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Factors influencing the acid–base (pH) balance in the Baltic Sea: a sensitivity analysis

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ABSTRACT

Using calculations based on the marine carbon system and on modelling, the sensitivity of Baltic Sea surface pH was examined. Transient long-term calculations demonstrated that the marine carbon system adjusts to lateral boundary conditions within some decades, as does salinity. Climate changes in temperature or salinity will only marginally affect the acid–base (pH) balance. Wetter or dryer climate will also play a minor role in the pH balance. The direct effect on seawater pH of acid precipitation over the Baltic Sea surface was demonstrated to be small. Acidification due to river transport of dissolved organic carbon (DOC) into the marine system seems marginal although mineralization of terrestrial DOC may cause extra marine acidification, but the effect has yet to be quantified. Increased nutrient load may increase the amplitude in the pH seasonal cycle and increase the acidification during winter time. Fossil fuel burning is likely to have both a direct and indirect effect through increased CO_2 levels, altering seawater pH as well as changing the river chemistry. This may severely threaten some species in the Baltic Sea, particularly in the Northern Baltic.

1. Introduction

Seawater pH is among the most important factors controlling life in marine systems, and acidification could severely alter and threaten marine ecosystems (Doney et al., 2009). Rising atmospheric carbon dioxide levels attributable to human activity have been demonstrated to have already reduced ocean pH by approximately 0.1 units, and are likely to reduce it even more in the future. According to recent estimates, a reduction of up to 0.4 pH units over the coming 100 yr is possible (IPCC, 2007). There are also suggestions that acid precipitation may increase the acidification of coastal seas, which then may lead to even more severe conditions (Doney et al., 2007) in the absence of other processes damping coastal acidification. Numerical model simulations have demonstrated that the CO_2 system of coastal seas will be significantly affected if atmospheric CO_2 levels increase simultaneously with changed river transport of organic matter and nutrients (Andersson et al., 2006). Model calculations indicate a shift in coastal seas, from being sources of atmospheric carbon in pre-industrial times to sinks in the modern era of industrialization and eutrophication (Andersson et al., 2006; Gypens et al., 2009; Omstedt et al., 2009). Model studies also illustrates that the carbon chemistry in coastal waters may respond stronger to eutrophication than ocean acidification (Borges and Gypens, 2010). Understanding pH changes in coastal regions characterized by high biological production and several anthropogenic mechanisms, such as climate change, land-use change, eutrophication and overfishing, is therefore crucial.

The sea water acid–base (pH) balance is characterized by the total alkalinity, A_T, which is defined as the excess of proton acceptors (anions of weak bases) over proton donors (strong acids). The major proton acceptors in seawater are hydrogen carbonate (HCO_3^-, 95.5%), carbonate (CO_3^{2-}, 4%) and borate ($B(OH)_4^-$, 0.5%) ions, whereas hydrogen ions (H^+) and hydrogen sulphate ions (HSO_4^-) act as proton donors. A_T is impacted by, for example, dissolution of limestone through the increase of carbonate ions. This addition of carbonate ions strengthens the buffering capacity (A_T) and increases the pH. The addition of weak acids such as CO_2, which does not affect A_T, lowers the pH. However, the effect is small since most of the added CO_2 reacts with CO_3^{2-} (buffer reaction: $CO_2 + CO_3^{2-} + 2H_2O \leftrightarrow 2HCO_3^-$) and only a small fraction of the CO_2 adds hydrogen ions to the system by dissociation of H_2CO_3 to HCO_3^- and H^+. The problem is that when enough carbonic acid (or any other acid) has been added, there are not enough carbonate and bicarbonate ions left, and with further additions, pH decreases more

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rapidly. This has been observed in freshwater systems exposed to airborne sulphuric acid, though freshwater systems have in general much weaker buffering capacities than do marine systems. Some fresh water systems may also have high A_T due to the geology in the drainage area. In addition, primary production (uptake of carbon dioxide) and mineralization (release of carbon dioxide) greatly influence the pH balance, with daily, seasonal and interannual variations being observed in coastal regions (Wootton et al., 2008). Large spatial gradients in pH and pCO_2 are also observed in coastal regions (e.g. Borges and Frankignoulle, 1999; Schneider et al., 2006)

The Baltic Sea ranges from marine to nearly limnic conditions, and the salinity is strongly influenced by freshwater input from rivers and direct precipitation. Brackish water is often defined as saline water that has a freezing point below the temperature of maximum density. The upper salinity limit is 24.7 and the lower limit is estimated to be 0.5 (Leppäranta and Myrberg, 2009). This range represents the surface salinities ranging from the Kattegat surface water to the river mouths in the northern Bothnia Bay. The A_T displays strong horizontal and vertical variation (Hjalmarsson et al., 2008) due to inflowing high-salinity and high-A_T waters that mix with waters from rivers with different A_T values due to the mineralogy of the different drainage basins. Calcium carbonate is almost under-saturated in the winter in the Baltic Sea, which may explain the absence of coccolithophores (Tyrell et al., 2007).

This study examines the sensitivity of the pH balance in the Baltic Sea surface water. To do this, we perform a study based on theoretical calculations from the marine carbon system and on modelling using a simple Baltic Sea box model and a transient, fully coupled Baltic Sea biogeochemical multi basin model. By using different models the sensitivity over a large variation can be investigated. We start by examining observed pH data from the central Baltic Sea and their variability. Then we investigate the pH sensitivity to changes in temperature, salinity, carbon dioxide partial pressure, and A_T. After this, we examine the influence of river water, Kattegat/Skagerrak water, and acid precipitation. Then the results of some long-term transient numerical experiments are presented and discussed. Finally, we summarize the study and present some conclusions.

2. Background

2.1. Observations and variability

Most statements about ocean acidification are based on model experiments, while field observational data are often lacking on longer time scales (e.g., decadal). Important time series, such as Bermuda-Atlantic Time-series Station (BATS), Hawaii Ocean Time Series (HOT) and European Station for time series in the Ocean at the Canary Islands (ESTOC), indicate a reduction in pH over the last decade in line with increases in atmospheric CO_2. However, only one longer time series of ocean pH is available at a high time resolution (i.e. hourly) (Wootton et al., 2008); it is based on eight years of measurements from Tatoosh Island (Washington state, USA). These data indicate clear daily, seasonal and interannual variations as well a declining trend in pH. The variability is much larger than would be expected from increasing atmospheric carbon dioxide concentrations, indicating that other processes are important, such as diurnal oscillation in photosynthesis and respiration, variation in seasonal cycles, interannual variation and upwelling.

Monitoring data for Baltic Sea pH are typically based on 1 or 2 measurements per month. The Swedish data are believed to be reliable starting from 1993 (Anderson, ed., 2008), with a measurement accuracy of ± 0.015 pH units. The corresponding accuracy for A_T is approximately $\pm 2.5\%$ (Wesslander, 2009, personal communication). Fig. 1 presents data from the central Baltic Sea, which indicate a clear seasonal cycle (Fig. 1b) and interannual variations (Fig. 1c) but no clear trend for this short period (Fig. 1a). The interannual variation is about ± 0.1 pH units and the seasonal variation is approximately ± 0.2 pH units.

The trend in pH based on model calculations from the start of industrialization, considering only increased atmospheric carbon dioxide, has been calculated to 0.1 pH units over the last 250 yr (e.g. IPCC, 2007). The corresponding trend calculated from 15 yr of observations is thus much smaller. Using decadal data for trend analysis and interpreting the results as indication of long-term climate change can therefore be misleading. In addition, trend analysis gives no information outside the observation interval and provides little mechanistic explanation (BACC, 2008). Similar warnings based on a model study of the North Atlantic were recently provided by Gruber (2009).

From the mechanisms controlling pH, we should expect that the seawater pH in coastal regions may exhibit regional differences as well as variability on all time scales. Variations on decadal and centennial time scales in the Baltic Sea–North Sea region are well known for several parameters, such as air temperature (BACC, 2008), wind (BACC, 2008; Siegismund and Schrum, 2001), salinity (Winsor et al., 2001, 2003), river runoff (Bergström and Carlsson, 1994 Hansson et al., 2010) and sea ice (Eriksson et al., 2007; Hansson and Omstedt, 2008). For example, a wavelet analysis by Eriksson et al. (2007) demonstrated that there was considerable variability in winter temperatures and in ice also on longer time scales.

