



Structure and functioning of the acid–base system in the Baltic Sea

Karol Kuliński¹, Bernd Schneider², Beata Szymczycha¹, and Marcin Stokowski¹

¹Institute of Oceanology, Polish Academy of Sciences, IO PAN,
ul. Powstańców Warszawy 55, 81-712 Sopot, Poland

²Leibniz Institute for Baltic Sea Research Warnemünde, IOW, Seestrasse 15, 18119 Rostock, Germany

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

Received: 6 April 2017 – Discussion started: 12 April 2017

Revised: 21 October 2017 – Accepted: 6 November 2017 – Published: 11 December 2017

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 a number of regionally specific anomalies. In this review article we collect and integrate existing knowledge of 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, make the acid–base system complex. In this study, we summarize the general knowledge of the marine acid–base system as well as 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 in total alkalinity, anomalies of borate alkalinity, and the acid–base effects of biomass production and mineralization. Finally, we identify research gaps and specify limitations concerning the Baltic Sea acid–base system.

1 Introduction

The acid–base system controlling 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, such as ocean acidification, calcium carbonate (CaCO_3) formation/dissolution and carbon dioxide (CO_2) exchange through the air–sea interface.

The steady increase in atmospheric CO_2 concentrations leads to enhanced dissolution of CO_2 in the ocean. Since

CO_2 dissolved in seawater forms 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. The EU Marine Strategy Framework Directive (MSFD, 2008) explicitly points out that the EU member states should place more attention on ocean acidification and emphasizes the necessity to include measurements of pH and of the CO_2 partial pressure ($p\text{CO}_2$) as descriptors for the environmental status of marine regions.

There is a general belief that the magnitude of ocean acidification can be sufficiently quantified from the atmospheric $p\text{CO}_2$ levels and the CO_2 exchange between seawater and the atmosphere (Zeebe, 2012; Riebesell et al., 2010; Caldeira and Wicket, 2003). This is generally true for oceanic waters. However, it is not the case for coastal seas because several other processes influence seawater pH such as CaCO_3 formation and/or dissolution, eutrophication or oligotrophication, total alkalinity (A_T) consumption and production, weathering, contribution by organic substances, and terrestrial inputs. The general structure and functioning of the acid–base system in seawater are relatively well identified; however, some aspects still show 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 Quére, 2016). The direction and magnitude of the CO_2 exchange through the air–sea interface depend largely on the $p\text{CO}_2$ difference between seawater and the atmosphere. The level of seawater $p\text{CO}_2$ is mainly controlled by the structure of the acid–base system, which 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 a very complex ecosystem. On the 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). A

considerable research effort was also made 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 diverse knowledge. Therefore, the goal of this review article is to collect and integrate the existing knowledge of 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 $p\text{CO}_2$, 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 $[\text{CO}_2^*]$ represents the sum of molecular dissolved CO_2 and undissociated carbonic acid (H_2CO_3):

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (1)$$

Measurements of C_T are usually based on the 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 1 kg of sample (Dickson, 1981):

$$\begin{aligned} A_T = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] \\ & + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] \\ & + [\text{HS}^-] + [\text{minor bases}] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] \\ & - [\text{H}_3\text{PO}_4] - [\text{minor acids}]. \end{aligned} \quad (2)$$

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 Andrew Dickson's laboratory, UC San Diego, USA (Dickson et al., 2007). pH measurements in seawater are usually calibrated against tris buffer. Its characteristics are 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 also takes into account 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 $p\text{CO}_2$ require the continuous flow of water, which makes this parameter difficult to measure in discrete samples.

All four variables interact 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 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 of limitations. To obtain high accuracy for the calculation of pH and $p\text{CO}_2$ 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 generally 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 4 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 ($22 \times 10^3 \text{ km}^3$). 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).

3.2 Dissociation constants in 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 , $p\text{CO}_2$ 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:

$$[\text{CO}_2^*] = k_0 \cdot f\text{CO}_2. \quad (3)$$

The solubility constant, k_0 , relates the concentration of CO_2^* in seawater to the CO_2 fugacity, $f\text{CO}_2$. In contrast to the CO_2 partial pressure, $p\text{CO}_2$, the fugacity accounts for the non-ideal behaviour of CO_2 at atmospheric conditions. It differs only slightly from the $p\text{CO}_2$ and in many cases can be replaced by the $p\text{CO}_2$. The solubility and thus k_0 decrease 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. Again using CO_2^* as a variable, the two dissociation equilibria are given by

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*], \quad (4)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]. \quad (5)$$

In these formulas the terms for the hydrogen ions are given in concentration units which include HSO_4^- ion concentration (Dickson, 1984).

