

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

Jens Daniel Müller,* Bernd Schneider, Gregor Rehder

Department of Marine Chemistry, Leibniz Institute for Baltic Sea Research, Warnemünde, Germany

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 (A_T) and thus mitigate the acidification signal. The Baltic Sea is an ideal study site for such A_T dynamics, due to its direct link to terrestrial processes, short water residence time and long history of A_T measurements dating back to the early 20th century. We compiled an extensive A_T data set that revealed the highest data quality and coverage for the past two decades. Within that period, surface water A_T 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 A_T increase observed in the Central Baltic Sea ($+3.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$) and the Gulf of Bothnia ($+7 \mu\text{mol kg}^{-1} \text{yr}^{-1}$) has compensated CO₂-induced acidification by almost 50% and 100%, respectively. Further, the A_T 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 A_T trends to potential changes in precipitation patterns, continental weathering driven by acidic rain and increasing atmospheric CO₂, agricultural liming and internal A_T sources.

Introduction

Alkalinity: global relevance and characteristics

Total alkalinity (A_T) is a measure of the acid-binding capacity of seawater. As one of four measureable parameters of the marine CO₂ system, A_T has gained increasing attention within the field of climate change research. The importance of A_T 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 (Khaliwala 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 A_T . Although more CO₂ could be taken up by high- A_T seawater, the degree of acidification would be smaller than at lower A_T . Knowledge about spatio-temporal A_T 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 A_T , as the excess of proton acceptors over proton donors (Dickson et al. 2007), is expressed by:

*Correspondence: Jens.Mueller@io-warnemuende.de

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$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] \\ + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+]_F - [\text{HF}] \quad (1) \\ - [\text{HSO}_4^-] - [\text{H}_3\text{PO}_4] + [\text{minor bases} - \text{minor acids}]$$

where $[\text{H}^+]_F$ 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 CO_2 system, like pCO_2 and pH , which do not necessarily obey linear mixing relationships. Further, A_T is not affected by the release or dissolution of CO_2 , because the A_T loss caused by the release of protons (H^+) from the dissociation of carbonic acid (H_2CO_3) is balanced by the gain from produced bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. Among the components that contribute to A_T according to Eq. 1, the major share can be attributed to HCO_3^- and CO_3^{2-} that originate not from the A_T -neutral dissolution of CO_2 , but from riverine input of continentally weathered carbonate and silicate minerals. On oceanic scales this input is currently balanced by CaCO_3 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., $2291 \pm 4 \mu\text{mol kg}^{-1}$ (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 $0.002 \text{ pH units yr}^{-1}$ can be predicted from future pCO_2 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 CO_2 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 CO_2

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, CaCO_3 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 alkalinity 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 CO_2 -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 subareas, 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 ~ 35 exists in the Kattegat region. With exception of the Gulf of Riga, the

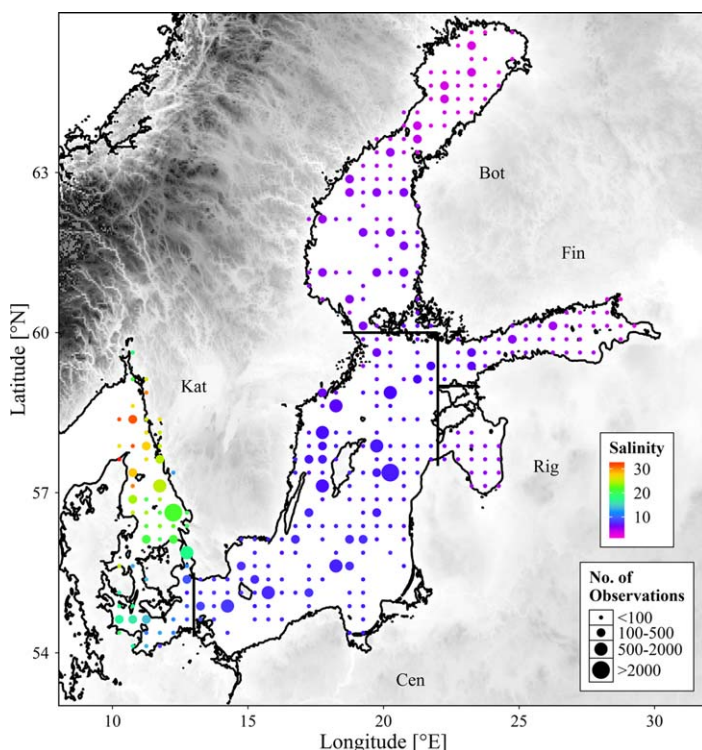


Fig. 1. Map of the Baltic Sea showing the spatial distribution of associated salinity and alkalinity observations. The geographical borders of the subareas Kattegat (Kat), Central Baltic Sea (Cen), Gulf of Bothnia (Bot), Gulf of Finland (Fin), and Gulf of Riga (Rig) that were assigned according to the hydrographical mixing regimes are indicated. The color scale represents the mean salinity and the point size the number of observations, both on a grid of 0.5° Lon and 0.25° Lat. The grey shading indicates the elevation of land above sea level.

