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The Baltic Sea marine system – human impact and natural variations

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Dedicated to the memory of my mother



Abstract

The environmental state of the Baltic Sea system is influenced by both natural and anthropogenic factors. Water exchange with the adjacent ocean and within the system depend on large-scale atmospheric circulation and properties of the straits separating the different sub-basins. Physical processes control the stratification and determine residence times of water and dissolved substances, which has a major impact on the oxygen situation. Deep water oxygen demand is coupled to the production of organic material, which in turn depends on the availability of plant nutrients in the sunlit surface layer. Plant nutrients are supplied from external waterborne and airborne sources, but there is also an internal supply of remineralized nutrients from the deep water resulting from decomposition of organic material previously produced in the surface layer. In large areas of the system the contemporary rate of deep water oxygen consumption exceeds the rate of oxygen supply, resulting in oxygen poor water hostile to higher forms of life.

Mathematical models of the marine system are the only tools able to determine the relative importance of the many different factors that influence the Baltic Sea environmental state. Without a proper system understanding and attribution of detected threats to their dominant sources, it is not possible to determine the future effects of ecosystem management strategies. The work in this thesis is a part of the development of Baltic Sea modelling tools that can address several different ecosystem threats, and thus serve as support concerning management decisions. In this case the foci are on eutrophication, acidification and climate change. Reconstructions of the factors forcing the system are used to do hindcast simulations up to half a millennium back in time. The ecosystem changes on longer time scales are mainly attributed to anthropogenic fuelling of phytoplankton production as the result of a massive increase in nutrient supply during the twentieth century. Model results indicate that eutrophication may have damped the effect of increasing atmospheric levels of carbon dioxide on surface water pH. The reconstruction of the Baltic Sea past suggests that the physical forcing, which is related to climate variability, so far mainly affects the oxygen situation on an inter-annual to decadal basis whereas significant long-term trends coupled to climate change have not been detected.

Preface

This thesis contains a summary (Part I) and four appended papers (Part II). In the summary, the papers are referred to by their roman numerals.

Paper I:

Gustafsson, E. and Omstedt, A., 2009. Sensitivity of Baltic Sea deep water salinity and oxygen concentration to variations in physical forcing. Boreal Environment Research, 14, 18–30.

Paper II:

Hansson, D. and Gustafsson, E., 2010. Salinity and hypoxia in the Baltic Sea since AD 1500. Submitted to Journal of Geophysical Research – Oceans.

Paper III:

Omstedt, A., Gustafsson, E. and Wesslander, K., 2009. Modelling the uptake and release of carbon dioxide in the Baltic Sea surface water. Continental Shelf Research, 29, 870–885, doi:10.1016/j.csr.2009.01.006.

Paper IV:

Gustafsson, E., 2010. Modelled long-term evolution of particulate organic carbon flux to the Baltic Sea deep water. Submitted to Journal of Marine Systems.

Omstedt initiated Paper I, whereas modelling was conducted by Gustafsson. The results were jointly interpreted while Gustafsson did most of the writing.

The idea for Paper II came from Omstedt. The paper was initiated by Hansson who wrote the first draft, in which most of the modelling was carried out by Gustafsson. The analysis has been extended by Gustafsson who also wrote the revised version of the paper.

Paper III was initiated by Omstedt. Gustafsson contributed with modelling, analysis of the results and part of the writing.

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Part I

Summary



Cyanobacteria bloom in the Baltic Sea observed from space (provided by the NASA/Goddard Space Flight Center, http://visibleearth.nasa.gov/).

