilities" to "capabilities"
Done

P10L27: Need to state that the differences are presumed! Citations needed here.
These are not presumed differences but the measured ones. Citation: Beldowski et al. (2010) is already given in the text.

P10L28: Lower alkalinity and lower buffer capacity are not necessarily the same thing. Either discuss the difference or remove the reference to buffer capacity.
Removed

P11L2: change to "This results in alkalinity…"
Changed

P11L3: remove "is"
Removed

P11L11: change to "characterization of the…"
Changed

P11L17: change to "depends"
Chenged

P11L20: this section discusses AT, so there is a need to explain the connection between AT and these CT concentrations- the link is not clear between the two.
Explanation added.

P12L8: need to provide the open ocean pH range with citations
We do not agree with the reviewer here as this sentence refers to the situation where seawater is in equilibrium with atmospheric CO_2. In this specific case more important is A_T range, which is already given in the text.

P13L9-11: this is nicely said.
Thank you

P13L11: change to "It also implies"
Changed

P13L1: needs citation
There is a citation given.

P15L17: change to "were 27-56: lower…"

Changed

P15L20: change to "2009), because they are…"
Changed

P15L23: change to "include an Aorg…"
Changed

P15L27: perhaps replace "catch also Aorg" with something like "include all inorganic and organic contributors, while subsequent…"
Changed

P15L31: change to "dissociation constants"
Changed

P16L5 and throughout: change to "They also estimated…"
Changed

P16L7: I don't really understand this sentence, please rephrase.
Changed

P16L8: change to "They also suggested that the method…"
Changed

P16L10: change to "They also showed…"
Changed

P16L13: change to "also found "
Changed

P16L23: change to "the anion"
Changed

P16L24: change to "means that…"
Changed

P16L28: change to "for oceanic waters"
Changed

P16L30-31: this is a great point
P16L33: change to "Baltic Sea, where the experimentally…"
Changed

P17L4: change to "effect of the anomaly"
Changed

P17L9: change to "In the case"
Changed

P17L10: change to "of pCO2, because the atmospheric CO2 is then the only driver…"
Changed

P17L29: change "enhances" to "raises"
Changed

P17L30: change to "This assimilation also decreases…"
Changed

P18L1: is this low P concentration specific for the Baltic?
No. This is a general remark, which refers also to the Baltic Sea.

P18L4: remove "thus"
Changed

P19L13: change to "produces CO2, and…"
Changed

P19L21: add space between "Eq.8"
Done

P20L6-26: It might improve readability to include the names of the reactions alongside the delta AT values, so it's obvious which reaction is which. For instance, change line 10 to "Manganese Reduction ΔAT=+472"
Done

P21L6: change to "sulphide or ammonia only influence the acid-base system locally"
Changed

P21L12: Change to "Challenges for future research…"
Changed

P21L21: change "perfect" to "model"
Changed

P21L29: change to "water are made available…"
Changed

P22L3: change "is" to "are"
Changed

P22L19: Aorg already defined
Corrected

P22L24: change to "would require substantial progress in analytical techniques, as the…"
Changed

P22L26: change to "Problems also arise…"
Changed

P23L3: remove "potentially missing"
Removed

P23L10: change to "Hence, agreement…"
Changed

P23L11: change to "indication of…"
Changed

P23L14: change to "was the focus…"
Changed

P23L17: change to "did not reflect"
Changed

P23L19: change to "This meant…", also remove comma after "production"
Changed

P23L23: change "upon" to "after"
Changed

P24L2: change "shown" to "proposed", change "confined to" to "explained by"
Changed

P24L3: change to "and, presumably, other marginal…"
Changed

P24L6-7: change to "in connected catchment areas."
Changed

P24L11: change to "to the immediate effect of riverine input of acidic substances. This riverine input refers mostly…"
Changed

P24L13: change to "et al. 2014), but also to boric…"
Changed

P24L16: remove "(ion anomaly)"
Removed

P24L17: change to "mineralization also have the potential…"
Changed

P24L19: remove "."
Done

P24L20-21: change to "which reduces the alkalinity, but the abundance…"
Changed

P24L24: remove ",which however is nothing specific for the Baltic Sea."
Removed

P24L26 remove ","
Removed

P24L31: change to "event and do not affect…"
Changed

P24L32: change to "do influence the…"
Changed

P24L33: remove "But"
Removed

P25L9: remove "and", change "It" to 'This"
Done

P25L13: change "hopeless" to "impossible"
Changed

P25L16: change to "in other coastal…"
Changed

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

Reviewer#2
The authors have addressed all comments and suggestions from the first revision round, and the revised manuscript has improved greatly in terms of structure, language, and readability. One of my main issues with the previous version was the lack of a concluding section. This has now been added. In my view, this manuscript is now suitable for publication after a few minor corrections.
P4L16-17: Switch to italic font
Done