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 $A_{T,0}$ 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). Fur-

ther, 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 ($+2 \mu\text{atm yr}^{-1}$) a slightly lower mean pH trend of -0.0019 yr^{-1} can be expected for the open ocean ($S = 35$, $T = 10^\circ\text{C}$, $A_T = 2300 \mu\text{mol kg}^{-1}$) compared to -0.0021 yr^{-1} in the Central Baltic Sea ($S = 7$, $T = 10^\circ\text{C}$, $A_T = 1650 \mu\text{mol kg}^{-1}$). However, the direct link to riverine A_T input (Hjalmarsson 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 $100 \mu\text{mol kg}^{-1}$ ($\sim 6\%$) 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; Hjalmarsson 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 (Melnzer 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 (Kuliński 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:

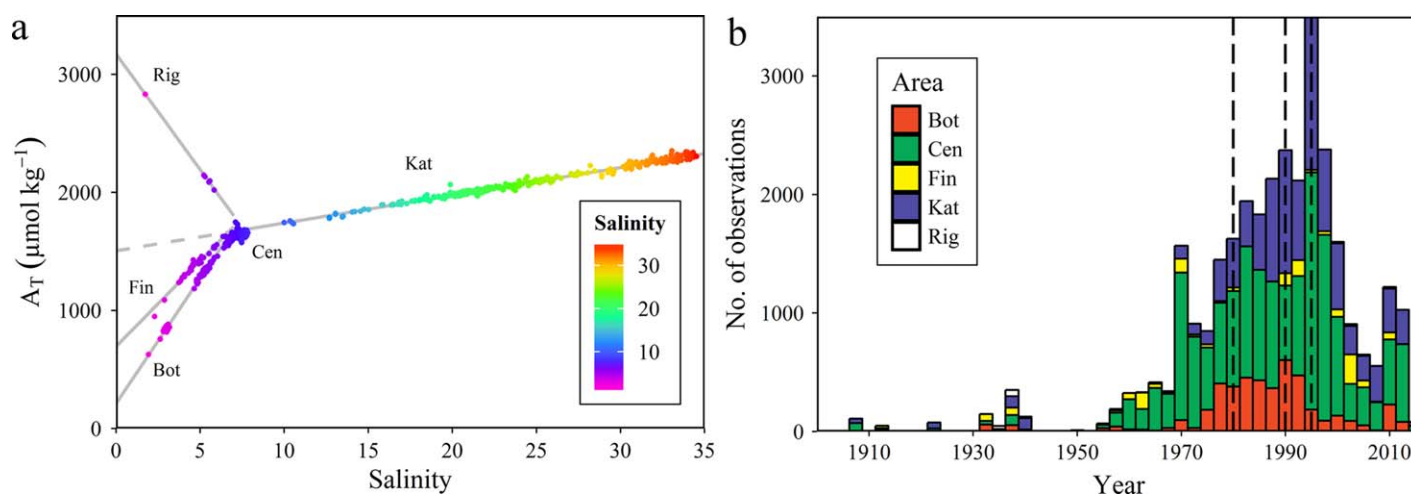


Fig. 2. (a) Exemplary A_T - S relationship in the Baltic Sea for observations from 2008/2009 with linear regression lines for the subareas Kat, Bot, Fin and Rig and (b) temporal distribution of available data over the past century (binwidth = 2.5 yr) with colors coding for the investigated subareas. The vertical dashed lines mark the periods (<1980, 1980–1990, 1990–1995, >1995) that were analysed separately.

- 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. Perttinen 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 A_T contributions from sulfide (S^{2-}) formed in stagnant bottom waters. The analysed data set comprises 31436 single observations. The spatio-temporal coverage of the data is presented in Figs. 1, 2b.

Quality control

The applied quality control focuses on the homogeneity of the A_T 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_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 A_T - S relationships to identify data that are obviously biased by analytical shortcomings. The precision of A_T observations can be estimated from the residuals when performing linear regression analysis for the A_T - 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. However, applying a threshold for the various subareas led to the exclusion of observations primarily from the period 1975–1995, whereas no precision deficiency could be identified for the past two decades. 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 A_T observations from the critical 1975–1995 period we risked to discard important information and thus decided to analyse the critical time

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 alkalinities 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 relation

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 analyse A_T trends at specific salinity levels. Therefore, all observations 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 val-

ues 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:

$$A_T(S, t) = A_{T(S_0, t_0)} + \left(\frac{\Delta A_T}{\Delta S} \right)_{t_0} \times (S - S_0) + \left(\frac{\Delta A_T}{\Delta t} \right)_{S_0} \times (t - t_0) + \frac{\Delta \left(\frac{\Delta A_T}{\Delta S} \right)}{\Delta t} \times (S - S_0) \times (t - t_0) \quad (3)$$

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 $(\Delta A_T / \Delta t)_{S_0}$ 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

Table 1. Summary and interpretation of the coefficients that characterize the applied 3d model.