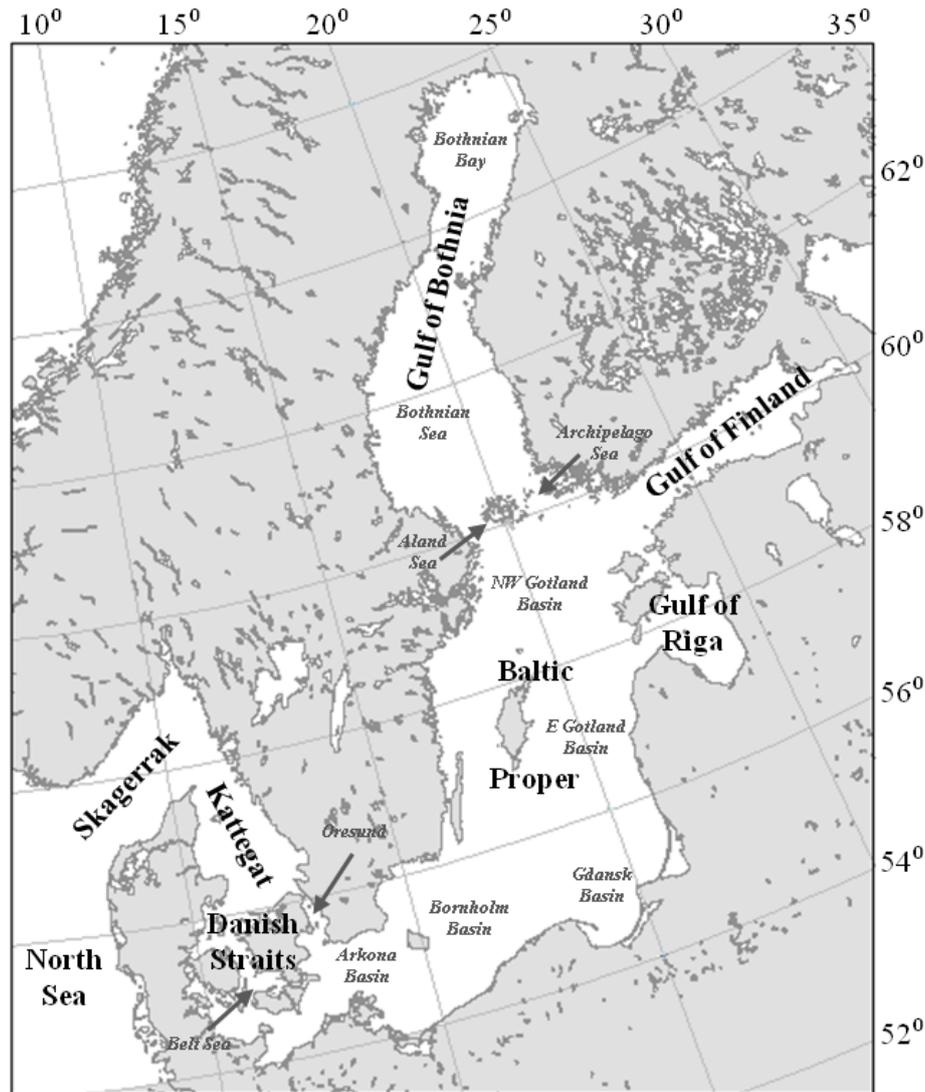


Figure 1. Map of the Baltic Sea showing its division into natural basins and sub-basins (modified after Kuliński and Pempkowiak, 2011).

Systematic studies concerning the dissociation constants of carbonic acid in seawater were already performed during the 20s and 30s 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 0. 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 “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. 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. This was the case 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 freshwater. 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 CO₂ research in brackish waters. The salinity and the temperature dependency of K_1 and K_2 are presented in Fig. 2a and b, 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):

$$\frac{K_1}{K_2} = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2^*] \cdot [\text{CO}_3^{2-}]} \quad (6)$$

Equation (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 of 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 $\text{p}K_1 - \text{p}K_2$, 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 that were available to Buch and his co-workers in the 20s and 30s of the last century.

When alkalinity is also used for the calculation of any variables of the CO₂ system, the contributions of non-CO₂ 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 sulfide anions are released during organic-matter mineralization at anoxic conditions (see Sect. 3.4.2). Both these constituents are strong proton acceptors forming mainly HS[−] and NH₄⁺. Since their concentrations may be on the order of several tens and up to a few hundred $\mu\text{mol L}^{-1}$ (Nausch et al., 2008), respectively, they have a strong effect on alkalinity and pH. Therefore, any calculations concerning the CO₂ system at anoxic conditions must account for the dissociation equilibria of H₂S–HS[−] (Millero et al., 1988) and NH₄⁺–NH₃ (Clegg and Whit-

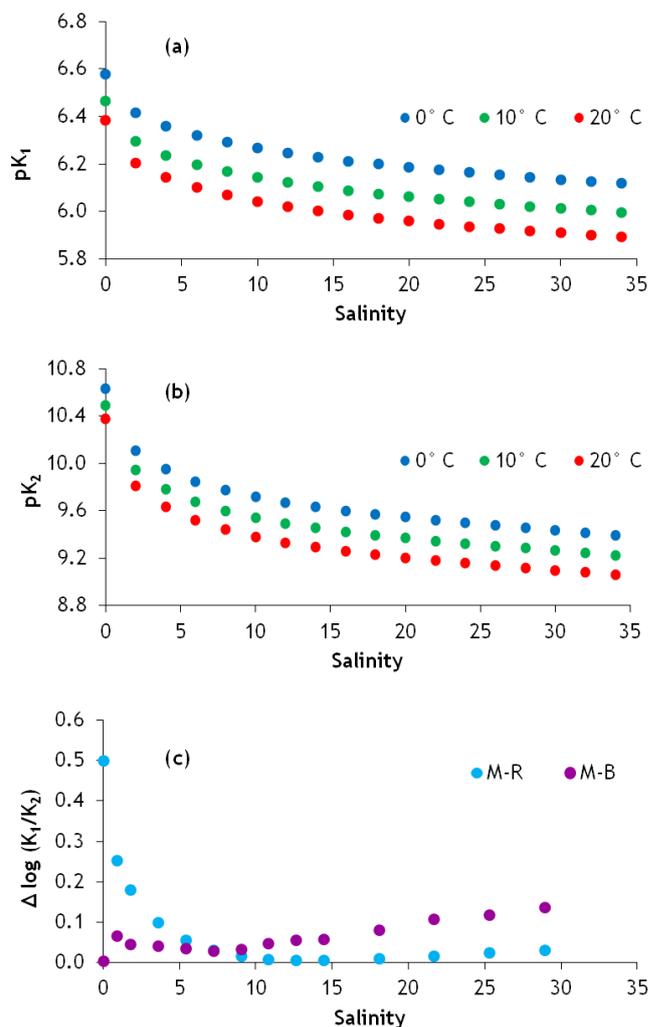


Figure 2. Dissociation constants (a) $\text{p}K_1$ and (b) $\text{p}K_2$ as a function of salinity calculated according to Millero (2010) for three different temperatures: 0, 10 and 20 °C; (c) differences in $\log(K_1 / K_2)$ between the dissociation constants obtained from Millero (2010) and Roy et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

field, 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. 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

