Modelling the Dissolved Inorganic Carbon System in the Baltic Sea

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Abstract

Oceans are capable of storing part of the emitted anthropogenic carbon dioxide (CO_2) due to the formation of carbonic acid and subsequent dissociation. CO_2 is also assimilated by biota and the inorganic carbon system is thus coupled to biogeochemical processes. Naturally, it is a substantial improvement of model realism if the inorganic carbon system is fully coupled to biogeochemistry in numerical models. The focus of this thesis has been to improve the accuracy of pH and the partial pressure of CO_2 (pCO_2) computations for a marine environment like the Baltic Sea, but the knowledge we have gained is generally applicable. A model system has been developed to consider several environmental threats simultaneously (eutrophication, acidification, and climate change) and the model skill has been certified by using objective skill metrics.

To improve the coupling between biogeochemical processes and the dissolved inorganic carbon system, generation and depletion of total alkalinity (A_T) due to several biogeochemical reactions was added to the model. *In situ* generation of A_T was found to be important, specifically in regions with permanent or periodic anoxia, as the major A_T changes were coupled to oxidation–reduction (redox) reactions. Without adding A_T from these processes, the correct pH could not be calculated in anoxic waters and the mean volume A_T content was found to be too low.

The improvements were put to use when several environmental threats were evaluated simultaneously in a study of possible future changes in the Baltic Sea pH and oxygen balances. A coupled model for the catchment and sea was set up and forced by meteorological and hydrological datasets and scenarios. The results showed that increased nutrient loads will not inhibit future Baltic Sea acidification, but the seasonal pH cycle will be amplified by increased biological production and mineralization. The study indicated future acidification of the whole Baltic Sea and that the main factor controlling the direction and magnitude of the change was the atmospheric CO_2 concentration. Through a previous investigation of the sensitivity of Baltic Sea surface water pH it was found that increased atmospheric CO_2 can affect pH also through changing the river chemistry, especially with regard to A_T. The latter could severely impact water in the northern Baltic region.

To improve modelled seasonal pCO_2 variations dissolved organic matter was added to a numerical model. The modelled phytoplankton were allowed to utilize the dissolved organic nutrients and the biological drawdown of CO_2 in the Eastern Gotland basin was much improved by this. When phytoplankton used the organic nutrients the CO_2 assimilation was higher during the summer months and the partial pressure of CO_2 decreased by ~200 μatm in the Eastern Gotland Basin as a result. In the Bothnian Bay, both the duration and magnitude of CO_2 assimilation was doubled when phytoplankton utilized dissolved organic nutrients.

KEYWORDS: Baltic Sea, Kattegat, pH, pCO_2, total alkalinity, biogeochemistry, dissolved inorganic carbon, eutrophication, acidification, climate change, numerical modelling

Svensk sammanfattning

Världshaven har förmåga att ta upp en del av den koldioxid (CO_2) som tillförts atmosfären från antropogena källor. Detta kommer av havsvattnets förmåga att lösa koldioxiden vilken därefter disassocierar. Även växligheten i havet (fotosyntetiserande fytoplankton) tar upp CO_2 och därmed kopplas den oorganiska koldioxiddynamiken till det marina biogeokemiska systemet. Det är uppenbart att realismen i numeriska modeller förbättras om koldioxidsystemet kopplas till de biogeokemiska processerna. Arbetet i denna avhandling har koncentrerats på att förbättra beräkningarna av pH och partialtrycket av CO_2 i Östersjön. Resultaten är allmänna, och därmed användbara även för liknande miljöer. Vi har utvecklat ett modellsystem som kan användas till att analysera flera miljöhot (övergödning, försurning och klimatförändringar) simultant. Modelresultatens kvalitet har kontrollerats kontinuerligt genom objektiva jämförelser med mätningar.

För att fördjupa kopplingen mellan biogeokemin och den oorganiska koldioxiddynamiken genomfördes en studie där produktion och förlust av total alkalinitet (A_T) orsakas av flera biogeokemiska processer i modellsystemet. De nya kopplingarna till biogeokemin visade sig vara viktiga för den totala alkaliniteten i havsvattnet, speciellt i områden som har periodisk eller permanent syrefria förhållanden. Förklaringen är att de största A_T förändringarna beror på vattnets redox-potential. Om man inte tog hänsyn till A_T tillskotten från redoxprocesserna beräknades felaktigt för låga pH värden i de syrefria vattenvolymerna och även volymmedelvärdet av A_T blev för lågt.

Vidare utvärderades flera miljöhot simultant i en studie över framtida pH- och syrgasförändringar i Östersjön. För att genomföra studien skapades en kopplad modell över Östersjöns och dess avrinningsområde. Modelsystemet drevs av meterologiska och hydrologiska observationer och scenarier, och resultaten visade att fortsatt övergödning inte kommer att dämpa Östersjöns försurning, utan endast kommer att öka amplituden i den årliga pH cykeln. Studien pekar på framtida försurning av hela Östersjöområdet och den viktigaste drivande faktorn var den ökade CO_2 koncentrationen i atmosfären. En tidigare känslighetsstudie visade att förhöjda atmosfäriska CO_2 koncentrationer även kan påverka havsvattnets pH genom att förändra kemin, speciellt den totala alkaliniteten, i det tillrinnande flodvattnet. Lägre tillförsel av A_T från flodvattnet skulle utgöra en allvarlig risk i norra Östersjön.

För att förbättra beräkningarna av den årliga koldioxidcykeln cykeln infördes variabler i modellen som representerade löst organiskt material. Modellens fytoplankton tilläts tillgodogöra sig det lösta organiskt kväve och fosfor som nu fanns tillgängligt, och det biologiska upptaget av CO_2 förbättrades märkbart i modellens östra Gotlandsbassäng. När primärproducenterna utnyttjade de organiska formerna av löst näring ökade CO_2 uttaget under sommarmånaderna och det resulterade i att det partiella koldioxidtycket minskade med ~200 μmol under denna period i den nämna bassängen. I Bottniska viken fördubblades både storleken och varaktigheten av CO_2 upptaget när den organiska näringen utnyttjades.

Preface

This project was initiated by an interest to investigate sea water acidification in the Baltic Sea region. The aim has been that this thesis should overlap the fields of oceanography and marine chemistry, reaping the benefits of both.

The thesis consists of a thesis summary and four appended papers. The latter are referred to by roman numerals in the text. Sections 1-3 in the summary are aimed to give papers I-IV background and context, while section 4 gives a preface to, and short summary of, the papers. Thereafter follow thesis conclusions and future perspectives on the scientific field.

Where else would I be?

List of publications

I. Omstedt, A., <u>M. Edman</u>, L. G. Anderson, and H., Laudon (2010). **Factors influencing the acid-base (pH) balance in the Baltic Sea: A sensitivity analysis**. Tellus, 62B, 280-295.

   Omstedt contributed with the idea for the paper. Edman had a minor role in writing, contributed with the main share of calculations and figures, took part in analyse, and commented on the text.

II. <u>Edman, M.</u>, and A. Omstedt (2013). **Modeling the dissolved CO_2 system in the redox environment of the Baltic Sea**. Limnol. Oceanogr., 58(1), 74–92.

   Both authors participated in forming the idea for the paper. Edman had the leading role in writing and submitting the paper, and led the revision. Edman also developed the model, analyzed the model results and prepared all figures.

III. Omstedt, A., <u>M. Edman</u>, B. Claremar, P. Frodin, E. Gustafsson, C. Humborg, H. Hägg, M. Mörth, A. Rutgersson, G. Schurgers, B. Smith, T. Wällstedt, and A. Yurova (2012). **Future changes in the Baltic Sea acid-base (pH) and oxygen balances**. Tellus, 64B, 1-23.

   The paper is the final product of the BONUS+/Baltic-C project. Edman participated in the project and wrote part of the text, contributed substantially to the analyze, and prepared several of the figures.

IV. <u>Edman, M.</u>, and L. G. Anderson (2013). **Effect on pCO_2 by phytoplankton uptake of dissolved organic nutrients in the central and northern Baltic Sea, a model study**. Submitted to Journal of Marine Systems.

   Both authors participated in forming the idea for the paper. Edman had the leading role in writing and submitting the paper. Edman also developed the model, analyzed the model results and prepared all figures.

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I. Summary

1. Introduction

1.1. The Baltic Sea – an overview

The Baltic Sea is situated in the densely populated northern Europe (see maps in Fig. 1). It is a semi-enclosed coastal sea that only connects to the world ocean through the Danish straits, here including Öresund. The straits act as a sill and cause the Baltic Sea to function similarly to a large fjord, (see also Fig. 2, that shows the Baltic Sea bathymetry along the transect shown in black in Fig. 1A). Bathymetrical constraints, such as sills or horizontal contractions, divide the Baltic Sea into several sub-basins. The long-term water exchange is dominated by outflow of low saline waters in surface layers and periodic inflow of dense water through the Danish straits. The inflowing water spreads through the system by filling up the deep basins at the vertical level where it finds neutral buoyancy. As one basin is filled up the water spills over to adjoining basins, often as a dense bottom current. Thus different depths are ventilated by each inflow event and only a few carries water dense enough to reach the deepest parts of the basins. This creates long stagnation periods for the bottom waters in some areas. The present understanding of climate and physical flows of Baltic Sea was reviewed in, e.g., Omstedt et al. (2004).

