Long-term alkalinity trends in the Baltic Sea and their implications for CO₂-induced acidification

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Abstract
Anthropogenic CO₂ emissions currently decrease open ocean pH, but on multi-millennial time scales intensified continental weathering is expected to contribute to increasing oceanic alkalinity (AT) and thus mitigate the acidification signal. The Baltic Sea is an ideal study site for such AT dynamics, due to its direct link to terrestrial processes, short water residence time and long history of AT measurements dating back to the early 20th century. We compiled an extensive AT data set that revealed the highest data quality and coverage for the past two decades. Within that period, surface water AT levels increased throughout the Baltic Sea. The rates of change were highest in the low-saline, northern areas and decreased gradually toward constant levels in the North Sea. The AT increase observed in the Central Baltic Sea (+3.4 µmol kg⁻¹ yr⁻¹) and the Gulf of Bothnia (+7 µmol kg⁻¹ yr⁻¹) has compensated CO₂-induced acidification by almost 50% and 100%, respectively. Further, the AT trends enhanced the CO₂ storage capacity and stabilized the CaCO₃ saturation state of the Baltic Sea over the past two decades. We discuss the attribution of the AT trends to potential changes in precipitation patterns, continental weathering driven by acidic rain and increasing atmospheric CO₂, agricultural liming and internal AT sources.

Introduction
Alkalinity: global relevance and characteristics
Total alkalinity (AT) is a measure of the acid-binding capacity of seawater. As one of four measurable parameters of the marine CO₂ system, AT has gained increasing attention within the field of climate change research. The importance of AT for the carbon cycle can be exemplified by its control over the CO₂ uptake and the pH of seawater. Currently, the oceans absorb around ~30% of the anthropogenic CO₂ released into the atmosphere (Khatiwala et al. 2013; Le Quéré et al. 2015), mainly due to equilibration between the atmosphere and the surface ocean mixed layer. The penetration of anthropogenic CO₂ into the ocean interior is controlled by the ocean circulation and today the ongoing process can be observed at locations where deep water is formed, e.g. in the high latitudes of the North Atlantic (Lee et al. 2003). When the fossil fuel derived CO₂ will invade the entire ocean interior on millennial time scales, the share of the oceanic uptake will increase to around 80% (Archer and Brovkin 2008). The oceanic uptake of CO₂ is beneficial, because it counteracts the rising atmospheric CO₂ levels and thus mitigates global warming. However, it comes at the expense of decreasing seawater pH. This process, termed ocean acidification (Doney et al. 2009), is expected to have global and potentially detrimental impacts on marine ecosystems (Hofmann et al. 2010; Kroeker et al. 2010). When CO₂ dissolves in water, carbonic acid is formed and protons are released. The alkalinity of seawater determines the share of these protons that are neutralized and thereby controls the CO₂ uptake and the degree of acidification. For a given increase in atmospheric pCO₂, more anthropogenic CO₂ can be stored in seawater with higher AT. Although more CO₂ could be taken up by high-AT seawater, the degree of acidification would be smaller than at lower AT. Knowledge about spatio-temporal AT dynamics is thus crucial for a comprehensive understanding of the global carbon cycle and the impact of anthropogenic CO₂ emissions on the marine CO₂ system.

The exact definition of AT, as the excess of proton acceptors over proton donors (Dickson et al. 2007), is expressed by:
\[ A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{Si(OH)}_4]^- + [\text{NH}_4^+] + [\text{HS}^-] - [\text{H}^+] - [\text{HF}] \quad (1) \]

where \([\text{H}^+]_0\) is the free concentration of hydrogen ions. This definition implies that \(A_T\) is a conservative quantity with respect to changes in temperature and pressure, although the share of the various alkalinity components can vary. As a conservative quantity, \(A_T\) behaves exactly like salinity (S) when two water parcels are mixed (Wolf-Gladrow et al. 2007). This is not the case for non-conservative parameters of the marine CO2 system, like pCO2 and pH, which do not necessarily obey linear mixing relationships. Further, \(A_T\) is not affected by the release or dissolution of CO2, because the \(A_T\) loss caused by the release of protons (H+) from the dissociation of carbonic acid (H2CO3) is balanced by the gain from produced bicarbonate (HCO3-) and carbonate (CO32-) ions. Among the components that contribute to \(A_T\) according to Eq. 1, the major share can be attributed to HCO3- and CO32- that originate from the \(A_T\)-neutral dissolution of CO2, but from riverine input of continentally weathered carbonate and silicate minerals. On oceanic scales this input is currently balanced by CaCO3 formation, sedimentation and burial as ultimate sinks (Sarmiento and Gruber 2006).

**Zooming in from oceanic to coastal systems**

The open ocean surface \(A_T\) is surprisingly stable, which reflects the long water residence time of \(\sim 10^5\) yr (Sundquist 1991; Sarmiento and Gruber 2006). Most of the variation in surface alkalinity can be attributed to precipitation and evaporation patterns (Millero et al. 1998; Jiang et al. 2014; Fry et al. 2015). Because \(A_T\) and salinity are affected similarly by these processes, the salinity normalized alkalinity (\(nA_T = A_T \times 35/S\)) shows remarkably little spatial variability in the subtropical gyres of the major ocean basins, e.g., 2291 \(\pm 4\) \(\mu\)mol kg\(^{-1}\) (mean \(\pm\) SD) between 30 °S and 30 °N in the Atlantic (Millero et al. 1998; Friis et al. 2003). Likewise, the surface \(nA_T\) in the Northern Atlantic did not exhibit significant temporal changes over the past three decades (Bates et al. 2012). Based on this constant \(A_T\) background in the open ocean, acidification trends around 0.002 pH units yr\(^{-1}\) can be predicted from future pCO2 scenarios “without major uncertainties” (Doney et al. 2009). These predictions match well with the currently observed pH trends at seven globally distributed time-series stations (Bates et al. 2014).

However, on longer time scales the oceanic alkalinity is expected to increase. On millennial time scales (10\(^3\) yr) anthropogenic CO2 will acidify the ocean interior and thus lift the carbonate lysocline. The resulting dissolution of carbonate sediments is expected to increase oceanic \(A_T\). On geological time scales (10\(^3\)–10\(^6\) yr) increased terrestrial weathering rates may further contribute to rising oceanic \(A_T\) levels (Lenton and Britton 2006). This postulated alkalinity gain is expected to increase the share of anthropogenic CO2 stored in the ocean to 90% (Archer and Brovkin 2008). However, it may not dampen ocean acidification occurring on shorter, centennial timescales.

In contrast to the subtropical open ocean, \(A_T\)–S relations in marginal seas are much more variable because processes like riverine alkalinity input, CaCO3 formation and denitrification (Cai et al. 2010; Gustafsson et al. 2014; Jiang et al. 2014) superimpose on evaporation and precipitation effects. The dominant effect of riverine \(A_T\) input in marginal seas is typically reflected in linear \(A_T\)–S relationships:

\[ A_T = A_{T,0} + a \times S \quad (2) \]

where \(A_{T,0}\) corresponds to the river end-member alkalinity at \(S = 0\), and \(a\) is the slope representing the alkalinity change per salinity unit. The direct link of coastal alkalinitities to the riverine \(A_T\) input (which is in turn often impacted by anthropogenic activities) and the shorter residence time of alkalinity in coastal environments (which is basically equal to the water residence time) suggest that temporal changes in \(A_T\)–S relationships may occur on timescales similar to that of CO2-induced ocean acidification. A more comprehensive understanding of alkalinity dynamics in such systems is thus essential to extent climate change research into the coastal zone.

