Earth System
Dynamics
Discussions

EGU

Open Access

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

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

3 [1]Institute of Oceanology, Polish Academy of Sciences, IO PAN, ul. Powstańców Warszawy

4 55, 81-712 Sopot, Poland

5 [2]Leibniz Institute for Baltic Sea Research, IOW, Seestrasse 15 Warnemünde, D-18119

6 Rostock, Germany

7 Correspondence to: Karol Kuliński (kroll@iopan.gda.pl)

8

11

12 **Abstract**

13 The marine acid-base system is relatively well understood for oceanic waters. Its structure and

14 functioning is less obvious for the coastal and shelf seas due to the number of regionally

15 specific anomalies. In this review article we collect and integrate existing knowledge on the

16 acid-base system in the Baltic Sea. Hydrographical and biogeochemical characteristics of the

17 Baltic Sea, as manifested in horizontal and vertical salinity gradients, permanent stratification

18 of the water column, eutrophication, high organic matter concentrations and high

19 anthropogenic pressure, makes the acid-base system complex. We summarize in this study the

20 general knowledge on the marine acid-base system as well as we describe the peculiarities

21 identified and reported for the Baltic Sea specifically. In this context we discuss issues such as:

22 dissociation constants in the brackish water, different chemical alkalinity models including

23 contributions by organic acid-base systems, long term changes of total alkalinity, anomalies of

24 borate alkalinity and thee acid-base effects of biomass production and mineralization. Finally,

25 we identify research gaps and specify bottlenecks concerning Baltic Sea acid-base system.

26

27

28

29

1. Introduction

The acid-base system is a complex net of interrelationships between chemical species and processes that control the seawater pH (Dickson et al., 2007). The understanding of its structure and functioning is a tool to investigate important issues that shape the Baltic Sea ecosystem and that are of interest for the present-day chemical oceanography like: ocean acidification, calcium carbonate formation/dissolution and/or 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 (buffer reaction), a significant fraction stays in the water column and thus causes a decrease of the 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 scientific community, but also in 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. 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. 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 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. Saturation state of calcite and aragonite is of crucial importance for organisms forming their exoskeletons from $CaCO_3$. Although pelagic calcifying organisms do

1   not occur in the Baltic Sea this aspect is still relevant as some benthic organisms can also build

2    $CaCO_3$ into their shells (Tyrrell et al., 2008). Moreover, calcifying processes not only depend

3   on the acid-base system structure but in turn can modify it by decreasing the concentration of

4   CO_3^{2-} and thus the alkalinity.

5   Carbon dioxide is a major player in the global carbon cycle and transport of CO_2 links all

6   Earth's compartments. It is believed that the world oceans absorb about 25 % of the

7   anthropogenic CO_2 emissions. However, there is still a debate on the role that the shelf seas

8   play in this context (Le Quéré, 2016). The direction and magnitude of the CO_2 exchange

9   through the air-sea interface depends largely on the pCO_2 difference between seawater and the

10   atmosphere. The level of seawater pCO_2 is mainly controlled by the structure of the acid-base

11   system that is influenced by the combined effect of biological activity (biomass production vs.

12   mineralization), CO_2 exchange with the atmosphere and temperature (Emerson and Hedges,

13   2008).

14   In this context the Baltic Sea can be considered as a very complex ecosystem, in which on one

15   hand the low buffer capacity makes the seawater vulnerable to acidification, and on the other

16   hand the sea is exposed to various anthropogenic influences which have the potential to change

17   the acid-base system and thus also seawater pH and all pH-related processes. This makes the

18   Baltic Sea different from the oceans for which the CO_2 system as part of the acid-base system

19   has been well characterized during the last decades. Considerable research effort was also

20   undertaken in recent years to investigate the Baltic Sea CO_2 system and its peculiarities.

21   However, this was done from different perspectives and resulted in specific problem-oriented

22   and divers knowledge. Therefore, the goal of this review article is to collect and integrate the

23   existing knowledge on the structure and functioning of the acid-base system in the Baltic Sea,

24   to point out the research gaps and thus also to address challenges for the future research in this

25   field.

26

27   **2. The standard acid-base model for ocean water**

28   Four measurable variables exist to describe the acid-base system of seawater. These are: pCO_2,

29   pH, total inorganic carbon concentration (C_T, known also as DIC) and total alkalinity (A_T). C_T

30   is the total concentration of all inorganic carbon forms present in seawater (Eq. 1), where

31   $[CO_2^*]$ represents the sum of molecular dissolved CO_2 and undissociated carbonic acid

32   (H_2CO_3):

Earth System
Dynamics
Discussions

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

2   Measurements of C_T usually base on acidification of the sample and coulometric or infrared

3   detection of the extracted CO_2 (Dickson et al., 2007). A_T is defined as the excess of proton

4   acceptors (bases formed from weak acids with a dissociation constant of $K \leq 10^{-4.5}$ at 25 °C)

5   over proton donors (acids with $K > 10^{-4.5}$) and expressed as the hydrogen ion equivalent in one

6   kilogram of sample (Dickson, 1981):

7    $A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + +[NH_3] +$

8    $[HS^-] + [\text{minor bases}] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] - [\text{minor acids}]$ (2)

9   A_T can be determined by open- or closed-cell acidimetric titration. For both C_T and A_T certified

10   reference materials are provided by the Andrew Dickson laboratory, UC San Diego, USA

11   (Dickson et al., 2007). Reference materials still do not exist for pH measurements in seawater.

12   In many cases pH is still measured potentiometrically on the NBS scale although

13   spectrophotometric measurements on the total scale (pH_{tot}), which takes into account also

14   HSO_4^- ions, are currently state of the art in the field of chemical oceanography. The

15   concentration of $CO_2{}^*$ in seawater is obtained from the partial pressure of CO_2 in air in

16   equilibrium with seawater. According to the standard operating procedure (Dickson et al.,

17   2007), measurements of pCO_2 require continuous flow of water, which makes this parameter

18   difficult to measure in discrete samples.

19   All four variables are interacting and control the pH by a set of equilibrium constants and mass

20   balance equations. In general the interrelationships between these four parameters facilitate the

21   calculation of any two variables, when the two others are known, e.g. through measurements,

22   and when the dissociation constants of the involved acid-base reactions are known for the

23   respective temperature and salinity. This fact is used in biogeochemical models aiming at

24   simulation of marine CO_2 system. All biogeochemical models are based on the transport and

25   transformations of A_T and C_T, because these variables are independent on temperature and

26   pressure and behave conservative with respect to mixing (mass conservation). Moreover,

27   straightforward techniques for sampling and analysis for A_T and C_T exist and are supported by

28   the availability of reference materials (Dickson et al., 2007). Hence, these two variables are

29   very well suited for studying the CO_2 system. However, the use of A_T and C_T for the CO_2

30   system studies is not free from limitations. To obtain high accuracy for the calculations of pH

31   and pCO_2 from measured or modelled A_T and C_T, all dissociation constants and total

32   concentrations of all non-CO_2 components of the acid-base system must be known. This

Earth System
Dynamics
Discussions

1 requirement is approximately fulfilled with regard to ocean studies where the total

2 concentrations of non-CO_2 acid-base components are there either negligible or can be

3 approximated by a functions of salinity (Riebesell et al., 2010). However, this issue is more

4 critical for coastal and shelf regions, where biogeochemical composition of seawater shows

5 regional peculiarities (e.g. Kuliński 2014; Hunt et al. 2011; Hernandez-Ayon et al., 2007; Cai

6 et al., 1998). This is the case for the Baltic Sea, which shows various unique biogeochemical

7 characteristics.

8

3. Peculiarities of the Baltic Sea acid-base system

3.1. Short introduction to relevant hydrographic settings

11 The Baltic Sea is one of the largest brackish ecosystems in the world. This is caused by both

12 limited inflows of saline oceanic water through the shallow and narrow Danish Straits and high

13 river runoff. The drainage basin of the Baltic Sea is almost four times larger than the area of

14 the sea itself, while the annual freshwater supply (428 km^3) constitutes about 2 % of the Baltic

15 Sea water volume ($22 \cdot 10^3$ km^3). This specific features of the Baltic Sea hydrology cause clear

16 horizontal and vertical salinity gradients. Salinity in surface layer fluctuate from 2 PSU in the

17 northern Bothnian Bay to >20 PSU observed in the Kattegat. Dense and highly saline water,

18 which irregularly enters the Baltic Sea, sinks and moves along the sea bottom. This deep water

19 is separated from the brackish surface water layer by a permanent halocline located at a depth

20 of 60-70 m, which is at the same time the maximum mixed layer depth in the Baltic Sea (Lass

21 and Matthäus, 2008). The stratification limits ventilation of the deep water masses.