P5L5-6: Somewhat strange wording, maybe write instead "…for simulations of the marine…"
Corrected

P8L11: Strange sentence, maybe write instead something like "Exceptions are…"
Corrected

P16L8: Correct the font of Aorg (subscript)
Corrected

P17L8: Change to "suggested also that the method" instead of "suggested also that method"
Corrected

P18L14: "controls for pH and pCO2" instead of "controls for the pH and the pCO2"?
Changed

P22L21: "knowledge of" instead of "knowledge on"?
Changed

P23L31: Aorg has already been defined
Corrected

P25L17: "catchment areas" instead of "catchments area"
Changed

P25L22: "The latter" should be removed
Removed

P26L10: "event are do not" – remove "do"
Removed

P26L12: "But On" should be "But on"
Corrected

P26L21: “alkalinity and together” – remove “and”
Done

P26L24: Change “get these” to “obtain this”?
Changed

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

Karol Kuliński[1], Bernd Schneider[2], Beata Szymczycha[1], Marcin Stokowski[1]

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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~~ a 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 brackish water, different chemical alkalinity models including contributions by organic acid-base systems, long term changes of total alkalinity, anomalies of borate alkalinity and the 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. The understanding of the structure and functioning of the acid-base system is necessary to investigate important issues that shape the Baltic Sea ecosystem and that are of interest in present-day chemical oceanography like: ocean acidification, calcium carbonate ($CaCO_3$) formation/dissolution and carbon dioxide (CO_2) 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 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 (e.g. Bates et al., 2014; Zeebe, 2012), 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 are influencing the seawater pH such as: $CaCO_3$ formation and/or dissolution, euthrophication or oligotrophication, total alkalinity (A_T) consumption and~~/or~~ production, weathering, contribution by organic substances and terrestrial inputs ~~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 states of calcite and aragonite 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 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 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. On one hand the low buffer capacity (Beldowski et al., 2010) makes the seawater vulnerable to acidification in most regions of the Baltic Sea, 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 (Bates et al., 2014; Riebesell et al., 2010; Dickson et al., 2007). 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 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):

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

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 (https://www.io-warnemuende.de/pinbal-home.html). 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 materials in seawater matrix still do not exist for pH measurements. 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 as described 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 for ~~the~~ simulations of the 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 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 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 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 either negligible or can be approximated as a function 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; 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. Hydrographic setting

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). The specific features of the Baltic Sea hydrology cause clear horizontal and vertical salinity gradients. Salinity in the surface layer fluctuate from 2 in the northern Bothnian Bay to >20 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 either 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, which leads to hypoxia or even anoxia in the bottom waters (HELCOM, 2009).