**Focus on the Baltic Sea**

The semi-enclosed Baltic Sea can be considered as one of the world’s largest estuaries. The brackish water system is an ideal study site for the investigation of alkalinity dynamics, due to the long history of biogeochemical studies including decades of alkalinity and salinity monitoring, a diverse, but well-defined bedrock structure in different parts of its large drainage basin and a variety of existing biogeochemical models. For this study we divide the Baltic Sea into five sub-areas, which accounts for the patterns of the surface \(A_T\)–S distribution (Beldowski et al. 2010). The geographical borders of the five subareas, which are the narrow Belt Sea and Kattegat region (Kat), Central Baltic Sea (Cen), Gulf of Bothnia (Bot), Gulf of Finland (Fin) and Gulf of Riga (Rig), are displayed in Fig. 1. The hydrography of the Baltic Sea is characterized by inflowing, high saline water from the North Sea that enters the deep basins of the Baltic Sea and generates a permanent halocline. The outflow of low-saline surface waters, caused by river-runoff and positive net precipitation, slightly exceeds the inflow. The mean salinity of the Baltic Sea shows decadal, large-scale variations of up to 1 salinity unit, but no long-term trend was found during the past century (Winsor et al. 2001, 2003). The surface salinity is controlled by the mixing of oceanic and river water and increases from a mean surface salinity around 3 in the northern-most part of the Gulf of Bothnia to around 10 in the south-western part of the Central Baltic (Fig. 1). A strong gradient to the oceanic salinity of \(\sim 35\) exists in the Kattegat region. With exception of the Gulf of Riga, the
surface $A_T$ decreases with decreasing salinity (Fig. 2). However, different $A_T$–$S$ signatures can be found in the surface waters of the various subareas, because the drainage basin composition – dominated by limestone in the south and granite in the northern parts – controls the $A_T$–$S$ levels in the river water. Linear $A_T$–$S$ regimes exist in the three gulfs (Bot, Fin and Rig) and the Kattegat region (Fig. 2a), whereas the Central Baltic Sea is the “mixing chamber” of waters from the other areas and consequently shows no strictly linear $A_T$–$S$ relation (Beldowski et al. 2010). During stagnation periods, $A_T$ increases temporarily when anoxic conditions prevail below the halocline (Edman and Omstedt 2013). In anoxic bottom waters sulfate ($SO_4^{2-}$) is used as electron acceptor for the oxidation of organic material. This reaction produces sulfide ($S^{2-}$) that contributes two moles of $A_T$ per mole of sulfate oxidized (Eq. 1), independent on the subsequent protonation of $S^{2-}$. However, under oxic conditions in the surface water, $S^{2-}$ is reoxidized to $SO_4^{2-}$ and the $A_T$ increase is reversed. In addition to this reversible $A_T$ contribution, recent modelling studies suggest that other significant internal $A_T$ sources (e.g., denitrification) may exist in the Baltic Sea (Edman and Omstedt 2013; Gustafsson et al. 2014). Further, it should be noted that planktonic calcifiers, which constitute the most important alkalinity sink in the oceanic environment, do not exist in the Baltic Sea (Tyrrell et al. 2008) except in the Kattegat area.

Due to its generally lower alkalinity the Baltic Sea is believed to be especially vulnerable to CO$_2$-induced acidification. Indeed, for the current atmospheric pCO$_2$ increase ($\sim 2$ µatm yr$^{-1}$) a slightly lower mean pH trend of $-0.0019$ yr$^{-1}$ can be expected for the open ocean ($S = 35$, $T = 10^\circ$C, $A_T = 2300$ µmol kg$^{-1}$) compared to $-0.0021$ yr$^{-1}$ in the Central Baltic Sea ($S = 7$, $T = 10^\circ$C, $A_T = 1650$ µmol kg$^{-1}$). However, the direct link to riverine $A_T$ input (Hjalmarssson et al. 2008) and the short water residence time of around 20 yr (Helcom 1993) suggest that in the Baltic Sea significant $A_T$ changes may occur on timescales similar to that of anthropogenic atmospheric pCO$_2$ perturbations (10–100 yr). This implies that a reliable acidification estimate cannot solely be based on the atmospheric pCO$_2$ evolution. Previous studies indeed suggested that the alkalinity in the eastern Gotland Sea increased by around 100 µmol kg$^{-1}$ (~6%) from 1930 to 2010 (Schneider et al. 2015). Extensive $A_T$ measurements were performed in the Baltic Sea region with investigations dating back to the early 20th century (Buch 1945; Hjalmarssson et al. 2008). Nevertheless, a comprehensive analysis of the $A_T$ evolution in the Baltic Sea has not yet been performed. More detailed knowledge about past $A_T$ changes in Baltic Sea is essential, e.g., to assess the anthropogenic, CO$_2$-based acidification potential (Melzner et al. 2012), to validate modelling approaches of alkalinity dynamics (Kuznetsov and Neumann 2013; Gustafsson et al. 2014) and to obtain more reliable estimates for the Baltic carbon budget (Kulinski and Pempkowiak 2011; Gustafsson et al. 2015).

This work thus aims at:

- Detecting temporal $A_T$ trends reflected in changes of the $A_T$–$S$ relationship
- Quantifying the implications for CO$_2$-induced acidification
- Attributing the detected $A_T$ trends to biogeochemical drivers

### Material and methods

The data handling, quality control, statistical analysis, and data visualization described in the following were performed with the statistical computing language R Version 3.1.1 (R Core Team 2014). The CO$_2$ system calculations were performed with the seacarb package (Lavigne et al. 2011), using the carbonate constants for estuarine waters (Millero 2010), $K_W$ from Dickson and Riley (1979) and $K_S$ from Dickson (1990).

### Data compilation

To compile the most comprehensive data set of $A_T$ observations from the Baltic Sea, we combined data from the following sources:
Canibal data set (Hjalmarsson et al. 2008 and references therein)

SMHI monitoring data (extracted from SHARK data base: http://produkter.smhi.se/pshark/datamap_nationell.php?language=s)

Baltic-C project (BALTEx Phase II (BONUS+), available at: https://ecds.se/)

FMI monitoring data (provided by M. Perttila pers. comm.)

The data set was compiled in April 2015. Identical data points appearing in more than one of the data bases were removed prior to analysis. The analysis was restricted to water depths < 20 m to avoid temporary AT contributions from sulfide (S\textsuperscript{2-}) formed in stagnant bottom waters. The analysed data set comprises 31436 single observations. The spatiotemporal coverage of the data is presented in Figs. 1, 2b.

Quality control

The applied quality control focuses on the homogeneity of the AT measurements as well as the accuracy and precision of the available data.

The homogeneity of the measurement method is a critical aspect, because the data used for our trend analysis originate from different sources and time periods. The oldest observations date back to the beginning of the 20th century when for the first time intense theoretical and experimental work including comprehensive field studies concerning the marine CO\textsubscript{2} system was performed (Buch 1945). A review of the analytical methods for the determination of alkalinity – termed commonly “excess base” at that time – was given by Gripenberg (1936). For the back titration method that became the standard procedure for many decades, Gripenberg (1936) reported a precision of only a few \( \mu \text{mol kg}^{-1} \). However, a systematic bias may have been associated with the choice of the indicator for the detection of the titration end-point and could amount up to 10 \( \mu \text{mol kg}^{-1} \) according to the data presented by Gripenberg (1936). The alkalinity data from the Swedish Monitoring Programme, which constitute the bulk of the more recent data used in our study, were based on the back titration method until 1995 and after that based on the direct titration. No significant bias was caused by this change in method, which was demonstrated for an extensive number of samples measured in parallel (M. Krysell pers. comm.). In combination with the use of certified carbon reference material (CRM, Dickson et al. 2007) the back titration facilitates an overall range of bias of \( \pm 5 \ \mu \text{mol kg}^{-1} \) (Dickson et al. 2007) and is currently state of the art. It was also the basis for the data collected within the Baltic-C project.