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)
$\left(\frac{\Delta A_T}{\Delta S} \right)_{(t_0)}$	$\mu\text{mol kg}^{-1}$	Slope $A_T \sim$ salinity (at the beginning of the observation period t_0)
$\left(\frac{\Delta A_T}{\Delta t} \right)_{(S_0)}$	$\mu\text{mol kg}^{-1} \text{ yr}^{-1}$	Slope $A_T \sim$ time (at the reference salinity S_0)
$\Delta \left(\frac{\Delta A_T}{\Delta S} \right)_{\Delta t}$	$\mu\text{mol kg}^{-1} \text{ yr}^{-1}$	Interaction term: (change of slope $A_T \sim$ salinity, if time increases by 1 yr, or change of slope $A_T \sim$ 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 CO_2 was computed from pCO_2 and A_T for the time period 1995–2014. The acidification estimates are based on a pCO_2 trend of $+2 \mu\text{atm yr}^{-1}$ (IPCC 2013). Calculations were performed for an increase from $\text{pCO}_{2,t0} = 380 \mu\text{atm}$ to $\text{pCO}_{2,t1} = 382 \mu\text{atm}$, reflecting the annual increase in the northern-hemisphere 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 (mA_T) of the observation period was computed for each salinity interval. Based on this mA_T , the pH trend was computed according to:

$$dpH_{(A_T=\text{constant})} = pH(mA_T, pCO_{2,t1}) - pH(mA_T, pCO_{2,t0}) \quad (4)$$

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

$$dpH_{(A_T=\text{variable})} = pH\left(\left(mA_T + \frac{\Delta A_T}{\Delta t} \times 1\text{yr}\right), pCO_{2,t1}\right) - pH(mA_T, pCO_{2,t0}) \quad (5)$$

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 homogenous 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 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

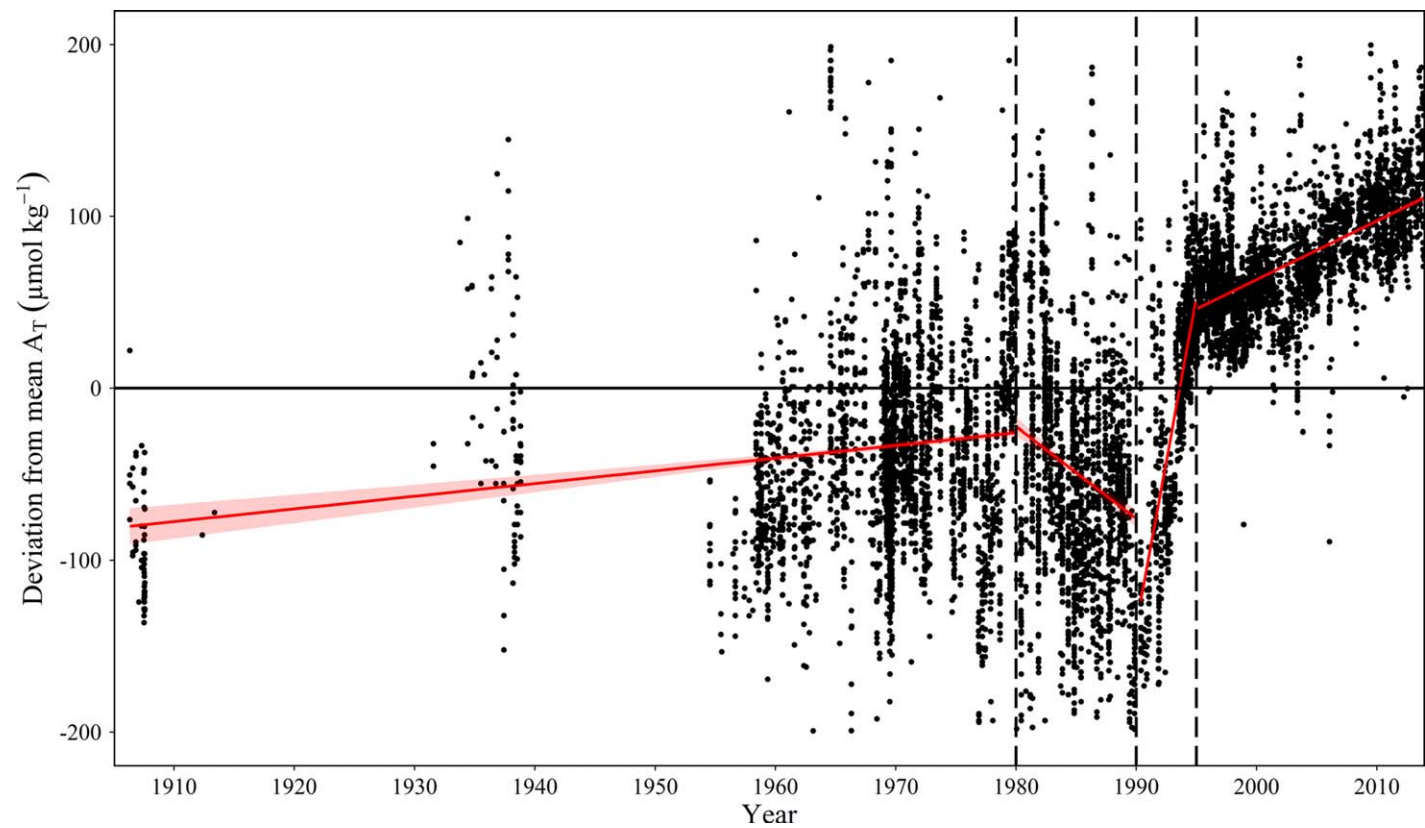


Fig. 3. Temporal alkalinity trends in the Central Baltic Sea from 1900 to 2015. Displayed are deviations (dA_T) of observed A_T from mean A_T . Linear regression models (red line + 95% confidence interval (red area)) were fitted separately within the four time frames indicated by the vertical dashed lines. For the coefficients of the regression analysis please refer to Table 2.

salinity 5 we found an A_T increase from 1340 to 1440 $\mu\text{mol kg}^{-1}$ ($+5.6 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$).