The deposition of sulphur compounds in the Baltic Sea drainage basin has decreased to less than half the levels recorded in the 1970s (Mylona, 1996). In southern Scandinavia, decreasing sulphate levels have been followed by increasing base cation concentrations and alkalinity (Fölster and Wilander, 2002; Finer et al., 2004). In the northern part of the region, acid deposition has generally been lower, and mainly been attributed to episodic acidification (Laudon et al., 2001). Although there has been a general amelioration of the episodic acidification of limnic water in recent decades (Laudon and Bishop, 2002), the effect of

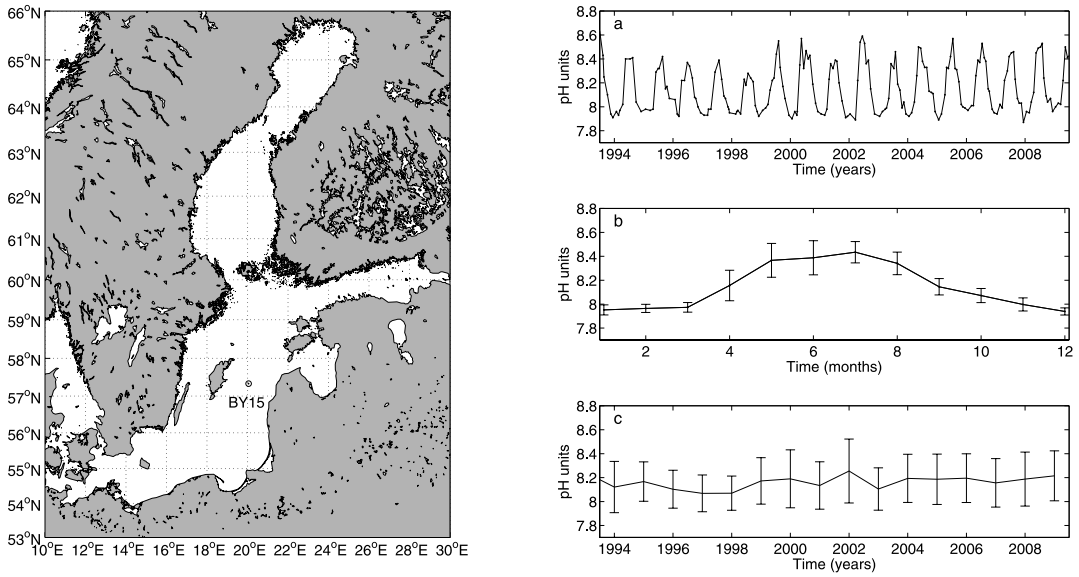

Fig. 1. Observed pH variation in the Gotland Deep in the central Baltic Sea, including a map. Panels (a)–(c) present measured pH during the period 1994 to 2008, bars indicate the standard deviation. (a) Actual time-series, (b) Seasonal variations and (c) Interannual variations.

the deposition decline on the sulphate trend of stream water in the region has been negligible (Fölster and Wilander, 2002; Vuorenmaa and Forsius, 2008). One exemption to the general acidification recovery can be found in coastal areas of both Sweden and Finland that have undergone isostatic uplift. Ditching and other human activity in these post-glacial sediments has resulted in the oxidation of marine sulphur (Mörth et al., 2008; Åström, 2005) and the consequent acidification of many coastal streams (Österholm and Åström, 2002).

The large interannual variability of water chemistry in limnic systems can mainly be attributed to climate variations. Large water fluxes produce a general decline in buffering capacity due to dilution, making streams and rivers more sensitive to pH decline (Buffam et al., 2007). The generally wetter years Scandinavia experienced in the 1990s and early 2000s could therefore have contributed to a more diluted buffering capacity in river runoff in this period. A common feature of many streams and rivers in recent decades has been increasing levels of dissolved organic carbon (DOC). This trend, found across northern latitudes (Monteith et al., 2007), has also been found in more regional studies such as from Sweden (Erlandsson et al., 2008a), and from Finland (Vuorenmaa et al., 2006; Lepisto et al., 2008). Several mechanisms explaining this increasing trend have been postulated. These include climate variability, declining acid deposition and land-use change. The increasing DOC trend has generated considerable interest, as it plays a central biogeochemical role in surface waters, including effects on light attenuation (Karlsson et al., 2009), trace metal complexation (Shafer et al., 1997) and microbial substrate sources (Berggren et al., 2007). DOC also strongly controls pH in most low-buffered boreal surface waters (Köhler et al., 2000; Hruska et al., 2003), so increasing DOC slows down or even reverses acidification recovery in many limnic systems (Erlandsson et al., 2008b).

With the increasing DOC levels observed in many surface waters follows a likely increase in the partial pressure of CO_2 (pCO_2). DOC and pCO_2 are strongly correlated in both lake water (Sobek et al., 2003) and river water (Laudon and Buffam, 2008), and most of these systems experience a large oversaturation compared to the pCO_2 of the atmosphere. Excluding small first-order streams (Öquist et al., 2009), this suggests that the pCO_2 is primarily controlled by the mineralization of organic carbon in the water and that increased DOC in lake or stream water will also likely lead to an increase in surface water pCO_2, implying that river runoff is often oversaturated when entering the Baltic Sea (Jones et al. 2003; Raymond et al., 2008; Humborg et al., 2010; Teodoru et al., 2009). River transport of DOC may contribute considerable to the carbon budget in the Baltic Sea (Algesten et al., 2006; Sandberg et al., 2004). Part of this organic material is available for bacterial mineralization and transformation to CO_2. Recent estimations indicate that the mineralization of the river transported organic matter takes place close to the river mouth (van Dongen et al., 2008). But the effect of river DOC on coastal seas acid-base balance has yet to be identified and further research is needed.

2.2. *Theory and limitations*

The pH balance under coastal and ocean conditions is often studied using solubility and dissociation constants for carbonic acids, dissociation constants for boric acid, and ionic product of water. This is also the main approach in this study.

We use the total pH scale $\{H^+\} = [H^+] + [HSO_4]$ throughout this section and in all calculations, except when noted. For the marine system, the constants are salinity and temperature dependent (Dickson et al., 2007). The constants are viable for the pH^{tot} scale when the following equilibrium constants are used: K_0 (see eq. 1; Weiss, 1974), K_1 and K_2 (see eqs 2 and 3; Millero et al., 2006), K_B (see eq. 4; Dickson, 1990), and K_W (see eq. 5; Hansson, 1973). Millero et al. (2006) constants are consistent with the constants for fresh water and developed for a wide salinity and temperature range. A limitation is that the constants assume that seawater is diluted with pure water. In this study, we concentrate on surface water properties and neglect the carbon chemistry in anoxic deep waters and sediments. The constants are given in Appendix A. The marine inorganic carbon system includes

$$K_0 \approx \frac{\left[CO_2^*\right]}{pCO_2} \tag{1}$$

$$K_1 = \frac{\left[HCO_3^-\right]\{H^+\}}{\left[CO_2^*\right]} \tag{2}$$

$$K_2 = \frac{\left[CO_3^{2-}\right]\{H^+\}}{\left[HCO_3^-\right]} \tag{3}$$

$$K_B = \frac{\left[B(OH)_4^-\right]\{H^+\}}{[B(OH)_3]} \tag{4}$$

$$K_W = \{H^+\}[OH^-], \tag{5}$$

where $CO_2^* = CO_2 + H_2CO_3$. The four carbon system parameters are: pH—a measure of the H^+ concentration, here according to the pH^{tot} scale (see eq. 6); A_T—total alkalinity, the surplus of proton acceptors over proton donors (see eq. 7); C_T—total dissolved inorganic carbon (see eq. 8); and pCO_2—the partial pressure of carbon dioxide.

$$pH_{tot} = -\log(\{H^+\}), \quad \text{where } \{H^+\} = [H^+] + [HSO_4] \tag{6}$$

$$A_T = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] - \{H^+\} + \left[OH^-\right] \tag{7}$$

$$C_T = [CO_3(aq.)] + \left[H_2CO_3\right] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right]. \tag{8}$$

For a more detailed description of the marine inorganic carbon system, see Zeebe and Wolf-Gladrow (2001). When investigating the effects of acid precipitation, $-[H^+]_P$ is added to eq. (7); see further discussion in Section 3.4.