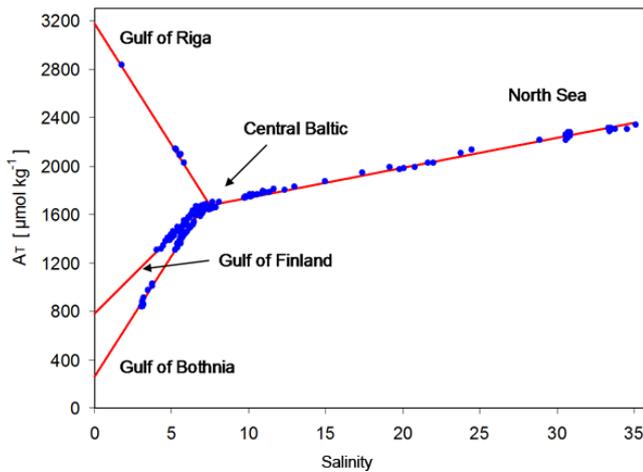


Figure 3. Different A_T vs. S regimes observed in the Baltic Sea (modified after Beldowski et al., 2010).

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 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 Gdąnsk Bay (Kuliński 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 alkalinity in the surface water of the Baltic Proper (salinity around 7) of about 1600–1700 $\mu\text{mol kg}^{-1}$.

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 in 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 the 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 some limitations still 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 ($5400 \mu\text{mol kg}^{-1}$ on average) in SGD seeping to the southern Baltic along the Polish coast. Although there might be

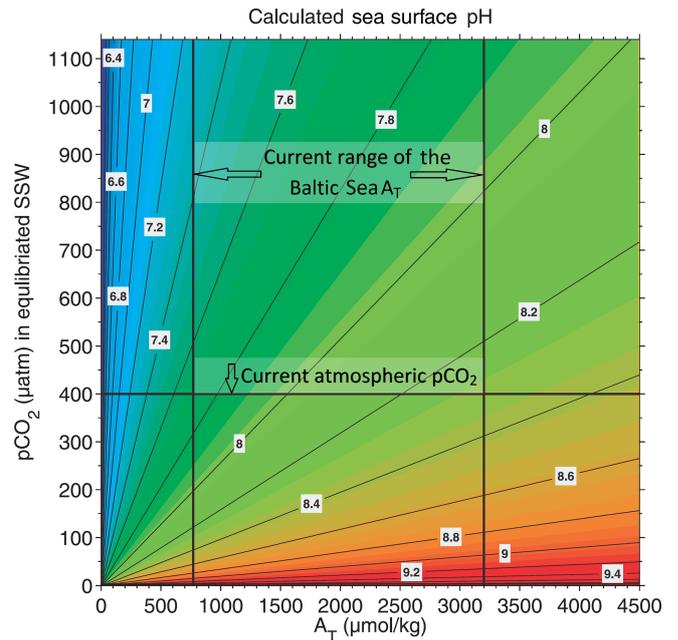


Figure 4. Distribution of pH_{tot} as a function of A_T and pCO_2 at a salinity of 7.5 and temperature of 0°C (modified after Omstedt et al., 2010). The A_T range represents findings by Beldowski et al. (2010). SSW is an abbreviation for surface seawater.

some contribution from CO_2 to this high C_T , it is very likely that SGD can, at least locally, play 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. $400 \mu\text{atm}$ 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: $2170\text{--}2460 \mu\text{mol kg}^{-1}$ (Riebesell et al., 2010). The reason for that is the high spatial variability in A_T in the surface Baltic Sea waters, from low A_T (below $1000 \mu\text{mol kg}^{-1}$) observed in the Bothnian Bay to the A_T -rich (more than $3000 \mu\text{mol kg}^{-1}$) 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 .

3.3.2 Long-term A_T changes – consequences for ocean acidification

Long-term high-resolution pH measurements at the BATS station (Bermuda Atlantic Time Series) in the subtropical North Atlantic have shown that ocean acidification occurs at a rate that is thermodynamically consistent with the increase