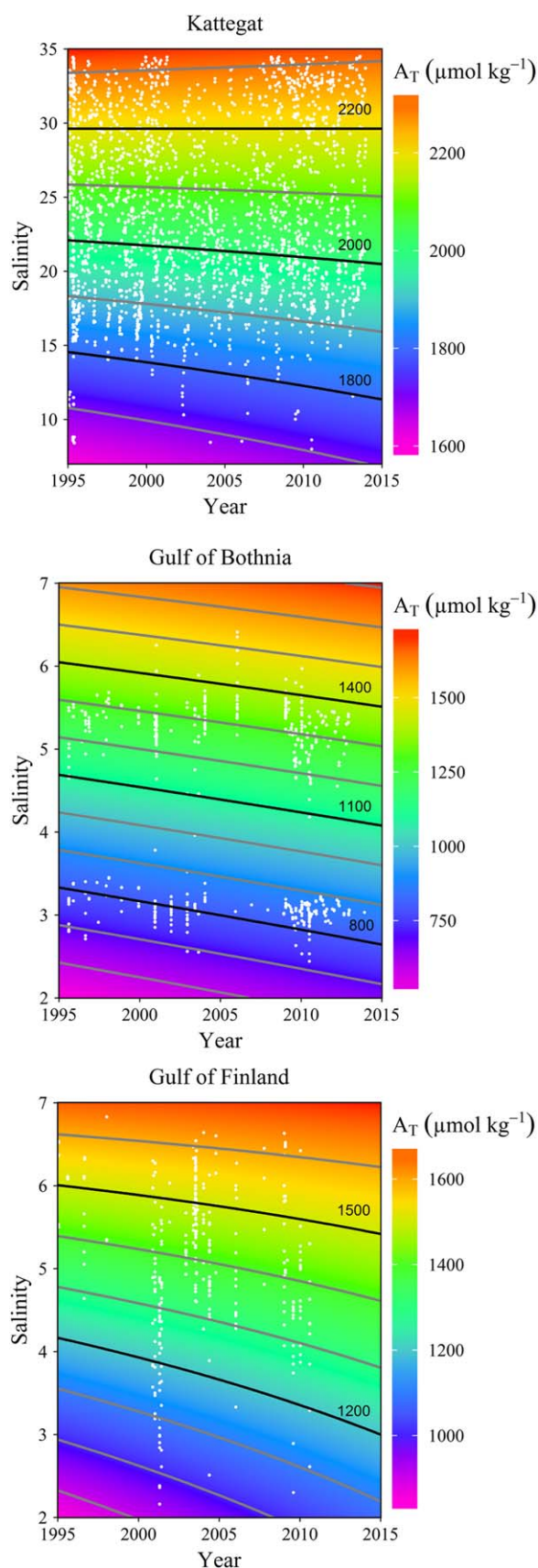
In the Gulf of Riga, the data coverage is not extensive enough for a reasonable application of the statistical 3d model. However, for the salinity range 5–6 and the limited time period 2000–2011, linear regression of A_T as function of time indicates a rate of change around $+8 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ (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

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	$A_{T(S_0, t_0)}$	$\left(\frac{\Delta A_T}{\Delta S}\right)_{(t_0)}$	$\left(\frac{\Delta A_T}{\Delta t}\right)_{(S_0)}$	$\frac{\Delta\left(\frac{\Delta A_T}{\Delta S}\right)}{\Delta t}$	R^2	Mean residual	No of observations
		yr	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1} \text{ yr}^{-1}$	$\mu\text{mol kg}^{-1} \text{ yr}^{-1}$		$\mu\text{mol kg}^{-1}$	
Cen	$dA_T = f(t)$	1900–1980	-	-	0.7	-	0.02	44	3876
		1980–1990	-	-	-5.2	-	0.04	51	2591
		1990–1995	-	-	38.4	-	0.61	27	1713
		1995–2014	-	-	3.4	-	0.33	20	4080
Kat	$A_T = f(S, t)$		1600	26.5	5.3	-0.2	0.98	16	3333
Bot		1995–2014	1610	220.9	5.1	-0.6	0.98	24	738
Fin			1662	163.0	1.7	-1.9	0.87	34	476



care, because the spread of the observations from before 1995 is much larger (mean residual $> 40 \mu\text{mol kg}^{-1}$) than for the last two decades (mean residual $< 20 \mu\text{mol kg}^{-1}$, 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 ($-5 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$) from around 1980–1990, and recovered more rapidly ($+38 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$) 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 $50\text{--}100 \mu\text{mol kg}^{-1}$ 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 $+100 \mu\text{mol kg}^{-1}$ 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 CO_2 -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 $-0.0020 \text{ pH units yr}^{-1}$ at salinity 35 to $-0.0022 \text{ pH units yr}^{-1}$ 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 $-0.0015 \text{ pH units yr}^{-1}$ 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.