The water of the Baltic Sea is brackish from river discharge and has strong vertical salinity dependent stratification in the southern and western parts of the system. The surface salinity at station BY15 in Fig. 1, representing the central Baltic Sea, is around 7, while bottom waters typically have salinity around 12. In these areas there is a permanent halocline at about 60 m depth. In the northern basins the water mass is more easily mixed due to a weaker salinity gradient in the vertical. These features are clearly visible in Fig. 2, were the salinity of the Baltic Sea is shown. The Baltic Sea salinity also has a horizontal salinity gradient from the saline water of the Skagerrak (salinity of 20-25), to the very low saline Gulf of Bothnia in the north (salinity of 3-4). In spring and summer solar radiation adds heat to near surface water layers and creates a seasonal thermocline, i.e., a temperature dependent stratification. In wintertime the surface layer is well mixed above the halocline.

The Baltic Sea collects fresh water and land derived matter from a drainage area that is some four times larger than the sea itself, see Fig. 1A. The influence from land is thus large, and the surrounding rivers bring biogenic material such as carbon (C), nitrogen (N), and phosphorous (P) to the Baltic Sea. However, the bedrock, soil type and land usage varies greatly in the catchment, and thus the composition of matter discharged by the rivers varies. These variations create horizontal biogeochemical gradients in the Baltic Sea and give the sub-basins different biogeochemical conditions. The strong vertical stratification in the southern and western parts of the Baltic Sea creates vertical gradients for most biogeochemical variables.

From a biogeochemical perspective shelf seas, such as the Baltic Sea, are far more important than what is justified by their surface area and volume. They are transition zones between the open ocean and land, and their shallow depths connect sediments, bottom waters, surface water and atmosphere on shorter time scales. These areas are thus very dynamical, with frequently changing environments, and they have higher natural variability than does the open oceans. Costal seas are also more fertile and humans value them for recreation, food supplies and transportation. They are

also exposed to anthropogenic changes and the Baltic Sea is sensitive to anthropogenic influence due to its enclosed nature and large drainage area, but also relatively well investigated (BACC Author Team, 2008). The diversity of the biogeochemical conditions and the availability of observational data is a good basis for the development and usage of biogeochemical models.
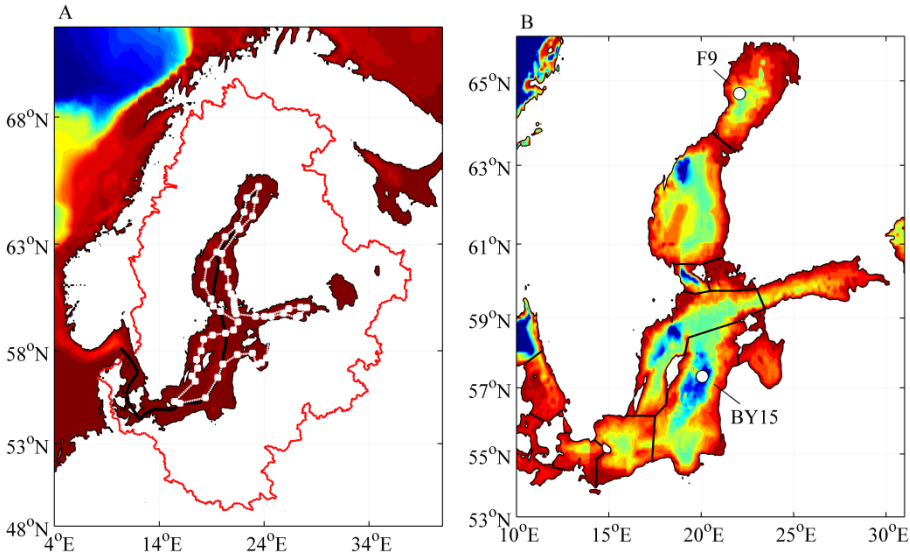

Figure 1. Maps of the Baltic Sea. A) Shows bathymetry down to 5000 m, the drainage area is marked by a red line, and two transect are marked by one white line with dots and one black line. B) Bathymetry down to 200 m, the PROBE-Baltic models sub-basin boundaries marked by black lines, and two measurement stations from the SHARK database are marked by white dots.
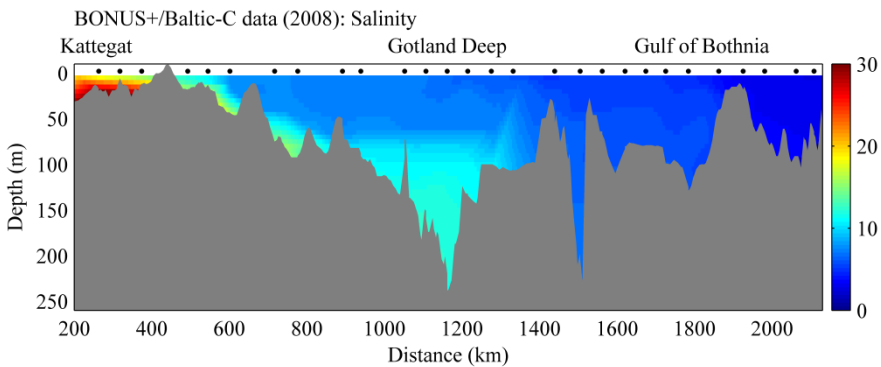

Figure 2. Baltic Sea salinity during the summer of 2008. Interpolated from data measured during the BONUS+/Baltic-C cruises. The transect follows the black path indicated in Fig. 1A. Black dots indicate the locations of the measurement stations.

1.2. Baltic Sea biogeochemistry

The organic material in the Baltic Sea is either produced *in situ* by primary producers, usually pelagic phytoplankton, in the sunlit surface waters, or originates from land biota in the catchment and transported by rivers. The latter is a substantial addition of organic materials, especially in the northern parts of the system. The soft organic matter mainly consists of lipids (fats) and carbohydrates (sugars, starch and fibres), but also proteins and phosphate ester groups. The composition of a generic organic material of marine origin was described in Redfield et al. (1963) and called the Redfield-Ketchum-Richard (RKR) ratio, often referred to as the Redfield ratio. It states that OM generally has a mean composition of 106 carbon atoms and 16 nitrogen atoms to every phosphorous atom (106:16:1). During primary production all of these three main components (and trace metals) need to be available at roughly the RKR ratio, but this is seldom the case. Thus, the growth of primary producing organisms will eventually be limited by depletion of one of the nutrients. As the Baltic is situated at quite high latitudes ($\sim$54°-66° N) biological production is also limited by light unavailability during winter and when this constraint is lifted in spring, phytoplankton growth increase rapidly, creating a spring bloom. The spring bloom lasts until production is restricted by lack of nutrients. This summer nutrient depletion in surface waters is caused by consumption of nutrients by primary producers and subsequent sinking of the dead organic matter through the water mass. Thus the nutrients become unavailable for primary producers. It follows that surface waters are almost entirely nutrient deprived during summer months. As autumn arrives there is sometimes an autumn bloom, fuelled by entrainment of nutrients accumulated in deeper water into the surface layer. This generally occurs as a result of the deepening of the summer thermocline.

In the northern parts of the Baltic Sea, especially in the Bothnian Bay, primary production is severely limited by low phosphorous concentrations, and the area is generally oligotrophic, even though it receives large amounts of organic matter from land. A large fraction of the production is instead assumed to be carried out by bacteria and other microorganisms which feed of land derived dissolved organic matter (Andersson et al., 1993). The southern and western parts of the Baltic Sea system are by comparison eutrophic, and even more so by the anthropogenic addition of nutrients (eutrophication) from the large drainage area. For most phytoplankton species nitrogen is limiting in these areas, but there are primary producers that can fix nitrogen from N_2 gas dissolved in sea water. These organisms are instead limited by the phosphorous availability.

Fig. 3 shows the horizontal and vertical distribution of oxygen (O_2), nitrate (NO_3) and phosphate (presented as dissolved inorganic phosphorous (DIP)), along the black transect in Fig. 1A. The data was obtained during the BONUS+/Baltic-C cruises in the summer of 2008 and was first used in Beldowski et al. (2010). The surface layers are nutrient poor, as is typical after the spring bloom. Also note the high concentrations of inorganic nitrogen in the Bothnian Bay, quite in contrast with the mostly nitrogen limited central Baltic Sea.

Sinking organic matter is the primary source of energy at depths where no photosynthesis can take place due to lack of light. The energy is stored in the chemical bounds of the organic molecules and can be released and utilized if these bounds are broken. Mineralization of this matter is carried out by microorganisms,

often bacteria, and the energy, and some of the matter, is used to sustain the organisms themselves. The remaining matter is released in inorganic form, and deep waters are therewith supplied with inorganic mineralization products such as nitrogen, phosphorous and inorganic carbon. A large fraction of the mineralization in the Baltic Sea is carried out in sediments, as has been shown by Schneider et al. (2010). Mineralization of OM requires an oxidation agent, often oxygen, for the electron transfer needed during the chemical reaction, and the sinking OM determine the oxygen demand in the water masses overlying the sediment.