In addition to available information about the analytical accuracy and precision for the alkalinity determination, one may use the characteristics of AT–S relationships to identify data that are obviously biased by analytical shortcomings. The precision of AT observations can be estimated from the residuals when performing linear regression analysis for the AT–S relation (Fig. 2a) in the subareas Kat, Bot, Fin and Rig (Fig. 1). Observations with low precision can be excluded, when the residual exceeds a predefined threshold. This analysis was performed separately for data from each cruise within the CANIBAL data set, which contributes the most questionable historic data. Accordingly, Swedish scientists reported unidentified sources of error for the observation period 1975–1995 (K. Wesslander and M. Krysell pers. comm.). However, apparently low precision can also reflect increased natural variability of the investigated parameter. By largely removing AT observations from the critical 1975–1995 period we risked to discard important information and thus decided to analyse the critical time period.
frames separately, comprehensively report the observed variability and interpret the respective findings with great care.

In contrast to the precision control described above, it is not possible to retrospectively test the accuracy of \( A_T \) observations. Since CRMs were introduced for monitoring purposes around 1995, an accuracy of better than 5 \( \mu \text{mol kg}^{-1} \) can be assumed (Dickson et al. 2007; Hjalmarsson et al. 2008). With respect to historic observations from before 1995, somewhat larger uncertainties are to be expected. However, even when assuming an inaccuracy twice as large as the current level, the detected trends are almost an order of magnitude larger than the potential bias.

**Alkalinity trend analysis**

The analysis of oceanic \( A_T \) trends is typically based on alkalinitis normalized to a salinity of 35 (\( nA_T = A_T \times 35/S \)) to account for local evaporation, precipitation and circulation patterns (Millero et al. 1998). Friis et al. (2003) highlighted that this approach has its limitations already in oceanic environments influenced by riverine input of alkalinity or the dissolution of biogenic carbonates. For a comprehensive analysis of \( A_T \) trends in estuarine systems, which receive significant amounts of \( A_T \) from freshwater end-members and thus cover a large range of variable \( A_T-S \) conditions, the classical alkalinity normalization is by no means adequate.

Taking the complex \( A_T-S \) distribution of the Baltic Sea into account, two types of subareas had to be investigated differently: (1) The Central Baltic Sea, which – as a mixing chamber for waters from the adjacent gulfs and the North Sea – reveals no distinct \( A_T-S \) relation and (2) the other subareas (Kat, Bot, Fin, Rig), which feature a linear \( A_T-S \) relationship (Fig. 2a).

**Central Baltic Sea: no defined \( A_T-S \) relationship**

A simple regression analysis of \( A_T \) trends at a given station in Central Baltic Sea is not meaningful, because changes in circulation patterns could alter \( A_T \). To identify potential \( A_T \) changes driven by biogeochemical processes, it is thus more informative to analyze \( A_T \) trends at specific salinity levels. Therefore, all observation were grouped into salinity intervals of 0.2 (range: 6.5–7.7). The interval width was chosen as narrow as necessary to avoid significant salinity dependence of \( A_T \) within the groups, but as wide as possible to increase the number of observations within each interval. The deviations (\( dA_T \)) of the individual values from the mean \( A_T \) were computed separately for each salinity interval. The \( dA_T \) values from the various salinity intervals were pooled and plotted as a function of time (Fig. 3). Based on the pooled \( dA_T \) values temporal trends were investigated by linear regression analysis. For the trend analysis the whole observation period was divided into four distinct periods. This division into up to four periods reduced the mean squared error (MSE), whereas a larger number of distinct periods did not further reduce the MSE significantly. The exact breakpoint between two adjacent time periods was determined with an iterative procedure (Crawley 2007) that we applied to identify the breakpoints resulting in the lowest MSE. The iterative procedure was repetitively applied to all breakpoints until no change in breakpoint position occurred. The three breakpoints 1980, 1990, and 1995 were identified with this iterative procedure.

**Subareas with linear \( A_T-S \) relationship**

For subareas with linear \( A_T-S \) relationships (Kat, Bot, Fin) a three dimensional (3d) statistical model was applied. The 3d model includes the dependency of \( A_T \) on salinity (\( S \)), time (\( t \)) and an interaction term of both parameters (\( S \times t \)), that accounts for the change of the \( A_T-S \)-slope with time, but can also be interpreted as the dependency of the temporal \( A_T \) trend on salinity. The applied linear 3d model is:

\[
A_T(S, t) = A_T(S_0, t_0) + \left( \frac{\Delta A_T}{\Delta S} \right)_{t_0} \times (S-S_0) + \left( \frac{\Delta A_T}{\Delta t} \right)_{S_0} \times (t-t_0) + \Delta \left( \frac{\Delta A_T}{\Delta S} \right)_{S_0} \times (S-S_0) \times (t-t_0)
\]

where \( t_0 \) and \( S_0 \) are the assigned reference year and salinity, respectively. The fitted coefficients and their interpretation are summarized in Table 1.

The 3d models were applied only to the time period 1995–2014, reflecting the usage of CRMs in the monitoring programs, the last breakpoint found in the Central Baltic Sea and a high spatio-temporal data coverage. Accordingly, the beginning of the observation period \( t_0 \) was set to 1995. The reference salinity \( S_0 \) was set to 7, allowing a direct comparison of the coefficient \( \Delta (A_T/\Delta S)_{S_0} \) to the slope found in the Central Baltic Sea (Table 2). It should be noted that the values assigned to \( S_0 \) and \( t_0 \) do change the specific coefficients obtained from the model, but have no impact on the general

| Coefficient | Unit | Interpretation |
|-------------|------|----------------|
| \( A_T(S_0, t_0) \) | \( \mu \text{mol kg}^{-1} \) | \( A_T \) intercept, (at the beginning of the observation period and reference salinity) |
| \( \frac{\Delta A_T}{\Delta S} \) | \( \mu \text{mol kg}^{-1} \) | Slope \( A_T \sim \text{salinity} \) (at the beginning of the observation period \( t_0 \)) |
| \( \frac{\Delta A_T}{\Delta t} \) | \( \mu \text{mol kg}^{-1} \text{yr}^{-1} \) | Slope \( A_T \sim \text{time} \) (at the reference salinity \( S_0 \)) |
| \( \Delta \left( \frac{\Delta A_T}{\Delta S} \right) \) | \( \mu \text{mol kg}^{-1} \text{yr}^{-1} \) | Interaction term: (change of slope \( A_T \sim \text{salinity} \), if time increases by 1 yr, or change of slope \( A_T \sim \text{time} \), if salinity increases by one unit) |
outcome of the model, i.e., the predicted $A_T$ at any given $S$ and $t$. The fitted 3d models and residuals are displayed in Figs. 4, 5, respectively.

To test the outcome of the 3d models described above, a more simplistic and less universal trend analysis was performed for the same time period after 1995. Therefore, linear regression models ($A_T = f(t)$) were applied for salinity intervals of 1 unit separately for each subarea. The slopes derived from these 2d linear regression models are compared to the slope obtained from the 3d models at the same salinity and subarea (Fig. 7a, Supporting Information Figs. S2, S3).

Due to insufficient spatio-temporal data records from before 1995 the 3d model could not be applied. The available historic data for the regions Bot, Fin, and Kat had thus to be presented according to the same principle as applied in the Central Baltic Sea: For area-specific salinity intervals we computed the deviations from mean $A_T$. In contrast to the Central Baltic Sea we did not pool the computed deviations thereafter, because different rates of change were expected at differing salinity intervals. We thus display the deviations as boxplots grouped by salinity intervals and decades for the subareas Kat, Bot, Fin and Rig (Fig. 6).