1 Introduction

Hypoxia refers to a state when the oxygen concentration in the water is too low to support higher forms of life. Though species-dependent, about 90 μ mol O_2 I^{-1} is generally defined as the limit for hypoxia. As higher organisms either abandon oxygen poor water or suffocate, "dead zones" are formed. Hypoxic conditions are mostly associated with areas where stratification of the water column and a constrained water exchange with adjacent regions result in a long residence time and a limited supply of oxygen to deeper layers. As organic matter decomposes, oxygen is consumed. The oxygen demand depends on phytoplankton blooms producing degradable particulate organic matter, which in turn is limited by the availability of plant nutrients in the productive zone of the ocean. Steadily increasing populations along the rims of coastal seas and within the catchment areas go hand in hand with eutrophication – an excess production of organic matter related to anthropogenic supply of plant nutrients to the ocean. Eutrophication is normally associated with leakage of industrial fertilizers, release of untreated sewage water and atmospheric deposition of plant nutrients. Eutrophied coastal seas is a worldwide phenomenon with an exponential expansion of "dead zones" as a consequence (Diaz and Rosenberg, 2008).

Eutrophication and hypoxia in the Baltic Sea have been studied intensely and a rich literature exists on the subject (cf. Savchuk (2010) and references therein). The contemporary net production of organic carbon has been estimated to be two times larger than during the 1930s (Schneider and Kuss, 2004). In addition, the sediment burial of organic carbon at the deep accumulation bottoms of the system has more than doubled during the last century (Emeis et al., 2000). The burial rate increased especially rapid during the 1950s, which is also the period when the use of industrial fertilizers begun to increase substantially. Before 1970, high quality data of nutrient loads are not available. However, according to reconstructions of the loads at the beginning of the twentieth century, the contemporary total external supplies of nitrogen and phosphorus may be two and three times larger respectively (Savchuk et al., 2008). It is widely recognised that anthropogenic fertilization of the sea is an important factor concerning the vast area of oxygen-poor deep water that has characterised the Baltic Proper since the 1950s (e.g. Boesch et al., 2006, HELCOM, 2009). On average, the area suffering from hypoxic conditions during the last decades was about 42 000 km² (Conley et al., 2009a). This is presently considered to be the largest "dead zone" in the world (Diaz and Rosenberg, 2008).

With approximately 85 million inhabitants in the catchment area, an anthropogenic influence on the oxygen conditions is inevitable. The relative importance of eutrophication compared to the physical factors that control water exchange however remains unclear. Sediment records indicate a correlation between climate variations and the state of the Baltic Sea, with strong stratification and hypoxic conditions associated with mild and dry periods in the past (Zillén et al., 2008). But, such periods are also associated with increased populations and consequently an increased utilization of arable land (Zillén and Conley, 2010). Recent changes in climate have occurred on the same time-scale as increases in nutrient loads, and the two effects may as a consequence be difficult to separate from one another (Conley et al., 2009a).

The Baltic Sea is a highly dynamic system with substantial inter-annual and long-term variability concerning for example stratification, salt content, as well as concentrations of oxygen and nutrients. One aim of this thesis is to examine how the oxygen situation in the deeper and temporarily isolated parts of the Baltic Sea responds to the physical forcing or in other words changes due to variations in the region's climate. In Paper I it is examined how the climate affects the stratification in the Baltic Sea and how the stratification in turn

influences oxygen conditions in the vast majority of water volume in this system. Paper II treats the Baltic Sea deep water history based on reconstructed climatic forcing. Oxygen conditions and salinity during the past 500 years are modelled, and long-term interactions between climate variability and deep water ventilation are analysed.

Another aim is to examine large-scale and long-term evolution of biogeochemical properties in the Baltic Sea. The vertical circulation is of major importance to this system's oxygen state, and the oxygen concentration largely controls the fluxes of nutrients within the water body and between the water and sediments. Thus, the ultimate control of nutrient dynamics to some degree lies within the physical circulation. But, anthropogenic fuelling of the ecosystem productivity amplifies the oxygen demand and accelerates the nutrient feedback processes. Another concern is the acidification of marine areas associated with increased levels of carbon dioxide in the atmosphere. In Paper III a biogeochemical model that includes nutrients and plankton interactions as well as the carbonate system is coupled to the physical circulation model described in Paper I & II. Here it is examined how eutrophication and acidification together affect the long-term acid-base balance in the Baltic Sea. In Paper IV the vertical flux and sediment accumulation of organic material during the last century are examined in relation to changes in climate and nutrient loads.