22 Simultaneously, the deeper water layers are supplied with large amounts of organic matter that

23 is either originating from terrestrial sources or derived from the biomass production in the

24 surface under the influence of high nutrient concentrations (eutrophication). Some fraction of

25 sedimentary organic matter mineralizes releasing CO_2 and consuming oxidants, what leads to

26 hypoxia or even anoxia in the bottom waters (HELCOM, 2009).

Earth System
Dynamics
Discussions
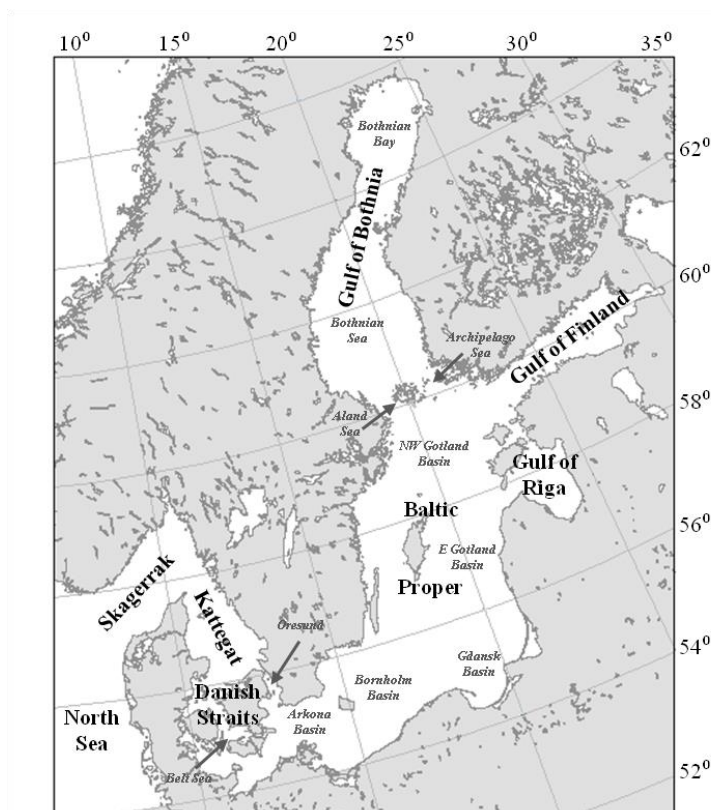
1

2   Fig. 1. Map of the Baltic Sea showing its division into natural basins and sub-basins

3   (modified after Kuliński and Pempkowiak, 2011).

4

3.2. Dissociation constants in the brackish water

6   If any variables of the marine CO_2 systems are to be used for biogeochemical studies, it is

7   advisable to measure these directly and not to derive it from the measurements of other

8   variables of the CO_2 system. However, sometimes direct measurements may be prevented by

9   technical reasons or routine analytical methods do not exist. The latter refers for example to

10   the determination CO_3^{2-} ion concentrations which are important for the assessment of the state

11   of the $CaCO_3$ saturation and thus for the dissolution or formation of $CaCO_3$ shells. In this case,

12   calculations on the basis other known variables such as C_T, A_T, pCO_2 or pH are indispensable

13   and require knowledge about the equilibrium constants of the CO_2 system. Here we examine

14   the availability of the necessary constants for low salinity brackish water. Three fundamental

Earth System
Dynamics

Discussions

Open Access

1   equations characterize the equilibria of the marine CO_2 system. The first refers to the solubility

2   of gaseous CO_2 in seawater:

3    $[CO_2^*] = k_0 * fCO_2$ (3)

4   The solubility constant, k_0, relates the concentration of CO_2^* in seawater to the CO_2 fugacity,

5   fCO_2. In contrast to the CO_2 partial pressure, pCO_2, the fugacity accounts for the non-ideal

6   behaviour of CO_2 at atmospheric conditions. It differs only slightly from the pCO_2 and in many

7   cases can be replaced by the pCO_2. The solubility and thus k_0 decreases with increasing

8   temperature and salinity and vice versa. Studies by Weiss (1974) that describe k_0 as a function

9   of temperature and salinity, have received widespread acceptance and are almost exclusively

10   used in chemical oceanography. The situation is somewhat more complicated for the

11   determination of the dissociation constants for carbonic acid because it is a diprotic acid. Using

12   again the CO_2^* as variable, the two dissociation equilibria are given by:

13   $K_1 = [H^+][HCO_3^-]/[CO_2^*]$ (4)

14   $K_2 = [H^+][CO_3^{2-}]/[HCO_3^-]$ (5)

15   In these formulas the terms for the hydrogen ions are given in concentration units which include

16   HSO_4^- ion concentration. This convention is called "total" hydrogen ion scale and its use is

17   currently state of the art.

18   Systematic studies concerning the dissociation constants of carbonic acid in seawater were

19   already performed during the twenties and thirties of the last century. One of the leading

20   scientists in this field was Kurt Buch from the former Finnish Institute for Marine Research,

21   whose research was mainly related to the Baltic Sea and consequently also his laboratory

22   studies on the CO_2 system focused on brackish water with salinities down to zero. The results

23   of his lab work and of field studies performed during 1927 to 1936 are summarized in Buch

24   (1945). The presented dissociation constants must be considered as "hybrid" constants because

25   the hydrogen ions are represented by the hydrogen ion activity whereas the CO_2 constituents

26   refer to concentrations.

27   With the upcoming awareness of the importance of the oceans for the uptake of anthropogenic

28   CO_2 and thus for climate change scenarios, large-scale measurement programmes concerning

29   the state of the marine CO_2 system on an oceanic scale were performed. These efforts were

30   accompanied by numerous laboratory studies that aimed at the determination of improved

31   dissociation constants. All these constants referred to the total hydrogen concentration scale

1   that includes the contribution by hydrogen sulphate ions. However, the validity of most of the

2   constants was confined to salinities that are encountered in ocean water. An exception are the

3   constants suggested by Roy et al. (1993), which were determined for salinities down to values

4   of 5 and could be used accordingly for brackish water. However, with regard to research in the

5   Baltic Sea where large areas, e.g. in the Gulf of Bothnia, have surface water salinities less than

6   5, the situation was unsatisfactory. It took until 2006 when Millero et al. (2006) published

7   dissociation constants that covered the salinity range from 0 to 50 and that were consistent with

8   the constants for fresh water. An update of these constants was performed in 2010 (Millero,

9   2010) and since then this set of dissociation constants is state of the art for CO_2 research in

10   brackish waters. The salinity and the temperature dependency of K_1 and K_2 are presented in

11   Fig. 2a and 2b, respectively.

12   A direct comparison between the dissociation constants that were used in the past for brackish

13   water is difficult because the constants by Buch (1945) are based on a pH scale that is based

14   on the hydrogen ion activity. Since it is difficult to convert the activities to total hydrogen ion

15   concentrations, we use the ratio K_1/K_2 (pK_1-pK_2) that does not include the hydrogen ion

16   activities or concentrations, for a comparison. The deviations of the (pK_1-pK_2) obtained from

17   Buch (1945) and Roy et al. (1993) from the (pK_1-pK_2) according to Millero (2010), indicated

18   as M-B and M-R, respectively, are shown in Fig. 2c. At salinities >7, M-R is less than 0.03,

19   but the differences increase rapidly at lower salinities and amount to 0.06 and 0.10 already at

20   S = 5.4 and S = 3.6, respectively. Such differences in pK_1-pK_2 (K_1/K_2) are equivalent to a

21   temperature change of 1 °C. The deviations of the Buch (1945) data from those of Millero

22   (2010) (M-B in Fig. 2c) ranged below 0.10 at salinities below 20. This is a surprisingly small

23   difference in view of the limited technical possibilities that were available to Kurt Buch and

24   his co-workers in the twenties and thirties of the last century.