**Calculation of acidification trends**

The annual acidification trend caused by increasing atmospheric $\text{CO}_2$ was computed from $\text{pCO}_2$ and $A_T$ for the time period 1995–2014. The acidification estimates are based on a $\text{pCO}_2$ trend of $+2 \ \mu\text{atm yr}^{-1}$ (IPCC 2013). Calculations were performed for an increase from $\text{pCO}_2,0 = 380 \ \mu\text{atm}$ to $\text{pCO}_2,1 = 382 \ \mu\text{atm}$, reflecting the annual increase in the northern-hemisphere $\text{pCO}_2$ roughly in the middle of the investigated period. Two $A_T$ scenarios were analysed:

1. Alkalinity was assumed to be constant. For this scenario the mean $A_T$ ($mAT_1$) of the observation period was computed for each salinity interval. Based on this $mAT$, the pH trend was computed according to:

$$dpH_{(A_T=\text{constant})} = pH(mAT, pCO_2,1) - pH(mAT, pCO_2,0)$$

2. The alkalinity trend ($\Delta A_T/\Delta t$) was taken into account and the pH trend was computed as:

$$dpH_{(A_T=\text{variable})} = pH \left( mAT + \frac{\Delta A_T}{\Delta t} \times \text{yr} \right), pCO_2,1) - pH(mAT, pCO_2,0)$$

The alkalinity trend for the second scenario was derived from the 3d models for the Kattegat region and the Gulf of Bothnia, and from the 2d model for the Central Baltic Sea (Table 2). The estimated pH trends for a constant and an increasing $A_T$ background are displayed in Fig. 7b.

**Results**

Within this chapter we first present $A_T$ trends for the time period 1995–2014 (Figs. 3, 4), for which we found the smallest mean residual ($\sim 20 \ \mu\text{mol kg}^{-1}$, Table 2) and a homogeneous spatial and temporal data coverage (Fig. 5). Further, we present $A_T$ changes before 1995 (Figs. 3, 6). Data from that period revealed much higher variability (mean residual $\sim 50 \ \mu\text{mol kg}^{-1}$, Table 2) and the spatio-temporal data coverage is more fragmentary compared to the recent two decades. Results from before 1995 should thus be interpreted with greater care. We therefore focus the following estimation of $\text{CO}_2$-induced acidification trends on the time period after 1995 (Fig. 7b). The chapter concludes with an evaluation of the applied models and uncertainties associated to our findings.

**Time period 1995–2014**

In the Central Baltic Sea we found an increase of the alkalinity deviations ($dA_T$) by $+70 \ \mu\text{mol kg}^{-1}$ for the time period 1995–2014, corresponding to a rate of $+3.4 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$ (Fig. 3; Table 2). The deviations of the $dA_T$ values from the applied linear model are evenly distributed over time (Fig. 5) and the mean residual is below $20 \ \mu\text{mol kg}^{-1}$ (Table 1).

In the Kattegat region at salinity 15, $A_T$ increased from 1812 to 1880 $\mu\text{mol kg}^{-1}$ over the time period 1995–2014. This corresponds to a trend of $+3.4 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$ (Fig. 4; Table 2) and matches the $A_T$ increase observed in the Central Baltic Sea at salinities around 7. The positive $A_T$ trend continuously decreases toward the high saline waters of the North Sea and levels off at salinity 30. At salinities higher 30, we found a minor decrease of $A_T$ over time (Fig. 4), which is smaller than the mean residual of the observed $A_T$ values from the fitted 3d model ($16 \ \mu\text{mol kg}^{-1}$, Table 2). The observations in the Kattegat region are evenly distributed over the salinity range from 15 to 35. Fewer observations cover the salinity range below 15, reflecting the steep salinity gradient and the small number of monitoring stations in the Belt Sea. Residuals are evenly distributed over time (Fig. 5).

In the Gulf of Bothnia we found an $A_T$ increase from 730 to 870 $\mu\text{mol kg}^{-1}$ at salinity 3 ($+7.4 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$), which is slightly higher than the increase from 1170 to 1290 $\mu\text{mol kg}^{-1}$ ($+6.2 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$) observed at salinity 5 (Fig. 4; Table 2). Most of the observations available from the Gulf of Bothnia fall within the two salinity intervals 2.5–3.5 and 4.5–6 (Fig. 4), indicating the prevailing surface salinity in the northern Bothnian Bay and the southern Bothnian Sea, respectively (Winsor et al. 2001, 2003). However, the $A_T$ trend is similar for both predominant salinity levels and should thus also hold true for the narrow transition zone.

In the Gulf of Finland, most of the available data are restricted to the salinity range 4–6.5 (Fig. 4) and only in 2001 extensive investigations covered lower salinities down to 2. The temporal $A_T$ changes in the Gulf of Finland outside the salinity range 4–6.5 thus remain speculative. However, at
salinity we found an $A_T$ increase from 1340 to 1440 \( \mu \text{mol kg}^{-1} \) (+5.6 \( \mu \text{mol kg}^{-1} \text{yr}^{-1} \)).

In the Gulf of Riga, the data coverage is not extensive enough for a reasonable application of the statistical 3d model. However, for the salinity range 5–6 and the limited time period 2000–2011, linear regression of $A_T$ as function of time indicates a rate of change around 1.8 \( \mu \text{mol kg}^{-1} \text{yr}^{-1} \) (Supporting Information Fig. S1).

Time period before 1995

In the Central Baltic Sea, we found that the increasing alkalinity trend observed over the past two decades, may have persisted for the entire past century. The alkalinity deviations increase by about 200 \( \mu \text{mol kg}^{-1} \) from early 1900 to the current levels, corresponding to an overall rate of change of about +2 \( \mu \text{mol kg}^{-1} \text{yr}^{-1} \) (Fig. 3). However, this overall trend observed in the Central Baltic Sea should be interpreted with caution.

Table 2. Summary of the statistical parameters obtained from the application of the 2d and 3d models to the Central Baltic Sea and subareas with linear $A_T$–$S$ relations (Kat, Bot, Fin), respectively.

| Area | Model | Time period | $A_T(S, t)$ | $\frac{\Delta A_T}{\Delta S}$ | $\frac{\Delta A_T}{\Delta t}$ | $\Delta \left( \frac{\Delta A_T}{\Delta S} \right)$ | $R^2$ | Mean residual | No of observations |
|------|-------|-------------|-------------|-------------------------------|-------------------------------|-------------------------------------|------|---------------|-------------------|
| Cen  | $dA_T = f(t)$ | 1990–1995 | - | - | - | - | - | - | - |
|     |       | 1995–2014 | - | - | 3.4 | - | 0.33 | 20 | 4080 |
| Kat  | $A_T = f(S)$ | 1995–2014 | 1610 | 220.9 | 5.1 | -0.6 | 0.98 | 24 | 738 |
| Bot  | $A_T = f(S, t)$ | 1995–2014 | 1662 | 163.0 | 1.7 | -1.9 | 0.87 | 34 | 476 |
| Fin  | $A_T = f(S, t)$ | 1990–1980 | - | - | 0.7 | - | 0.02 | 44 | 3876 |
|     |       | 1980–1990 | - | - | -5.2 | - | 0.04 | 51 | 2591 |
|     |       | 1990–1995 | - | - | 38.4 | - | 0.61 | 27 | 1713 |

Fig. 3. Temporal alkalinity trends in the Central Baltic Sea from 1900 to 2015. Displayed are deviations ($dA_T$) of observed $A_T$ from mean $A_T$. Linear regression models (red line + 95% confidence interval (red area)) were fitted separately within the four time frames indicated by the vertical dashed lines. For the coefficients of the regression analysis please refer to Table 2.
care, because the spread of the observations from before 1995 is much larger (mean residual > 40 μmol kg\(^{-1}\)) than for the last two decades (mean residual < 20 μmol kg\(^{-1}\), Table 1). Despite the large scatter of the earlier observations, we detected a break in the overall increasing \(A_T\) trend: \(A_T\) anomalies seem to have decreased (−5 μmol kg\(^{-1}\) yr\(^{-1}\)) from around 1980–1990, and recovered more rapidly (+38 μmol kg\(^{-1}\) yr\(^{-1}\)) thereafter from 1990 to 1995 (Table 2).

In the Kattegat and the Gulf of Finland, the majority of \(A_T\) observations before 1935 are around 50–100 μmol kg\(^{-1}\) below the long-term average (Fig. 6). \(A_T\) levels similar to the long-term mean were first observed in the 1940 decade and around 1970 respectively for the Kattegat and Gulf of Finland region. In the Gulf of Bothnia, the historic \(A_T\) evolution follows a contrasting trend. \(A_T\) residuals in the 1910 decade are almost entirely positive, but decrease thereafter and become consistently negative at all salinity levels around 1950 (Fig. 6). From the few observations available from Gulf of Riga it can be assumed that \(A_T\) was considerably lower in the 1925–1945 period, than in the recent decades.