The central and western Baltic Sea system is sufficiently eutrophic to produce enough OM to cause oxygen deficiency in the periodically stagnant basins. This is exemplified in the upper panel in Fig. 3. During stagnation periods there is also accumulation of nutrients (see the lower panel in Fig. 3) and inorganic carbon. When oxygen is entirely depleted, the ambient redox state (i.e. the availability of effective oxidation agents) in the water mass changes. The transition zone between oxic and anoxic environments is called the redoxcline and it moves upward as the anoxic bottom water volume increases. In the anoxic environment below the redoxcline many biogeochemical pathways change due to the changed redox state. During anoxic conditions organic matter is mineralized by bacteria that can utilize oxidation agents other than oxygen. Bacteria tend to use the reaction which offers the best energy return, and thus both the availability and the strength of the oxidation agents set the redox sequence. The best option is oxygen, and thereafter follows nitrate (NO_3), iron oxides and manganese oxides. The latter two are however scarce in the free water mass, while nitrate usually accumulates in deep water layers until oxygen levels approaches zero. Mineralization with NO_3 is called denitrification and is usually the dominant mineralization process in the vicinity of the redoxcline. The middle panel of Fig. 3 shows a situation where the deep anoxic water is already depleted in NO_3. In an anoxic environment nitrogen is accumulated in the form of NH_4, because even if NH_3 is oxidized to NO_3 (i.e., nitrification) by, e.g., Mn_4^+, it will soon be consumed by denitrification. Thus anoxic waters generally have low nitrogen content.

Nitrogen is self-regulating in the central Baltic Sea due to two processes; N_2-fixation and denitrification. N_2-fixation in surface waters can add bioavailable nitrogen to the water mass when needed. If surface waters are instead eutrophicated, anoxic deep waters are likely to develop, and nitrogen is then removed through denitrification. The controlling factor for the biogeochemical system is thus phosphorous. This is ultimately caused by the special combination of constrained and poorly ventilated deep basins, together with brackish surface water in which N_2-fixing cyanobacteria can thrive.

Phosphorous is not sensitive to the ambient redox state in itself, but binds to metal oxides that are involved in redox reactions. In the Baltic Sea mineralization mainly takes place in sediments where these metal oxides can be quite abundant, and thus a substantial share of the released phosphorous is bound in the sediment instead of returned to the free water mass. But in an anoxic environment these metals are reduced when they are used by microbes to oxidize organic matter, and phosphorous is released. Thus anoxic waters often have high phosphorous content. The sediments in shelf seas, such as the Baltic Sea, are often anoxic even if the overlaying water is

not. This often causes movement of phosphate within the sediment, but as long as the surface is oxidized, it cannot escape.
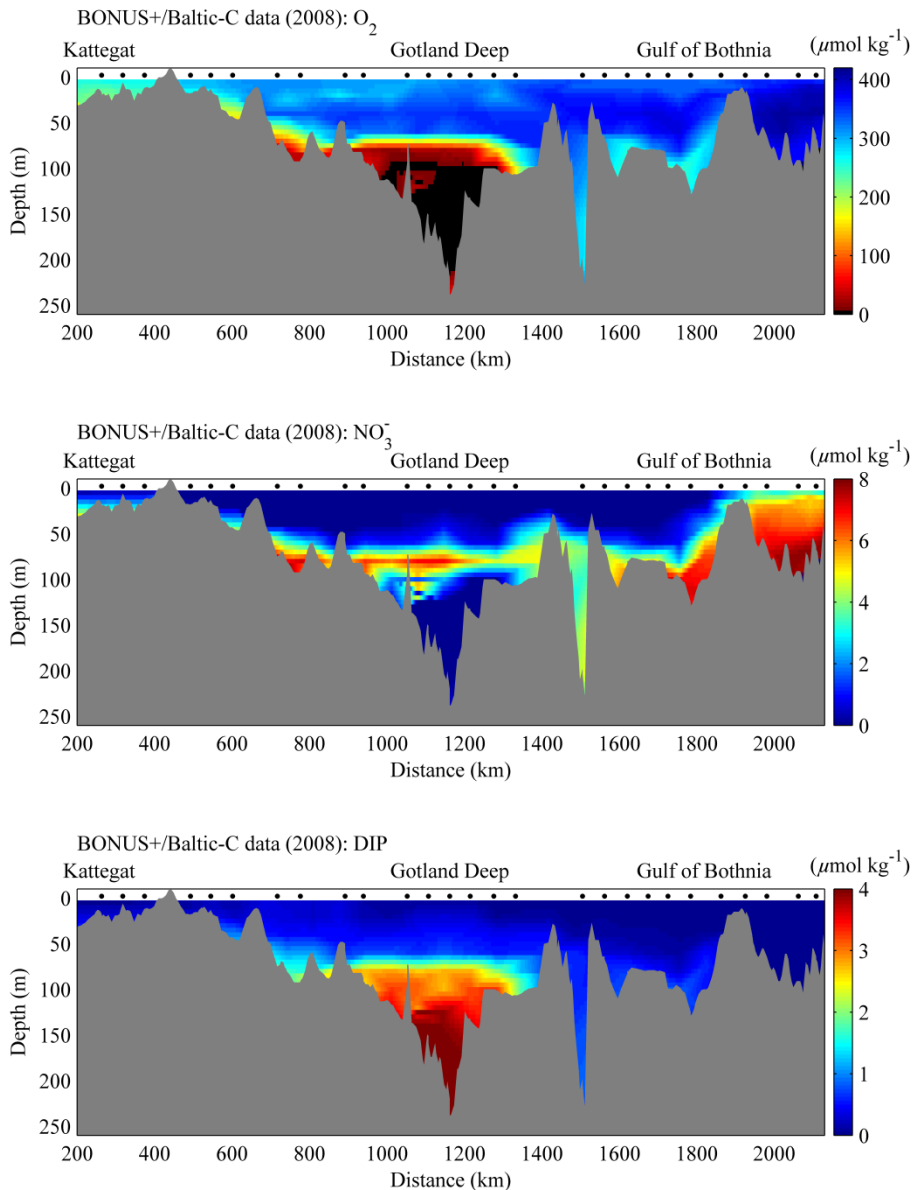

Figure 3*. Observed oxygen, nitrate and dissolved inorganic phosphorous (DIP) concentrations in the Baltic Sea during the summer of 2008. Interpolated from data measured during the BONUS+/Baltic-C cruises. The transect follows the black path indicated in Fig. 1A. Black dots indicate the locations of the measurement stations.*

Release of phosphorous from sediments during anoxia in the Gotland deep has been shown by Conley et al. (2002) during the first stages of anoxia. The flux from the sediment decreases as the stored phosphorous is depleted. What remains is then the continuous release of new mineralization products. This has been shown by Viktorsson et al. (2013) and the differences between phosphorous released from periodically and continuously anoxic bottoms was discussed. This study also pointed out internally regenerated P as a dominating source of dissolved inorganic phosphorus in the Baltic Sea. Substantial release of phosphate will occur if previously oxic bottoms become anoxic.

1.3. Baltic Sea pH

Already in 1945 Karl Buch published pH measurement from the Gulf of Bothnia, and since then scientists have continued to measure pH in the Baltic Sea. Recently, pH was measured as part of the BONUS+/Baltic-C project during the summers of 2008-2010. Measurement of pH is also part of monitoring programs and pH data is available from the SHARK data base hosted by the SMHI. The quality of the SHARK pH data have increased since 1993, since they have been found to have less noise from then and onwards (Anderson et al., 2008). Both the SHARK and Baltic-C data are measured on the pH^{NBS} scale, which means that the titration of pH has been performed with an NBS (National Bureau of Standards) buffer solution (ISO 10523, 1994; Grasshoff et al., 1999). To approximately convert the values to the pH^{tot} scale, which is widely used in models, 0.13 pH units can be subtracted. Unfortunately, the NBS buffers are not ideal for measuring pH in low saline waters as the difference of ionic strength between buffer and sample causes errors. The transect in Fig. 4 (upper panel) shows pH measured in the summer of 2009 and follows the white transect shown in Fig. 1A. It circles the Baltic Sea from the tip of the Bornholm Island, to the west of Gotland, up to the northern Bothnian Bay and returns through the eastern Baltic Sea basins.

Baltic Sea surface pH is typically higher in the southern parts of the system as a result of higher total alkalinity (A_T) and primary production in these areas. There is also a seasonal variation in surface waters, with higher pH being associated with primary production and assimilation of CO_2 during summer. Thus surface pH is usually at its lowest during winter when additional CO_2 is added from mineralisation and the cold temperatures also cause dissolution of more CO_2. There are also horizontal variations in pH due to up-welling from deeper water layers and outflow of river water. In deeper water layers pH is lower due to accumulation of dissolved inorganic carbon (CO_2). This is especially the case for enclosed deep waters, seen in Fig. 4 in the deep basins to the west and east of Gotland. Waters can here be as low as pH of 6.9. Thus the natural variability of pH in the Baltic Sea is substantial both in the vertical and horizontal directions.