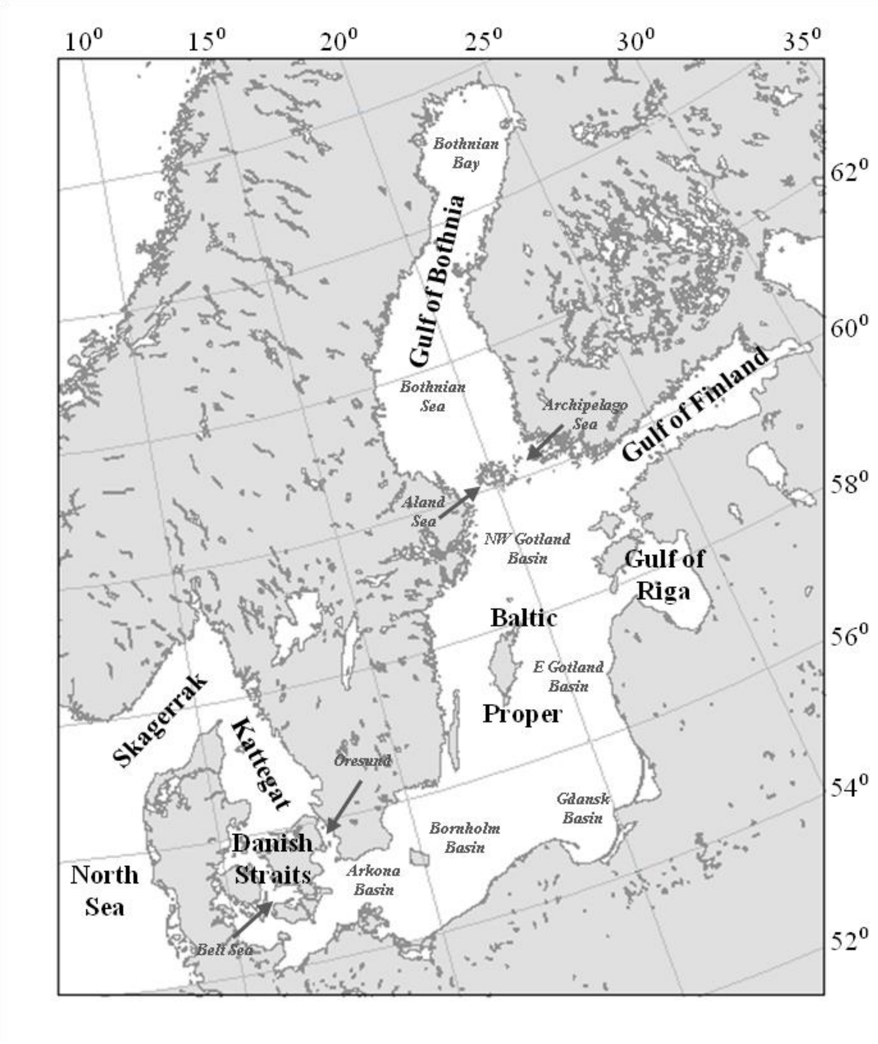


Fig. 1. Map of the Baltic Sea showing its division into natural basins and sub-basins (modified after Kuliński and Pempkowiak, 2011).

3.2. Dissociation constants in ~~the~~ brackish water

If any variables of the marine CO_2 system 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 (Dickson et al., 2007). 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 of 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 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 (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 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 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 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^- (Dickson, 1984). However, the validity of most of the constants was confined to salinities that are encountered in ocean water. ~~An exception~~Exceptions 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 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):

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

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.

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 $\log(K_1/K_2)$ 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 capabilities~~possibilities~~ that were available to Buch and his co-workers in the twenties and thirties of the last century.