For around three decades from 1965 to 1995 the \(A_T\) observations show remarkably lower precision in all three subareas discussed above (Kat, Bot, Fin) and we thus refrain from interpreting any temporal changes during that time (Fig. 6). The recent observations from the last decade reveal positive \(A_T\) residuals for the Gulfs of Bothnia and Finland around +100 μmol kg\(^{-1}\) throughout all salinity intervals. In the Kattegat such positive evolution was only found at the lowest salinity (Fig. 6), which is in good agreement with the results from the applied 3d model (Fig. 4).

**Implications for CO2-induced acidification trends**

When assuming constant alkalinity levels in the Baltic Sea over the past two decades, the computed mean acidification trend (i.e., decrease in pH over time) caused by an increasing atmospheric pCO\(_2\) is in a similar order of magnitude as in oceanic environments and increases only slightly from −0.0020 pH units yr\(^{-1}\) at salinity 35 to −0.0022 pH units yr\(^{-1}\) at salinity 5 (Fig. 7b). In contrast, if the observed positive \(A_T\) trends are taken into account, the estimated acidification is generally lower. In the Kattegat region, increasing \(A_T\) levels mitigate the acidification trend to around −0.0015 pH units yr\(^{-1}\) at salinity 15. Slightly higher mitigation effects of around 50% were found for the Central Baltic Sea (Fig. 7b). In the low saline areas of the Bothnian Sea, the alkalinity increase fully compensated the CO\(_2\)-induced acidification signal during the last two decades (Fig. 7b).

**Fig. 4.** Surface water alkalinity as a function of salinity and time in the Kattegat, Gulf of Bothnia and Gulf of Finland from 1995 to 2014. The colors and black contour lines display \(A_T\) levels as derived from the best fitting 3d models. White dots represent the observations included in the analysis. For the fitting coefficients please refer to Table 2.
3d model advantages and uncertainties

The applied 3d models have several advantages, compared to the simple regression analysis of $A_T$ as a function of time within specific salinity intervals: (1) The 3d models are more robust against outliers, due to the high number of observations contributing to each fit. (2) The 3d models require only four fitted coefficients per subarea, whereas simple linear regression requires 2 coefficients per salinity interval and area. (3) The 3d models do not group the $A_T$ observations into salinity intervals as it is required for 2d regression analysis. Thus, each observation is included into the fitting procedure with the exact corresponding salinity. This difference explains the slight deviations between 3d and 2d models (Fig. 7a), which can best be exemplified for the salinity range $3 \pm 0.5$ in the Bothnian Sea: Within that salinity interval the 2d model underestimates the slope by around $1–2 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$, due to a larger number of observations with high salinities and thus higher $A_T$ at the beginning of the period (visualized in Supporting Information Fig. S3). This limitation of the 2d model also applies in the Kattegat region (Supporting Information Fig. S2), but is less pronounced than in the gulfs, because the $A_T$–$S$ slope is about fivefold less steep. In conclusion we found the 3d models to be more reliable to analyse $A_T$ trends in estuarine systems covering large salinity ranges.

Fitting the statistical 3d models ($A_T = f(S, t)$) to $A_T$ observations from the past two decades revealed trends ($50–150 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$) that were – in the typical salinity range of the Baltic Sea – by an order of magnitude larger than the measurement uncertainties.

In the Kattegat, we derived a slightly negative $A_T$ trend for the North Sea end member, which is around $-15 \ \mu\text{mol kg}^{-1}$ for the time period 1995–2014 at salinity 33. Because this estimate is in the same order of magnitude as the mean residual it was considered to be not significant.

When extrapolating the 3d models for the Kattegat and Bothnian Sea to the mean salinity 7 of the Central Baltic Sea an alkalinity trend of $+3.2 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$ at salinity 7 was derived for both areas. This is somewhat higher than the rate ($+3.4 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$) found by direct observations from the Central Baltic Sea. The deviation can potentially be attributed to the increasing uncertainty generally associated to the extrapolation of regression analysis.

Discussion

We found a consistent increase of surface water $A_T$ in the Baltic Sea over the past two decades (1995–2014), with increasing rates of change from the North Sea toward the low-saline areas in most northern parts. In the Central Baltic Sea, the $A_T$ trend amounts to $+3.4 \ \mu\text{mol kg}^{-1} \ \text{yr}^{-1}$ for the past two decades. In contrast to this consistent positive trend, the evaluation of historic $A_T$ data (1900–1995) suggests regional differences. The $A_T$ increase in the Central Baltic Sea, Kattegat and Gulf of Finland seems to be a persistent long-term trend, whereas $A_T$ levels in the Gulf of Bothnia have dropped during the first half of the century and increased only over the last two decades. The perception of the historic data is in agreement with previous studies (Ohlson and Anderson 1990; Kremling and Wilhelm 1997; Hjalmarsson et al. 2008).
Fig. 6. Surface water alkalinity trends in the Kattegat and the three Gulfs of Bothnia, Finland and Riga from 1905 to 2015. The boxplots represent the deviations ($\delta AT$) of observed AT from mean AT per salinity interval and decade. The number in the grey box on top of the panels indicates the middle of the decades, which cover ±5 yr. The salinity intervals are indicated by color. Within the grey bar below each plot the number of observations is given.
In the following discussion, we will first focus on the attribution of the detected surface water $A_T$ trends to biogeochemical processes and subsequently address their implications for the evolution of the Baltic Sea CO$_2$ system.

**Attribution of the detected $A_T$ trends**

Within the following chapters the potential drivers for the observed trends are discussed, but a quantitative attribution to the numerous possible biogeochemical processes and anthropogenic impacts is beyond the scope of this study. The qualitative discussion covers processes that affect terrestrial weathering rates (changes in precipitation patterns, acidic rain deposition, and atmospheric CO$_2$ increase), liming activities and finally internal alkalinity generation.

**Weathering in the Baltic drainage basin**

With respect to terrestrial weathering processes the Baltic Sea drainage basin can be divided into a northern and southern part that intersect at the easternmost end of the Gulf of Finland [for details see e.g., Håkanson et al. (2003)]. The Gulf of Bothnia and the Gulf of Riga are thus drained exclusively from the northern and southern part, respectively. All other subareas receive freshwater input from both drainage areas.

The bedrock of the northern part mainly consists of granite and is covered only with a thin layer of soil. Boreal forests are the predominant vegetation. The terrestrial weathering process in the northern catchment can be exemplified by the reaction of albite with carbonic acid (Berner and Berner 1987), which produces the secondary mineral kaolinite, dissolved silica, sodium ions and bicarbonate:

\[
2NaAlSi$_3$O$_8$ + 2H$_2$CO$_3$ + 9H$_2$O \rightarrow Al$_2$Si$_2$O$_5$ + 2Na$^+$ + 2HCO$_3^-$ + 4H$_4$SiO$_4$
\]

The bedrock of the southern part consists of limestone, clay and sandstone, covered with a thick soil layer that forms the...
Foundation for intense agricultural activities. The dominant weathering process in the southern part is the reaction of carbonate minerals with carbonic acid, which produces calcium ions and bicarbonate:

\[ CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \]  (7)

The weathering reactions exemplified in Eqs. 6 and 7 are driven by carbonic acid. That carbonic acid is produced by soil respiration processes, and thus ultimately originates from photosynthetically fixed atmospheric CO2. The fundamental difference in both weathering reactions with respect to the formation of alkalinity is that bicarbonate produced by the weathering of granite (Eq. 6) is entirely derived from carbonic acid. In contrast, roughly half of the alkalinity produced by the weathering of carbonate minerals (Eq. 7) originates from carbonic acid and the carbonate mineral, respectively. If the weathering is driven by a strong acid (e.g., H2SO4) instead of by carbonic acid, the weathering of carbonate minerals produces bicarbonate and the anion of the strong acid (e.g., sulfate), whereas the weathering of granite produces only the anion of the strong acid. In contrast to bicarbonate ions, the anions of the strong acids do not contribute to alkalinity. Thus, the weathering of carbonate minerals with a strong acid produces alkalinity, whereas the weathering of granite with a strong acid does not produce alkalinity, but neutralizes the delivered protons [for details see e.g., Berner and Berner (1987)]. This difference in the weathering processes is essential to understand the potential impacts of acidic rain on riverine alkalinity in the Baltic Sea drainage basin.