A_T along the same transect is shown in the lower panel. The alkalinity is strongly co-related to salinity, which is seen when Fig. 2 is compared with Fig. 1, but the A_T content also varies between rivers in the drainage basin, e.g., rivers in the northern part of the Baltic Sea catchment have been found to carry low A_T (Hjalmarsson et al., 2009).
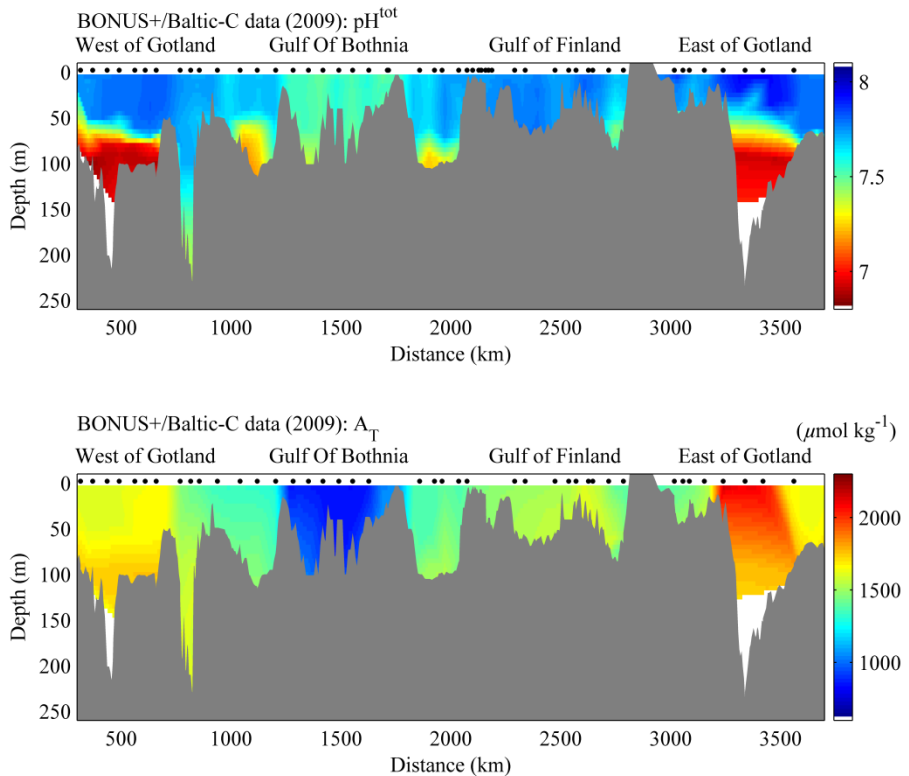
Figure 4. *Observed pH and A_T in the Baltic Sea during the summer of 2009. Interpolated from data measured during the BONUS+/Baltic-C cruises. The transect follows the white path indicated in Fig. 1A. Black dots indicate the locations of the measurement stations.*

1.4. Why model carbon?

There is hope that the ocean can store a large amount of the anthropogenic CO_2 emissions and thus decrease the climatic impact of human actions. The world ocean is the largest storage in the carbon cycle, including soil, biota, atmosphere, and oceans (Seigenthaler and Sarmiento, 1993). Considering anthropogenic CO_2 emissions, it has become important to fully understand the ocean reservoir and the mechanisms controlling it. However, when more carbon is stored in the oceans, the pH of sea water decreases. This process is already initiated (Solomon et al, 2007) and as the CO_2 emissions are expected to continue to increase (IPCC, 2007), future changes of sea water pH (ocean acidification) needs to be considered. This issue can only be investigated by models if the inorganic carbon system is computed.

The problem of ocean acidification has gained recognition since falling pH could affect biota, especially those organisms with calcium carbonate shells. It has however been hard to determine the actual impact on marine organisms and ecosystems (Doney et al., 2009). The impact on biota from possible future acidification is thus still uncertain, even if the ability to predict future pH changes has increased during

later years (e.g., paper III). Research on the inorganic carbon system is also motivated by a pure scientific interested in how the equilibrium balance of carbonic acid functions in a media rich in ions and complexing agents (the saltiness of sea water). These circumstances has led to CO_2 being one of the most abundantly measured gases of the oceans, and modern measurements of partial pressure of CO_2 (pCO_2) in the Baltic Seas have recently been made available through the Finnmaid project at IOW (Schneider et al., 2009). This means that pCO_2 can be validated, which also offers an opportunity to validate biogeochemical models through the seasonal pCO_2 variations, if the inorganic carbon system calculated. Since carbon is a central link in the biogeochemical system, this is very valuable.

Carbon is the main constituent in OM as it is a dominating component of the structure of both lipids and carbohydrates. Carbon is assimilated during marine primary production, mainly in the form of CO_2, and this uptake lowers the pCO_2 in the water. Often primary production has been modelled based only on the RKR ratio and the amount of inorganic nutrients available just before the start of the productive season. But since at least one of the essential nutrients N and P will be in short supply, i.e. limiting, for primary production, that nutrient will be recycled within the euphotic zone at a much higher rate than carbon. This recycling leads to difficulties estimating the actual amount of OM being produced, while using the abundantly available element carbon (C) as indicator, is more reliable. The idea was first put forward in Leinweber et al. (2005) were they demonstrated the importance of including the dissolved CO_2 system in ecosystem models, and also the value of validating the calculations by the observed partial pressure of CO_2. This approach is also used by the present author, especially in paper IV, and was introduced by Omstedt et al. (2009) to model the uptake and release of CO_2 in Baltic Sea surface water. A god estimation of surface OM primary production is essential to correctly estimate the process rates in the deeper sub-surface waters. In deep waters the mineralization rate, and thus the redox-state, is dependent on the amount of sinking organic matter. It is important that this basis, the amount of sinking OM, is correct. By estimating the biogeochemical fluxes with carbon as the indicative variable, and validate the primary production with pCO_2 variations, the development of biogeochemical modelling takes a more realistic direction.

In conclusion; including carbon variables in biogeochemical models enables us to model the concentration of OM more accurately, and this is essential for realistic estimation of the concentration of biogeochemical variables and the biogeochemical pathways in models. It also allows us to evaluate the total environmental threat to marine system, as it takes into account eutrophication, and anthropogenic CO_2 complications (acidification and climate change) simultaneously. This latter ability was used in paper III, where a coupled catchment–sea model system which was set up and forced by meteorological and hydrological datasets and scenarios to predict future acidification and oxygen conditions of the Baltic Sea.

1.5. Baltic Sea biogeochemical models

Many of the Baltic Sea biogeochemical models which are currently used started as physical numerical models focused on describing the water and heat balances of the Baltic Sea. As the awareness of dead bottoms and eutrophication grew, the idea of modelling also biogeochemical aspects of the system arose. Biogeochemical modelling of the Baltic Sea then took an important step forward when Stigebrandt

and Wulff (1987) coupled physical transports to nutrient dynamics in the Baltic Proper. Several other studies followed, e.g., Savchuk and Wulff (2001).

The biogeochemical aspects have either been integrated directly into models, or they have been developed as separate modules. Two examples of the former approach are the simple as necessary Baltic long-term large-scale (SANBALTS) model (Savchuk and Wulff, 2009) which calculates average concentrations in homogeneous boxes and focuses on rapid estimates of eutrophication for decision support, and the Baltic Sea long-term large-scale eutrophication model (BALTSEM) (Savchuk and Wulff, 1999; Savchuk, 2002), after Stigebrandt and Wulff (1987). Also the PROBE-Baltic, the model used in this thesis, is part of this category, as it started out as a purely physical process model which has continued to expand by including chemical and biological variables.

Some biogeochemical models have instead been developed, and especially presented, as biogeochemical modules. These biogeochemical modules can be coupled to different physical model solvers, which give the advantage of upgrading the physical modelling as calculation capacity increase and new physical model solvers are developed. Examples are the ecological regional ocean model (ERGOM), and the Rossby Centre ocean model (RCO) coupled to Swedish coastal and ocean biogeochemical model (SCOBI). Both ERGOM and SCOBI currently have three-dimensional set-ups, such as the RCO-SCOBI (Meier et al., 2003; Eilola et al., 2009) or ERGOM coupled to the modular ocean model (MOM) circulation model (Pacanowski and Griffies, 2000). An evaluation of the performance of BALTSEM, ERGOM, and RCO-SCOBI biogeochemical cycles can be found in Eilola et al. (2011).

The main focus of SANBALTS, BALTSEM, SCOBI and ERGOM has previously been nutrient and ecosystem dynamics, but now ERGOM calculates dissolved CO_2 system parameters and also BALTSEM has developed in this direction (Gustafsson et al., 2013). Still, only PROBE-Baltic has integrated the inorganic carbon system fully coupled to the wider biogeochemical system.
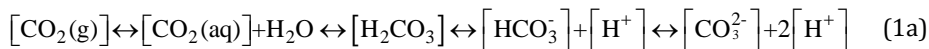
Some models have been more directly developed to include carbon fluxes and the dissolved inorganic carbon system. Examples of such models are the carbon and nitrogen regulated ecosystem model (CN-REcoM) (Schartau et al., 2007), which focuses on nitrogen and carbon decoupling, and more general coastal dissolved CO_2 system models, such as the shallow–water ocean carbonate model (SOCM) (Andersson et al., 2005) and the coastal MIRO-CO2 model coupled to the river model RIVERSTRAHLER model (R-MIRO-CO2) (Gypens et al., 2009).