An analytical expression for pH, based on a simplification in which only the inorganic carbon system (without $[B(OH)_4^-]$ and neglecting minor contributions to A_T and C_T) is considered, can be derived, starting with eq. (3), as follows:

$$[H^+] \approx K_2\left(\frac{C_T}{\Delta} - 1\right) \approx K_2\frac{C_T}{\Delta}, \quad \text{where } \Delta = A_T - C_T. \tag{10}$$

This expression allows for an estimated, and more direct, understanding of what drives pH change, which is helpful when interpreting the results. Usually Δ, the difference between the concentration of A_T and C_T, is assumed to have the main influence on pH, but it should be noted that the actual magnitude of C_T is also present in eq. (10). This means that an increase in C_T gives an increase in H^+ (lower pH) when Δ is constant or changes slightly. Another implication is that an increase/decrease of Δ will increase/decrease pH.

A biologically important parameter closely related to the carbon system is the saturation state (Ω) of calcium carbonates. A saturation of 1.0 indicates that the solid face of the calcium carbonate in question is in equilibrium with the dissolved components. The saturation state of calcite and aragonite in seawater can be calculated from:

$$\Omega = \frac{\left[CO_3^{2-}\right][Ca^{2+}]}{K_{C/A}}, \tag{11}$$

where $K_{C/A}$ is the solubility product for either calcite or aragonite. The CO_3^{2-} concentration is dependent on the speciation of the carbon system, while the calcium ion concentration, expressed in mmol kg^{-1}, is dependent on salinity according to the relationship $Ca^{2+} = 0.331S + 0.392$ for the central Baltic Sea (Dyrssen, 1993). The solubility constants ($K_{C/A}$) are dependent strongly on pressure, temperature and, especially, salinity; this study uses the temperature and salinity relationships derived in Mucci (1983) and neglect pressure effects that are important only for the deep water CO_2 system.

2.3. Analytical and model calculations

The sensitivity study will be performed using three different tools. We will first investigate steady-state response characteristics, and the analytical calculations will use the equations presented in Section 2.2. Second, we will use a simple box model system (see Appendix B and Fig. 2) to calculate the solutions for different forcing conditions. The box model divides the Baltic Sea into a surface box and a deep water box. The box model takes into account fresh water and deep water inflows to the Baltic Sea and corresponding transports of A_T and C_T . The flows are generally kept constant throughout the box-model calculations, while the chemical properties that are not varied and are kept at their representative values according to Table 2, where also the ranges

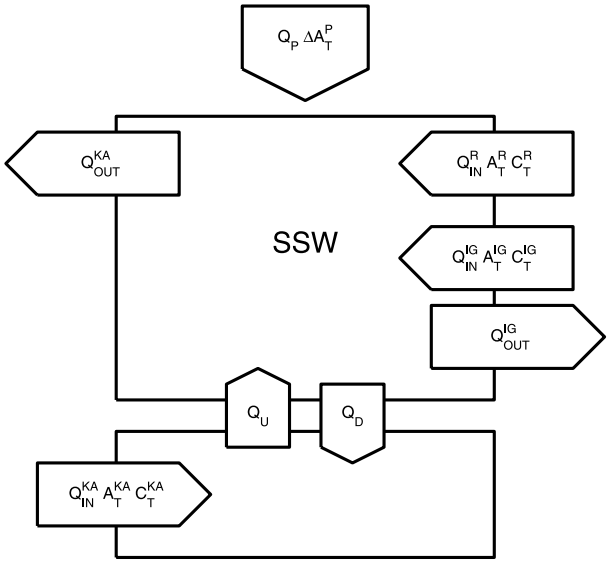

Fig. 2. Schematic depiction of the steady-state two-box model used in this study. In the model description, the letter Q indicates flows and the indices U and D stand for internal exchange between the boxes, that is, up and down flows. The indices IN and OUT indicate the in- and outflows. KA and IG stand for the Kattegat and the Inner Gulfs of the Baltic. P stands for precipitation and R indicates river properties. ΔA_T is the titration power of acid rain, or in other words, negative alkalinity associated with precipitation. SSW is an abbreviation of Surface Sea Water.

Table 1. The parameters defining the modelled area. All values are from Hjalmarsson et al. (2008) except where noted

Parameter	Baltic proper (winter)	Units
Basic set-up values that define the area		
S_S	7.5	–
S_D	9.81	–
S_{KA}	23.7	–
S_{IG}	5.66	–
T	0	°C
Area	8.97	10^{10} m^2
Q_F[a]	3.90	10^3 m^3 s^{-1}
Q_R	3.60	10^3 m^3 s^{-1}
Q_P	1.71	10^3 m^3 s^{-1}
$Q_{IN}{}^{KA}$	9.00	10^3 m^3 s^{-1}
$Q_{IN}{}^{IG}$	56.1	10^3 m^3 s^{-1}
$Q_{OUT}{}^{KA}$	24.8	10^3 m^3 s^{-1}
$Q_{OUT}{}^{IG}$	44.1	10^3 m^3 s^{-1}
Q_U	57.1	10^3 m^3 s^{-1}
Q_D	48.1	10^3 m^3 s^{-1}
Chemical forcing that defines the area		
$A_T{}^{KA}$	2007	μmol kg^{-1}
$A_T{}^{R}$	3221	μmol kg^{-1}
$A_T{}^{IG}$	1345	μmol kg^{-1}
ΔA_T[b]	–31.6	μmol kg^{-1}
$pCO_2{}^{KA}$	380	μatm
$pCO_2{}^{R}$	760	μatm
$pCO_2{}^{IG}$	380	μatm

[a]Freshwater inflow $Q_F = Q_R$ +Area(Precipitation – Evaporation).
[b]Values for $pH_P = 4.5$ and precipitation = 600 mm yr^{-1}.

in the sensitivity study are given. Some check values are given in Table 3. The only flow that has been varied is the volume flow of precipitation (Q_P). Temperatures and salinities are kept constant according to Table 1.

Third, the transient response characteristics will be investigated using a fully coupled physical–biogeochemical Baltic Sea multi basin model (Omstedt et al., 2009). The transient model is built on conservation equations in their one-dimensional, time-dependent form and divides the Baltic Sea into thirteen natural subbasins with vertical resolution in each. The coupling between the subbasins is effected through strait flow models. The vertical structures are resolved using time-dependent boundary conditions calculated from observed meteorological conditions, sea levels from the Kattegat and Baltic Sea river inflow. The physical part of the model includes six equations representing conservation of momentum (two equations), heat, salinity, turbulent kinetic energy, and dissipation of turbulent energy. The chemical part includes two equations for acid and basic carbon (which are transformed to total alkalinity and total inorganic carbon), oxygen, and nutrients (three equations). The biological part includes two equations representing the depth- and time-dependent phytoplankton abundance. The first equation is a measure of species that are limited by both nitrogen and phosphorus availability, whereas the second treats species that are able to fix N_2 and thus are limited by phosphorus only. The full description is given in Omstedt et al. (2009).