Precipitation patterns

Increasing precipitation and run-off were found to affect riverine alkalinity (AT) in two counteracting ways: The lower contact time of water with the soil and bedrock reduces the concentration of weathering products and as such AT. However, this effect is generally overcompensated by an increase in river discharge, which results in an increasing AT flux (Berner and Berner 1987; Cai et al. 2008). In a classical estuarine system consisting of an unchanged marine- and one variable freshwater endmember, increasing precipitation should thus directly increase the slope and decrease the intercept of the AT-S relationship, as both are controlled by AT but independent of the AT flux. In contrast, the Baltic Sea has a complex and diverse drainage basin structure, and the surface water AT-S distribution (Fig. 2a) also depends on the mixing ratio and thus the AT flux of the various discharging rivers.

The precipitation and total river run-off in the Baltic Sea area do not show a significant long-term trend over the past 100 years, but the recent two decades were relatively wet and the total runoff increased (The BACC II Author Team 2015). This recent increase in run-off was pronounced in the Nordic countries (Wilson et al. 2010), whereas the southern catchment revealed a contrasting tendency for a decrease in run-off (Gailius et al. 2011; The BACC II Author Team 2015). Due to the increased run-off in the Nordic countries we would expect a decrease of AT in the Gulf of Bothnia. Likewise, the northward shift in run-off should favor decreasing AT levels in the Central Baltic Sea, as it reduces the contribution from the AT-rich rivers draining the southern catchment area. Both expected trends are in contrast to our observations and we thus do not expect a significant impact of changes in precipitation patterns on the observed AT trends.

Hansson et al. (2011) report that runoff to the Baltic Sea is strongly linked to temperature and therefore suggest that southern regions will become drier and that the northern- and Gulf of Finland area will experience higher runoff with rising temperature. It can thus not be ruled out that changes in precipitation patterns (The BACC II Author Team 2015) will influence the future AT-S distribution in the Baltic Sea.

Impacts of acidic rain

Anthropogenic emissions of sulphur oxides (SOX) and nitrogen oxides (NOX) cause acidic rain, because both react with water and form strong sulphuric acid (H2SO4) and nitric acid (HNO3). European SO2 emissions steadily increased to peak emissions of > 50 Mt SO2 yr⁻¹ around 1980. Emissions decreased thereafter to today’s < 10 Mt SO2 yr⁻¹ with highest reduction rates in the 1990–2000 period (Vestreng et al. 2007). NOX emissions showed a much lower decrease rate (Granier et al. 2011). The decrease of SOX and NOX emissions is reflected by an increased precipitation pH, e.g., in Germany from 4.3 during 1978–1990 to 4.8 in 1990–2010 (Lajtha and Jones 2013). A recent modelling study revealed that the history of SOX and NOX emissions is well-mirrored in the direct atmospheric deposition of acids in the Baltic Sea basin (Omstedt et al. 2015).

According to the peculiarities of the weathering processes described above, we expect that increasing acidic precipitation until 1980 enhanced the dissolution of carbonate minerals and thus the riverine AT input from the southern drainage basin. In contrast, we expect a decreasing AT input from the northern drainage basin until 1980 that reflects the direct removal of alkalinity by acidic precipitation. After 1980, the recovery from acid deposition should have an inverse effect (Stets et al. 2014). Superimposed on the potentially delayed signals from terrestrial weathering processes, the direct input of acidic precipitation into the Baltic Sea can be considered an immediate AT sink that peaked around 1980 (Omstedt et al. 2015). In the following, we estimate the upper limits for acidic rain induced AT changes for two simplified processes: (1) The potential AT increase in rivers from the southern, limestone-dominated drainage basin and (2) the potential AT removal by direct acidic precipitation into the Gulf of Bothnia.
1. To quantify the relationship between acidic precipitation and alkalinity generation in the southern, limestone-rich catchment area, we first considered the weathering without any acidic precipitation and attributed the reference $A_T$ formation solely to the weathering with carbonic acid. Subsequently, we computed the additional dissolution of calcium carbonate due to acidic rain that causes higher $A_T$ levels (for a detailed description of the calculation procedure see the Supporting Information). We performed the respective calculations for various precipitation pH levels, temperatures and reference $A_T$ concentrations (Supporting Information Fig. S4). Assuming a reference river water $A_T$ of 3000 $\mu$mol kg$^{-1}$, $T = 10 \, ^{\circ}C$ and precipitation pH values of 3, 4, and 5 we estimated an $A_T$ increase of 410, 47 and 5 $\mu$mol kg$^{-1}$, respectively. Comparing these estimates with the temporal trends in $A_T$ as detected in the Central Baltic Sea and Gulf of Finland, a decline of the precipitation pH to values below 4 would be required. However, according to Winkler (1983), who analysed precipitation pH data going back to the late 1930s, such low pH have not been observed. Hence, increased weathering due to acidic precipitation might have contributed to the $A_T$ increase observed over the first half of the 20th century in subareas receiving river water from the southern drainage basin, but it is questionable that this is the major driver.

2. Acidic precipitation has the reverse effect on $A_T$ when the weathering in the northern, granite-dominated drainage basin and the direct input into seawater are considered. In this case, $A_T$ is reduced directly by the excess of proton donors over proton acceptors in rain water, approximated by the precipitation pH. The following estimate constitutes an upper limit, because we neglected that protons may partially be neutralized by increased weathering of granite rocks, which does however not produce additional alkalinity. For a precipitation pH of 4, the input of hydrogen ions into the Gulf of Bothnia and its drainage basin was estimated. Based on a precipitation rate of 600 mm yr$^{-1}$ and a surface area of 490,000 km$^2$ (The BACC Author Team 2008), the annual $A_T$ removal amounts to $\sim$29 Gmol yr$^{-1}$. This removal of $A_T$ is in the same order of magnitude as the mean input of $A_T$ by river water into the Gulf of Bothnia (43 Gmol yr$^{-1}$, Hjalmarsson et al. 2008) and indicates that the observed $A_T$ loss in the Gulf of Bothnia during the first half of the 20th century (Fig. 6) may indeed be attributed to acidic precipitation. Reversely, the increasing $A_T$ in the Gulf of Bothnia over the past two decades (Fig. 4) may constitute a relaxation effect from acidic precipitation.

In summary, our estimates support the concept of acidic rain impacts on the $A_T$ system of the Baltic Sea, as suggested by previous studies (Ohlson and Anderson 1990; Kremling and Wilhelm 1997; Hjalmarsson et al. 2008). Hjalmarsson et al. (2008) compiled the Canibal data set – which contains observations from 1911 to 2003 and was also included in our analysis – and investigated the $A_T$ signature of the rivers entering the Baltic Sea. They derived the flow-weighted $A_{T,0}$ in rivers entering a specific region from the intercept at $S = 0$, when extrapolating a regression analysis of $A_T$ vs. salinity. Hjalmarssoon et al. (2008) found an increase in $A_T$ in rivers entering the Gulf of Finland ($+2.6 \, \mu$mol L$^{-1}$ yr$^{-1}$) and a decrease in $A_T$ in rivers entering the Gulf of Bothnia ($-2.7 \, \mu$mol L$^{-1}$ yr$^{-1}$). These rates of change estimated for river water $A_T$ and the trends we observed in the Baltic Sea are of similar magnitude. However, it should be noted that the extrapolated river water alkalinity analysed by Hjalmarsson et al. (2008) suffers from at least the same uncertainty as the historic data included in our study. Ohlson and Anderson (1990) applied a similar principle to the Kattegat region and derived the flow-weighted calcium and $A_T$ concentrations of all rivers entering the Baltic Sea. They found that the Ca-$A_T$ ratio increased from around 0.4 (1938 and 1967) to 0.7 in 1986. This was attributed to an increase in weathering driven by acidic rain, which increases the ratio of weathered calcium to produced alkalinity compared to CO$_2$-driven weathering (Eq. 7). An according trend was found by Kremling and Wilhelm (1997), who reported a mean Ca concentration increase of about 4% from 1970 to 1995 in the Central Baltic Sea.