1
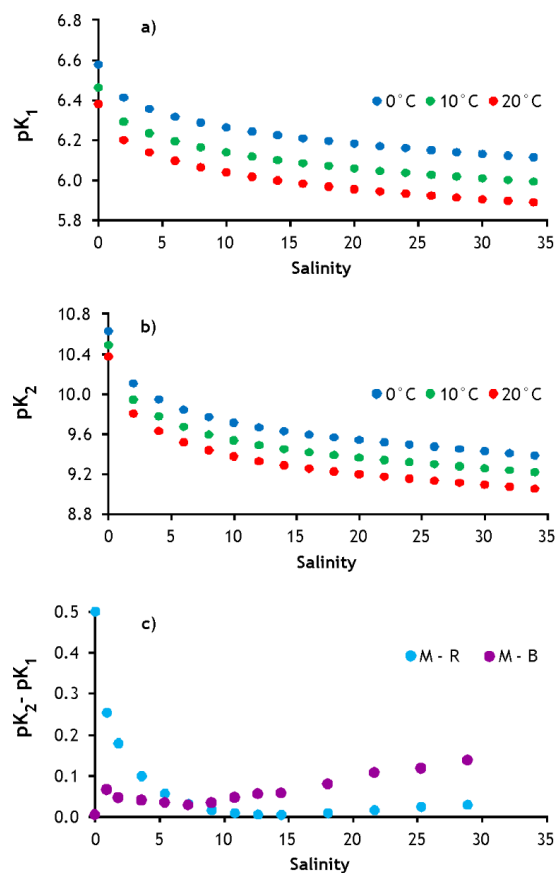
Fig. 2. (a) pK_1 and (b) pK_2 as a function of salinity calculated according to Millero (2010) for three different temperatures: 0, 10 and 20 ºC; (c) deviations of ($pK_1 - pK_2$) obtained from Roy et al. (1993) (M-R, blue dots) and from Buch (1945) (M-B, purple dots) with regard to the ($pK_1 - pK_2$) obtained from by Millero (2010) at different salinities.

6

7   In case that also alkalinity is used for the calculation of any variables of the CO_2 system, the

8   contributions of non-CO_2 acid-base components to A_T (Eq. 2), which are generally low, must

9   be taken into account. This requires knowledge about the concentration of the individual acid-

10   base pairs and about the corresponding dissociation constants. In the deep basins of the central

11   Baltic Sea, ammonia and sulphide anions are released during organic matter mineralization at

12   anoxic conditions (see Chapter 3.4.2). Both these constituents are strong proton acceptors

13   forming mainly HS^- and NH_4^+. Since their concentrations may be in the order of several tens

14   and up to a few hundred µmol L^{-1} (Nausch et al., 2008), respectively, they have a strong effect

1   on alkalinity and pH. Therefore, any calculations concerning the CO_2 system at anoxic

2   conditions must account for the dissociation equilibria of H_2S-HS^- (Millero et al., 1988) and

3   NH_4^+-NH_3 (Clegg and Whitfield, 1995; Johansson and Wedborg, 1980). The concentrations of

4 S^{2-} at the pH of anoxic water are extremely small and can be neglected.

5

6   **3.3. The central role of alkalinity**

7   **3.3.1. Regional A_T vs. S distribution, consequences for pH distribution pattern**

8   There are several different A_T vs. S regimes in the Baltic Sea (Fig. 3, Beldowski et al., 2010).

9   They reflect different A_T concentrations in the respective rivers, which can be deduced from

10   extrapolation of regional A_T vs. S relationships to zero salinity. Low alkalinities are observed

11   in rivers entering the Gulf of Bothnia whereas rivers from south-eastern part of the Baltic

12   catchment, as shown by A_T vs. S plot for the Gulf of Riga (Fig. 3), are rich in alkalinity. These

13   differences are a consequence of the geological conditions and weathering processes in the

14   respective catchment areas. As a result lower alkalinities (low buffer capacity) and lower mean

15   pH are observed in the Gulf of Bothnia and Finland, whereas higher mean alkalinities and thus

16   somewhat higher pH are found in the Gulf of Riga and also in the Gdansk Bay (Kulinski et al.,

17   2014; Beldowski et al., 2010; Hjalmarsson et al., 2008). First investigations made in the Polish

18   rivers (own data) suggest additionally that A_T concentrations in river water decrease

19   substantially in western direction.

20   The central Baltic Sea acts as a mixing chamber for the different water masses, including water

21   originating from the North Sea, resulting in an alkalinity in the surface water of the Baltic

22   Proper (salinity around 7 PSU) of about 1600-1700 μmol kg^{-1}. However, the river A_T

23   characteristics in the Baltic Proper are not well defined because several A_T vs. S regimes are

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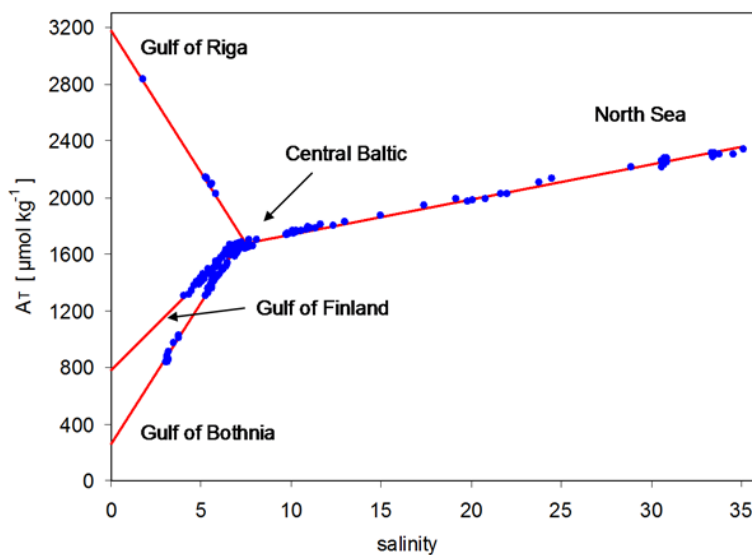
Fig. 3. Different A_T vs. S regimes observed in the Baltic Sea (modified after Beldowski et al., 2010)

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 data which are regularly collected by some Baltic Sea states within the framework of HELCOM monitoring program. In some countries like Sweden the monitoring data are publically 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 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 been reported in the Baltic Sea so far.

Earth System
Dynamics
Discussions

1   At equilibrium with the atmospheric CO_2, the A_T controls the C_T and thus the pH. Hence, the

2   pH may be depicted as a function of A_T and pCO_2. A sensitivity study performed by Omstedt

3   et al., (2010) indicates that the pH of the Baltic Sea surface water that is at equilibrium with

4   the atmosphere (pCO_2 of ca. 400 µatm at 0 °C) can vary between 7.7 and 8.3 depending on the

5   A_T (Fig. 4). This range is significantly higher than that observed in the open ocean. The reason

6   for that is the high spatial variability of A_T in the surface Baltic Sea waters, from low A_T (below

7   1000 µmol kg^{-1}) observed in the Bothnian Bay to the A_T-rich (more than 3000 µmol kg^{-1})

8   estuaries of the large continental rivers. The diagram presented in Fig. 4 shows also that higher