3. Theoretical calculations

3.1. Influence of salinity and temperature on pH

The pH sensitivity to temperature and salinity changes is depicted in Fig. 3. In the calculations, A_T and pCO_2 are kept constant, so the calculations only represent the temperature and salinity dependency of the solubility and dissociation constants. Temperature variation of 5 °C may change the pH by only approximately ±0.01 pH units, while a change in salinity of 5 units implies a pH change of less than 0.1 units. We may conclude that direct climate change within the currently estimated ranges of temperature (several degrees) and salinity (some salinity units) (BACC, 2008) will only marginally affect the pH balance. Climate change will instead change pH through other processes, as discussed in the following sections. We may also conclude that oscillations and trends in pH data on annual and decadal time

Table 2. Presentation of the parameters that are varied in the analytical and box-model calculations

Parameter	Unit	Constant representative values	Range
Analytical variations			
Temperature	°C	0	0–30
Salinity	–	7.5	0–30
pCO_2	μatm	380	38–1140
A_T	μmol kg^{-1}	1550	180–4500
Box-model variation			
$fCO_2{}^R$	μatm	760	0–2280
$A_T{}^R$	μmol kg^{-1}	3221	0–4500
$A_T{}^{KA}$	μmol kg^{-1}	2007	0–4500
pH_P	–	4.5	3.0–6.0
Precipitation	mm yr^{-1}	600	0–1800
A_T-dependent derived C_T variation for the box model			
$C_T{}^R$	μmol kg^{-1}	–	$\begin{bmatrix} 0 & 0 \\ 183.7 & 4667 \end{bmatrix}$
$C_T{}^{KA}$	μmol kg^{-1}	–	32–4321

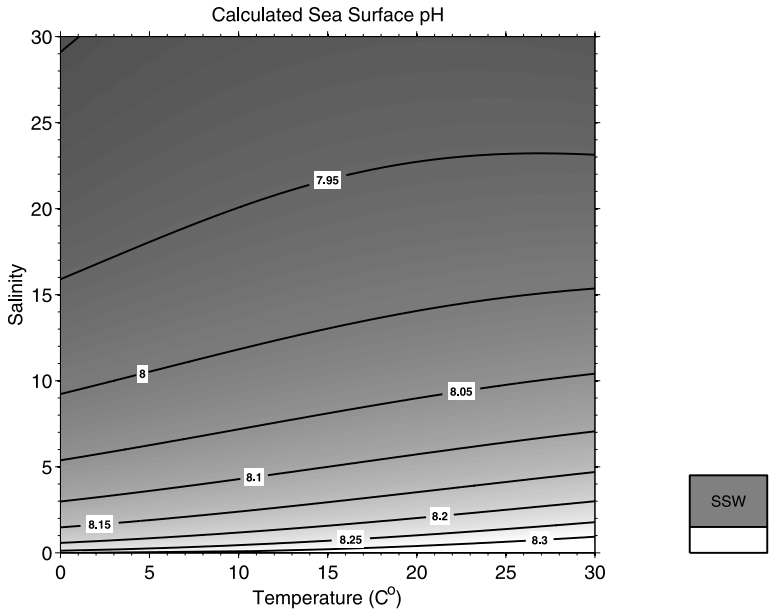

Fig. 3. Change of pH^{tot} with variation in salinity and temperature. A_T is kept at 1550 μmol kg^{-1} and atmospheric pCO_2 is kept at 380 μatm throughout the calculations. SSW is an abbreviation of Surface Sea Water.

scales cannot be explained by temperature and salinity changes alone.

3.2. *Influence of atmospheric carbon dioxide and surface water alkalinity on pH*

In these calculations, we have varied pCO_2 and A_T in the surface sea water but kept salinity and temperature constant and equal to 7.5 (psu) and 0 °C, respectively. As atmospheric carbon dioxide levels increase, they will equilibrate with surface waters and result in increased surface water pCO_2, though other processes can work in the opposite direction. If limestone goes into solution, the buffer effect may increase and pH may increase. By knowing two variables (in this case, A_T and pCO_2), one can calculate pH directly from the carbonate system (Section 2.2). This has been done and the results are presented in Fig. 4. The pH sensitivity to change in A_T varies throughout the Baltic Sea, the greatest impact being anticipated in the north where A_T is the lowest. The buffer effect is illustrated by the pH curves becoming less steep at high A_T values.

In general, pCO_2 is affected by several different processes and thus often deviates from atmospheric CO_2 levels, raising the question of whether the Baltic Sea is a sink or source of atmospheric CO_2. Modelling suggests that the water partial pressure

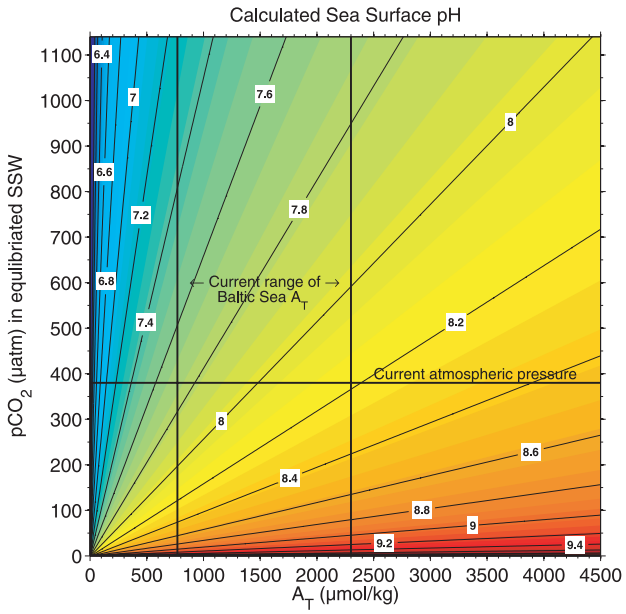

Fig. 4. Change of pH^{tot} with variation in water carbon dioxide pressure and A_T. Salinity is kept at 7.5 and temperature at 0 °C throughout the calculations. Indicator lines show the current status of the area with regard to A_T (Hjalmarsson et al., 2008) and atmospheric carbon dioxide pressure. SSW is an abbreviation of Surface Sea Water.

of carbon dioxide were above atmospheric values before industrialization, with a net release of CO_2 to the atmosphere. Seasonal variability increased in the modern industrialization era with the inclusion of eutrophication, making the Baltic Sea both a sink and source of CO_2 to the atmosphere (Omstedt et al., 2009). Calculation based on measurements also indicates that the difference between the partial pressure in water and in air changes over seasonal, interannual and regional scales (Algesten et al., 2004). However, if a long-term change in the atmosphere pCO_2 occurs, the surface water pCO_2 are expected to follow this increase and to assume equilibrium is an approximation.

An increase in atmospheric CO_2 levels of 100 μatm from pre-industrial (280 μatm) to present levels, assuming an A_T of 1550 μmol kg^{-1}, will result in a decrease of ~0.1 pH units in Baltic Sea surface waters, if no other processes interact. For the same A_T, doubling or tripling pre-industrial atmospheric CO_2 levels (560 and 840 μatm, respectively) will result in a decrease from pre-industrial conditions of ~0.3 and ~0.5 pH units, respectively (see Table 3).

Reducing the winter surface water pH by ~0.1 pH units by means of a change in A_T would require that A_T be lowered by ~165 μmol kg^{-1} in the low-buffered northern parts of the Baltic Sea (A_T ~ 800 μmol kg^{-1}) and by ~425 μmol kg^{-1} in the high-buffered Kattegat (A_T ~ 2000 μmol kg^{-1}). Increased atmospheric CO_2 levels in combination with reduced A_T concentrations may cause severe pH decline.

Table 3 presents some results of the present sensitivity study of the winter saturation state of $CaCO_3$, starting from Baltic Sea winter conditions. When CO_2 is taken up by from the atmosphere the CO_3^{2-} concentration decreases, according to $CO_2 + CO_3^{2-} \rightarrow 2HCO_3^-$, and the saturation state decreases. Only at high A_T or pre-industrial atmospheric CO_2 levels is the calcite saturation state above 1.0 during winter conditions. The solubility of CO_2 decreases when the surface water warms up in the spring resulting in an increase in pCO_2 that drives a flux of CO_2 to the atmosphere. However, spring bloom in the Baltic Sea coincides with the start of surface warming and since the biological effect on the in pCO_2 dominates over the temperature effect surface waters are undersaturated during spring and the flux of CO_2 to the atmosphere does not occur. Furthermore when primary production occurs CO_2 is consumed that further decreases the concentration of CO_2. Hence spring and summer values of the saturation state of $CaCO_3$ are higher than those during winter.

3.3. *Influence of river water and seawater on pH*

The effect on pH of increasing DOC concentrations in river runoff into the Baltic Sea was estimated using a dissociated organic acid anion model developed by Hruska et al. (2003) and used to calculate the effect on changes in the pH of river water by Laudon and Buffam (2008). Varying the DOC concentration by 50% while keeping pCO_2 and remaining inorganic chemistry constant resulted in a less than 0.03 pH unit increase/decrease in seawater pH. Although the organic acid anion model not primarily was developed for marine systems, the results provide an indication that the DOC increase will not have a direct pH effect. However, the mineralization of DOC to dissolved inorganic carbon (DIC) may reduced pH further, but the effect has yet to be quantified and merits further research.