in the atmospheric CO_2 (Bates et al., 2014). There is therefore 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 timescales 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, which 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 ($7.0 \mu\text{mol kg}^{-1} \text{yr}^{-1}$), followed by $3.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ 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 $480 \mu\text{mol CL}^{-1}$, while those in the surface water (top 100 m) of the Atlantic Ocean are much lower and range between 50 and $80 \mu\text{mol CL}^{-1}$ (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 an 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 ($\text{p}K_a > 4.5$), their dissociation releases the equivalent of organic acids, which are 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 $\text{p}K_a$ 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 the case of the carbonate alkalinity, this means a reduction in CO_3^{2-} and an increase in H_2CO_3 and thus 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 $25\text{--}35 \mu\text{mol kg}^{-1}$ 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 $50 \mu\text{mol kg}^{-1}$ 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 0 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 use 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 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 (Edman and Omstedt, 2013; Kuznetsov and Neumann, 2013; Omstedt et al., 2009, 2012) 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} parameterization in biogeochemical models were 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, 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 a 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 DOC, a commonly measured parameter. According to their studies, slightly corrected by Ulfssbo et al. (2015), pK_{DOM} in the Baltic Sea amounts to 7.34. They also estimated experimentally that 12 % of DOC acts as a carrier for acidic functional groups in the Baltic Sea DOM. The model studies by Ulfssbo et al. (2015) showed that this experimentally derived share fits the share estimated from the hypothetical structure of the fulvic acids. They also suggested 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 that organic matter (as represented by the fulvic acids) also contains some functional groups having pK_a already below 4.5. According to the definition (Dickson, 1981), they should be considered strong acids. In experimental studies Hammer et al. (2017) also found 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 the titration of 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 usually focus 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 the form of weak boric acid, $\text{B}(\text{OH})_3$, and the anion, $\text{B}(\text{OH})_4^-$. The high pK_a (8.60 at salinity 35 and temperature 25 °C) means that at a 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 ($S = 1.80655 \cdot \text{Cl}$). First measurements of boron concentrations in the Baltic Sea were reported by Buch (1945), who found that $B_T [\text{mg kg}^{-1}] = 0.133 \cdot S$. This finding was confirmed recently by Lee et al. (2010) for 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 $B_T [\text{mg kg}^{-1}] = 0.128 \cdot S$. 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 the experimentally determined 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 of pH changes referring to equilibrium with the atmosphere, it may be meaningful to consider the pH at a given alkalinity as a function of $p\text{CO}_2$ because the atmospheric 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 pH and $p\text{CO}_2$. 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 $p\text{CO}_2$ in the upper water layers and causes a $p\text{CO}_2$ 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 $p\text{CO}_2$ disequilibrium with the atmosphere throughout the year. In spring and summer, seawater is undersaturated with respect to atmospheric CO_2 with two characteristic $p\text{CO}_2$ minima and two pH maxima (Fig. 5), which reflect the spring bloom and the midsummer nitrogen fixation period. In autumn and winter the Baltic Sea surface water $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 raises the pH during biomass production (Brewer and Goldman, 1976). This assimilation also decreases the $p\text{CO}_2$ and therefore reinforces the drop in $p\text{CO}_2$ 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 may also consume CO_3^{2-} ions in the calcification processes. This causes an A_T reduction and in consequence a $p\text{CO}_2$ increase and also a 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.

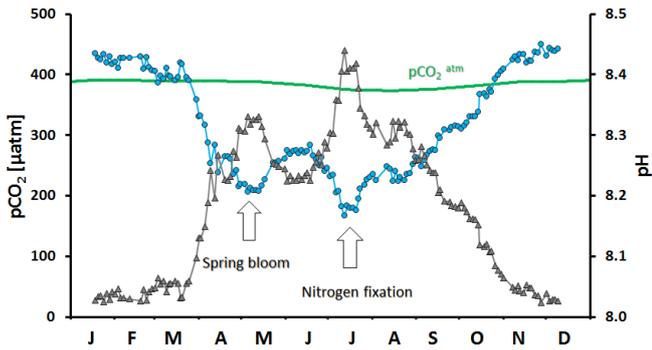


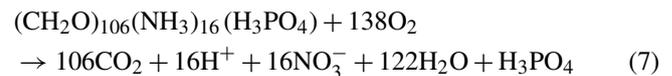
Figure 5. Typical seasonality of $p\text{CO}_2$ in surface water (blue line) and the atmosphere (green line) in the Eastern Gotland Sea modified after Schneider (2011) and presented together with pH calculated from the shown $p\text{CO}_2$ data and the mean A_T value.

3.4.2 Remineralization

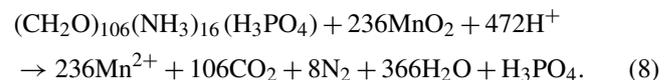
In contrast to biomass production, CO_2 is released during the remineralization processes and causes an increase in C_T . Consequently, this leads to a pH decrease and $p\text{CO}_2$ increase. Some fraction of organic matter produced in situ undergoes remineralization in the upper water layers. Particulate organic matter (POM) may be mineralized directly or via the prior release of 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 340 Gmol of organic carbon from land annually. 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 it 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 that the latter result likely refers to the mixture of terrestrial and marine DOC.

Whereas the A_T in surface water is mainly controlled by the mixing of different water masses, the deep-water A_T distribution additionally depends 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, 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 in pH or $p\text{CO}_2$ during the mineralization process without knowledge of the oxidant. In the presence of oxygen, mineralization takes place according to Eq. (7),

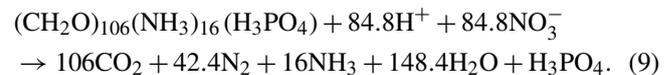
which reverses the bulk photosynthesis reaction. However, in sediments and in deep-water layers of some basins of the central Baltic, where longer periods (years) of stagnation occur, oxygen may be entirely depleted. Organic matter can then be mineralized in a certain thermodynamically controlled sequence 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 an oxidant (Eq. 9). After nitrate is consumed, the mineralization process may be continued by iron (III) oxide (Eq. 10) before sulfate oxidizes the organic matter and generates hydrogen sulfide (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 sulfate concentration has approached 0, is confined to deeper sediment layers only. Except for oxic mineralization, all other processes are connected with a simultaneous A_T increase caused either by the release of strong bases (S^{2-}) or by the 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 $p\text{CO}_2$ 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 a level of about 7 (Hammer et al., 2017).



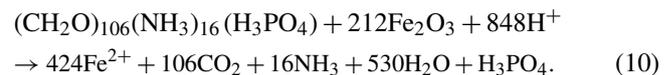
Oxic mineralization, $\Delta A_T = -16$.