2. The dissolved inorganic carbon system

2.1. Theory

The marine dissolved inorganic carbon system is the description of the equilibrium between the inorganic carbon species that results from carbon dioxide (CO_2) being dissolved in sea water, and the dissolution of carbonate minerals, such as calcite or aragonite. Dissolved inorganic carbon is added to seawater from both weathering of carbonate minerals in the river drainage basins and from in situ dissolution of
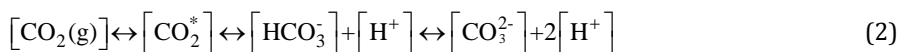
biogenic produced calcium carbonates. Atmospheric CO_2 is transferred through the sea surface until equilibrium is reached, i.e., the partial pressure of CO_2 in sea water and atmosphere are equal. Some of the gaseous (g) CO_2 is dissolved to form aquatic (aq) CO_2, which react with water to form carbonic acid (H_2CO_3). The acid then mostly dissociates to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. This is described in the following reaction.

$$\left[CO_2(g)\right] \leftrightarrow \left[CO_2(aq)\right] + H_2O \leftrightarrow \left[H_2CO_3\right] \leftrightarrow \left[HCO_3^-\right] + \left[H^+\right] \leftrightarrow \left[CO_3^{2-}\right] + 2\left[H^+\right] \quad (1a)$$

This formation and dissociation of carbonic acid is the main reason why inorganic carbon is so effectively stored in solution, and thus why the ocean is the largest reservoir in the carbon cycle. Dissolved CO_2 and H_2CO_3 are hard to differentiate. We introduce the variable $[CO_2^*]$ to denote both states according to reaction Re. 1b.

$$\left[CO_2^*\right] = [H_2CO_3] + \left[CO_2(aq)\right] \quad (1b)$$

Re. 1a can, and will, hereafter be written as Re. 2.

$$\left[CO_2(g)\right] \leftrightarrow \left[CO_2^*\right] \leftrightarrow \left[HCO_3^-\right] + \left[H^+\right] \leftrightarrow \left[CO_3^{2-}\right] + 2\left[H^+\right] \quad (2)$$

Note that the arrows depicted in Re. 2 go both ways, indicating that these reactions are reversible. If pCO_2 increases, more of the gas will go into solution and the equilibrium shifts to the right. If more carbonate is added from increased weathering on land, the equilibrium shifts to the left. At a pH typical for the Baltic Sea (and the ocean at large)(7-8, see Fig. 4, upper panel) the speciation of the inorganic carbon system is dominated by bicarbonate.

Disassociation means that hydrogen ions (H^+) part from the acid until equilibrium is reached with the acid-base state of the ambient environment. This is dependent on temperature and equilibrium constants, and for a marine system, also on salinity (Dickson et al. 2007). At this stage the dissolved CO_2 system starts to be affected by the ambient conditions. All acids and basis in solution are interdependent through the shared pool of donated (from acids) or accepted (to bases) hydrogen ions (H^+) in solution. The amount of H^+ donated to the solute from each acid is regulated by the acids strength (i.e. an acids willingness to give of H^+) and the concentration of H^+ already released. The H^+ concentration is thus a result of the acid-base balance.

pH is an alluring property to use as indicator of the acid-base balance, but it is tricky to define and measure in the marine environment since sea water is rich in ions and other complexing agents. Thus pH is defined on several different scales, depending on how you chose to define and measure it. In this thesis we have used the total scale throughout, defined as in Eq. 3a. The free scale is when only $[H^+]$ is taken into account, and there is also a sea water scale which takes hydrogen fluoride into consideration

$$\left\{H^+\right\}^{tot} = \left\{H^+\right\}^{free} + \left[HSO_4^-\right] \quad (3a)$$

{H+} represents the activity of the hydrogen ions, but for modelling purposes this can be equalled with the concentration [H$^+$]. Since this thesis is focused on what is important from a modelling perspective, we define pH as in Eq. 3b.

$$pH^{tot} = -\log\left(\left[H^+\right]^{tot}\right) \tag{3b}$$

We have now defined two properties of the inorganic carbon system; pH – a measure of the proton (H$^+$) concentration, here according to the total pH scale (pH^{tot}); and pCO$_2$ – the partial pressure of carbon dioxide in seawater. We need to define two more properties to fully describe the system. The first one is the concentration of total dissolved inorganic carbon (C$_T$) described in Eq. 4. It is a summation of the dissolved inorganic carbon species.

$$C_T = \left[CO_2^*\right] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right] \tag{4}$$

The last property is the total alkalinity (A$_T$), defined as the surplus of proton acceptors over proton donors as is shown in Eq. 5.

$$A_T = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[HPO_4^{2-}\right] + 2\left[PO_4^{3-}\right] + \left[NH_3\right] +$$
$$\left[HS^-\right] + \left[OH^-\right] + ... - \left[H^+\right] - ... \tag{5}$$

Total alkalinity is here presented generally, rather than in detail; it is the summation of all steps in chemical reactions that may donate or take up protons, including dissolved organic matter (DOM). It thus estimates the possibility for the system to find acceptors for new H$^+$ ions. For a smaller A$_T$ value, the availability of proton acceptors is less, and thus the system have less ability to re-adjust and maintain its pH when changes occur.

Since the concentration of H$^+$ is regulated by all dissolved acids and bases, we may also need to define other major acids and bases in solution, apart from the carbonates. To decide which to take into consideration, one has to consider the research question, area and computation resources. In paper I we used; B$_T$ – total dissolved inorganic boron; and in papers II, III and IV we aslo added; NH$_T$ – the sum of ammonia and ammonium; HS$_T$ – the sum of hydrogen sulphide and di-hydrogen sulphide and; PO$_T$ – the sum of phosphoric acid constituents. To take these properties into consideration we also need the constants that define their equilibriums.

For a more comprehensive description of the marine dissolved CO$_2$ system, see (Zeebe and Wolf-Gladrow 2001; Dickson et al. 2007).

3. Modelling

3.1. Modelling philosophy

Numerical models are simplified representations of the real world. By simplifying the problem we aim to solve, we are forced to choose, and by doing so we prescribe a set of strengths and weaknesses for the model. Model results are thus a representation of the process understanding we already have, but by delegating the mathematical calculations to the machines, we can see further implications of that understanding and gain new knowledge of the system as a whole. By comparing model results with observations we can evaluate if our current process understanding is enough, but it can also highlight the strength of model investigations by clearly stating a model systems capability.

3.2. Evaluating model skill

During the thesis work model skill has been evaluated continuously. The method was introduced in paper II, used in paper III to evaluate the quality of future scenarios and in paper IV to evaluate development efforts. It was inspired by the guidelines and recommendations found in Oschlies et al. (2010), a study which aim to ensure that the validation of models is objective and their quality quantifiable. We calculate two dimensionless skill metrics for a set of key physical and biogeochemical state variables and display them graphically. The graphical presentation is inspired by Taylor diagrams (A graphical summation of how well a distribution matches observations; Taylor, 2001), but simplified to achieve a bulls-eye effect were the model skill is inversely related to the distance from origin. Through this approach some information is sacrificed (comparing standard deviations), but the graphical presentation is straightforward and thus easier to use when many options are considered (paper III, 31 models runs evaluated). The method was first applied to vertical mean profiles, which was suitable for papers II and III, while in paper IV it was also applied to annual mean surface variations.

The objective skill metrics were chosen to evaluate both the shape and level of a modelled distribution compared to observational data. To quantify the models ability to return the correct shape of a distribution we use the correlation coefficient, *r*, between observations and model, as is suggested in Stowe et al. (2009). As a complement to the correlation coefficient, we use the mean of a cost function (*C*) to evaluate a models skill to return the magnitude of a parameter. The cost function normalizes the bias between the model results (P_i) and observed data (O_i) by the standard deviation (SD) of *n* observations, see Eq. 6.

$$C = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{P_i - O_i}{SD(O_i)} \right| \tag{6}$$

The use of this formulation for the cost function was inspired by Eilola et al. (2009) and to interpret the outcome we follow the ranges suggested in that study. When applied to the mean depth profiles, the averaging of Eq. 6 has been volume weighted. This method have been very useful both in the development phases and to present the result. Examples of this approach can be found in papers II-IV.

3.3. The PROBE-Baltic model

The PROBE-Baltic model uses the equation solver PROBE (first presented by Svensson (1978)), which is a well-documented program and freely available (Omstedt 2011). Also the full model and the versions used in papers II (version 2.8), III (version 3.0) and IV (version 3.1), are freely available on request, which also follow the recommendations by Oschlies et al. (2010).

The PROBE-Baltic is a physical-biogeochemical model for the Baltic Sea that resolves the transient vertical profiles of thirteen coupled Baltic Sea sub-basins, see Fig. 1B. The thirteen basins are based on natural boundaries and approximately follow bathymetrical constraints and the ecosystem-based regions defined by Ojaveer and Kalejs (2008). The vertical resolution is adapted to basin depth and stratification (i.e., a few meters). The model applies a process based approach and is aimed to function as a numerical experimental environment to test and implement new system understanding. It is well suited for climate impact studies, but does not resolve horizontal variations within the sub-basins.