9   A_T reduces vulnerability of the seawater pH upon changes in pCO_2.

10

11
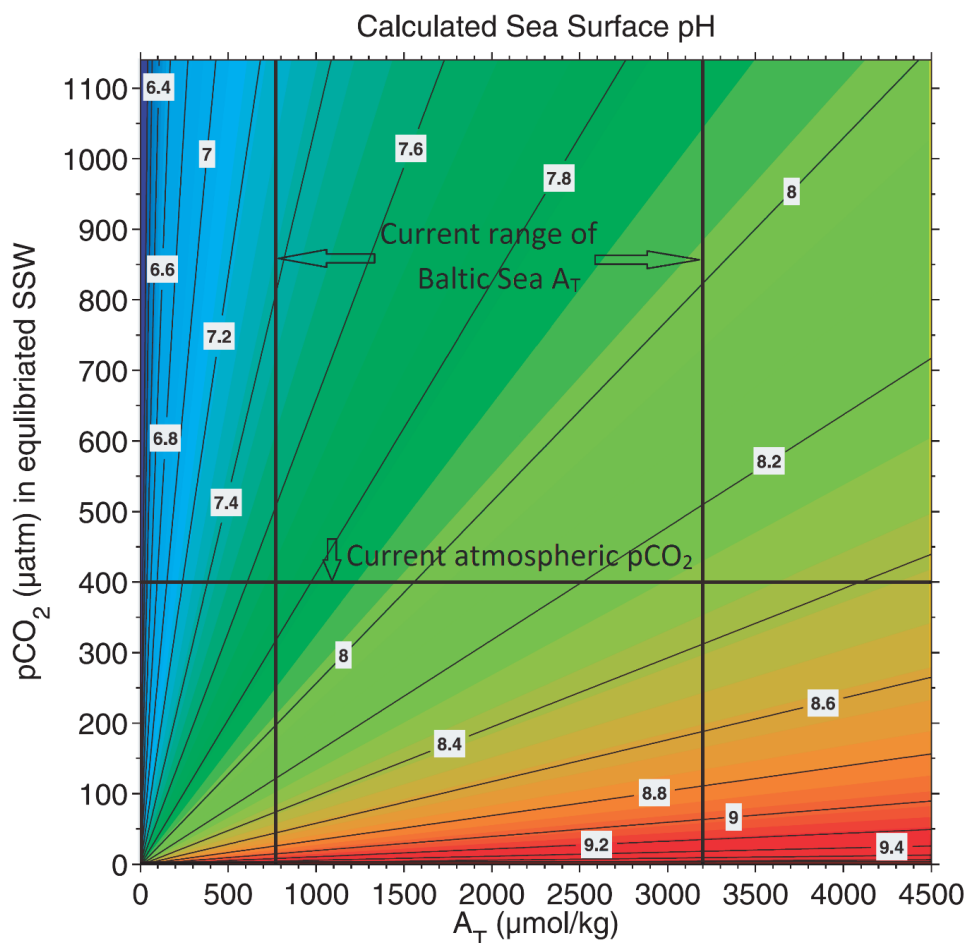
1   Fig. 4. Distribution of pH_{tot} as a function of A_T and pCO_2 at salinity of 7.5 and temperature of

2   0 °C (modified after Omstedt et al., 2010). The A_T range represents findings by Beldowski et

3   al. (2010). SSW is an abbreviation of surface sea water.

4

5   **3.3.2. Long-term A_T changes, consequences for ocean acidification**

6   Long-term high resolution pH measurements at station BATS (Bermuda Atlantic Time Series)

7   in the sub-tropical North Atlantic have shown that ocean acidification occurs at a rate that is

8   thermodynamically consistent with the increase of the atmospheric CO_2 (Bates, 2014). This

9   gave reason to expect that the future development of ocean acidification can be assessed on the

10   basis of CO_2 emission scenarios and the modelling of the effect on the atmospheric CO_2. It

11   implies that changes in alkalinity will not occur in the future. On time scales of decades this

12   may be a reasonable assumption for the oceans which react very slowly upon internal or

13   external changes. However, the situation is different for the Baltic Sea that is under the

14   immediate influence of natural or anthropogenic processes on land. First hints for increasing

15   alkalinity in the surface water of central Baltic Sea were reported by Schneider et al. (2015)

16   who argued that this may have mitigated considerably the acidification by increasing

17   atmospheric CO_2. Müller et al. (2016) took up this idea and performed a thorough and

18   comprehensive statistical analysis of all alkalinity data that were available since the very

19   beginning of the CO_2 research in the Baltic Sea at the beginning of the last century. The authors

20   focused on high-quality data measured after 1995 and they detected a distinct A_T trend that

21   showed a clear regional gradient. The highest trend was found in the Gulf of Bothnia (7.0 µmol

22   kg^{-1} yr^{-1}), followed by 3.4 µmol kg^{-1} yr^{-1} in the central Baltic, whereas no trend could be

23   detected in the Kattegat. Müller et al. (2016) estimated that the changes in A_T have reduced the

24   acidification effect in the central Baltic Sea by about 50 % and that the Gulf of Bothnia was

25   not subjected at all to acidification during the last 20 years. Several reasons for the increasing

26   A_T are discussed by Müller et al. (2016), but a major player could not be identified and, hence,

27   it remains unclear whether the trend will continue in the future.

28

29   **3.3.3. Effect of organic alkalinity**

30   The Baltic Sea water contains 3-5 times more organic matter than open ocean waters. This is a

31   result of both high inputs of terrestrial organic matter and eutrophication driven by nutrient

32   supply from land (Hoikkala et al., 2015; Kuliński and Pempkowiak, 2011; Kuliński et al.,

Earth System
Dynamics
Discussions

1   2011). Organic substances contain functional groups. Some of them (carboxylic, phenolic,

2   amines) have acidic character and can dissociate in seawater releasing protons (H^+). This

3   contributes to pH decrease. However, as most of these groups are believed to act as weak acids

4   ($pK_a > 4.5$), their dissociation releases also an equivalent of organic anions being strong bases.

5   This, according to Eq. 2, causes no change in A_T concentration since an equivalent amount of

6   protons have been released. It affects the internal structure of A_T by changing the contributions

7   of different A_T components according to their individual dissociation constants (Cai et al.,

8   1998; Hunt et al., 2011; Kuliński et al., 2014). The lower the pK_a of an organic acid added to

9   the system is, the greater are the shifts in the internal A_T distribution. As a consequence bases

10   forming the acid-base system are partially protonated and their concentration decreases while

11   the concentration of the corresponding undissociated acid is increasing. In case of the carbonate

12   alkalinity this means a reduction of CO_3^{2-} and an increase of H_2CO_3 and thus of the pCO_2.

13   Kuliński et al. (2014) estimated the organic alkalinity (A_{org}) in the Baltic Sea as an excess

14   alkalinity calculated from the difference between measured A_T and that calculated from C_T and

15   pH or pCO_2. They found A_{org} of 25-35 μmol kg^{-1} in the surface Baltic Sea water (from the

16   Arkona Basin to the Bothnian Bay) without any clear spatial distribution pattern. This Aorg

17   contribution amounted from 1.5 % to 3.5 % of the measured A_T values. Even higher values of

18   more than 50 μmol kg^{-1} were found by Hammer et al. (2017) in the Baltic Sea surface mixed

19   layer during the spring phytoplankton bloom. They reported also that A_{org} decreases with depth

20   and approaches zero below the permanent halocline due to pH decrease.

21   In sensitivity studies Kuliński et al. (2014) showed for the Baltic Sea that calculations

22   concerning the CO_2 system that are using measured A_T, may lead to significant errors if A_{org} is

23   ignored. Highest deviations between calculated and observed values were found when A_T was

24   used together with C_T for computations of pCO_2 and pH. The pCO_2 values obtained in that way

25   were by 27-56 % lower than the measured ones, while pH was overestimated by more than 0.4

26   units. These results are especially important as this combination (A_T and C_T) is used in

27   biogeochemical models because they are conservative variables. This means that they are

28   independent on pressure and temperature and follow the law of conservation of mass during

29   mixing, which are prerequisites for variables transported in models. The sensitivity of

30   biogeochemical models with regard to the inclusion/negligence of A_{org}, however, has not yet

31   been reported.

32   The source of the calculation errors related to ignoring A_{org} is due to the fact that measurements

33   catch also A_{org} while subsequent calculations using the standard chemical A_T model and

Earth System
Dynamics
Discussions

1   respective software, interpret the measured A_T only as inorganic alkalinity. Including organic

2   substances into the A_T model is, however, challenging as there are number of organic

3   substances having acidic functional groups and, according to the A_T definition, for each of them

4   the information on concentration and dissociation constant must be available. Accounting for

5   A_{org} in the chemical A_T model is less important for oceanic research because the low

6   concentrations of dissolved organic matter (DOM) in the oceans cause only minor effects. As

7   a first approximation of the acid-base properties of DOM for the Baltic Sea water, Kuliński et

8   al. (2014) proposed to use one single bulk dissociation constant, pK_{DOM} and relate A_{org} to the

9   concentration of dissolved organic carbon (DOC), a commonly measured parameter.