To evaluate how the Baltic Sea carbon system responds to land-derived changes, the inorganic forcing associated with rivers, pCO_2^R and A_T^R, were simultaneously varied in the box model. All other parameters were kept constant (see Tables 1

Table 3. Changes in pH^{tot} and the saturation state (Ω) of calcite and aragonite that occur as some of the investigated parameters are varied

Winter conditions: $S = 7.5$ and $T = 0$ °C		Analytical and box modelling		
Varied variable	Variations	pH	Ω (Calcite|Aragonite)	
Analytical				
pCO_2 in atmosphere (μatm) while $A_T = 1550$ (μmol kg^{-1})	280	8.15	1.19	0.65
	380	8.02	0.90	0.49
	560	7.86	0.62	0.34
	840	7.68	0.42	0.23
A_T (μmol kg^{-1}) while $pCO_2 = 380$ (μatm)	1000	7.83	0.38	0.21
	1500	8.01	0.84	0.46
	2000	8.13	1.47	0.80
Box-model				
$pCO_2{}^R$(μatm) while other parameters are keep constant (Table 2)	380	7.99	0.82	0.45
	760	7.97	0.79	0.43
	1000	7.96	0.78	0.42
$A_T{}^R$ (μmol kg^{-1}) while other parameters are keep constant (Table 2)	2700	7.97	0.77	0.42
	3200	7.97	0.79	0.43
	3700	7.97	0.81	0.44
$A_T{}^{KA}$ (μmol kg^{-1}) while other parameters are keep constant (Table 2)	1500	7.95	0.72	0.39
	2000	7.97	0.79	0.43
	2500	8.00	0.87	0.48
pH_P while other parameters are keep constant (Table 2)	3.5	7.92	0.70	0.38
	4.5	7.97	0.79	0.43
	5.5	7.98	0.80	0.44
Precipitation (mm yr^{-1}) while other parameters are keep constant (Table 2)	400	7.97	0.80	0.43
	600	7.97	0.79	0.43
	800	7.97	0.79	0.43

Notes: The chemical properties not varied are kept at their representative values according to Table 2. Temperature and salinity are kept at the area-defining values in Table 1. A_T and pCO_2 in the surface box are within the variability of the surface water parameters detected at station BY15 (see Fig. 1) for the 1994–2004 period, during which the listed box-model variations occurred.

and 2). Temperature and salinity were also kept constant at 0 °C and 0 (psu), respectively, to mimic winter river conditions, for which C_T from rivers was calculated from different combinations of pCO_2^R and A_T^R. The resulting seawater pH is shown in Fig. 5. The pH sensitivity to changes in pCO_2^R is quite small; for example, with a change in pCO_2^R in rivers from 380 to 1000 μatm, while A_T^R is kept at 3221 μmol kg^{-1}, the change in pH is only 0.03 (see Table 3).

To estimate to what extent sea surface pH in the Baltic Proper is affected by inflowing A_T^R concentrations from the Kattegat, or from the A_T^R of inflowing river water, these two sources of A_T were varied in the box model. All other parameters, including pCO_2, were kept constant according to Tables 1 and 2. Figure 6 shows that Baltic Sea pH generally increases as A_T in the rivers, or in the inflows from the Kattegat to the deep water, increases. However, the results indicate that pH in Baltic Sea surface waters is more sensitive to changes in the inflowing waters from the Kattegat, because this inflow volume is much greater and thus has a larger impact. Table 3 provides some numerical results exemplifying this phenomenon.

3.4. Influence of acid precipitation on pH

Acid precipitation affects the ocean surface carbonate system by titrating some of the A_T. Thus, acid precipitation can be considered as the addition of a given volume of water having a specific negative A_T (see eq. 7). In this way, an indirect and negative concentration of A_T can be assigned to precipitation of a

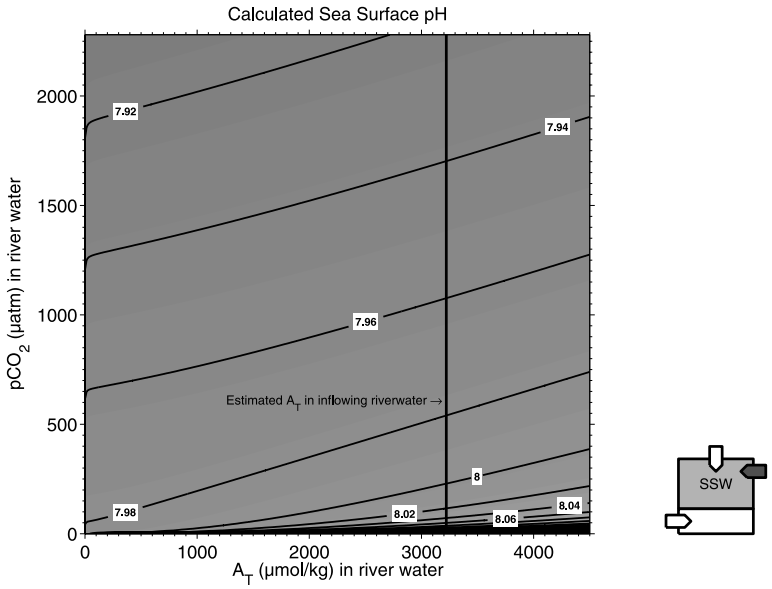

Fig. 5. The change of pH^{tot} in the surface box when pCO_2 and A_T are varied in river water of 0 °C and with zero salinity. All other inflowing concentrations, as well as salinity and temperature, are kept constant according to Table 2. Indicator line shows the current status of the area with regard to A_T^R (Hjalmarsson et al., 2008). SSW is an abbreviation of Surface Sea Water.

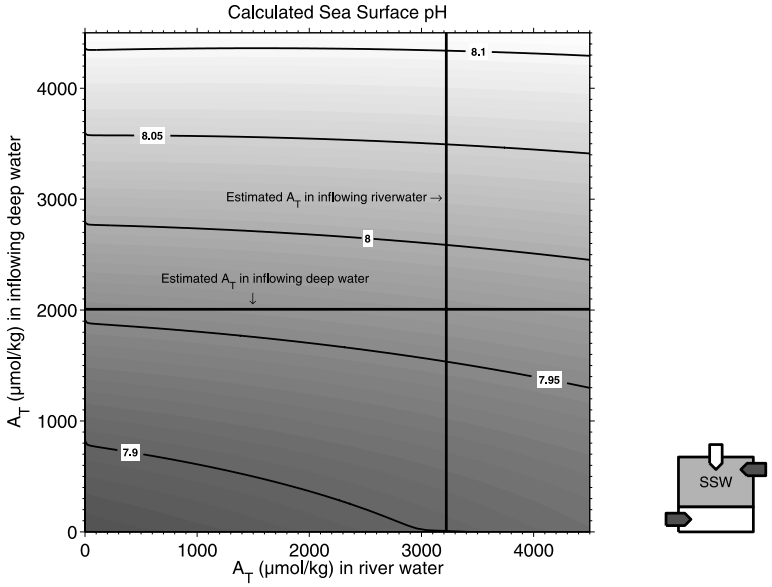

Fig. 6. The change of pH^{tot} in the surface box when A_T^R and A_T^{KA} are varied in water of 0 °C; the salinities of the different water sources are according to Table 1. All other inflowing concentrations, as well as salinity and temperature, are kept constant according to Table 2. Indicator lines show the current status of the area with regard to A_T^R and A_T^{KA} (Hjalmarsson et al., 2008). SSW is an abbreviation of Surface Sea Water.

certain pH value (pH_P). The H^+ activity coefficient was assumed to be unity throughout these calculations, for simplicity. Using estimated values of the pH of precipitation, we write

$$[H^+]_P = 10^{-\mathrm{pH}_P}. \tag{12}$$

Since A_T, per definition, is the excess of proton acceptors over proton donors, an increasing concentration of H^+ results in a corresponding decrease in A_T per m^3 of precipitation

$$\Delta A_T = -[H^+]_P. \tag{13}$$

C_T is not affected by acid rain, if one assumes no out gassing of CO_2 due to decreasing pH, and will therefore remain unchanged.