The physical model is described in Omstedt and Axell (2003) and the biogeochemical model has been progressively developed through the work of Gustafsson (2011) and papers II, III and IV. The model is fully coupled and all variables are solved at the same grid level and time step. The biogeochemical part of the model originally calculated the transient concentrations of oxygen, nitrate, total ammonia, phosphate, two phytoplankton types, C_T and A_T. A third phytoplankton type, zooplankton and detritus in three fractions were introduced in Gustafsson et al. (2011), and the four variables describing dissolved organic matter were introduced in paper IV. The partial pressure of CO_2 and pH are calculated from the state variables.

The state variables are forced by relevant additions from river water and sea water exchange between the basins. The basins are connected via strait flow models that calculate the volume flux at different depths. If applicable, the transient profiles are also regulated by atmosphere–sea fluxes through the seawater interface. The transfer velocity formulation needed for the gas exchange of CO_2 and O_2 is according to Wanninkhof et al. (2009). Most state variables are also affected by sources and sinks within the water mass, and these are used to couple the biogeochemical variables. The rate of chemical and biologically relevant reactions is parameterized and used to generate or deplete the state variables. A thorough listing and description of all variables and processes is given in the thesis papers and web appendixes.

3.4. Modelling the dissolved inorganic carbon system

If two parameters from the dissolved inorganic carbon system are known, the other two can be calculated by using the solubility constant for CO_2, the dissociation constants for the acids and bases in solution, and the ionic product of water. The set of constants that have been recommended as most suitable for the Baltic Sea are listed in Table 1. They have been experimentally derived for a range of salinity and temperature combinations and the constants from Millero et al. (2006) are consistent with the constants for freshwater and developed for a wide salinity range. This makes it possible to determine the state of the dissolved CO_2 system in estuarine waters.

In this thesis the marine dissolved inorganic carbon system has mainly been solved from the two state variables C_T and A_T, following the praxis in marine chemistry. Previously in the PROBE-Baltic model the system has been solved from the state variables acid carbon (${}^aC$) and basic carbon (${}^bC$), and this was also the case in paper I. The acid and basic carbon variables are explained in Walin (1991) and used in Omstedt et al. (2009) and more recently in Hieronymus et al. (2013). Both sets of variables have their own strengths and weaknesses; C_T and A_T are defined together with pH and pCO_2 to describe different aspects of the inorganic carbon system, as has been discussed in section 2, while ${}^aC$ and ${}^bC$ are defined to facilitate modelling by directing the sinks and sources from a biogeochemical process to only one of the state variables. However, in paper II the advantage of the Walin approach was lost since the alkalinity from ions that are not part of the carbonate system affects both ${}^aC$ and ${}^bC$. Instead A_T and C_T were used. The inorganic carbon system is also widely solved by the CO2SYS software (Lewis and Wallace, 1998).

Table 1. Equilibrium constants and their references.

Constant	Equilibrium	Reference
K_W	$\left[H_2O \right] \leftrightarrow \left[H^+ \right] + \left[OH^- \right]$	Hansson (1973)
K_0	Solubility of CO_2	Weiss (1974)
K_1	$\left[CO_2 * \right] \leftrightarrow \left[H^+ \right] + \left[HCO_3^- \right]$	Millero et al. (2006)
K_2	$\left[HCO_3^- \right] \leftrightarrow \left[H^+ \right] + \left[CO_3^{2-} \right]$	Millero et al. (2006)
K_B	$\left[B(OH)_3 \right] \leftrightarrow \left[H^+ \right] + \left[B(OH)_4^- \right]$	Dickson (1990)
K_{NH}	$\left[NH_4^+ \right] \leftrightarrow \left[H^+ \right] + \left[NH_3 \right]$	Clegg and Whitfield (1995)
K_{HS}	$\left[H_2S \right] \leftrightarrow \left[H^+ \right] + \left[HS^- \right]$	Millero (1988)
K_{1P}	$\left[H_3PO_4 \right] \leftrightarrow \left[H^+ \right] + \left[H_2PO_4^- \right]$	Millero (1995)
K_{2P}	$\left[H_2PO_4^- \right] \leftrightarrow \left[H^+ \right] + \left[HPO_4^{2-} \right]$	Millero (1995)
K_{3P}	$\left[HPO_4^{2-} \right] \leftrightarrow \left[H^+ \right] + \left[PO_4^{3-} \right]$	Millero (1995)

To compute the system, the state variables are first solved numerically, and the H^+ concentration is then calculated through an iterative procedure, after which pCO_2 and seawater pH can be computed. To set up the iteration scheme for calculating H^+ concentrations, we follow Dickson et al. (2007) and derive the H^+ concentration from the definition of A_T. The resulting iterative equation is presented in papers II and IV. The iteration is solved by a combination of bisection and Newton–Raphson schemes. The first bisection phase of the calculation narrows down the starting value for the Newton–Raphson iteration and thus ensures convergence. This approach also gives an acceptable calculation speed for the PROBE-Baltic model.

4. Contributions to system understanding of the Baltic Sea

4.1. Baltic Sea pH sensitivity (paper I)

As an introduction and guidance, we performed a study of the Baltic Sea pH sensitivity in paper I. We used several methods to evaluate possible causes of acidification. The PROBE-Baltic was used to investigate the effect of eutrophication and the spin-up time for the dissolved inorganic carbon system, and we also used a simple steady-state box model to investigate the pH of surface waters. Calculations on the effect of acidification due to DOC in limnic waters were also added.

The transient calculations with PROBE-Baltic demonstrated that the marine dissolved inorganic carbon system adjusts to lateral boundary conditions within some decades in the Baltic Sea, just like salinity, and that increased nutrient load may increase the amplitude in the pH seasonal cycle and increase the acidification during winter time. We also found that acidification due to river transport of dissolved organic carbon (DOC) was small, although mineralization of the terrestrial DOC may cause additional acidification. The later possibility was yet to be quantified. The steady-state box model calculations showed that climate changes will only marginally affect pH. This was investigated both by testing the pH changes caused by salinity and temperature induced changes of the equilibrium constants, and by looking at the effect of a wetter or drier climate. The direct effect on seawater pH of acid precipitation over the Baltic Sea surface was also demonstrated to be small.

The greatest sensitivity was attributed to changes in water pCO_2 and total alkalinity. The box-model was used to calculate surface pH for a range of pCO_2 and A_T combinations for constant temperature and salinity. The result is shown in Fig. 5. The bold black lines indicate the current atmospheric pCO_2, which were assumed also for the water, and the range of Baltic Sea A_T. The figure indicate that Baltic Sea surface pH is in the range of just above 8 to 7.5 and this agrees rather well with what is shown in Fig. 4.

Since changes of pCO_2 and A_T showed the greatest sensitivity, we concluded that fossil fuel burning, resulting in CO_2 emissions, is likely to have both a direct effect through increased CO_2 levels, as well as by possibly changing the river chemistry. If the pCO_2 of river waters increase, the transport of total alkalinity to the sea could increase in some parts of the drainage basin, where the bedrock and soils allow additional weathering, but in others the river water could become more acidic. This later scenario is applicable in the northern parts of the drainage basin and CO_2 emissions could thus severely threaten these marine environments. Paper I thus underlines the importance of considering CO_2 emissions and A_T concentrations when the future pH of the Baltic Sea is studied.
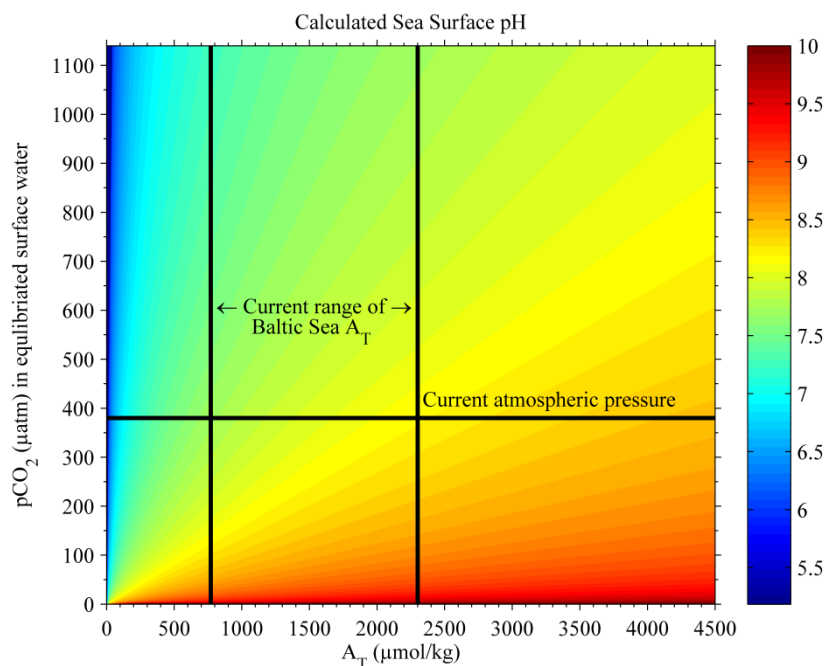
Figure 5. *Change of pH^tot as a result of variation in water pCO₂ and A_T. Salinity is kept at 7.5 and temperature at 0 °C throughout the calculations. Bold black lines show the current status of the area with regard to A_T (Hjalmarsson et al., 2008) and atmospheric pCO₂. (Redrawn from paper I)*

4.2. Considering in situ A_T changes (paper II)

The importance of total alkalinity for Baltic Sea pH was stated in paper I, and thus the study of Thomas et al. (2009) inspired us to consider the chemicals reactions which govern *in situ* generation and depletion of A_T. This study mentions several biogeochemical reactions that are common in the Baltic Sea deep waters as being sources of A_T. The total alkalinity distribution in the Baltic Sea has a strong salinity dependent A_T signal (Hjalmarsson et al., 2008), but it seemed interesting to investigate if biogeochemical processes in the marine environment could modify it to any substantial degree. *In situ* changes of total alkalinity (A_T) were thus added to the PROBE-Baltic model.