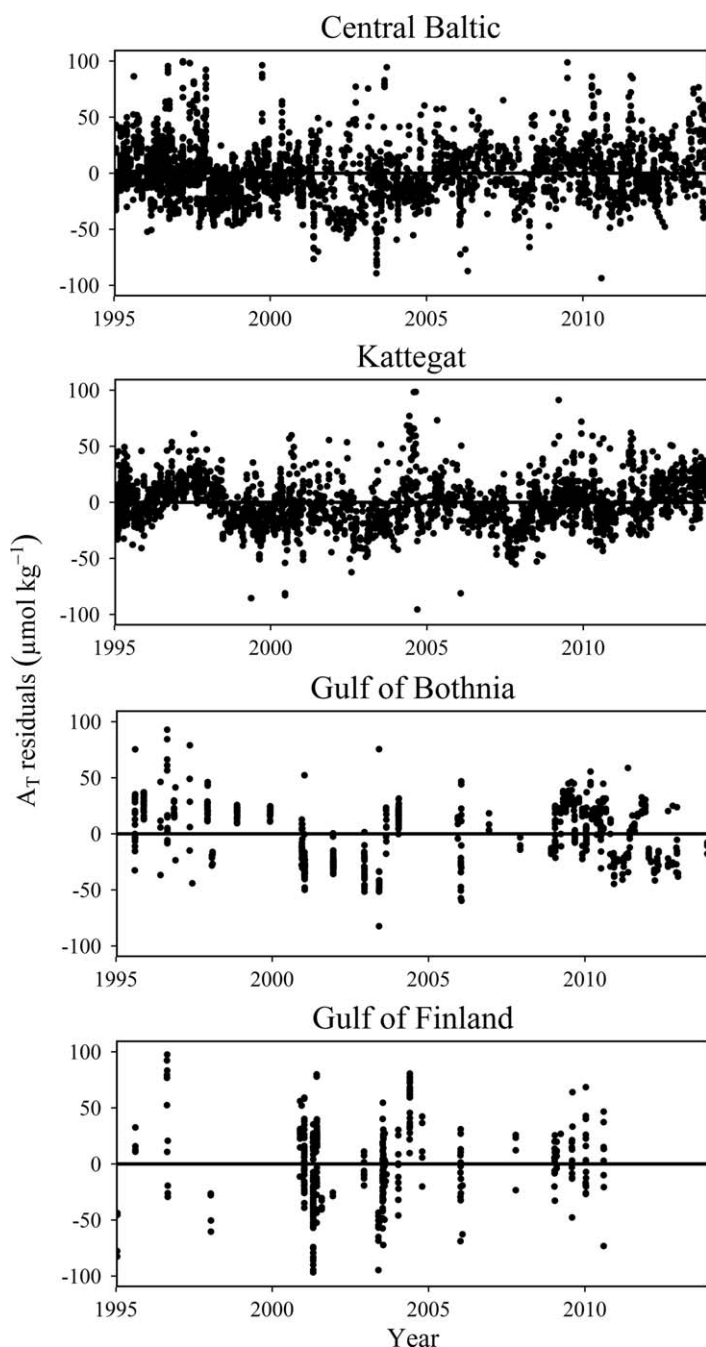


Fig. 5. Residuals of observed surface water alkalinity from the statistical models over the time period 1995–2014. In the Central Baltic Sea, the residuals correspond to the 2d linear regression model applied to the A_T deviations. In the Kattegat, Gulf of Bothnia and Gulf of Finland the residuals correspond to the statistical 3d models. Due to the scaling of the y-axis 38 (0.9%), 14 (0.4%), 10 (1.4%), and 15 (3.2%) observations are not displayed for Cen, Kat, Bot and Fin area, respectively.

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 ± 0.5 in the Bothnian Sea: Within that salinity interval the 2d model underestimates the slope by around $1\text{--}2 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$, 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 ($50\text{--}150 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$) 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 $+5.2 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ 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).