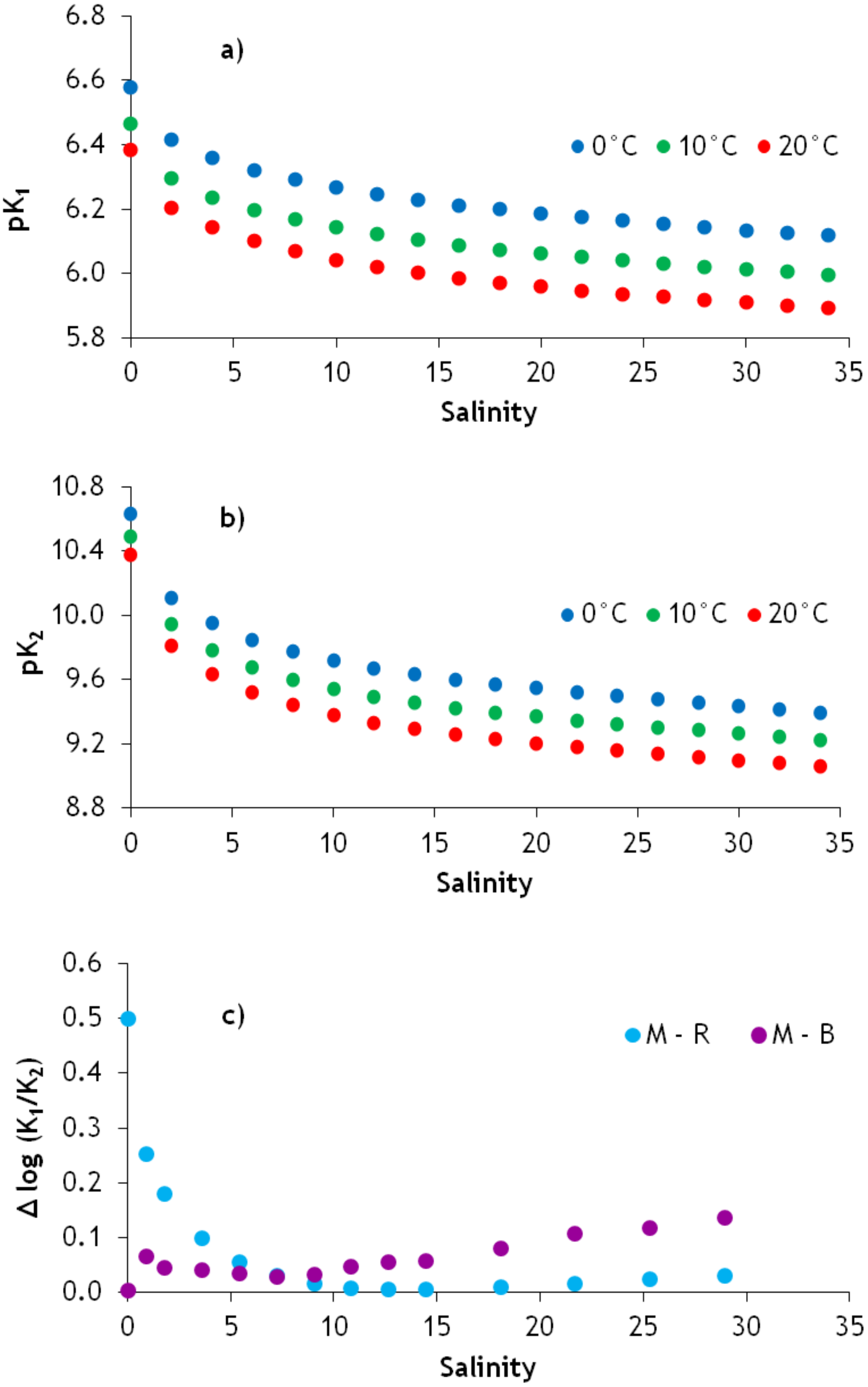


Fig. 2. Dissociation constants (a) pK_1 and (b) pK_2 as a function of salinity calculated according to Millero (2010) for three different temperatures: 0, 10 and 20 ºC; (c) differences in $\log(K_1/K_2)$ between the dissociation constants obtained from Millero (2010) and Roy et al. (1993) (M-R, blue dots) and between Millero (2010) and Buch (1945) (M-B, purple dots) at different salinities.

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 Section 3.4.2). Both these constituents are strong proton acceptors forming mainly HS^- and NH_4^+. Since their concentrations may be 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).

The central Baltic Sea acts as a mixing chamber for the different water masses, including water originating from the North Sea. This results in ~~causes that~~ alkalinity in the surface water of the Baltic Proper (salinity around 7) ~~is~~ of about 1600-1700 µmol kg^{-1}.