The definition of total alkalinity was widened, and A_T changes could then be added due to primary production, respiration, nitrification, oxic mineralization, denitrification, sulphate reduction, reoxidation of sulphide and the adsorption and release of phosphate. We found that the mean annual generation and depletion were almost balanced, though the transient rates were much faster. This is caused by the reversibility of sulphate reduction and the close coupling of creation and destruction of OM. The A_T that is added from biological uptake during primary production is almost entirely depleted again during mineralization and nitrification, and the result

is mostly a vertical displacement of the A_T distribution. Sulphate reduction is a reversible process that takes place to mineralize OM during anoxia, and the generated A_T is depleted as the products are re-oxidized when the water is ventilated. The effect is however very important during anoxic periods, as the added A_T partly buffer the acidification caused by the CO_2 released during mineralization. This is shown in Fig. 6 were A_T and pH are shown as functions of oxygen concentrations. When the new functionally was added (black dots) the model was able to better recreate the observed behaviour of the pH and A_T variables.

Modelled and observed A_T is also shown in Fig. 7, indicating much more realistic distributions due to additions of A_T during oxygen poor conditions. The mean volume integrated A_T content also increased with up to 50 μmol kg^{-1} when generation and depletion of total alkalinity were in use. This is probably caused by irreversible denitrification around the redoxcline.

Paper II led us to conclude that model predictive capability in marine environments with strong biogeochemical gradients is improved by coupling the dissolved inorganic carbon system to biogeochemical reactions. It enables simultaneous evaluation of eutrophication, acidification, and climate change, and is essential in regions with permanent or periodic anoxia, such as the Baltic Sea.
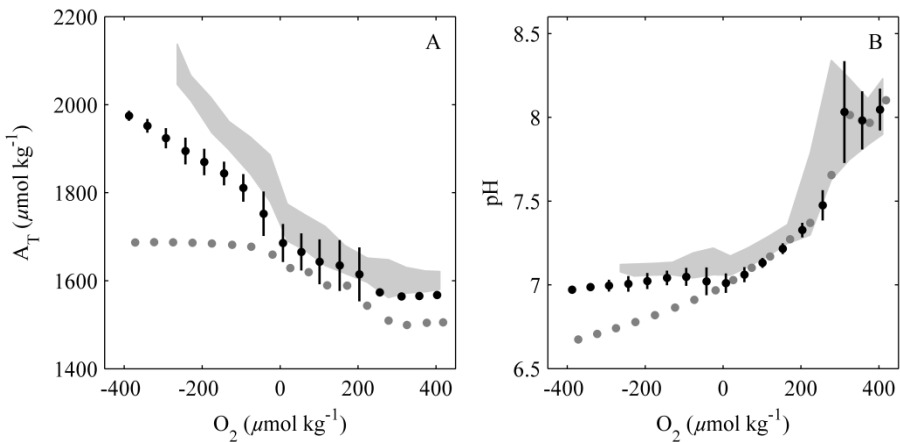
Figure 6. A) Total alkalinity (A_T) and B) pH as functions of oxygen concentration for 0–250 m at station BY15, the Gotland Deep. The observational data (1995–2004) are indicated light grey area, the black markers and lines represent a model run including internal generation of A_T, and the grey markers represent a model run excluding internal generation of A_T. (Figure from paper II)
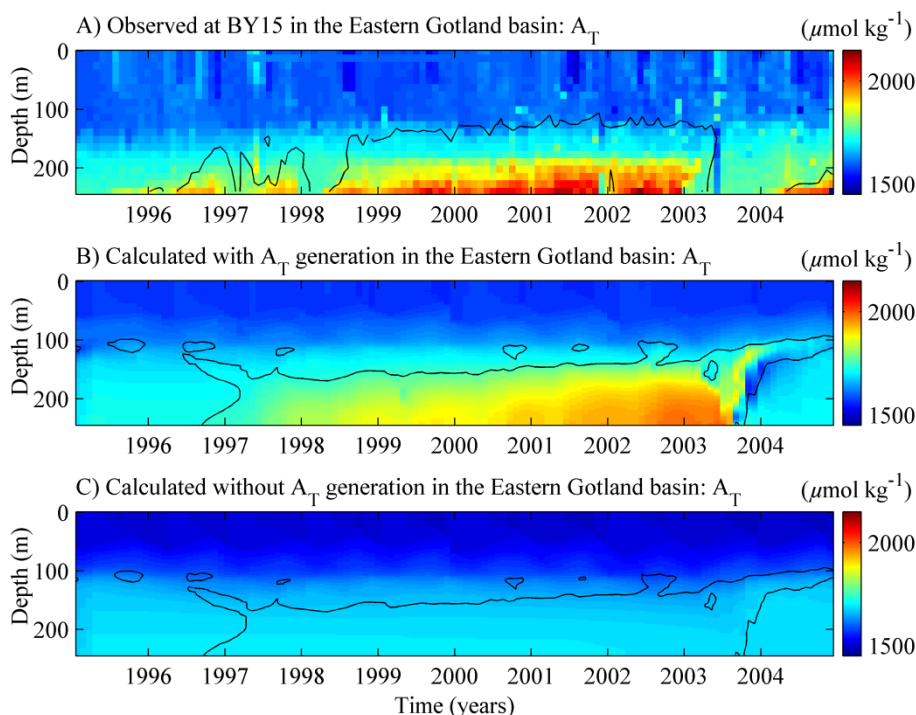
Figure 7. *Total alkalinity at the BY15 station in the Eastern Gotland basin. The redoxcline is indicated by thin black lines. A) Observations (SHARK-data). B) Model results with internal A_T generation and depletion. C) Model results without internal A_T generation and depletion. (Figure from paper II)*

4.3. The future – Use the skill and knowledge (paper III)

The PROBE-Baltic model was now fully coupled and the development presented in paper II and Gustafsson et al. (2011) were combined to create a capable scenario model. It was evaluated by objective skill metrics during a control period and used to analyse possible future changes in Baltic Sea pH and oxygen concentrations. This paper was a product of the BONUS+/Baltic-C project, and the marine model was coupled to the CSIM catchment model, which was in turn coupled to the vegetation model LPJ-GUESS, to create a catchment–sea model which was forced with meteorological and hydrological datasets and scenarios (for details about the different models see paper III).

All examined scenarios indicated future acidification of the whole Baltic Sea and the result was insensitive to the chosen global climate model. The results indicated that increased nutrient load would amplify the seasonal pH cycle by increased biological production and mineralization, which could be expected from the results in paper I. Climate change and land-derived changes affected pH mainly by altering the seasonal cycle and deep-water conditions. Apart from pH, also other environmental indices were examined. All future scenarios indicated decreased saturation state of calcium

carbonate, decreased respiration index, and an increasing hypoxic area. All these factors threaten the marine ecosystem.

It was concluded that the main factor controlling the direction and magnitude of future pH changes was the atmospheric CO_2 concentration and all examined scenarios indicated future acidification of the whole Baltic Sea. This is shown in Fig. 8 where the modelled present day pH is presented to the left and the estimated future change in pH is shown to the right. If the Baltic Sea Action Plan (BSAP) is implemented, and an optimistic (B1) CO_2 emission scenario followed, we can expect pH changes in the range of -0.2 in surface waters, while the effect will be less in deep water masses dominated by inflows. The oxygen conditions remained the same as today for this scenario. If we instead continue with business as usual (BAU), we should expect a pH decrease of about -0.5, and substantial deterioration of the bottom water oxygen conditions. However, there is a limit set by stratification and bathymetry for how much the anoxic water volume can increase.