10   According to their studies, slightly corrected by Ulfsbo et al. (2015), pK_{DOM} in the Baltic Sea

11   amounts to 7.34. They estimated also experimentally that 12 % of DOC acts as a carrier for

12   acidic functional groups in the Baltic Sea DOM. The model studies by Ulfsbo et al. (2015)

13   showed that this experimentally derived share fits to the hypothetical structure of the fulvic

14   acids. They suggested also that method proposed by Kuliński et al. (2014) is the best available

15   approach for representing organic alkalinity in biogeochemical models at the current state of

16   knowledge. They showed also that organic matter (as represented by the fulvic acids) contains

17   also a lot of acidic functional groups having pK_a already below 4.5. According to the definition

18   (Dickson, 1981) they should be considered as strong acids. In experimental studies Hammer et

19   al. (2017) found also that humic and/or fulvic substances are more acidic than the bulk DOM

20   naturally occurring in the Baltic Sea. This may also be a source of uncertainty in the A_T

21   measurements as the determination of the titration end-point requires to titrate the samples

22   through this pH region.

23

3.3.4. Role of borate alkalinity

25   The carbonate system plays a central role in the marine acid-base system. Thus, studies on

26   seawater pH and buffering capacity focus usually on the carbon species. Less attention is paid

27   to boron, though borates are, after bicarbonates and carbonates, the third most abundant

28   constituent of seawater A_T (Eq. 2). Boron exists in seawater in form of weak boric acid,

29   $B(OH)_3$, and their anions, $B(OH)_4^-$. The high pK_a (8.60 at salinity 35 PSU and temperature 25

30   °C) causes that at seawater pH of about 8 the undissociated boric acid predominates. The boron

31   concentration, B_T, in seawater is approximated as a function of salinity or, for the historical

32   data, as a function of chlorinity ($S = 1.80655 * Cl$). First measurements of boron concentrations

33   in the Baltic Sea were reported by Buch (1945), who found that B_T [mg kg^{-1}] = 0.133 * S. This

15

1   finding was confirmed recently by Lee et al. (2010) for the oceanic waters. Another relationship

2   linking B_T and S and often used in acid-base system studies, is that by Uppström, (1974), who

3   reported that B_T [mg kg^{-1}] = 0.128 * S. All these formulas suggest a fixed B_T/S ratio which is

4   only the case if the river water that enters the Baltic Sea contains no boron. However, the

5   studies by Kremling (1970, 1972) indicated that this is not the case and that a B_T concentration

6   anomaly exists in the Baltic Sea. He found that the experimentally determined T_B vs. S

7   relationship yielded a river water B_T (anomaly term) of 0.15 – 0.20 mg kg^{-1} at S = 0. This

8   anomaly is not included in the chemical A_T model commonly used for numerical simulations

9   of the CO_2 system and similarly to the effect of ignoring A_{org}, may lead to wrong conclusions.

10   This can be especially critical at low salinities, where the effect of anomaly is the largest.

11

12   **3.4. Modulation of the acid-base system by organic matter production/mineralization**

13   **(concurrent A_T and C_T changes)**

14   **3.4.1. Biomass production**

15   As pointed out before, in case that pH changes are discussed that refer to equilibrium with the

16   atmosphere, it may be meaningful to consider the pH at a given alkalinity as a function of pCO_2

17   because the atmospheric pCO_2 is then the driver for any pH changes. However, when assessing

18   pH changes as the consequence of internal biogeochemical transformations, it is more

19   appropriate to consider A_T and C_T as control for the pH and the pCO_2. Biomass production

20   alter primarily C_T because phytoplankton (but also other plants) consume CO_2 in the course of

21   photosynthesis (Fig. 5). As a consequence it increases the pH and lowers the pCO_2 in the upper

22   water layers and causes a pCO_2 disequilibrium between seawater and the atmosphere. This

23   leads to CO_2 uptake by the seawater and thus counteracts the effect of biomass production and

24   dampens the pH decrease. However, the CO_2 exchange through air/sea interface is much slower

25   than the effects of biological processes. Therefore, the Baltic Sea water is in almost permanent

26   pCO_2 disequilibrium with the atmosphere throughout the year. In spring and summer seawater

27   is undersaturated with respect to atmospheric CO_2 with two characteristic pCO_2 minima and

28   two pH maxima (Fig. 5) which reflect the spring bloom and the mid-summer nitrogen fixation

29   period. In autumn and winter the Baltic Sea water pCO_2 increases over the atmospheric values

30   as a consequence of less active production in the upper water column and transport of deeper

31   CO_2-enriched water to the surface by mixing (Fig. 5; Schneider, 2011).

16

Earth System
Dynamics
Discussions

1   Another way in which biomass production influences seawater pH and pCO_2 is related to

2   nitrate consumption. Since phytoplankton assimilates nitrates for its growth an equivalent of

3   H^+ is also transported to the cells to keep the charge balance neutral. According to Eq. 2 this

4   increases the seawater A_T and thus enhances the pH during biomass production (Brewer and

5   Goldman, 1976). At the same time it decreases the pCO_2 and therefore reinforces the drop in

6   pCO_2 by biomass production.

7   Biological production may consume also CO_3^{2-} ions in the calcification processes. This causes

8   A_T reduction and in consequence pCO_2 increase and thus also pH decrease. However, this

9   mechanism has been recognized as less important in the Baltic Sea. According to studies by

10   Tyrrell et al. (2008) the Baltic Sea surface water is undersaturated in winter with respect to

11   both aragonite and calcite which are biogenic modifications of $CaCO_3$. This prevents possibly

12   the growth of calcifying plankton and is the reason for the absence of coccolithophores in the

13   Baltic Sea.
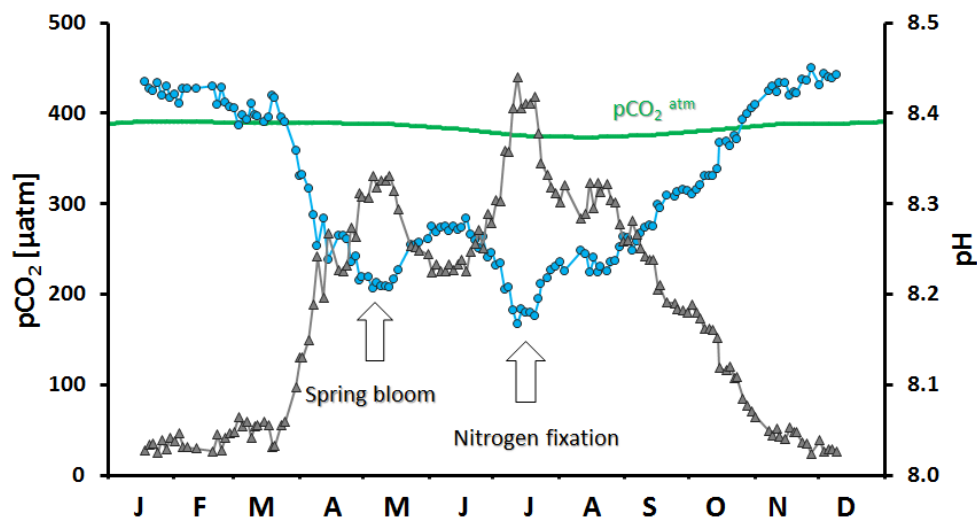
15   Fig. 5. Typical seasonality of pCO_2 in surface water (blue line) and the atmosphere (green line)

16   in the Eastern Gotland Sea modified after Schneider (2011) and presented together with pH

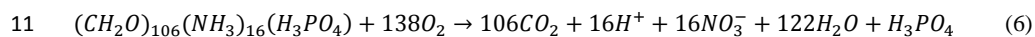17   calculated from the shown pCO_2 data and the mean A_T value.