Figure 7 presents the calculated pH values in Baltic Proper surface waters during variations in precipitation rates and precipitation pH. Compiling current pH_P data and EMEP model results (Björn Carlsson, 2009, personal communication) yields a mean pH_P of approximately 4.5 over the last two decades throughout the Baltic Sea. It has been demonstrated that, at the current pH of precipitation, an increase or decrease of precipitated freshwater volume over the Baltic Sea will make almost no difference for sea surface pH values in the Baltic Proper. As well, at the current precipitation rate, the pH_P over the Baltic Sea must decrease to levels lower than those of the 1980s for any significant change in Baltic Sea pH to occur. A change in pH_P from 3.5 to 5.5, as seen in Table 3, will have a small impact on Baltic Sea surface pH levels.

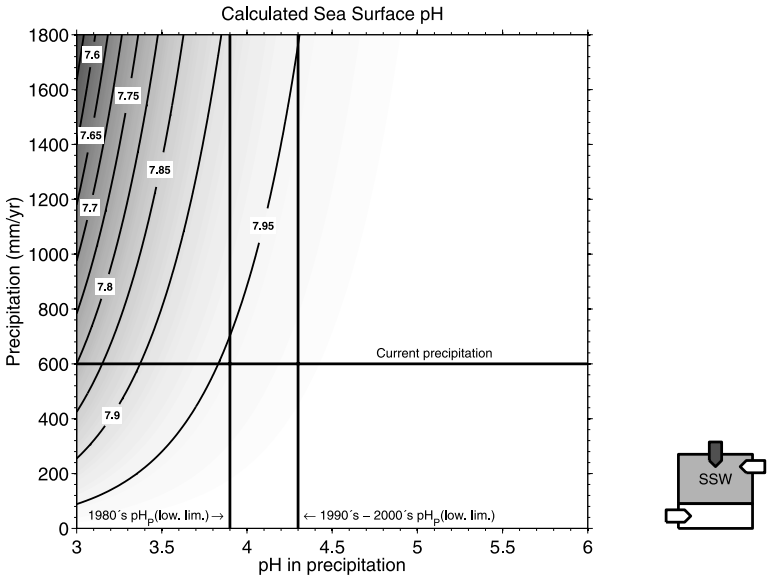

Fig. 7. The change of pH^{tot} in the surface box when the pH of precipitation and the precipitation volume are varied. All other inflowing concentrations, and salinity and temperature, have constant values according to Table 2. Indicator lines show the current and past pH_P status of the area (Björn Carlsson, 2009, pers. com.) and the annual precipitation (climate value of 0.6 yr^{-1} m^{-1}). SSW is an abbreviation of Surface Sea Water.

3.5. The transient dynamic

This work also used the fully coupled physical–biogeochemical model developed by Omstedt et al. (2009) to examine the transient pH dynamics in greater detail. In this model version we have made three major changes. First, the model includes new carbon constants where the dissociation constants K_1 and K_2 are now calculated according to Millero et al. (2006), see Appendix A. Secondly, the lateral boundary conditions for river run off are changed assuming that the total inorganic carbon concentration of river water is oversaturated and equal to 1350 μatm according to Humborg et al. (2010). Thirdly, the combination of new CO_2 constants and a new lateral boundary condition for river C_T indicated that the C:N:P ratios in primary production can be calculated using standard Redfield ratios (106:16:1) which were then applied in the present calculations.

The validation results are first illustrated in Fig. 8. From the calculations for the period since 1993, when observations are reliable, the figure depicts a clear seasonal cycle (Fig. 8 b1) with seasonal variation of approximately ±0.2 pH units, while the interannual variation (Fig. 8 c1) is ±0.1 pH units. The modelled and observed data are in good agreement (Fig. 8 a1). The variability can be further analysed when expanding the model data into a 100-yr simulation. In this model run, the atmospheric carbon dioxide concentrations were in line with observations, and at 1950, the nutrient input increased to present levels, representing modern industrialization with eutrophication (Omstedt et al., 2009). The model variability in seasonal pH increased by a factor of two, approximately ±0.1 pH units before 1950 (Fig. 8 b3) and by approximately ±0.2 pH units after 1950 (Fig. 8 b2). Increased biological production due to eutrophication can thus increase the pH variability considerably.

The stratification spin-up times were then analysed, by assuming that the Baltic Sea inside the Drogden and Darss sills was filled with freshwater, that is, salinity, A_T, C_T, and nutrients all equal zero, while outside the sills these properties were at ocean levels. The initial date in the calculation was put equal to AD 1700 and the numerical simulation ended in AD 2008. Similar experiments for salinity and temperature, earlier conducted by Omstedt and Hansson (2006a,b), found two important time scales to be considered: one associated with the water balance (salinity), with an e-folding time of approximately 33 yr; the other associated with the heat balance, with an e-folding time of approximately one year.

The results of the spin-up experiment are depicted in Fig. 9. The transient dynamics of A_T follow the salinity spin-up time with an e-folding time of some decades. Then the simulation stabilizes on the same level as has been observed in recent decades and close to observations. The pH calculations indicate oscillations in the initial state, but soon adjust to a level close to observations. The results illustrate that the surface water CO_2 system becomes adjusted to lateral boundary conditions within some decades similar to salinity. Long-term calculations are therefore mainly dependent on the lateral conditions, and thus on changes on land, in sediments, in the atmosphere, and outside the Baltic Sea.

The sensitivity of the pH balance to changes in nutrient load is examined in Fig. 10, where the standard run is compared with a run that assume reduced nutrient load according to pre industrial conditions. The standard run were forced using meteorological data, sea level data, river run off data and realistic atmospheric partial pressure of carbon dioxide increase. The load of nutrients was based on data regarding dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN) for the 1980–2000 period. For the period before 1950, we assumed pre-industrial

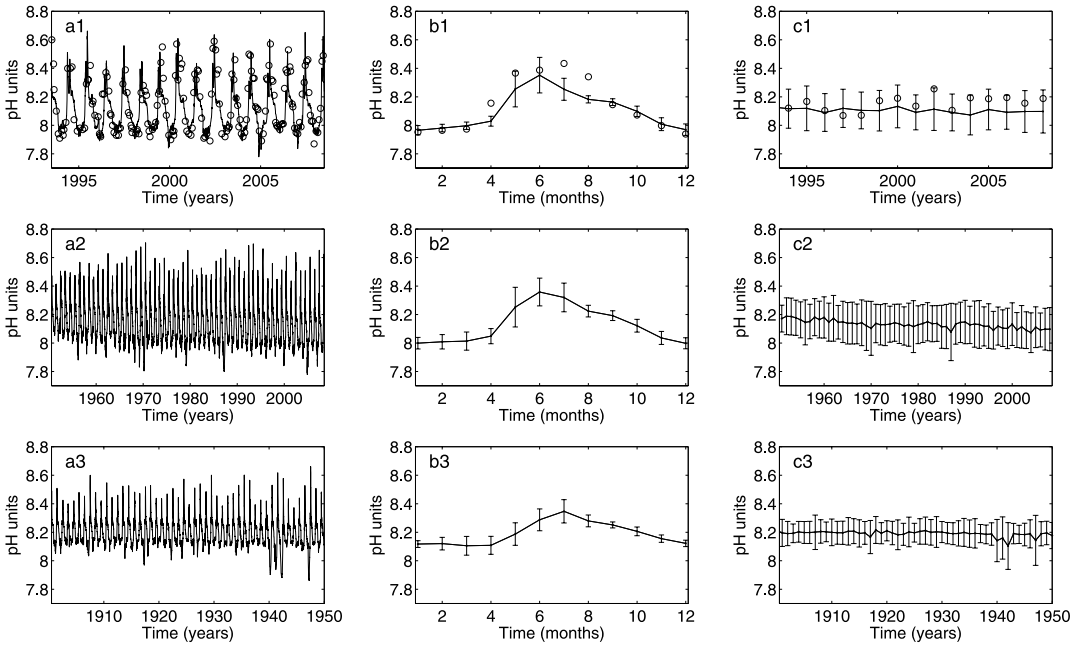

Fig. 8. Observed (circles) and modelled (fully drawn lines) pH variation from the Eastern Gotland Basin. Columns: (a) Actual time-series, (b) Seasonal variations and (c) Interannual variations. Rows: (1) The 1993–2008 period (for which observed data are available), (2) The 1950–2008 period representing the modern era of industrialization and eutrophication and (3) the 1900–1949 period representing the modern era of industrialization without eutrophication. The bars indicate the standard deviation.

conditions (total phosphorus and total nitrogen loads a third respectively a half of present conditions according to Savchuk et al., 2008) and a reduction in deep water mineralization rates. In the run with reduced nutrient load we assumed pre-industrial conditions for the whole period 1700–2008. The results illustrates that increased nutrient loads can increase the amplitude in the pH seasonal cycle with increased acidification during winter time but with only minor decadal changes.