Again it was shown that substantial reductions of CO_2 emissions are needed to minimize future pH decrease, and that nutrient load reduction is needed in order to avoid further increase of hypoxic and anoxic deep water volumes. Paper III thus in many ways supported what was indicated already in paper I.
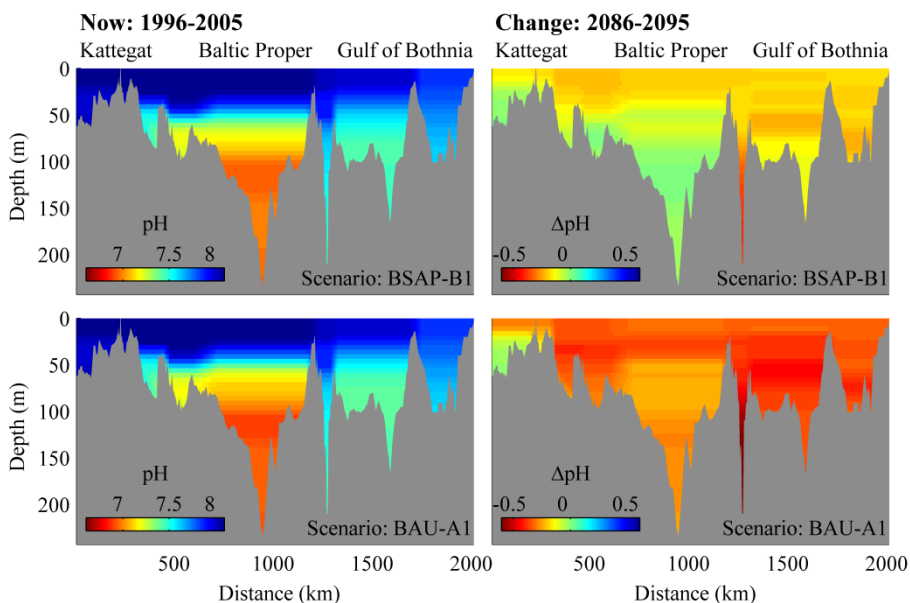
Figure 8. *Current pH (1996-2005) and scenario pH changes (2086-2095) along the black transect in Fig. 1A for the BSAP-B1 (Baltic Sea Action Plan) and BAU-A2 (Business as usual) scenarios. (Figure from paper III)*

4.4. Looking North (paper IV)

When evaluating the present skill of the PROBE-Baltic model and studying literature describing other efforts to model the Baltic Sea (e.g., Eilola et al. 2011), one area always stood out. The Bothnian Bay. Many of the biogeochemical models for the Baltic Sea have problems to return realistic nutrient concentrations, and the PROBE-Baltic had the same issues, as had been obvious in papers II and III. At the same time the co-operation with other research disciplines in the Baltic-C project had hinted that dissolved organic matter (DOM) needed to be considered.

Thus DOM was added to the modelled biogeochemical system in an attempt to realistically model the pCO_2 in the Eastern Gotland basin (BY15) and the Bothnian Bay. The aim was to improve the regenerated production during summer months by allowing phytoplankton to utilize the pool of dissolved organic nutrients. In the Bothnian Bay this would be a substantial addition of available nutrients which could improve the modelling of the inorganic fractions.
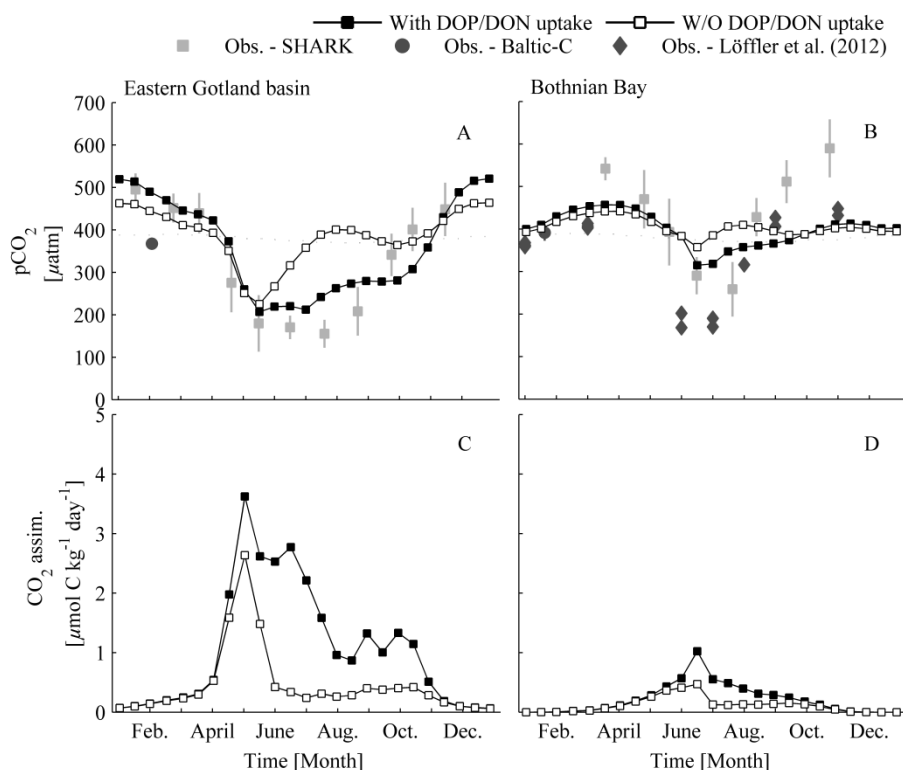
Figure 9. Seasonal variations in surface water (5 m) in the Eastern Gotland Basin and the Bothnian Bay. Modelled mean values for the years 2000-2011. The reference case is marked by a solid black line and black squares, the run with no phytoplankton DOM uptake is marked by a solid black line and white squares. Observations are shown with markers. (Redrawn from paper IV)

Due to scarce DOC measurements in the Baltic Sea it was hard to validate the new variables, but the model could recreate the general magnitude and distribution as far as we knew them. The objective skill metrics showed improved quality in the modelling of both vertical mean profiles and mean seasonal variation in surface waters. The new model version (black line and black squares) is shown in Fig. 9 together with an experiment where the phytoplankton were not allowed to assimilate dissolved organic nutrients (black line and white squares). If dissolved organic nitrogen and phosphate were utilized, the CO_2 assimilation was higher during the summer months and the pCO_2 decreased with about 200 μatm in the Eastern Gotland basin. In the Bothnian Bay, both the duration and magnitude of CO_2 assimilation were doubled when phytoplankton used DOP and DON as nutrient sources.

Paper IV led us to conclude that dissolved organic matter improves the modelling of phytoplankton dynamics, and therewith the CO_2 draw down. But there is still something illusive missing in the modelling of the biogeochemistry of the Bothnian Bay that call for further research efforts.

5. Conclusions

The conclusions from the separate papers have been mentioned previously. The most important general conclusions from this thesis are:

- Objective and uniform evaluation of performance of numerical models helps model development and clearly states the quality of model results. Transparency in the model community is also essential.

- Coupling of the dissolved inorganic carbon system to other biogeochemical reactions improves model skill substantially. It is also needed when several environmental threats are considered simultaneously (eutrophication, acidification, and climate change).

- Acidification of the entire Baltic Sea can be expected (- 0.2 to -0.5 units at the end of the century), and the relevant forcing factor is CO_2 emissions.

- Direct changes in water temperature and salinity will not affect Baltic Sea surface pH to any greater extent. However, climate change may change precipitation and evaporation patterns over the drainage area. With more net precipitation in north and less in south this may reduce the total alkalinity, which would lower the pH of Baltic Sea.

- Acidification will not be dampened by eutrophication. The increased nutrient load will only amplify the seasonal pH cycle.

- In marine systems with strong redox gradients, especially periodic anoxia, *in situ* A_T changes will partly buffer acidification.

- Dissolved inorganic matter is an important nutrient source in the Bothnian Bay, as well as in the Eastern Gotland basin. In the Eastern Gotland basin the improvement is caused by more realistic re-cycling of nutrient in the model.

- Marin sciences at large will benefit from closer links between monitoring and modelling. They are essential to each other, and both areas would benefit from problems in both fields being acknowledged sooner.

6. Future perspective

The dissolved inorganic carbon system is at present being implemented in several biogeochemical models computing the Baltic Sea, and I anticipate further progress in this direction. These models will benefit from having pCO_2 and pH as an indicative variables for the biogeochemical system. I have also experienced that there is a knowledge gap considering our current understanding of the processes governing total alkalinity in the Baltic Sea area. The main distribution patterns may have strong salinity dependence, but I believe that there could be other factors affecting the distribution. I state this because we do not seem to model A_T correctly as effortlessly as we should at present. The sources and sinks that were introduced in paper III is an important step forward, but I think more effort is needed. The effect of dissolved organic molecules on total alkalinity promises to be an interesting area of research and this is probably part of what we are missing.

There is also a current focus on adding dissolved organic matter to models, and the combination of these two developments could produce many interesting research question in the coming years. The introduction of the previously neglected nutrient pool of dissolved organic matter will affect how we model plankton dynamics.

There are remaining problems with our ability to model the northern Baltic Sea, and more work in this region is definitely necessary, but there seem to be good prospects. The main problem is the parameterization of the holding capacity of the sediment with regard to phosphorous. If we come to understand why the sediments seemingly hold more phosphorous in these parts of the Baltic, I think it would greatly improve the biogeochemical modelling of these areas.

Finally, I hope that modellers will work closely with experimental and measurement based sciences and make good use of data from monitoring programs. I sincerely think that this will benefit all. A large hindrance for further development of the parameterizations of the processes we already have in the biogeochemical models is that we cannot evaluate the model result with more accuracy. This leaves us with too many uncertainties, and thus we do not see where the important improvements should be done. Reliable empirical and reanalysed data-sets are needed to force models and marine measurements are needed for validation purposes. Immediate use of monitoring data will also be an effective quality check of measurement procedures, and I am sure data quality would benefit from this type of feedback.

Acknowledgments

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