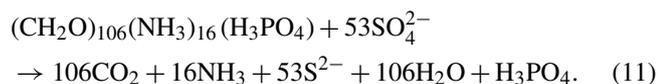
Manganese reduction, $\Delta A_T = +472$.



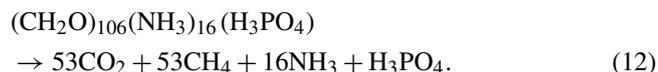
Denitrification, $\Delta A_T = +100.8$.



Iron reduction, $\Delta A_T = +864$.



Sulfate reduction, $\Delta A_T = +122$.



Methanogenesis, $\Delta A_T = +16$.

Generally, benthic processes linked to early diagenesis of organic matter can be an important source of A_T to the water column (Brenner et al., 2016). This corresponds to the findings by Gustafsson et al. (2014b), who, in a model study, found 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 sulfide or ammonia only influences the acid–base system locally. Upon contact with oxic water, most of the A_T -generating processes – except for denitrification – are reversed and do not constitute a permanent A_T source. Some minor increase in 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 future research

General knowledge of the marine acid–base system has been gained mainly from 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), which 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 limitations but also define challenges for marine biogeochemists working in these regions.

In this context the Baltic Sea can be considered a 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 entangled. The challenges are related to analytical methods, interpretation of the data and parameterization of the acid–base-system-related processes for use in numerical models. Great effort has recently been made to adapt spectrophotometric pH measurements based on m-cresol purple to Baltic Sea conditions. This was done by Hammer et al. (2014) and was recently improved within the framework of the BONUS PINBAL project. Further progress can be expected if pH reference materials for brackish water 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 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 ($\pm 2 \mu\text{mol kg}^{-1}$) 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 commonly found in the Baltic Sea, have relatively high concentrations of acid–base constituents, which have $\text{p}K_a$ values close to the $\text{p}K_a$ 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, the 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 an 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 A_{org} becomes a noticeable component of A_T (Kuliński et al., 2014). The challenge remains to include the contribution by DOM in 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 substantial progress in analytical techniques, as the characterization of the structure and composition of DOM is still far from being satisfactory (Nebbio and Piccolo, 2013). Problems also arise 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 reactions: $\text{H}_2\text{S}-\text{HS}^- - \text{S}^{2-}$ and $\text{NH}_4^+ - \text{NH}_3$, 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 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, $p\text{CO}_2$. The $p\text{CO}_2$ is an ideal validation variable because on the one hand, it can easily be measured with high spatiotemporal resolution (e.g. on Voluntary Observing Ships, VOSs) and, on the other hand, it reflects the biogeochemical transformations such as biomass production. Hence, agreement between simulated and measured $p\text{CO}_2$ data gives an indication 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 the focus of several model studies which initially failed to reproduce the observed $p\text{CO}_2$ 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 did not reflect the reality. Omstedt et al. (2009) solved the problem by including a fractional nutrient release into their model. This 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 $p\text{CO}_2$. A further study by Gustafsson et al. (2014a) investigated the changes in the simulated CO_2 air–sea flux 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; Kuznetsov 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 Chap. 3.3.2; Müller et al., 2016).

5 Summary and conclusions

With our review we have proposed that the Baltic Sea acid–base system cannot be 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 connected catchment 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 the intense production/mineralization of organic matter or to the immediate effect of riverine input of acidic substances. 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), but 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.

Internal biogeochemical processes such as organic-matter production or mineralization also have 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 reduces the alkalinity, but the abundance of calcifying plankton in the Baltic Sea is restricted to the high-salinity Kattegat region. Although the effect of organic-matter production on alkalinity is minor, it is the major control for the seasonal modulation of the acid–base properties such as pH and $p\text{CO}_2$.

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 mineralization of organic matter generates large amounts of alkalinity by the formation of sulfide ions and the release of ammonia. This reduces the increase in the $p\text{CO}_2$ 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 do not affect the acid–base system of the Baltic Sea as a whole, they do influence the deep-water redox chemistry, which is partly controlled by the pH. On the other hand, the existence of a pelagic redoxcline has other further-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., 2014b).

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 CO₂ system based on measurements of alkalinity together with another variable. 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 obtain this information. But in view of our limited knowledge concerning the composition of the dissolved organic matter, it is currently impossible 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 other coastal seas. Another important limitation, especially for the biogeochemical modelling, is also an insufficient knowledge of the short- and long-term development of alkalinity loads from land caused by processes occurring in the catchment.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. The study was completed thanks to funding provided by the National Science Centre, Poland, grant nos. 2015/19/B/ST10/02120 and 2014/13/D/ST10/01885. Significant financial support was provided also by BONUS and the Polish National Centre for Research and Development – sponsors of BONUS PINBAL project (grant no. BONUS-INNO-2012-03/2014). The contribution of B. Schneider to this study was supported by the Foundation for Polish Science within the Alexander von Humboldt Polish Honorary Research Scholarship. This study comprises a part of the Baltic Earth – Earth System Science for the Baltic Sea Region. We thank both anonymous reviewers for insightful and constructive comments and suggestions.