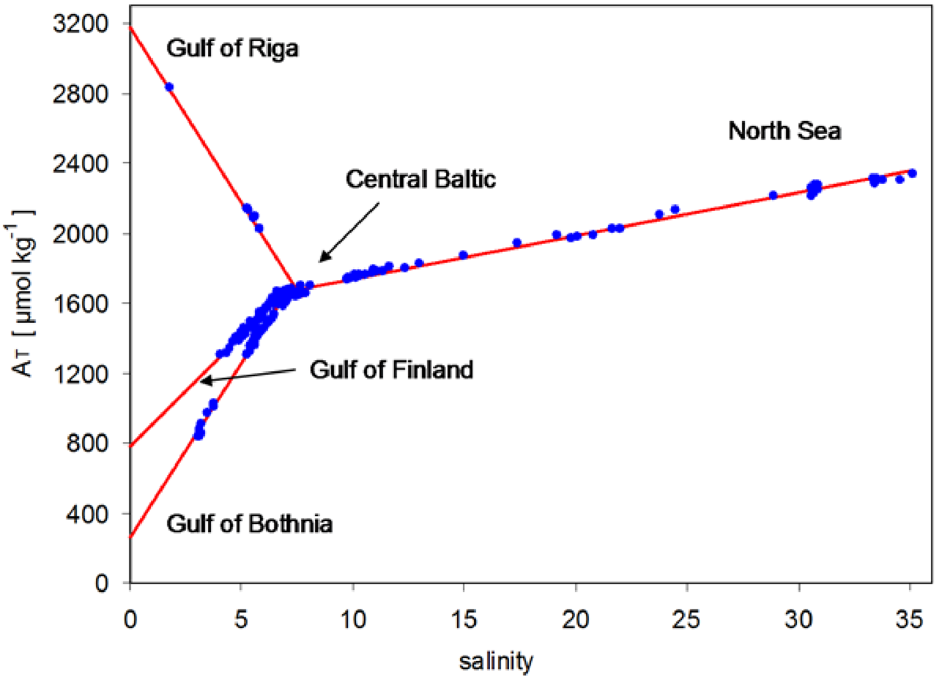


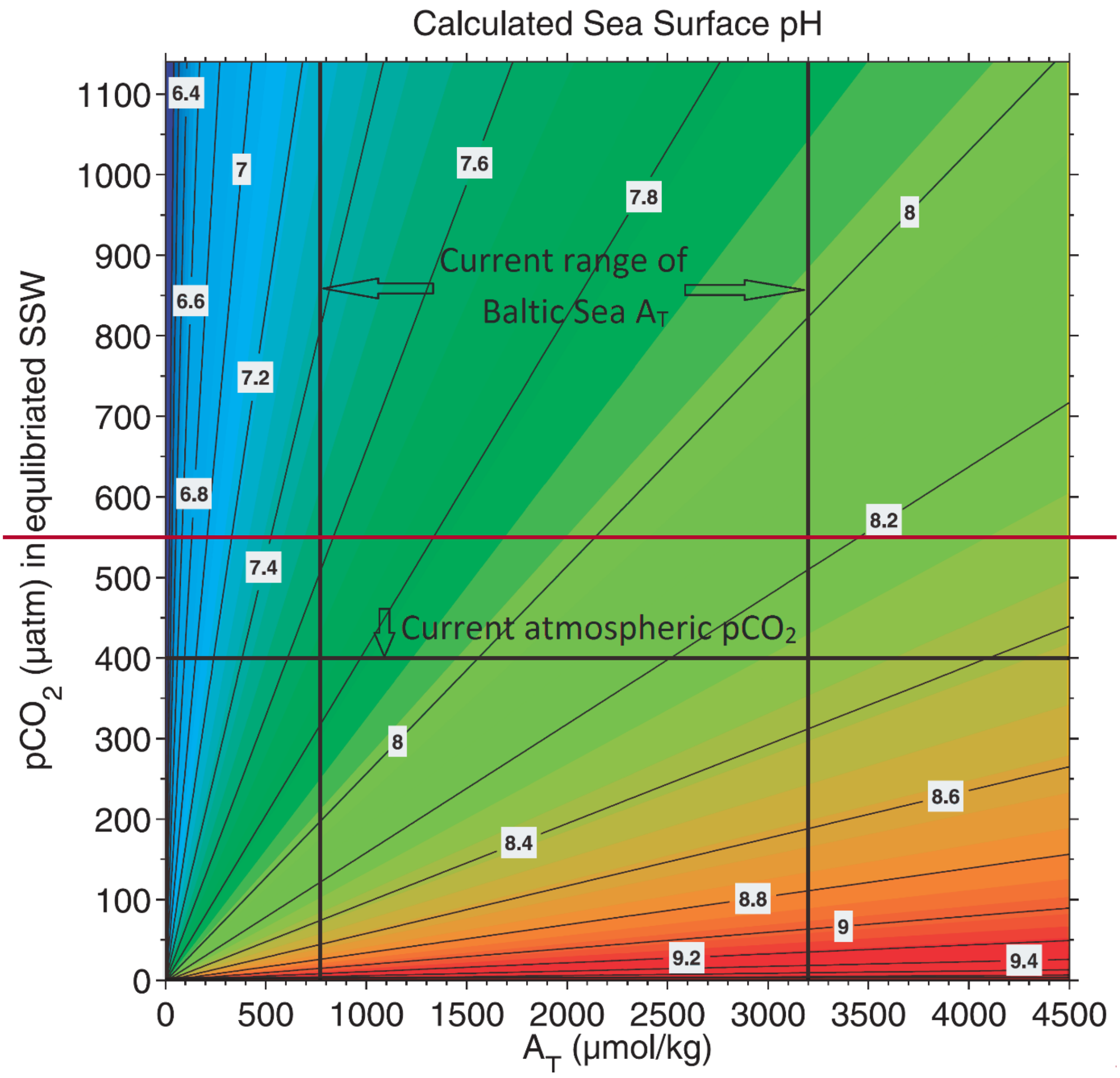
Fig. 3. Different A_T vs. S regimes observed in the Baltic Sea (modified after Beldowski et al., 2010)