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 undergo 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 (tDOC). The model studies by Gustafsson et al. (2014a) suggest that as much as 39.5% of tDOC 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 and 34 % of DOC present in the Baltic Sea is bioavailable. 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 depend additionally on the organic matter transformations by various redox processes. 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 depend 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 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), followed by denitrification were nitrate acts as oxidant (Eq. 8). After also nitrate is consumed, the mineralization process may be continued by iron (III) oxide (Eq. 9) before sulphate is oxidizing the organic matter and generating hydrogen sulphide (Eq. 10). In the Baltic Sea these processes may take place in the water column where a pelagic redoxcline can develop during longer periods of stagnation. Only the final mineralization, that is an internal oxidation and generates methane (methanogenesis, Eq. 11) after also sulphate concentration have approached zero, is confined to deeper sediment
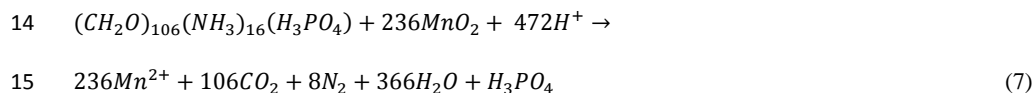
Earth System
Dynamics
Discussions

1   layers only. Except oxic mineralization, all other processes are connected with a simultaneous

2   A_T increase caused either by release of strong bases (S^{2-}) or by consumption of H^+ (see Eq. 2)

3   (Ulfsbo et al., 2011; Schneider et al., 2015; Lukawska-Matuszewska, 2016). The change in A_T

4   (ΔA_T) for different mineralization pathways is given in moles A_T per 106 moles of released

5   CO_2 (Eqs. 6 – 11). It shows large differences and is highest when the insoluble oxides of iron

6   (III) and manganese (IV) are reduced during the mineralization process. As a consequence of

7   the higher A_T level, the pCO_2 increase and pH decrease by increasing C_T during the

8   mineralization is mitigated or may even be reversed. In the eastern Gotland Sea this

9   mechanisms stabilize the pH in the deep, anoxic water layers at level of about 7 (Hammer et
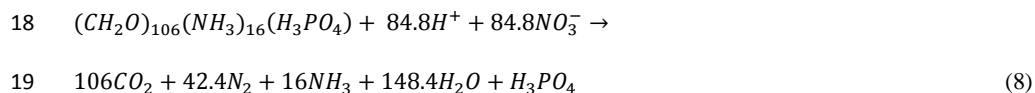
10   al., 2017).

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

12   $\Delta A_T = -16$

13

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

15   $236Mn^{2+} + 106CO_2 + 8N_2 + 366H_2O + H_3PO_4$ (7)

16   $\Delta A_T = +472$

17

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

19   $106CO_2 + 42.4N_2 + 16NH_3 + 148.4H_2O + H_3PO_4$ (8)

20   $\Delta A_T = +100.8$

21

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

23   $424Fe^{2+} + 106CO_2 + 16NH_3 + 530H_2O + H_3PO_4$ (9)

24   $\Delta A_T = +864$

25

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

27   $106CO_2 + 16NH_3 + 53S^{2-} + 106H_2O + H_3PO_4$ (10)

28   $\Delta A_T = +122$

1
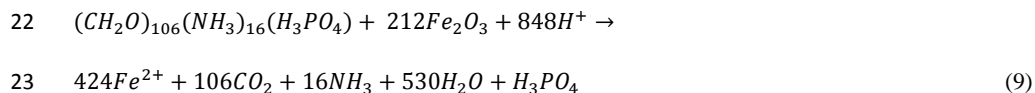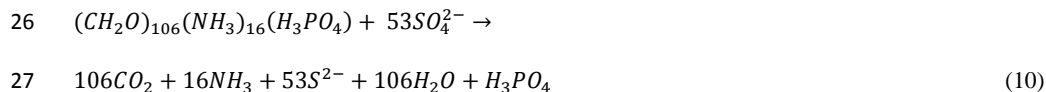
2 $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$ (11)

3 $\Delta A_T = +16$

4

5 Generally, benthic processes linked to early diagenesis of organic matter can be an important

6 source for A_T to the water column (Brenner et al., 2016). This corresponds to the findings by

7 Gustafsson et al. (2014b), who found by a model study that external sinks and sources of A_T in

8 the Baltic Sea are imbalanced and cannot reproduce the observed A_T inventory of the Baltic

9 Sea, and that an internal A_T source must exist in the Baltic Sea. However, it must be taken into

10 account that alkalinity released from sediments as sulphide and/or ammonia, influence the acid-

11 base system only locally. Upon contact with oxic water most of the A_T generating processes –

12 except denitrification - are reversed and do not constitute a permanent A_T source.

13

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

15 The general knowledge on the marine acid-base system was gained mainly from the oceanic

16 research. It has been integrated and documented in the form of a guide (Dickson et al., 2007)

17 and included in different software packages (Orr et al., 2015), that allow for computations of

18 two out of the four (pCO_2, pH, A_T, C_T) the acid-base system parameters, when the other two

19 are known e.g. by measurements. Although this works nicely for the open ocean waters,

20 problems appear when that knowledge is used for the studies of the acid-base system related

21 processes in coastal and shelf seas. This uncovers research gaps and bottlenecks but also define

22 challenges for marine biogeochemists working in these regions.

23 In this context the Baltic Sea can be considered as a perfect experimental field, where strong

24 horizontal and vertical salinity gradients, permanent stratification of the water column,

25 eutrophication, high organic matter concentrations and high anthropogenic pressure make the

26 acid-base system even more tangled. The challenges are related to analytical methods,

27 interpretation of the data and parametrization of the acid-base system related processes for the

28 use in numerical models. Great effort has recently been made to adapt pH spectrophotometric

29 measurements based on m-cresol purple to the Baltic Sea conditions. This was done by

30 Hammer et al. (2014) and was recently improved within a framework of BONUS PINBAL

31 project. Further progress can be expected if pH reference material for brackish water will be

32 available in the future. For the pCO_2 measurements the state-of-the-art method that is based on

1 measuring CO_2 content in the air equilibrated with the seawater is commonly used (e.g.

2 Schneider et al., 2014). Due to a relatively long response time, this method may, however, be

3 not fast enough to resolve steep horizontal pCO_2 gradients in the vicinities of river mouths. The

4 development of accurate and precise sensors for pCO_2, like optodes, could improve our

5 understanding of the CO_2 system in the transition area from the coast to the open sea.

6 Additionally, it would facilitate pCO_2 measurements in the discrete samples, which is highly

7 desired for investigations of the organic matter mineralization processes in the water column,

8 but difficult to obtain with common underway measurement techniques. The determination of

9 A_T by titration with an acid (HCl) allows a high accuracy (2 µmol kg^{-1}) for the ocean water.

10 This is difficult to achieve for Baltic Sea water because the detection of the endpoint of the A_T

11 titration is more difficult due to the influence of the organic acid-base constituents. The studies

12 by Ulfsbo et al. (2015) showed that fulvic and humic acids, substances widely spread in the

13 Baltic Sea, have relatively high concentration of acid-base constituents, which have pK_a values

14 close to the pK_a of carbonic acid and may thus impede the correct detection of the titration

15 endpoint. C_T measurements are less critical since reference materials exist and the analytical

16 procedure is relatively straightforward. However, development of high accuracy underway

17 methods for C_T (but also A_T) would improve the horizontal coverage of the data.

18 Interpretations of the acid-base system data requires appropriate parametrization of the acid-

19 base system related processes and chemical reactions. With regard to the Baltic Sea some

20 peculiarities of the composition of the acid-base system must be taken into account which are

21 neglectable in ocean waters. An example is the influence of DOM on the acid-base system. In

22 the oceans it is ignored due to the low DOM concentrations but in the Baltic Sea organic

23 alkalinity, A_{org}, becomes a noticeable component of A_T (Kuliński et al., 2014). The challenge

24 remains to include the contribution by DOM to the chemical A_T model. The approach suggested

25 by Kuliński et al. (2014) to use the so called bulk dissociation constant, K_{DOM}, is only a first

26 approximation, as K_{DOM} has no real thermodynamic meaning. It also does not allow for

27 distinguishing the influence of individual substances. Respective improvements would require,

28 however, also a progress in analytical methods as the characterization of the structure and

29 composition of DOM is still far from being satisfactorily (Nebbioso and Piccolo, 2013).

30 Problems arise also due to the ion anomalies observed in the Baltic Sea (Kremling 1970, 1972)

31 that are not taken into account in the A_T model. An example is boron, whose concentration is

32 usually approximated by the assumption of a constant boron/salinity ratio. However, the

33 function linking both these parameters does not account for river water as a source of boron.

Earth System
Dynamics
Discussions

1   Furthermore, common software for CO_2 system calculations omit also seawater constituents

2   that are generated at anoxic conditions. These are mainly the acid-base systems: H_2S-HS^--S^{2-}

3   and NH_4^+-NH_3 which require hence consideration in computational models. All these

4   shortcomings may cause uncertainties in any calculations of the CO_2 system including those in

5   biogeochemical models when A_T is used as a controlling variable. It is also recommended to

6   perform sensitivity studies in order to estimate the quantitative importance of potentially

7   missing or inadequate chemical characterization of A_T.