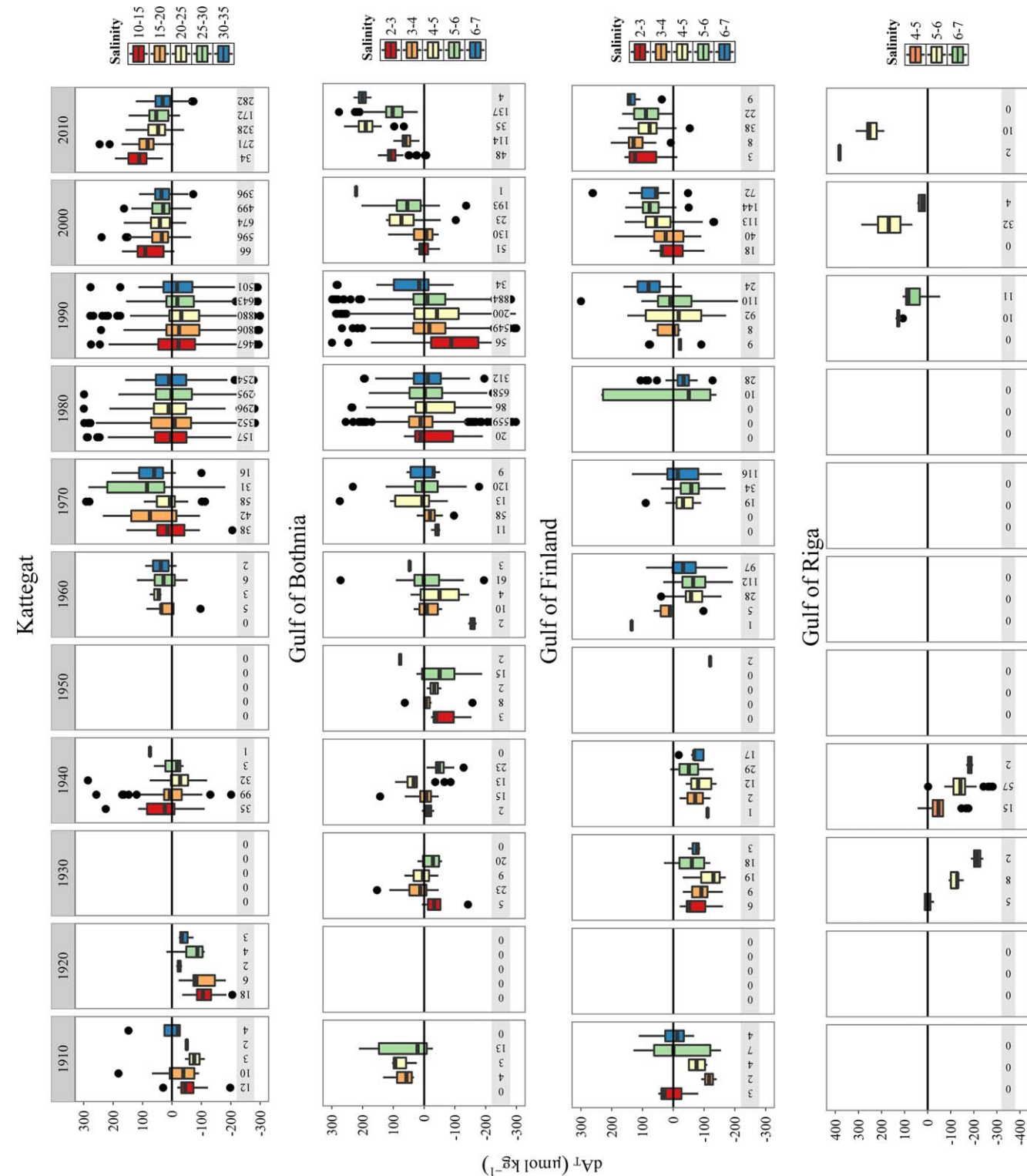


Fig. 6. Surface water alkalinity trends in the Kattegat and the three Gulfs of Bothnia, Finland and Riga from 1905 to 2015. The boxplots represent the deviations (dA_T) of observed A_T from mean A_T per salinity interval and decade. The number in the grey box on top of the panels indicates the middle 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.