Edited by: Marcus Reckermann

Reviewed by: two anonymous referees

References

- Bates, N. R., Astor, Y. M., Church, M. J., Currie, K., Dore, J. E., Gonzalez-Davila, M., Lorenzoni, L., Muller-Karger, F. E., Olafsson, J., and Santana-Casiano, J. M.: A time-series view of changing surface ocean chemistry due to ocean uptake of anthropogenic CO₂ and ocean acidification, *Oceanography*, 27, 126–141, 2014.
- Beldowski, J., Loeffler, A., Schneider, B., and Joensuu, L.: Distribution and biogeochemical control of total CO₂ and total alkalinity in the Baltic Sea, *J. Marine Syst.*, 81, 252–259, 2010.
- Brenner, H., Braeckman, U., Le Guitton, M., and Meysman, F. J. R.: The impact of sedimentary alkalinity release on the water column CO₂ system in the North Sea, *Biogeosciences*, 13, 841–863, <https://doi.org/10.5194/bg-13-841-2016>, 2016.
- Brewer, P. G. and Goldman, J. C.: Alkalinity changes generated by phytoplankton growth, *Limnol. Oceanogr.*, 21, 108–117, 1976.
- Buch, K.: Kolsyrejamvikten i Baltiska Havet, *Fennia*, 68, 5, 29–81, 1945.
- Cai, W. J., Wang, Y. C., and Hodson, R. E.: Acid–base properties of dissolved organic matter in the estuarine waters of Georgia, USA, *Geochim. Cosmochim. Ac.*, 62, 473–483, 1998.
- Caldeira, K. and Wickett, M. E.: Anthropogenic carbon and ocean pH, *Nature*, 425, 365–365, 2003.
- Carlson, C. A., Hansell, D. A., Nelson, N. B., Siegel, D. A., Smetie, W. M., Khaliwala, S., Meyers, M. M., and Halewood, E.: Dissolved organic carbon export and subsequent remineralization in the mesopelagic and bathypelagic realms of the North Atlantic basin, *Deep-Sea Res. II*, 57, 1433–1445, 2010.
- Clegg, S. L. and Whitfield, M.: Chemical model of seawater including dissolved ammonia and the stoichiometric dissociation constant of ammonia in estuarine water and seawater from –2 to 40 °C, *Geochem. Cosmochim. Ac.*, 59, 2403–2421, 1995.
- DeValls, T. A. and Dickson, A. G.: The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol (‘tris’) in synthetic sea water, *Deep-Sea Res. Part I*, 45, 1541–1554, 1998.
- Dickson, A. G.: An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data, *Deep-Sea Res. I*, 28, 609–623, 1981.
- Dickson, A. G.: pH scales and proton-transfer reactions in saline media such as sea water, *Geochim. Cosmochim. Ac.*, 48, 2299–2308, 1984.
- Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO₂ measurements, PICES Special Publication 3, North Pacific Marine Science Organization, Sidney, British Columbia, 191 pp., 2007.
- Edman, M. and Omstedt, A.: Modeling the dissolved CO₂ system in the redox environment of the Baltic Sea, *Limnol. Oceanogr.*, 58, 74–92, <https://doi.org/10.4319/lo.2013.58.1.0074>, 2013.
- Emerson, S. R. and Hedges, J. I. (Eds.): *Chemical Oceanography and the Marine Carbon Cycle*, Cambridge University Press, Cambridge, 470 pp., 2008.
- Gustafsson, E., Deutsch, B., Gustafsson, B. G., Humborg, C., and Mörth, C. M.: Carbon cycling in the Baltic Sea – the fate of allochthonous organic carbon and its impact on air–sea CO₂ exchange, *J. Marine Syst.*, 129, 289–302, 2014a.
- Gustafsson, E., Wällstedt, T., Humborg, Ch., Mörth, C. M., and Gustafsson, B. G.: External total alkalinity loads versus internal generation: The influence of nonriverine alkalinity sources in the Baltic Sea, *Global Biogeochem. Cy.*, 28, 1358–1370, 2014b.
- Gustafsson, E., Omstedt, A., and Gustafsson, B. G.: The air–water CO₂ exchange of a coastal sea–A sensitivity study on factors that influence the absorption and outgassing of CO₂ in the Baltic Sea, *J. Geophys. Res.-Ocean.*, 120, 5342–5357, 2015.
- Hammer, K., Schneider, B., Kuliński, K., and Schulz-Bull, D. E.: Precision and accuracy of spectrophotometric pH measurements