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 of 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 A_T monitoring data which are regularly collected by some Baltic Sea states within the framework of the HELCOM monitoring program. In some countries such as Sweden the monitoring data are 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, as in river water, depends 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 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. Although there might be some contribution from CO_2 to this high C_T, it is very likely ~~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 not been reported in the Baltic Sea so far.

At equilibrium with the atmospheric CO_2, A_T controls C_T and thus pH. Hence, 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 that higher A_T reduces shifts in seawater pH caused by changes in pCO_2.


Calculated Sea Surface pH
pCO2 (µatm) in equlibriated SSW
AT (µmol/kg)
0
100
200
300
400
500
600
700
800
900
1000
1100
0
500
1000
1500
2000
2500
3000
3500
4000
4500
6.4
7
6.6
7.2
6.8
7.4
7.6
7.8
8
8
8.2
8.4
8.6
8.8
9
9.2
9.4
Current range of
Baltic Sea AT
Current atmospheric pCO2

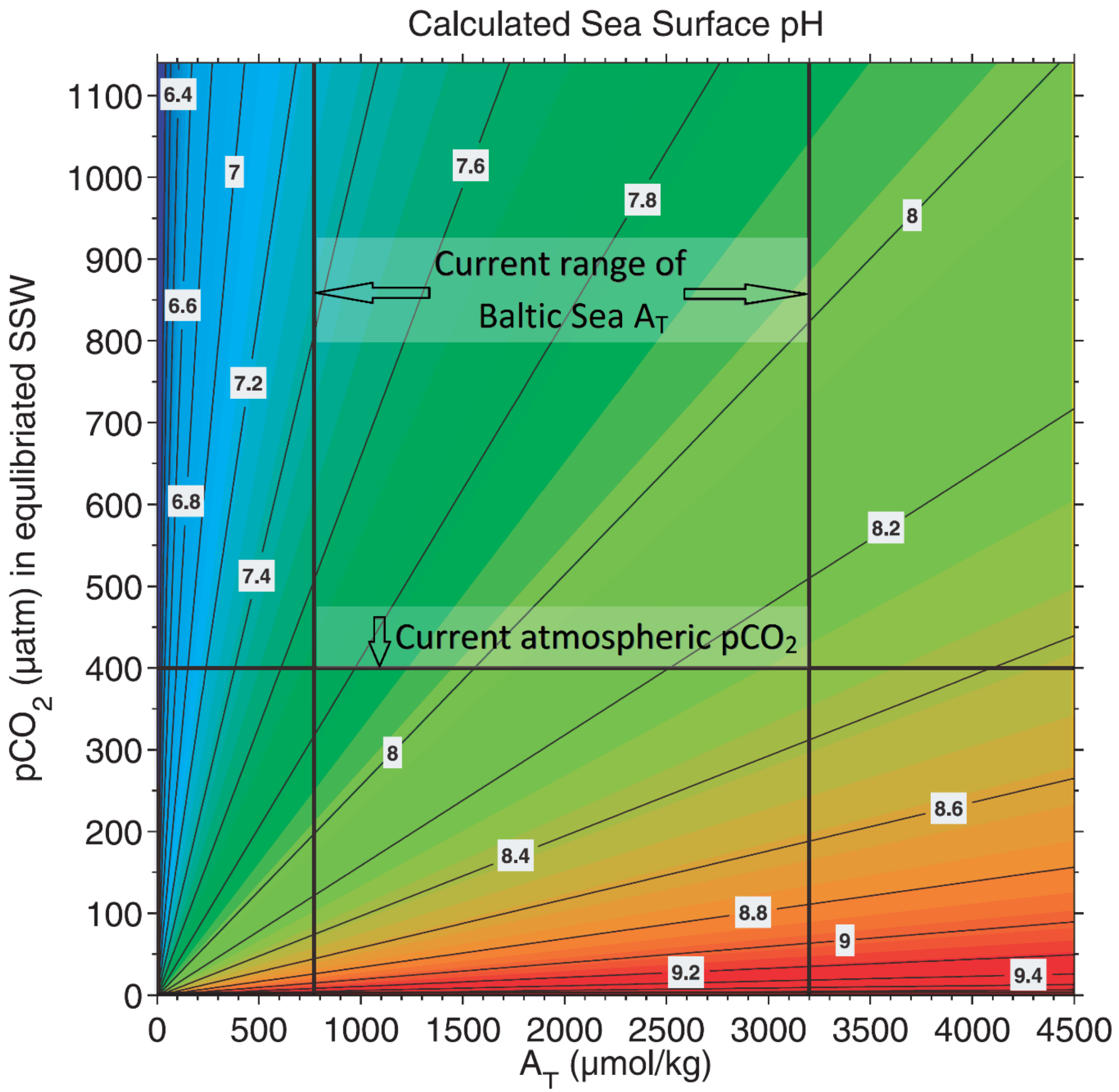


Fig. 4. Distribution of pH_{tot} as a function of A_T and pCO_2 at salinity of 7.5 and temperature of 0 °C (modified after Omstedt et al., 2010). The A_T range represents findings by Beldowski et al. (2010). SSW is an abbreviation for surface seawater.

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 gives reason to expect that the 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 also 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 to internal or external changes. However, the situation is different for the Baltic Sea that is under the immediate influence of natural and anthropogenic processes on land. The first hints 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 the acidification 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 start of 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 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 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, 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 A_{org} 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) because