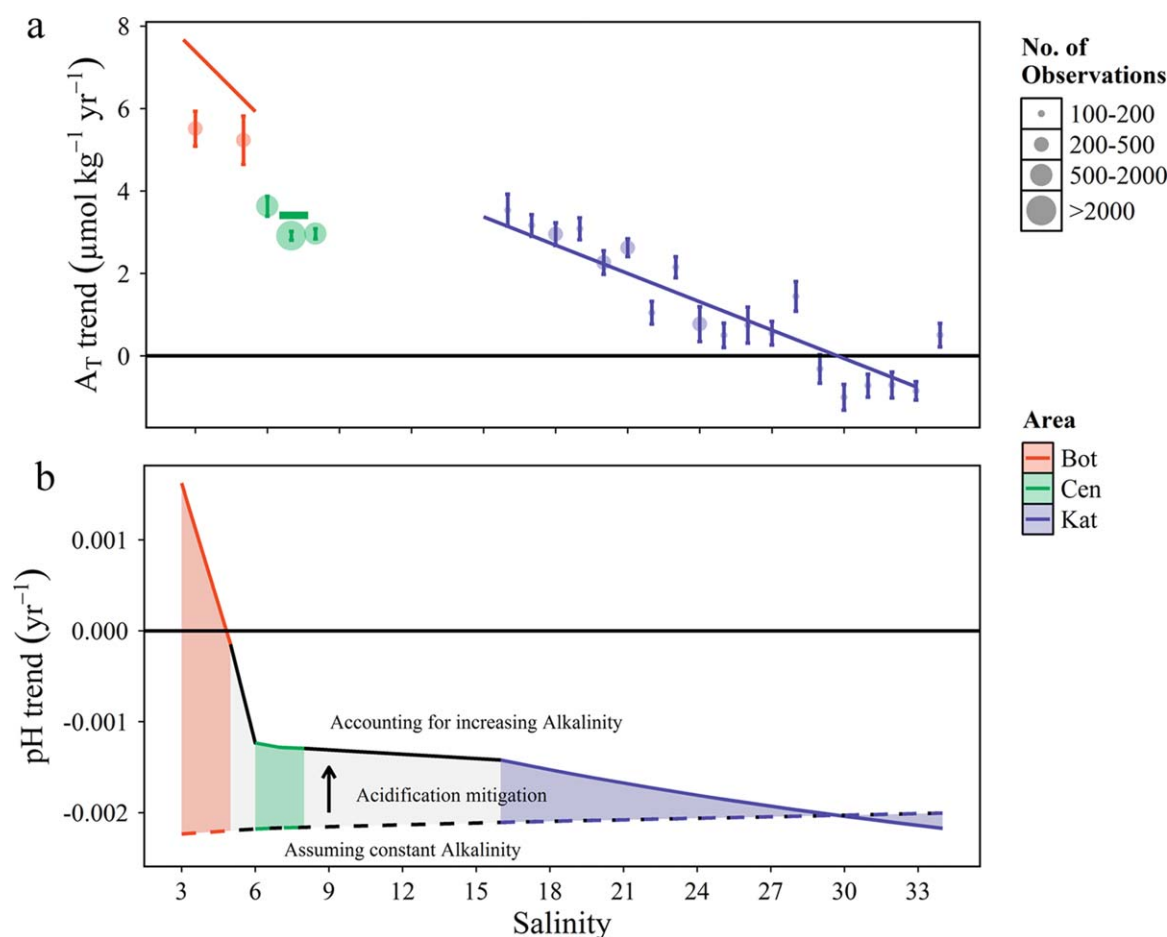


Fig. 7. Mean surface water alkalinity trends (a) and acidification mitigation (b) in the Kattegat, Central Baltic Sea and Gulf of Bothnia for the time period 1995–2014. (a) A_T trends displayed as points ($\pm\text{SE}$) correspond to the slope of linear regression models fitted separately at each salinity interval (given value ± 0.5), whereas the lines represent the A_T slopes derived from the 3d models. The point size depicts the number of observations. (b) Mean annual acidification trend assuming an atmospheric pCO_2 increase of $2 \mu\text{atm yr}^{-1}$. The dashed line represents the acidification trend assuming that the mean A_T was constant, whereas the solid line depicts a mean annual pH decrease taking the observed A_T changes into account. The filled area corresponds to the acidification mitigation that increases toward lower salinity.

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

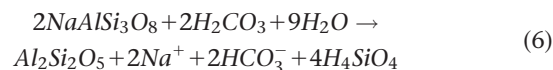
Within the following chapters the potential drivers for the observed trends are discussed, but a quantitative attribution to the numerous possible biogeochemical processes and anthropogenic impacts is beyond the scope of this study. The qualitative discussion covers processes that affect terrestrial 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 south-

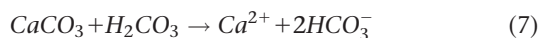
ern part that intersect at the easternmost end of the Gulf of Finland [for details see e.g., Håkanson et al. (2003)]. The Gulf of Bothnia and the Gulf of Riga are thus drained exclusively from the northern and southern part, respectively. All other subareas receive freshwater input from both drainage 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:



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:



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 CO_2 . 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., H_2SO_4) 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 ($A_{T,0}$) in two counteracting ways: The lower contact time of water with the soil and bedrock reduces the concentration of weathering products and as such $A_{T,0}$. However, this effect is generally overcompensated by an increase in river discharge, which results in an increasing A_T 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 A_T - S relationship, as both are controlled by $A_{T,0}$ but independent of the A_T flux. In contrast, the Baltic Sea has a complex and diverse drainage basin structure, and the surface water A_T - S distribution (Fig. 2a) also depends on the mixing ratio and thus the A_T 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 (Gailiusis 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 $A_{T,0}$ in the Gulf of Bothnia. Likewise, the northward shift in run-off should favor decreasing A_T levels in the Central Baltic Sea, as it reduces the contribution from the A_T -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 A_T 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 A_T - S distribution in the Baltic Sea.