2 Area description

2.1 The Baltic Sea system

Conceptually, the Baltic Sea can be described as a large estuary composed of a number of sub-basins (Figure 1). Five macro-regions can be identified: the transition area, the Baltic Proper, and its three major gulfs (the Gulf of Bothnia, the Gulf of Finland and the Gulf of Riga), cf. Table 1.

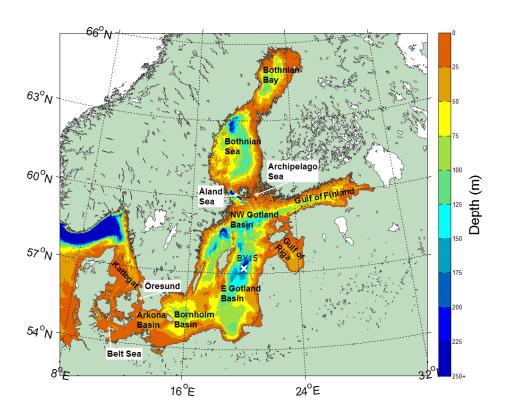


Figure 1. A major division of the Baltic Sea system of sub-basins. Depths down to 250 meters are shown though the maximum depth does exceed 250 meters at a few locations. White cross marks the location of measurement station BY15.

There is a positive water balance in this system, that is, river runoff and precipitation exceed evaporation. On average, the net freshwater input amounts to 500 km³ annually. A large fraction of the total freshwater input enters the Gulf of Finland and Gulf of Bothnia through major rivers (Table 1). This freshwater surplus results in a net outflow through the Danish Straits. The exchange with the ocean is mainly forced by pressure gradients resulting from differences in water level outside and inside the straits. On average, about 1 000 km³ of brackish Baltic Sea surface water leaves the system annually while ~500 km³ of denser water enters the system. There is thus a net outflow of approximately 500 km³ through the straits that on a long-term basis balances the net freshwater input. The inflowing denser water is typically a mixture of one part Kattegat deep water and two parts recirculated Baltic Sea surface water (Stigebrandt and Gustafsson, 2003). The annual input of "new water" amounts to approximately 660 km³, resulting in a mean flushing time of more than thirty years for the

¹ Net freshwater input plus the part of inflowing deepwater that is not recirculated surface water.

system. The large supply of fresh water to the gulfs together with the inflow of partly oceanic water through the Danish Straits result in a horizontal salinity gradient in the system. During a normal ice season all three major gulfs become completely covered by ice, as opposed to the central basin which is only covered during extremely severe winters².

Table 1. Properties of the five macro-regions and their sub-basins³.

Sub-basin		area	Volume	Mean	depth	River runoff ⁴
	(km^2)		(km ³)	(m)		$(km^3 yr^{-1})$
Transition area	43 070		800	19		36
Kattegat	22 000		500	23		32
Öresund	2 3 3 0		30	13		0
Belt Sea	18 740		270	14		4
Baltic Proper	213 690		13 250	62		113
Arkona Basin	19 070		440	23		6
Bornholm Basin	38 990		1 780	46		24
Eastern Gotland Basin	90 810		6 450	71		68
North-Western Gotland Basin	64 820		4 590	71		14
Gulf of Riga	17 910		410	23		32
Gulf of Finland	29 600		1 100	38		114
Gulf of Bothnia	116 300		6440	55		190
Archipelago Sea	8 300		200	23		0
Åland Sea	5 200		410	79		0
Bothnian Sea	66 000		4 340	68		91
Bothnian Bay	36 800		1 490	43		100

2.2 The Eastern Gotland Basin

The Eastern Gotland Basin is the largest sub-basin in the system (Table 1). Within this basin, the Gotland Deep between Gotland and Latvia is with its 249 meters one of the deepest pits in the system. Oceanographic measurements at the station BY15 (Figure 1) in the Gotland Deep cover more than a century, but with large gaps during the two world wars. Because of its representativeness for the central Baltic Sea and also because of the vast amount of observational data, most of the work in this thesis has been focused on the Eastern Gotland Basin. The volume of the deep water is small. The water below 125 metres or in other words the lower half of the water column comprises only 5 percent of the total basin volume. Almost 65 percent of the volume resides above 60 meters, which is the typical depth for the upper part of the permanent halocline.