they are conservative variables. This means that they are independent 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 an A_{org} parametrisation in biogeochemical models have been made by Gustafsson et al., (2015) and Omstedt et al. (2015). However, the sensitivity of the models with regard to the inclusion/negligence of A_{org} has not yet been reported.

The source of the calculation errors related to ignoring A_{org} is due to the fact that measurements include all inorganic and organic contributors, ~~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 constants 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 also 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 share estimated from the hypothetical structure of the fulvic acids. They also suggested ~~also~~ that the 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 also showed ~~also~~ that organic matter (as represented by the fulvic acids) contains also ~~a lot of acidic~~some 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) also 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 the~~ir~~ anion~~s~~, $B(OH)_4^-$. The high pK_a (8.60 at salinity 35 and temperature 25 ^oC) ~~causes~~ means 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, where~~. He found that~~ the experimentally determined ~~T_B~~ B_T 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 of ignoring A_{org}, may lead to wrong conclusions.. This can be especially critical at low salinities, where the effect of the 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

In the case that pH changes 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 ~~p~~CO_2 is then the only 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 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 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. As phytoplankton assimilate nitrate for 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~~ raises the pH during biomass production (Brewer and Goldman, 1976). ~~At the same time it~~This assimilation also 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 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 the growth of calcifying plankton and is the reason for the absence of coccolithophores in the Baltic Sea.