8   Furthermore, we promote the implementation of the acid-base system (or marine CO_2 system)

9   into biogeochemical models. This includes the simulations of the surface water CO_2 partial

10   pressure, pCO_2. The pCO_2 is an ideal validation variable because on the one hand it can easily

11   be measured with high spatiotemporal resolution (e.g. on Voluntary Observation Ships, VOS),

12   and on the other hand it reflects the biogeochemical transformations such as biomass

13   production. Hence, the agreement between simulated and measured pCO_2 data give an

14   indication for the quality of the biogeochemical process parameterization. Or, vice versa,

15   unsatisfactory agreement gives reason to rethink the description of the respective processes in

16   the model.

17   The latter aspect was in the focus of several model studies which initially failed to reproduce

18   the observed pCO_2 draw down during spring and summer (Fig. 5). This indicated that the

19   traditional parameterization of the biomass production that is based on the Redfield (1963)

20   C/N/P ratios and on nutrient concentrations at the start of the productive period, does not reflect

21   the reality. Omstedt et al. (2009) solved the problem by including a fractional nutrient release

22   into their model. This means that nutrients that have been used for production, are partly

23   released from the POM and reused for new production. In another study Kuznetsov et al. (2011)

24   introduced an additional cyanobacteria group and flexible C/N/P ratios into their model in order

25   to achieve approximate agreement between the simulated and measured pCO_2. A further study

26   by Gustafsson et al. (2014a) investigated the changes in the simulated CO_2 air-sea flux upon

27   including organic alkalinity and changes in external inputs of carbon, alkalinity and nutrients.

28   Modelling the CO_2 system was also used to simulate the vertical distribution of total CO_2 and

29   alkalinity in stagnant waters of the deep basins (Edman and Omstedt, 2013) and to assess the

30   importance of internal alkalinity generation (Gustafsson et al., 2014b). Finally, model

31   calculations were used to estimate future changes in the Baltic Sea CO2 system and in

32   particular in the development of the ocean acidification effect (Omstedt et al., 2012; Kuznetsov

33   and Neumann, 2013). Both simulations indicated that the increasing atmospheric CO_2 will

Earth System
Dynamics
Discussions

1   control mainly long-term changes in pH, of course, not taking into account the recently reported

2   current increase in alkalinity (see Chapter 3.3.2; Müller et al., 2016).

3

12

13 **References**

14 Bates, N. R., Astor, Y. M., Church, M. J., Currie, K., Dore, J. E., Gonzalez-Davila, M.,

15   Lorenzoni, L., Muller-Karger, F. E., Olafsson, J., and Santana-Casiano, J. M.: A time-

16   series view of changing surface ocean chemistry due to ocean uptake of anthropogenic

17   CO_2 and ocean acidification, Oceanography, 27, 126-141, 2014.

18 Beldowski, J., Loeffler, A., Schneider, B. and Joensuu, L.: Distribution and biogeochemical

19   control of total CO_2 and total alkalinity in the Baltic Sea, J. Mar. Syst., 81, 252–259,

20   2010.

21 Brenner, H., Braeckman, U., Le Guitton, M. and Meysman, F.J.R.: The impact of sedimentary

22   alkalinity release on the water column CO_2 system in the North Sea., Biogeosciences,

23   13, 841-863, 2016.

24 Brewer, P. G., and Goldman, J. C.: Alkalinity changes generated by phytoplankton growth,

25   Limnol. Oceanogr., 21, 108–117, 1976.

26 Buch, K.: Kolsyrejamvikten i Baltiska Havet., Fennia, 68, 5, 29–81, 1945.

27 Cai, W.J., Wang, Y.C. and Hodson, R.E.: Acid–base properties of dissolved organic matter in

28   the estuarine waters of Georgia, USA, Geochim. Cosmochim. Ac., 62, 473–483, 1998.

1   Clegg, S. L. and Whitfield, M.: Chemical model of seawater including dissolved ammonia and
2   the stoichiometric dissociation constant of ammonia in estuarine water and seawater
3   from -2 to 40°C, Geochem. Cosmochim. Ac., 59, 2403-2421, 1995.

4   Dickson, A. G., Sabine, C. L. and Christian, J. R.: Guide to best practices for ocean CO_2
5   measurements, PICES Special Publication 3, North Pacific Marine Science
6   Organization, Sidney, British Columbia, 2007.

7   Dickson, A.G.: An exact definition of total alkalinity and a procedure for the estimation of
8   alkalinity and total inorganic carbon from titration data, Deep Sea Res., Part A, 28,
9   1981.

10   Edman, M., and Omstedt, A.: Modeling the dissolved CO_2 system in the redox environment of
11   the Baltic Sea, Limnol. Oceanogr., 58, 2013.

12   Emerson, S. R. and Hedges, J. I. (Eds.): Chemical Oceanography and the Marine Carbon
13   Cycle, Cambridge University Press, Cambridge, 470, 2008.

14   Gustafsson, E., Deutsch, B., Gustafsson, B.G., Humborg, C. and Morth, C.M.: Carbon cycling
15   in the Baltic Sea - the fate of allochthonous organic carbon and its impact on air-sea
16   CO_2 exchange, J. Mar. Syst., 129, 289–302, 2014a.

17   Gustafsson, E., Wällstedt, T., Humborg, Ch., Mörth, C. M., and Gustafsson, B. G.: Glob.
18   Biogeochem. Cycles 28, 1358-1370, 2014b.

19   Hammer, K., Schneider, B., Kuliński, K. and Schulz-Bull, D.: Acid-base properties of Baltic
20   Sea dissolved organic matter, J. Mar. Syst., under review, 2017.

21   Hammer, K., Schneider, B., Kuliński, K. and Schulz-Bull, D.E.: Precision and accuracy of
22   spectrophotometric pH measurements at environmental conditions in the Baltic Sea,
23   Estuar. Coast. Shelf S., 146, 24-32, 2014.

24   HELCOM: Eutrophication in the Baltic Sea, Balt. Sea Environ. Proc. 115B, 2009.

25   Hernandez-Ayon, J. M., Zirino, A., Dickson, A. G., Camiro-Vargas, T. and Valenzuela-
26   Espinoza, E.: Estimating the contribution of organic bases from microalgae to the
27   titration alkalinity in coastal seawaters, Limnol. Oceanogr. Methods, 5, 225–232, 2007.

28   Hjalmarsson, S., Wesslander, K., Anderson, L. G., Omstedt, A., Perttila, M., and Mintrop, L.:
29   Distribution, long-term development and mass balance calculation of total alkalinity in
30   the Baltic Sea, Cont. Shelf Res., 28, 593–601, 2008.

Earth System
Dynamics
Discussions

1   Hoikkala, L., Kortelainen, P., Soinne, H. and Kuosa, H.: Dissolved organic matter in the Baltic
2   Sea, J. Mar. Syst., 142, 47–61, 2015.

3   Hunt, C. W., Salisbury, J. E., and Vandemark, D.: Contribution of non-carbonate anions to
4   total alkalinity and overestimation of pCO_2 in New England and New Brunswick rivers,
5   Biogeosciences, 8, 3069–3076, 2011.

6   Johansson, O. and Wedborg, M.: The Ammonia-Ammonium equilibrium in sea water at
7   temperatures between 5-25°C, J. Solution Chemistry, 9, 37-44, 1980.

8   Koeve W. and Oschlies, A.: Potential impact of DOM accumulation on fCO_2 and carbonate
9   ion computations in ocean acidification experiments, Biogeosciences, 9, 3787–3798,
10   2012.

11 Kremling, K.: Untersuchungen über die chemische Zusammensetzung des Meerwassers aus
12   der Ostsee II. Frühjahr 1967 – Frühjahr 1968. Kiel Meeresforsch, 26, 1-20, 1970.

13 Kremling, K.: Untersuchungen über die chemische Zusammensetzung des Meerwassers aus
14   der Ostsee III. Frühjahr 1969 – Herbst 1970. Kiel Meeresforsch, 27, 99-118, 1972.

15 Kuliński, K. and Pempkowiak, J.: The carbon budget of the Baltic Sea, Biogeosciences, 8,
16   3219-3230, 2011.

17 Kuliński, K., Hammer, K., Schneider, B. and Schulz-Bull, D.: Remineralization of terrestrial
18   dissolved organic carbon in the Baltic Sea, Mar. Chem., 181, 10-17, 2016.

19 Kuliński, K., Schneider, B., Hammer, K., Machulik, U. and Schulz-Bull, D.: The influence of
20   dissolved organic matter on the acid-base system of the Baltic Sea. J. Marine Syst., 132,
21   106-115, 2014.