The direct effects on changes in river runoff were analysed by running two numerical experiments that changed the runoff by $\pm 30\%$, one simulating a wetter climate and one simulating a dryer climate. All calculations started 1700 and were run to 2008 similar as the standard run. The variations in river runoff are quit large and the numerical simulations showed large changes in salinity, A_T and C_T. The result (Fig. 11) indicated however only minor decadal changes in pH due to compensating effects in the marine carbon system. Direct changes in the fresh water inflow to the Baltic Sea may thus only have minor effects on the pH balance but other effects associated with changes in river chemistry may cause larger effects.

4. Summary and conclusions

Factors influencing the pH balance in the Baltic Sea surface water were analysed based on theoretical considerations. This was performed in a sensitivity study based on calculations from the marine carbon system and from modelling using a simple box model and a transient, fully coupled biogeochemical model. By using different models the sensitivity over large variations were possible to investigate. The study started by examining observed pH data from the central Baltic Sea and their variability. Then the pH sensitivity to changes in temperature, salinity, partial carbon dioxide pressure and A_T were examined. The influence of river water, Kattegat/Skagerrak water, and acid precipitation were also tested. Then the results of some long-term transient numerical experiments were analysed and discussed. The conclusions of the study can be summarized as follows.

- The surface Baltic Sea carbon system becomes adjusted to the lateral boundary conditions within some decades. Long-term calculations are therefore dependent on changes on land, in sediments, in the atmosphere, and outside the Baltic Sea.
- Climate changes in temperature or salinity will only marginally affect the pH balance. Wetter or dryer climate will also play a minor role in the pH balance. Climate change may instead influence pH through other processes.
- The direct effect on seawater pH of acid precipitation over the Baltic Sea surface area is small, even with changed precipitation rates. Indirect effects on land (i.e. from acid precipitation and land-use change), however, may influence the pH balance.
- Acidification due to river transport of DOC into the marine system appears marginal. However, the mineralization of DOC into DIC may increase the acidification, though the effect in coastal seas has yet to be quantified.

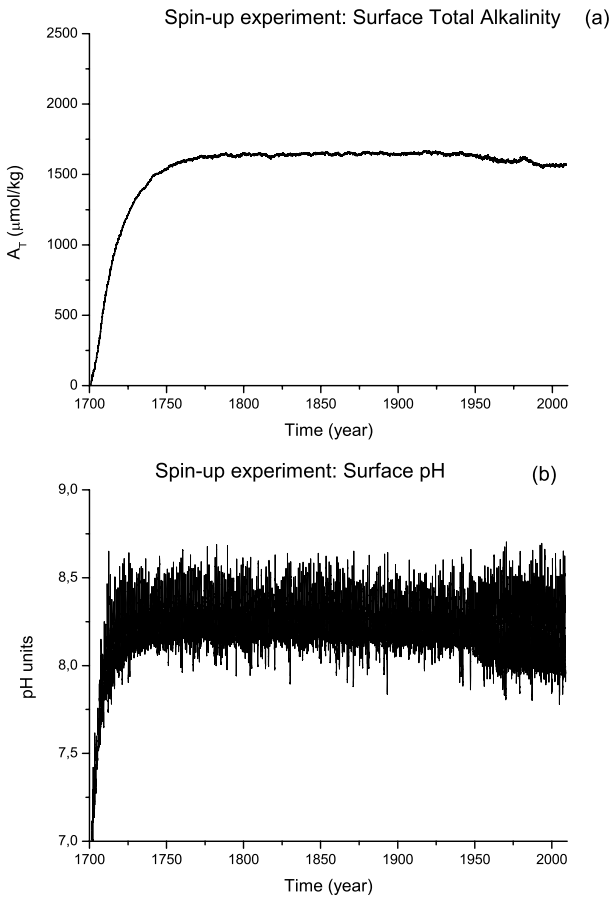

Fig. 9. Calculated total alkalinity (a) and pH (b) of the surface layer in Eastern Gotland Basin.

- Increased nutrient loads may increase the amplitude in the pH seasonal cycle and cause increased acidification during winter time.
- Increased atmospheric CO_2 levels reduce the pH of surface water, as reduced/increased A_T concentrations will decrease/increase the pH of surface water. A combination of increased atmospheric CO_2 levels and decreased A_T concentrations may cause severe reductions in water pH.
- The low-alkalinity regimes of the northern Baltic Sea are much more sensitive, resulting in larger changes in pH in response to any given perturbation of the driving conditions than in other Baltic Sea subbasins.

The study demonstrated that both atmospheric and land processes should be considered when evaluating measurements, designing monitoring programs, and developing models. Climate change and increased atmospheric CO_2 levels will not only influence the atmosphere–sea interaction but also changes in growth on land and changes in land–sea loads. This warrants further and more holistic research approaches that include the interacting effects of atmosphere, land, ocean and sediment processes as well as climate change scenarios.

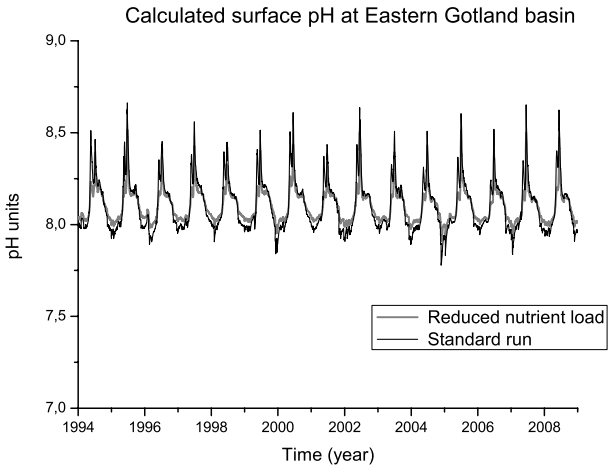

Fig. 10. Calculated surface water pH in Eastern Gotland Basin for reduced nutrient loading according to pre-industrial values (grey line) and present loading (black line).

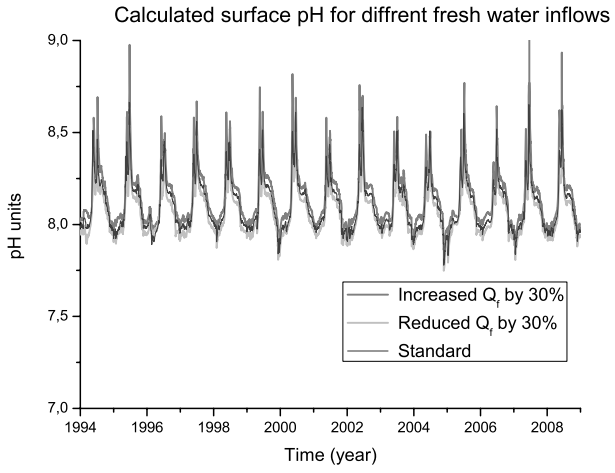

Fig. 11. Calculated surface water pH in Eastern Gotland Basin for different fresh water inflows to the Baltic Sea.

5. Acknowledgments

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Appendix A: The Carbon System Constants

Over the years several groups have determinated the stability constants for the marine inorganic carbon system, and the constants dependency on temperature and salinity. The results are not always directly comparable, since there are differences in pH and concentration scales among researchers. This appendix will be restricted to constants for concentrations expressed in

mol (kg seawater)$^{-1}$ and the total hydrogen ion concentration pH scale (pH^{tot}). Temperatures are expressed in Kelvin. Equations (A1)–(A5) presents the constants with their salinity (S) and temperature (T) dependency separated for easier access to the structure of the fittings. All five constants are expressed as logarithms, either the natural logarithm (ln) or with a base of ten (lg).