- at environmental conditions in the Baltic Sea, *Estuar. Coast. Shelf S.*, 146, 24–32, 2014.
- Hammer, K., Schneider, B., Kuliński, K., and Schulz-Bull, D.: Acid-base properties of Baltic Sea dissolved organic matter, *J. Marine Syst.*, 173, 114–121, 2017.
- HELCOM: Eutrophication in the Baltic Sea, *Balt. Sea Environ. Proc.*, 115 pp., 2009.
- Hernandez-Ayon, J. M., Zirino, A., Dickson, A. G., Camiro-Vargas, T., and Valenzuela-Espinoza, E.: Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters, *Limnol. Oceanogr.-Meth.*, 5, 225–232, 2007.
- Hjalmarsson, S., Wesslander, K., Anderson, L. G., Omstedt, A., Perttilä, M., and Mintrop, L.: Distribution, long-term development and mass balance calculation of total alkalinity in the Baltic Sea, *Cont. Shelf Res.*, 28, 593–601, 2008.
- Hoikkala, L., Kortelainen, P., Soenne, H., and Kuosa, H.: Dissolved organic matter in the Baltic Sea, *J. Marine Syst.*, 142, 47–61, 2015.
- Hunt, C. W., Salisbury, J. E., and Vandemark, D.: Contribution of non-carbonate anions to total alkalinity and overestimation of pCO₂ in New England and New Brunswick rivers, *Biogeosciences*, 8, 3069–3076, <https://doi.org/10.5194/bg-8-3069-2011>, 2011.
- Johansson, O. and Wedborg, M.: The Ammonia-Ammonium equilibrium in sea water at temperatures between 5–25 °C, *J. Solution Chem.*, 9, 37–44, 1980.
- Koeve, W. and Oschlies, A.: Potential impact of DOM accumulation on fCO₂ and carbonate ion computations in ocean acidification experiments, *Biogeosciences*, 9, 3787–3798, <https://doi.org/10.5194/bg-9-3787-2012>, 2012.
- Kremling, K.: Untersuchungen über die chemische Zusammensetzung des Meerwassers aus der Ostsee II, Frühjahr 1967–Frühjahr 1968, *Kiel Meeresforsch.*, 26, 1–20, 1970.
- Kremling, K.: Untersuchungen über die chemische Zusammensetzung des Meerwassers aus der Ostsee III, Frühjahr 1969–Herbst 1970, *Kiel Meeresforsch.*, 27, 99–118, 1972.
- Krumins, V., Gehlen, M., Arndt, S., Van Cappellen, P., and Regnier, P.: Dissolved inorganic carbon and alkalinity fluxes from coastal marine sediments: model estimates for different shelf environments and sensitivity to global change, *Biogeosciences*, 10, 371–398, <https://doi.org/10.5194/bg-10-371-2013>, 2013.
- Kuliński, K. and Pempkowiak, J.: The carbon budget of the Baltic Sea, *Biogeosciences*, 8, 3219–3230, <https://doi.org/10.5194/bg-8-3219-2011>, 2011.
- Kuliński, K., She, J., and Pempkowiak, J.: Short and medium term dynamics of the carbon exchange between the Baltic Sea and the North Sea, *Cont. Shelf Res.*, 31, 1611–1619, 2011.
- Kuliński, K., Schneider, B., Hammer, K., Machulik, U., and Schulz-Bull, D.: The influence of dissolved organic matter on the acid-base system of the Baltic Sea, *J. Marine Syst.*, 132, 106–115, 2014.
- Kuliński, K., Hammer, K., Schneider, B., and Schulz-Bull, D.: Remineralization of terrestrial dissolved organic carbon in the Baltic Sea, *Mar. Chem.*, 181, 10–17, 2016.
- Kuznetsov, I., Neumann, T., Schneider, B., and Yakushev, E.: Processes regulating pCO₂ in the surface waters of the central eastern Gotland Sea: A model study, *Oceanologia*, 53, 745–770, 2011.
- Kuznetsov, I. and Neumann T.: Simulation of carbon dynamics in the Baltic Sea with a 3D model, *J. Marine Syst.*, 111–112, 167–174, 2013.
- Lass, H.-U. and Matthäus, W.: General Oceanography of the Baltic Sea, in: *State and Evolution of the Baltic Sea, 1952–2005: Detailed 50-Year Survey of Meteorology and Climate, Physics, Chemistry, Biology and Marine Environment*, edited by: Feistel, R., Nausch, G., and Wasmund, N., John Wiley & Sons, Inc., USA, 5–43, 2008.
- Le Quééré, C., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Peters, G. P., Manning, A. C., Boden, T. A., Tans, P. P., Houghton, R. A., Keeling, R. F., Alin, S., Andrews, O. D., Anthoni, P., Barbero, L., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P., Currie, K., Delire, Ch., Doney, S. C., Friedlingstein, P., Gkritzalis, T., Harris, I., Hauck, J., Haverd, V., Hoppema, M., Goldewijk, K. K., Jain, A. K., Kato, E., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lombardozi, D., Melton, J. R., Metzl, N., Millero, F., Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S., O’Brien, K., Olsen, A., Omar, A. M., Ono, T., Pierrot, D., Poulter, B., Rödenbeck, Ch., Salisbury, J., Schuster, U., Schwinger, J., Séférian, R., Skjelvan, I., Stocker, B. D., Sutton, A. J., Takahashi, T., Tian, H., Tilbrook, B., van der Laan-Luijckx, I. T., van der Werf, G. R., Viovy, N., Walker, A. P., Wiltshire, A. J., and Zaehle S.: Global Carbon Budget 2016, *Earth Syst. Sci. Data*, 8, 605–649, <https://doi.org/10.5194/essd-8-605-2016>, 2016.
- Lee, K., Kim, T. W., Byrne, R. H., Millero, F. J., Feely, R. A., and Liu, Y. M.: The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans, *Geochim. Cosmochim. Ac.*, 74, 1801–1811, 2010.
- Lukawska-Matuszewska, K.: Contribution of non-carbonate inorganic and organic alkalinity to total measured alkalinity in pore waters in marine sediments (Gulf of Gdansk, S-E Baltic Sea), *Mar. Chem.*, 186, 211–220, 2016.
- Millero, F. J.: Carbonate constants for estuarine waters, *Mar. Freshwater Res.*, 61, 139–142, 2010.
- Millero, F. J., Plese, T., and Fernandez, M.: The dissociation of hydrogen sulfide in seawater (Note), *Limnol. Oceanogr.*, 33, 269–274, 1988.
- Millero, F. J., Graham, T. B., Huang, F., Bustos-Serrano, H., and Pierrot, L. D.: Dissociation constants of carbonic acid in seawater as a function of salinity and temperature, *Mar. Chem.*, 100, 80–94, 2006.
- Mosley, L. M., Husheer, S. L. G., and Hunter, K. A.: Spectrophotometric pH measurement in estuaries using thymol blue and cresol purple, *Mar. Chem.*, 91, 175–186, 2004.
- MSFD: Directive 2008/56/EC of the European Parliament and of the Council (Marine Strategy Framework Directive), EUR-Lex – 32008L0056 – EN, available at: <http://data.europa.eu/eli/dir/2008/56/oj>, 2008.
- Müller, J. D., Schneider, B., and Rehder, G.: Long-term alkalinity trends in the Baltic Sea and their implications for CO₂-induced acidification, *Limnol. Oceanogr.*, 61, 1984–2002, 2016.
- Nausch, G., Nehring, D., and Nagel, K.: Nutrients Concentrations, Trends and Their Relation to Eutrophication, in: *State and Evolution of the Baltic Sea, 1952–2005: Detailed 50-Year Survey of Meteorology and Climate, Physics, Chemistry, Biology, and Marine Environment*, edited by: Feistel, R., Nausch, G., and Wasmund, N., John Wiley & Sons, Inc., USA, 2008.