22 Kuliński, K., She, J. and Pempkowiak, J.: Short and medium term dynamics of the carbon
23   exchange between the Baltic Sea and the North Sea, Cont. Shelf Res., 31, 15, 1611–
24   1619, 2011.

25 Kuznetsov, I. and Neumann T.: Simulation of carbon dynamics in the Baltic Sea with a 3D
26   model, . J. Marine Syst., 111–112, 167–174, 2013.

27 Lass, H.-U. and Matthäus, W.: General Oceanography of the Baltic Sea, in: State and Evolution
28   of the Baltic Sea, 1952-2005: Detailed 50-Year Survey of Meteorology and Climate,
29   Physics, Chemistry, Biology and Marine Environment, Feistel, R., Nausch, G. and
30   Wasmund, N., John Wiley & Sons, Inc., USA, 2008.

Earth System
Dynamics
Discussions

1   Le Quéré, C., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Peters, G. P.,
2   Manning, A. C., Boden, T. A., Tans, P. P., Houghton, R. A., Keeling, R. F., Alin, S.,
3   Andrews, O. D., Anthoni, P., Barbero, L., Bopp, L., Chevallier, F., Chini, L. P., Ciais,
4   P., Currie, K., Delire, Ch., Doney, S. C., Friedlingstein, P., Gkritzalis, T., Harris, I.,
5   Hauck, J., Haverd, V., Hoppema, M., Goldewijk, K. K., Jain, A. K., Kato, E.,
6   Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lombardozzi, D.,
7   Melton, J. R., Metzl, N., Millero, F., Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M.
8   S., Nakaoka, S., O'Brien, K., Olsen, A., Omar, A. M., Ono, T., Pierrot, D., Poulter, B.,
9   Rödenbeck, Ch., Salisbury, J., Schuster, U., Schwinger, J., Séférian, R., Skjelvan, I.,
10   Stocker, B. D., Sutton, A. J., Takahashi, T., Tian, H., Tilbrook, B., van der Laan-Luijkx,
11   I. T., van der Werf, G. R., Viovy, N., Walker, A. P., Wiltshire, A. J., Zaehle S.: Global
12   Carbon Budget 2016, Earth Syst. Sci. Data, 8, 605-649, 2016.

13   Lee, K., Kim, T.W., Byrne, R.H., Millero, F.J., Feely, R.A. and Liu, Y.M.: The universal ratio
14   of boron to chlorinity for the North Pacific and North Atlantic oceans, Geochim.
15   Cosmochim. Ac., 74, 1801–1811, 2010.

16   Lukawska-Matuszewska, K.: Contribution of non-carbonate inorganic and organic alkalinity
17   to total measured alkalinity in pore waters in marine sediments (Gulf of Gdansk, S-E
18   Baltic Sea), Mar. Chem., 186, 211-220, 2016.

19   Millero, F.J., Graham, T.B., Huang, F, Bustos-Serrano, H. and Pierrot, L.D.: Dissociation
20   constants of carbonic acid in seawater as a function of salinity and temperature, Mar.
21   Chem, 100, 1-2, 80-94, 2006.

22   Millero, F.J., Plese, T., Fernandez, M.: The dissociation of hydrogen sulfide in seawater (Note),
23   Limnol. Oceanogr., 33, 2, 269-274, 1988.

24   Millero, F.J.: Carbonate constants for estuarine waters, Mar. Freshwater Res., 61, 139–142,
25   2010.

26   MSFD, Directive 2008/56/EC of the European Parliament and of the Council (Marine Strategy
27   Framework Directive), 2008.

28   Müller, J.D., Schneider, B. and Rehder, G.: Long-term alkalinity trends in the Baltic Sea and
29   their implications for CO_2-induced acidification, Limnol. Oceanogr., 61, 1984-2002,
30   2016.

Earth System
Dynamics

Discussions

1   Nausch, G., Nehring, D. and Nagel K.: Nutrients Concentrations, Trends and Their Relation to
2   Eutrophication, in: State and Evolution of the Baltic Sea, 1952-2005: Detailed 50-Year
3   Survey of Meteorology and Climate, Physics, Chemistry, Biology, and Marine
4   Environment, Feistel, R., Nausch, G. and Wasmund, N., John Wiley & Sons, Inc., USA,
5   2008.

6   Nebbioso, A. and Piccolo, A.: Molecular characterization of dissolved organic matter (DOM):
7   a critical review, Anal. Bioanal. Chem, 405, 109–124, 2013.

8   Omstedt, A., Edman, M., Anderson, L. G. and Laudon H.: Factors influencing the acid–base
9   (pH) balance in the Baltic Sea: a sensitivity analysis, Tellus B 62, 280-295, 2010.

10   Omstedt, A., Edman, M., Claremar, B., Frodin, P., Gustafsson, E., Humborg, C., Hagg, H.,
11   Morth, M., Rutgersson, A., Schurgers, G., Smith, B.,Wallstedt T. and Yurova, A.:
12   Future changes in the Baltic Sea acid–base (pH) and oxygen balances, Tellus B 64,
13   19586, 2012.

14   Omstedt, A., Gustafsson, E. and Wesslander, K.: Modelling the uptake and release of carbon
15   dioxide in the Baltic Sea surface water, Cont. Shelf Res., 29, 870-885, 2009.

16   Orr, J. C., Epitalon, J.-M. and Gattuso, J.-P.: Comparison of ten packages that compute ocean
17   carbonate chemistry, Biogeosciences, 12, 1483–1510, 2015.

18   Redfield, A. C., Ketchum, B. H. and Richards, F. A.: The influence of organisms on the
19   composition of sea water, in: The Sea, Hill, M. N. (Ed.), Interscience, New York, USA,
20   26–77, 1963.

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

24   Roy, R.N., Roy, L.N., Vogel, K.M., Porter-Moore, C., Pearson, T., Good, C.E., Millero, F.J.
25   and Campbell, D.M.: The dissociation constants of carbonic acid in seawater at
26   salinities 5 to 45 and temperatures 0 to 45°C: Mar. Chem., 44, 2–4, 249–267, 1993.

27   Schneider, B., Eilola, K., Lukkari, K., Muller-Karulis, B. and Neumann T.: Environmental
28   Imapacts – Marine Biogeochemistry, in: BACC II Author Team, Second Assessment
29   of Climate Change for the Baltic Sea Basin, Springer, Heidelberg, 337-361, 2015.

Earth System
Dynamics
Discussions

1 Schneider, B., Gülzow, W., Sadkowiak, B. and Rehder, G.: Detecting sinks and sources of CO_2
2   and CH_4 by ferrybox-based measurements in the Baltic Sea: Three case studies, J.
3   Marine Syst., 140, 13-25, 2014.

4 Schneider, B.: The CO_2 system of the Baltic Sea : biogeochemical control and impact of
5   anthropogenic CO_2, in: Global change and Baltic coastal zones. Ed. by G. Schernewski,
6   J. Hofstede and T. Neumann. Dordrecht: Springer Science+Business Media (Coastal
7   research library): 33-49, 2011.

8 Schulz, H.D. and Zabel, M., Marine geochemistry, Springer-Verlag Berlin Heidelberg, 574,
9   2006.

10 Szymczycha, B., Maciejewska, A., Winogradow, A. and Pempkowiak, J.: Could submarine
11   groundwater discharge be a significant carbon source to the southern Baltic Sea?,
12   Oceanologia, 56, 2, 327-347, 2014.

13 Tyrrell, T., Schneider, B., Charalampopoulou, A. and Riebesel, U.: Coccolithophores and
14   calcite saturation state in the Baltic and Black Seas, Biogeosciences, 5, 485–494, 2008.

15 Ulfsbo, A., Hulth S. and Anderson, L.G.: pH and biogeochemical processes in the Gotland
16   Basin of the Baltic Sea, Mar. Chem., 127, 20-30, 2011.

17 Ulfsbo, A., Kuliński, K., Anderson, L.G. and Turner, D.R.: Modelling organic alkalinity in the
18   Baltic Sea using a Humic-Pitzer approach, Mar. Chem., 168: 18-26, 2015.

19 Uppström, L.R.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, Deep-
20   Sea Res., 21, 161–162, 1974.

21 Weiss, RF.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar.
22   Chem., 2, 203-215, 1974.