The solubility constant for CO_2 in sea water according to Weiss (1974) is expressed as follows:

$$\begin{aligned}
&\ln K_0 = A_0 + B_0 S \\
&A_0 = -60.2409 + 93.4517\frac{100}{T} + 23.3585\ln\left(\frac{T}{100}\right) \\
&B_0 = 0.023517 - 0.023656\frac{T}{100} + 0.0047036\left(\frac{T}{100}\right)^2.
\end{aligned} \tag{A1}$$

The dissociation constants K_1 and K_2 according to Millero et al., (2006) are presented in eqs (A2) and (A3). They have a range of 0–50 in T and 1–50 in S, thus this fitting of the constants make it possible to determine the state of the acid–base system in estuarine waters.

$$\begin{aligned}
&-\lg K_1 = A_1 + \frac{B_1}{T} + C_1 \ln T \\
&A_1 = -126.34048 + 13.4191 S^{0.5} + 0.0331 S \\
&\qquad -(5.33 \times 10^{-5}) S^2 \\
&B_1 = 6320.813 - 530.1228 S^{0.5} - 6.103 S \\
&C_1 = 19.568224 - 2.06950 S^{0.5}
\end{aligned} \tag{A2}$$

$$\begin{aligned}
&-\lg K_2 = A_2 + \frac{B_2}{T} + C_2 \ln T \\
&A_2 = -90.18333 + 21.0894 S^{0.5} + 0.1248 S \\
&\qquad -(3.687 \times 10^{-4}) S^2 \\
&B_2 = 5143.692 - 772.483 S^{0.5} - 20.051 S \\
&C_2 = 14.613358 - 3.3336 S^{0.5}.
\end{aligned} \tag{A3}$$

Equation (A4) gives the dissociation constant K_B according to Dickson (1990),

$$\begin{aligned}
&\ln K_B = A_B + \frac{B_B}{T} + C_B \ln T + D_B T \\
&A_B = 148.0248 + 137.1942 S^{0.5} + 1.62142 S \\
&B_B = -8966.90 - 2890.53 S^{0.5} - 77.942 S + 1.728 S^{1.5} \\
&\qquad -0.0996 S^2 \\
&C_B = -24.4344 - 25.085 S^{0.5} - 0.2474 S \\
&D_B = 0.053105 S^{0.5}
\end{aligned} \tag{A4}$$

and the constant for dissociation of water, K_W, according to Hansson (1973) is presented in eq. A5.

$$\begin{aligned}
&\ln K_W = A_W + B_W S^{0.5} - C_W S \\
&A_W = 148.9802 - \frac{13847.26}{T} - 23.6521 \ln T \\
&B_W = -97.9429 + \frac{4149.915}{T} + 14.8269 \ln T \\
&C_W = -0.023694.
\end{aligned} \tag{A5}$$

To facilitate the understanding of this set of constants during different combinations of salinities and temperatures, they are presented graphically in Fig. 12.

Appendix B: The box model

A simple steady-state two-box model, which consists of a surface water box and a deep water box, is formulated and adapted for the Baltic Proper (see Fig. 2). It takes into consideration a freshwater inflow (Q_F), which consists of the river inflow (Q_R) and the net precipitation, deep water inflow (Q_{IN}^{KA}) from Kattegat, a southern outflow into the Kattegat (Q_{OUT}^{KA}), and a combined general exchange with the inner gulfs of the Baltic Sea (the Bothnian Sea, the Gulf of Finland, and the Gulf of Riga), which is divided into an outflow (Q_{OUT}^{IG}) and a surface inflow (Q_{IN}^{IG}).

Flows between the two boxes, and in/outflows, are assumed to be constant and according to Hjalmarsson et al. (2008). They are based on the conservation of salt and volume in a system of coupled box models mimicking the Baltic Sea system; for further details, see Hjalmarsson et al. (2008).

The chemical forcing for the box model focuses on concentrations of A_T and pCO_2, but calculations must be based on chemical species that behave conservatively when they come in contact with media differing in various properties, such as ionic strength and temperature. This implies that C_T and A_T should be used as known chemical properties in the actual box-model calculations. Therefore, C_T concentrations are calculated for each combination of pCO_2 and A_T in the chemical forcing flows. Variations of pCO_2 and A_T and the general flow conditions during the calculations are given in Tables 2 and 3. The model is forced with concentrations of A_T and C_T in Q_R, Q_{IN}^{KA}, Q_{IN}^{IG} and the actual precipitation, Q_P. The flows themselves are generally not varied in this study, the exception being Q_P, which is not involved in the set-up of the box-model flow calculation.

The inorganic carbon system is solved in the surface box from C_T and A_T concentrations, and these concentrations are calculated according to eqs (B1) and (B2), derived from mass balance considerations for C_T and A_T.

$$A_T = \frac{\left(A_T^{KA} Q_{IN}^{KA} + A_T^{R} Q_R + A_T^{IG} Q_{IN}^{IG} - \Delta A_T^{P} Q_P\right)}{\left(Q_{OUT}^{IG} + Q_{OUT}^{KA}\right)} \tag{B1}$$

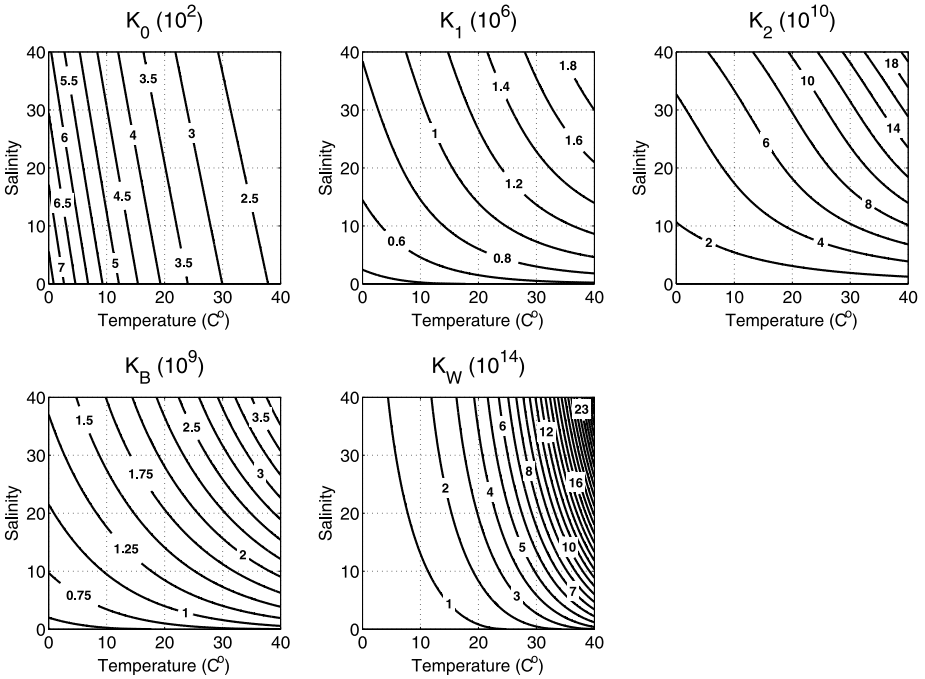

Fig. 12. Graphic presentation of the carbon system stability constants for salinities between 0 and 40 and temperatures (°C) between 0 and 40. Top left to bottom right: Solubility constant (K_0) for CO_2 in sea water according to Weiss (1974), disassociation constants K_1 and K_2 according to Millero et al. (2006), disassociation constant K_B according to Dickson (1990) and disassociation constant K_W according to Hansson (1973).

$$C_T = \frac{(C_T^{KA} Q_{IN}^{KA} + C_T^{R} Q_R + C_T^{IG} Q_{IN}^{IG})}{(Q_{OUT}^{IG} + Q_{OUT}^{KA})}. \quad \text{(B2)}$$

As can be seen, the concentrations in the surface box are dependent on the balance between the specific flows and the A_T and C_T concentrations in the flows. The precipitation, Q_P, is derived from a climate value of 0.6 m/yr m^2 of rain over the Baltic Sea area and the specific surface area of the investigated region. These values are among the defining properties of the basin and are therefore listed in Table 1.

To achieve comparable results throughout the study, each parameter is varied over an interval determined by implementing a fixed relative range on an appropriate central value for each parameter. In effect, this is computed from a maximum decrease of 100% and a maximum increase of 200% imposed on a central value for the parameter. When a parameter is not varied it is set to a constant representative value. See Table 2 for representative values and resulting ranges.

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