Impacts of acidic rain

Anthropogenic emissions of sulphur oxides (SO_x) and nitrogen oxides (NO_x) cause acidic rain, because both react with water and form strong sulphuric acid (H_2SO_4) and nitric acid (HNO_3). European SO_2 emissions steadily increased to peak emissions of $> 50 \text{ Mt SO}_2 \text{ yr}^{-1}$ around 1980. Emissions decreased thereafter to today's $< 10 \text{ Mt SO}_2 \text{ yr}^{-1}$ with highest reduction rates in the 1990–2000 period (Vestreng et al. 2007). NO_x emissions showed a much lower decrease rate (Granier et al. 2011). The decrease of SO_x and NO_x 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 SO_x and NO_x 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 A_T input from the southern drainage basin. In contrast, we expect a decreasing A_T 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 A_T sink that peaked around 1980 (Omstedt et al. 2015). In the following, we estimate the upper limits for acidic rain induced A_T changes for two simplified processes: (1) The potential A_T increase in rivers from the southern, limestone-dominated drainage basin and (2) the potential A_T 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 $3000 \mu\text{mol kg}^{-1}$, $T = 10^\circ\text{C}$ and precipitation pH values of 3, 4, and 5 we estimated an A_T increase of 410, 47 and $5 \mu\text{mol kg}^{-1}$, 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 $490,000 \text{ km}^2$ (The BACC Author Team 2008), the annual A_T removal amounts to $\sim 29 \text{ Gmol yr}^{-1}$. 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. Hjalmarsson et al. (2008) found an increase in A_T in rivers entering the Gulf of Finland ($+2.6 \mu\text{mol L}^{-1} \text{ yr}^{-1}$) and a decrease in A_T in rivers entering the Gulf of Bothnia ($-2.7 \mu\text{mol L}^{-1} \text{ yr}^{-1}$). 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 ($-30 \mu\text{mol kg}^{-1}$) may have occurred in the south-western Baltic Sea around 1990 (Omstedt 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 $\sim 300 \mu\text{atm}$ at the beginning of the 20th century (MacFarling Meure et al. 2006) to today's $400 \mu\text{atm}$ (IPCC 2013). Increasing $p\text{CO}_2$ decreases the pH of a water mass, but has itself no direct effect on the alkalinity. Likewise, atmospheric $p\text{CO}_2$ should have only a minor direct effect on terrestrial weathering processes, because the high groundwater $p\text{CO}_2$ levels and thus the weathering rates are controlled by soil respiration processes, rather than directly by atmospheric $p\text{CO}_2$. However, there is growing evidence that increasing atmospheric $p\text{CO}_2$ stimulates plant growth and soil respiration and thus indirectly raises soil $p\text{CO}_2$ (Andrews and Schlesinger 2001; Oh et al. 2007). Increased soil $p\text{CO}_2$ 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 $p\text{CO}_2$ (+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 mid-continental 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 $\mu\text{mol kg}^{-1}$ ($\sim 47 \mu\text{mol kg}^{-1} \text{yr}^{-1}$) 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 $p\text{CO}_2$, enhanced plant growth, elevated soil $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 (Svenson et al. 1995). Converting this to an alkalinity equivalent (twice the amount of $[\text{CO}_3^{2-}]$) 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} , Hjalmarsson 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 $>5 \text{Mt yr}^{-1}$ 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 ($\sim 100 \text{km}^3 \text{yr}^{-1}$), the complete dissolution of the applied CaCO_3 would be equivalent to an alkalinity contribution of roughly 1000 $\mu\text{mol kg}^{-1}$. 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 $\sim 440 \mu\text{mol kg}^{-1}$ in the Mississippi river from 1953 to 2002 and attributed it to changes in land-use. The increase rate ($\sim 1.3 \mu\text{mol kg}^{-1} \text{yr}^{-1}$) 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.

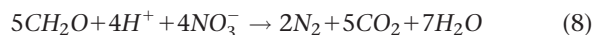
Internal alkalinity generation

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 modelling 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.

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



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.

- 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:



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_2O_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 alkalinities 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

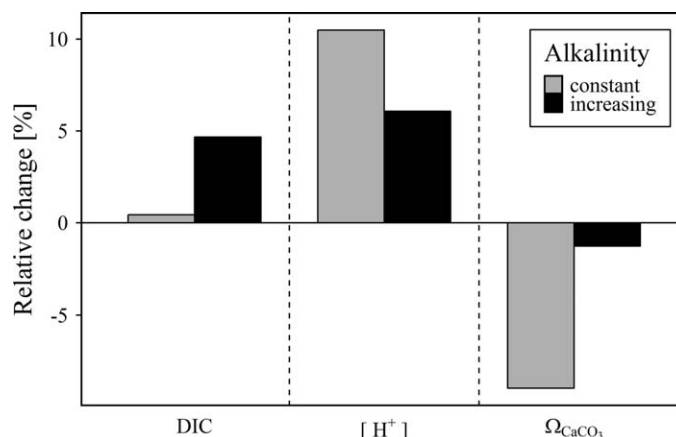


Fig. 8. Combined influence of simultaneous changes in atmospheric pCO_2 and seawater A_T on dissolved inorganic carbon (DIC), proton concentration $[\text{H}^+]$, and calcium carbonate saturation (Ω_{CaCO_3}) in the Central Baltic Sea from 1995 to 2014. Based on an atmospheric pCO_2 increase from 360 to 400 μatm , the relative changes in DIC, $[\text{H}^+]$, and Ω_{CaCO_3} were computed for two A_T scenarios: The observed A_T trend of $+3.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ was taken into account (black bars) and the A_T was assumed to be constant at mean A_T (grey bars). Computations were performed for $S = 7$, $T = 10^\circ\text{C}$ and with the dissociation constants from Millero (2010).

2014 the mean salinity and A_T were 7 and 1587 $\mu\text{mol kg}^{-1}$, respectively. Taking the positive A_T trend of $+3.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ into account, the A_T rose from around 1550 to 1620 $\mu\text{mol kg}^{-1}$. 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 $\mu\text{mol kg}^{-1}$ 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 $\mu\text{mol kg}^{-1}$, which corresponds to a relative change of 5% (Fig. 8). The DIC gain of around 70 $\mu\text{mol kg}^{-1}$ 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 concentration. 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 $\mu\text{mol kg}^{-1}$, but with A_T increasing in parallel this is reduced to a marginal change from

40.9 to 40.4 $\mu\text{mol kg}^{-1}$. 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 (Ω_{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 20th 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 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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Conflict of Interest

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