A recent modelling study that focused on the direct deposition of acids into the Baltic Sea indicated that most pronounced $A_T$ changes ($-30 \, \mu$mol kg$^{-1}$) may have occurred in the south-western Baltic Sea around 1990 (Omonted et al. 2015). This proposed direct acid deposition signal coincides with the $A_T$ drop that we observed – although with a high degree of uncertainty – in the Central Baltic Sea around 1990.

**Atmospheric CO$_2$ impacts on weathering**

In contrast to acidic precipitation – that peaked around 1980 – atmospheric CO$_2$ concentrations continuously increased over the whole observation period from $\sim$300 ppm at the beginning of the 20th century (MacFarling Meure et al. 2006) to today’s 400 ppm (IPCC 2013). Increasing pCO$_2$ decreases the pH of a water mass, but has itself no direct effect on the alkalinity. Likewise, atmospheric pCO$_2$ should have only a minor direct effect on terrestrial weathering processes, because the high groundwater pCO$_2$ levels and thus the weathering rates are controlled by soil respiration processes, rather than directly by atmospheric pCO$_2$. However, there is growing evidence that increasing atmospheric pCO$_2$ stimulates plant growth and soil respiration and thus indirectly raises soil pCO$_2$ (Andrews and Schlesinger 2001; Oh et al. 2007). Increased soil pCO$_2$ finally accelerates mineral weathering, which increases $A_T$ irrespective of the weathered mineral (Eqs. 6, 7).

Free-Air CO$_2$ Enrichment (FACE) experiments were performed to investigate this effect. In a pine plantation area, where the bedrock consists mainly of feldspar and should
thus be comparable to conditions in the northern drainage basin of the Baltic Sea, Andrews and Schlesinger (2001) found that under elevated atmospheric pCO$_2$ (+200 μatm) the soil respiration increased by 27%. This in turn accelerated mineral weathering and increased alkalinity by 162%. Likewise, Macpherson et al. (2008) observed steadily increasing $A_T$ levels in limestone-hosted groundwaters in the midcontinental North American grassland, which is rather comparable to the southern drainage basin of the Baltic Sea. The pronounced alkalinity increase from around 5400 to 6100 μmol kg$^{-1}$ ($\sim$47 μmol kg$^{-1}$ yr$^{-1}$) over the study period 1991–2005 was attributed to a 20% increase in groundwater CO$_2$ and enhanced weathering rates.

This positive feedback chain – increased atmospheric pCO$_2$ enhanced plant growth, elevated soil pCO$_2$ and finally raised groundwater $A_T$ – can potentially be amplified by atmospheric warming. Indeed, the surface air temperatures in the Baltic Sea region increased during the past 100 yr, with the strongest warming trend taking place during spring season (The BACC II Author Team 2015). As the duration of the cold season has decreased and the duration of the growing season increased (The BACC II Author Team 2015), it can be speculated that warming and increasing pCO$_2$ favored primary production on land in concert and act in the same direction with respect to $A_T$ changes in the Baltic Sea.

Although a quantitative assessment of the CO$_2$-driven $A_T$ contribution is currently impossible for the Baltic Sea, due to various types of landscapes and the lack of experimental work performed, we suggest that a positive feedback between atmospheric pCO$_2$ and weathering rates might have also contributed to the long-term increasing $A_T$ trends in our study area.

**Liming activities**

In Sweden, a large scale liming programme was implemented to counteract the acidification of sensitive freshwater systems caused by acidic rain. Around 0.2 Mt yr$^{-1}$ of limestone were introduced to Swedish freshwater systems from 1985 to 1995 (Svensson et al. 1995). Converting this to an alkalinity equivalent (twice the amount of [CO$_3^{2-}$]) reveals a potential $A_T$ source of around 4 Gmol yr$^{-1}$. This anthropogenic $A_T$ source might have mitigated acidification in Swedish lakes, but it is an order of magnitude smaller than the riverine input of $A_T$ into the Baltic Proper (43 Gmol yr$^{-1}$, Hjalmarrson et al. 2008) and should thus have contributed only marginally to the observed $A_T$ changes in the Baltic Sea.

Limestone is also applied for agricultural purposes mainly in the southern drainage area to improve soil pH and facilitate the nutrient uptake by plants. We could not compile a complete overview on agricultural liming statistics for the whole Baltic Sea drainage basin. However, liming rates in Germany – of which only a minor portion drains into the Baltic Sea – could be approximated by marketing of CaCO$_3$ (Supporting Information Fig. S5). The amount of marketed limestone rose from around 2 Mt yr$^{-1}$ in 1950 to >5 Mt yr$^{-1}$ in 2014 (Statistisches Bundesamt 2015, www.destatis.de), with a pronounced drop after the reunification of Germany in 1990. Similar trends in liming are reported from Eastern Europe and Russia. At present, the amount of limestone marketed in Germany is equal to 50 Gmol yr$^{-1}$ of CaCO$_3$. In relation to the annual run-off from this area (~100 km$^3$ yr$^{-1}$), the complete dissolution of the applied CaCO$_3$ would be equivalent to an alkalinity contribution of roughly 1000 μmol kg$^{-1}$. This estimate constitutes an upper limit, because it neglects the interdependency to the subsequent weathering of bedrock minerals, but it highlights the potentially immense contribution of agricultural liming on riverine $A_T$ concentrations. We hypothesize that the overall increase in liming rates over the second half of the 20th century significantly contributed to the observed $A_T$ trends in the Central Baltic Sea. This hypothesis is in agreement with findings from the intensively agricultural-used watersheds of the Ohio river basin, where Oh and Raymond (2006) estimated that 29% of the total riverine bicarbonate export could be attributed to liming activities. Likewise, Raymond and Cole (2003) reported an alkalinity increase from ~380 to ~440 μmol kg$^{-1}$ in the Mississippi river from 1953 to 2002 and attributed it to changes in land-use. The increase rate (~1.3 μmol kg$^{-1}$ yr$^{-1}$) estimated for the Mississippi river is in the same order of magnitude but lower than the trends we found in the Baltic Sea. Recently, Stets et al. (2014) extended the analysis and concluded that $A_T$ increase was a widespread phenomenon in large rivers of the conterminous U.S. Among the diverse drivers that were investigated, Stets et al. (2014) highlighted that recovery from acidification and agricultural liming are important contributions that act in concert on river water $A_T$ concentrations.

**Internal alkalinity generation**

In addition to the external $A_T$ sources discussed so far, recent modelling studies suggest that biogeochemical processes can act as significant internal alkalinity sources in the Baltic Sea (Edman and Omstedt 2013; Gustafsson et al. 2014). With respect to $A_T$ trends in the surface water over the past two decades, we discuss potential changes in $A_T$ contributions from (1) primary production, (2) denitrification, and (3) net sulfate reduction.