- Nebbioso, A. and Piccolo, A.: Molecular characterization of dissolved organic matter (DOM): a critical review, *Anal. Bioanal. Chem.*, 405, 109–124, 2013.
- Omstedt, A., Gustafsson, E., and Wesslander, K.: Modelling the uptake and release of carbon dioxide in the Baltic Sea surface water, *Cont. Shelf Res.*, 29, 870–885, 2009.
- Omstedt, A., Edman, M., Anderson, L. G., and Laudon H.: Factors influencing the acid–base (pH) balance in the Baltic Sea: a sensitivity analysis, *Tellus B*, 62, 280–295, 2010.
- Omstedt, A., Edman, M., Claremar, B., Frodin, P., Gustafsson, E., Humborg, C., Hagg, H., Morth, M., Rutgersson, A., Schurgers, G., Smith, B., Wallstedt T., and Yurova, A.: Future changes in the Baltic Sea acid–base (pH) and oxygen balances, *Tellus B*, 64, 19586, <https://doi.org/10.3402/tellusb.v64i0.19586>, 2012.
- Omstedt, A., Edman, M., Claremar, B., Rutgersson, A., Modelling the contributions to marine acidification from deposited SO_x , NO_x , and NH_x in the Baltic Sea: Past and present situations, *Cont. Shelf Res.*, 111, 234–249, 2015.
- Orr, J. C., Epitalon, J.-M., and Gattuso, J.-P.: Comparison of ten packages that compute ocean carbonate chemistry, *Biogeosciences*, 12, 1483–1510, <https://doi.org/10.5194/bg-12-1483-2015>, 2015.
- Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of sea water, in: *The Sea*, edited by: Hill, M. N., Interscience, New York, USA, 26–77, 1963.
- Reed, D. C., Gustafsson, B. G., and Slomp, C. P.: Shelf-to-basin iron shuttling enhances vivianite formation in deep Baltic Sea sediments, *Earth Planet. Sc. Lett.*, 434, 241–251, 2016.
- Riebesell, U., Fabry, V. J., Hansson, L., and Gattuso J.-P.: Guide to best practices for ocean acidification research and data reporting, 260 pp., Luxembourg, Publications Office of the European Union, 2010.
- Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., and Campbell, D. M.: The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45 °C, *Mar. Chem.*, 44, 249–267, 1993.
- Schneider, B.: The CO_2 system of the Baltic Sea : biogeochemical control and impact of anthropogenic CO_2 , in: *Global change and Baltic coastal zones*, edited by Schernewski, G., Hofstede, J., and Neumann, T., Dordrecht: Springer Science+Business Media (Coastal research library), 33–49, 2011.
- Schneider, B., Gülzow, W., Sadkowiak, B., and Rehder, G.: Detecting sinks and sources of CO_2 and CH_4 by ferrybox-based measurements in the Baltic Sea: Three case studies, *J. Marine Syst.*, 140, 13–25, 2014.
- Schneider, B., Eilola, K., Lukkari, K., Muller-Karulis, B., and Neumann, T.: Environmental Impacts – Marine Biogeochemistry, in: *BACC II Author Team, Second Assessment of Climate Change for the Baltic Sea Basin*, Springer, Heidelberg, 337–361, 2015.
- Schulz, H. D. and Zabel, M.: *Marine geochemistry*, Springer-Verlag Berlin Heidelberg, 574 pp., 2006.
- Szymczycha, B., Maciejewska, A., Winogradow, A., and Pempkowiak, J.: Could submarine groundwater discharge be a significant carbon source to the southern Baltic Sea?, *Oceanologia*, 56, 327–347, 2014.
- Thomas, H., Schiettecatte, L.-S., Suykens, K., Koné, Y. J. M., Shadwick, E. H., Prowe, A. E. F., Bozec, Y., de Baar, H. J. W., and Borges, A. V.: Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments, *Biogeosciences*, 6, 267–274, <https://doi.org/10.5194/bg-6-267-2009>, 2009.
- Tyrrell, T., Schneider, B., Charalampopoulou, A., and Riebesell, U.: Coccolithophores and calcite saturation state in the Baltic and Black Seas, *Biogeosciences*, 5, 485–494, <https://doi.org/10.5194/bg-5-485-2008>, 2008.
- Ulfso, A., Hulth S., and Anderson, L. G.: pH and biogeochemical processes in the Gotland Basin of the Baltic Sea, *Mar. Chem.*, 127, 20–30, 2011.
- Ulfso, A., Kuliński, K., Anderson, L. G., and Turner, D. R.: Modelling organic alkalinity in the Baltic Sea using a Humic-Pitzer approach, *Mar. Chem.*, 168, 18–26, 2015.
- Uppström, L. R.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, *Deep-Sea Res.*, 21, 161–162, 1974.
- Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, 2, 203–215, 1974.
- Winsor, P., Rodhe, J., and Omstedt, A.: Baltic Sea ocean climate: an analysis of 100 yr of hydrographic data with focus on the freshwater budget, *Clim. Res.*, 18, 5–15, 2001.
- Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Körtzinger, A., and Dickson, A. G.: Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, *Mar. Chem.*, 106, 287–300, 2007.
- Zeebe, R. E.: History of Seawater Carbonate Chemistry, Atmospheric CO_2 , and Ocean Acidification, *Annu. Rev. Earth Pl. Sc.*, 40, 141–165, 2012.