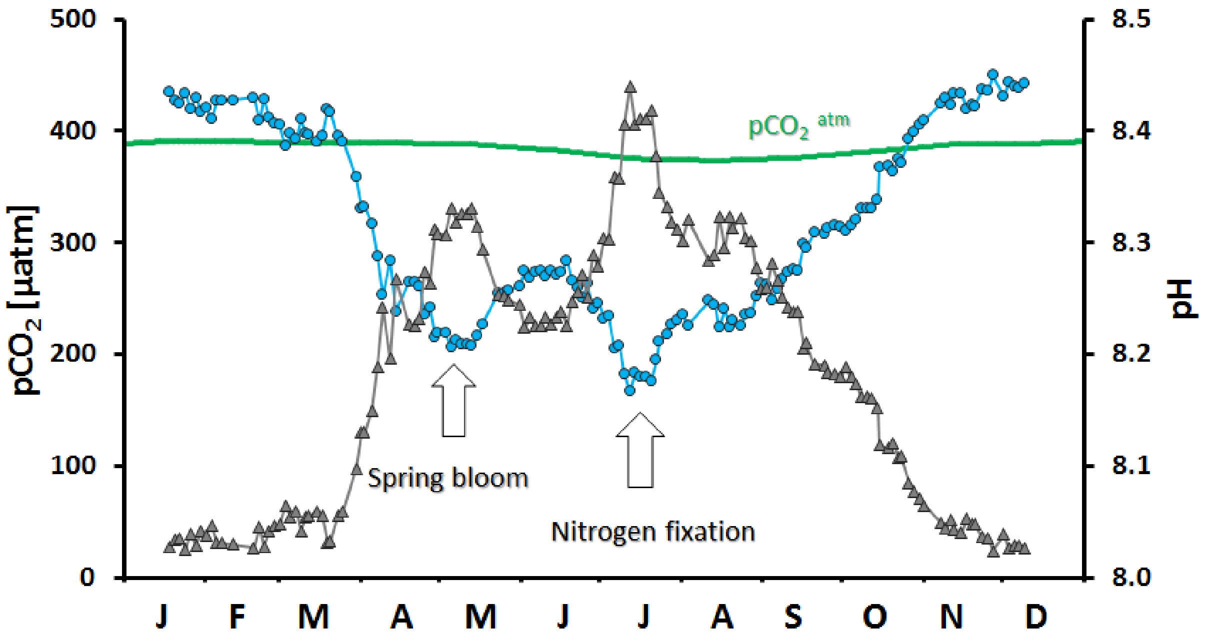


Fig. 5. Typical seasonality of pCO_2 in surface water (blue line) and the atmosphere (green line) in the Eastern Gotland Sea modified after Schneider (2011) and presented together with pH calculated from the shown pCO_2 data and the mean A_T value.

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 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 organic carbon from land. The model studies by Gustafsson et al. (2014a) suggested that as much as 39.5% of terrigenous organic carbon that enters the Baltic Sea undergoes mineralization without distinguishing between mineralization pathways. This makes that it is difficult to estimate all the consequences of that terrestrial organic carbon loss for the Baltic Sea acid-base system. The incubation experiments performed by Kuliński et al. (2016) indicated that ca. 20 % of terrestrial dissolved organic carbon and 34 % of DOC present in the Baltic Sea is bioavailable. 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 changes the alkalinity. The change in 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. 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. 8), followed by denitrification where nitrate acts as oxidant (Eq. 9). After nitrate is consumed, the mineralization process may be continued by iron (III) oxide (Eq. 10) before sulphate oxidizes the organic matter and generates hydrogen sulphide (Eq. 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. 12) after the sulphate concentration 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. 7 – 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 these mechanisms stabilize the pH in the deep, anoxic water layers at level of about 7 (Hammer et al., 2017).

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

Oxic mineralization, ΔA$_T$ = -16

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

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

Manganese reduction, ΔA$_T$ = +472

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

$$106CO_2 + 42.4N_2 + 16NH_3 + 148.4H_2O + H_3PO_4 \quad (9)$$

Denitrification, ΔA$_T$ = +100.8

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

$$424Fe^{2+} + 106CO_2 + 16NH_3 + 530H_2O + H_3PO_4 \quad (10)$$

Iron reduction, ΔA$_T$ = +864

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

$$106CO_2 + 16NH_3 + 53S^{2-} + 106H_2O + H_3PO_4 \quad (11)$$

Sulphate reduction, ΔA$_T$ = +122

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4 \quad (12)$$

Methanogenesis, ΔA$_T$ = +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 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, 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~~,~~ only 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~~ future research ~~on the acid-base system in the Baltic Sea~~.

The general knowledge ~~on~~ of 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), 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 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~~ model 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 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~~are made 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 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 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 discrete samples, which ~~is~~ are 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 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 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 appropriate parameterization of the 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 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~~ substantial progress in analytical ~~methods~~ techniques, as the characterization of the structure and composition of DOM is still far from being satisfactory (Nebbioso and Piccolo, 2013). Problems also 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 also omits 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 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 of 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~~ Observing 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~~ of 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~~ did not reflect the reality. Omstedt et al. (2009) solved the problem by including a fractional nutrient release into their model. This ~~means~~ meant 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~~ after 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 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~~ proposed that the Baltic Sea acid-base system cannot be ~~confined to~~explained by 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, presumably, 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 catchment~~s~~ areas 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 the immediate effect of riverine input of acidic substances~~ with acid acid-base properties~~. ~~The latter.~~ This riverine input 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),~~. B~~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 also 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, which ~~that~~ reduces the alkalinity~~. B~~, 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. Anoxic ~~M~~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 affect~~ing~~ the acid-base system of the Baltic Sea as a whole, they ~~are influencing~~do 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 ~~This 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~~obtain this information. But in view of our limited knowledge concerning the composition of the dissolved organic matter, it is currently ~~hopeless ~~imposible 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.

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