1. Primary production increases $A_T$, mainly because the uptake of nitrate (NO$_3^-$) has to be balanced by H$^+$ uptake (Wolf-Gladrow et al. 2007). This $A_T$ source is reversed when the produced organic material is remineralized. Pelagic primary production can however contribute to surface water $A_T$, when the organic matter is exported. With respect to alkalinity trends in the Baltic Sea surface water, it is reasonable to assume that nitrate based primary production and thus the $A_T$ contribution increased along with nutrient inputs that peaked around 1980 (Gustafsson
et al. 2012; Schneider et al. 2015). However, recent modeling studies suggest that the previously increasing nitrogen uptake by phytoplankton levelled off around 1990 (Gustafsson et al. 2012). Thus, we do not assume that changes in primary production contributed significantly to the observed $A_T$ trends since 1995.

2. Denitrification increases $A_T$ by 1 mole per mole of nitrate converted (Wolf-Gladrow et al. 2007) and is described by the reaction:

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 7H_2O$$

Denitrification is an irreversible process and can consequently contribute to surface water $A_T$ changes irrespective of where it occurs in the water column. However, the denitrification of nitrate that was originally introduced to the system by nitrogen fixation and nitrification has no net effect on $A_T$. Since the 1980s the nitrogen input to the Baltic Sea was continuously reduced, which is reflected in decreasing winter nitrate concentrations in the surface water (Helcom 2015). It is therefore plausible to assume that rates of denitrification not compensated by nitrogen fixation have rather decreased than increased and thus not contributed to the positive $A_T$ trend since 1995.

3. Oxygen deficiency in the bottom waters results in sulfate reduction, when all nitrate is depleted as alternative electron acceptor. The reaction produces sulfide, which contributes to alkalinity:

$$2CH_2O + SO_4^{2-} \rightarrow S^{2-} + CO_2 + H_2O$$

However, sulfate reduction is reversed under oxic conditions and does therefore not contribute directly to surface water $A_T$, which was the focus of this study. However, the process can act as a permanent alkalinity source, if the reduced sulfide is buried as FeS$_2$. In this case, the removal of iron – which represents a negative $A_T$ contribution when oxidized to Fe$_2$O$_3$ – constitutes the permanent $A_T$ source. Unfortunately, no reliable estimate of this removal processes and its relation to organic matter sedimentation is available by now and it is thus premature to speculate about the potential contribution to $A_T$ trends.

**Acidification mitigation**

In the Central Baltic Sea, almost 50% of the CO$_2$-induced acidification trend was mitigated by increasing alkalinitities over the past two decades (Fig. 7b). In terms of proton concentration this corresponds to an increase of 6% instead of 10.5% (Fig. 8). Toward the low-saline and low-alkaline Gulf of Bothnia – where pH levels are generally lower – the alkalinity increase fully compensated the CO$_2$-induced acidification.

In addition to the mitigation of CO$_2$-induced acidification, the observed alkalinity increase has further implications for the CO$_2$ system. Focusing on the Central Baltic Sea from 1995 to 2014 the mean salinity and $A_T$ were 7 and 1587 μmol kg$^{-1}$, respectively. Taking the positive $A_T$ trend of $+3.4$ μmol kg$^{-1}$ yr$^{-1}$ into account, the $A_T$ rose from around 1550 to 1620 μmol kg$^{-1}$. Over the same time period atmospheric pCO$_2$ increased from roughly 360 to 400 μatm. Assuming equilibrium with the atmosphere, this pCO$_2$ increase would raise the dissolved inorganic carbon (DIC) in the Central Baltic Sea only marginally from 1554 to 1560 μmol kg$^{-1}$ under a constant mean $A_T$ background (Fig. 8). However, with $A_T$ and pCO$_2$ rising in parallel, the DIC increased from 1522 to 1593 μmol kg$^{-1}$, which corresponds to a relative change of 5% (Fig. 8). The DIC gain of around 70 μmol kg$^{-1}$ is very similar to the change in $A_T$ and reflects the tight control of $A_T$ on the CO$_2$ storage capacity of seawater.

The potentially harmful effect of decreasing seawater pH on marine organisms has been reported extensively (Kroeker et al. 2010 and references therein). Consequently, increasing $A_T$ levels and the mitigation of CO$_2$-induced acidification can be judged beneficial to individual organisms and ecosystem stability. Specific concerns were raised about calcifying organisms, because they are believed to be sensitive not only to decreasing pH but also to decreasing carbonate concentrations, which may hinder the calcification process (Thomsen et al. 2015). The $A_T$ increase we observed in the Central Baltic Sea over the past two decades not only mitigated acidification by 50%, but also stabilized the carbonate concentrations. At constant mean $A_T$ levels the pCO$_2$ increase from 1995 to 2014 would have caused a drop in carbonate concentration from 42.7 to 38.8 μmol kg$^{-1}$, but with $A_T$ increasing in parallel this is reduced to a marginal change from
40.9 to 40.4 \mu mol \text{ kg}^{-1}. \) Assuming a constant calcium concentration of 2.7 mmol kg\(^{-1}\) (Dyrssen 1993), the changes in the carbonate concentration are directly reflected in the saturation state of calcium carbonate \((\Omega_{\text{CaCO}_3})\), which is defined as the solubility product divided by the product of \([\text{Ca}^{2+}]\) and \([\text{CO}_3^{2-}]\). With respect to the solubility product of calcite (Mucci 1983), the increasing \(A_T\) kept the saturation state stable at 1.5. In contrast, the non-mitigated CO\(_2\) uptake would have decreased the saturation state by around 0.2, corresponding to relative change of \(-9\%\) (Fig. 8). The observed \(A_T\) increase can thus be judged twofold beneficial to calcifying organisms, because it helps to stabilize both, pH and the CaCO\(_3\) saturation state.

### Conclusion

We found a consistent \(A_T\) increase in the Baltic Sea over the last two decades. Historic observations indicate that this positive \(A_T\) evolution might have persisted for extended periods of the 20\(^{th}\) century, except for the Gulf of Bothnia.

We suggest that these trends were driven by an interplay of acidic precipitation, increasing atmospheric CO\(_2\) and liming activities. The fundamental difference between those drivers is that acidic precipitation decreases the \(A_T\) input from the northern catchment area and increase the \(A_T\) input from the southern catchment area, whereas increasing atmospheric CO\(_2\) and liming activities are entirely positive drivers. Further, the temporal development of the drivers differs: Acidic precipitation peaked in the 1980s, atmospheric pCO\(_2\) increased steadily since the onset of industrialization and liming rates, at least in Germany, have increased since the 1950s, with a drop after 1990. Finally, all three drivers have in common that they act on the Baltic Sea alkalinity by changing the freshwater-derived \(A_T\) contributions. Because this freshwater \(A_T\) input is delayed by the groundwater residence time, disentangling the various processes in time and space will be a future challenge for holistic biogeochemical models taking the land-sea interaction into account.

Irrespective of the difficulties in attributing the Baltic Sea \(A_T\) trends, we put them into context with increasing atmospheric pCO\(_2\) and estimated the combined effect of both parameters on the seawater CO\(_2\)-system. For the Central Baltic Sea, we estimated that the \(A_T\) increase over the past two decades compensated the CO\(_2\)-induced acidification by 50\%, stabilized the saturation state of calcium carbonate, and increased the CO\(_2\) storage capacity. However, we emphasize that our findings should not be misinterpreted as suggesting a permanent protection against CO\(_2\)-induced acidification and related processes in coastal seas. As discussed above, only a portion of the observed alkalinity trend might be driven by processes that have a positive feedback to atmospheric CO\(_2\) and can thus be expected to proceed in the course of future CO\(_2\) emissions.

We conclude that the predictability of future acidification processes in coastal seas is limited by the variability of CO\(_2\) system constituents, especially the alkalinity, which forms the backbone of the CO\(_2\)-pH-interdependency. The continued monitoring of the carbonate system and the introduction of automated, high-quality observation techniques are thus essential requirements for the detection and understanding of future changes in the CO\(_2\) system of estuarine environments like the Baltic Sea. A comprehensive monitoring of such large estuarine systems would not only be beneficial for the understanding of the particular ecosystem itself, but could also serve as valuable indicators for expected changes in the open ocean on geological time scales.

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