Annually averaged measurements of salinity, temperature and oxygen concentration at BY15 since the early nineteen hundreds are shown below (Figures 2, 3 and 4). Data were extracted from the SMHI database Swedish Ocean Archive (SHARK) and the Baltic Environmental Database (BED). Before 1940, the resolution of measurements is poor. Typically there is just

² http://www.smhi.se/kunskapsbanken/oceanografi/isforhallanden-i-ostersjon-1.7024

³ Information on areas and volumes available in the online version of the Swedish National Encyclopaedia: http://www.ne.se/%C3%B6stersj%C3%B6n/%C3%B6stersj%C3%B6ns-havsomr%C3%A5den

⁴ Mean river runoff based on data from the BALTEX hydrological data centre for the period 1950-1998.

one or a few profiles each year, and measurements are biased towards the warmer months. A consequence of this is that summer conditions dominate when annual means are formed, resulting in high temperatures, low salinities and low oxygen concentrations in the surface layer. In addition, the spatial resolution is limited for early oxygen measurements (Figure 4) – samples were then normally taken only every 50 meters.

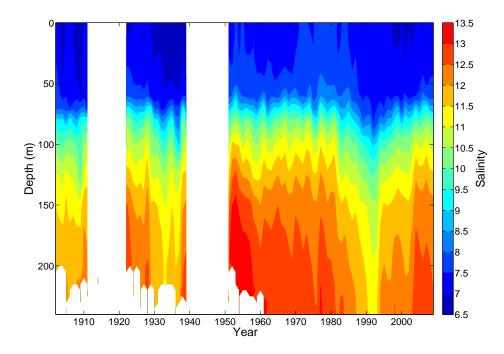


Figure 2. Annual means of salinity measured at BY15 since the beginning of the twentieth century. White colour represents missing values.

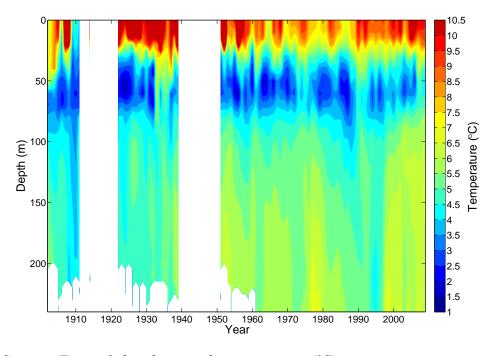


Figure 3. Same as Figure 2, but this time for temperature (°C).

3 Dynamics of the Baltic Sea marine system

3.1 Water exchange

On a first-order process level, the Baltic Sea system can mechanistically be described as a number of sub-basins connected by straits through which the flows are controlled by the dominant physical processes. Flows between basins are driven by horizontal pressure gradients, either barotropically due to differences in water level, or baroclinically as a result of differences in vertical stratification between adjacent basins. In barotropic flows, the horizontal pressure gradient is balanced by topographic resistance and bed friction. Depending on strait topography, different physical processes control the baroclinic flows. Most straits separating the major sub-basins of the Baltic Sea are sufficiently wide for the earth rotation to affect flows between basins, resulting in surface or bottom currents running along the basin walls. In these baroclinic geostrophic flows, the internal horizontal pressure gradient is balanced by the Coriolis force, and the flows are controlled by stratification and earth rotation (Stigebrandt, 2001).

The complex dynamics of inflowing water entering the system (e.g. Reissman et al., 2009) can as a first approximation be described as a dense current flowing along the bottom from basin to basin: Water with sufficiently high density passing through the Danish Straits – due to barotropic or baroclinic processes – replenishes the bottom pool of the Arkona Basin inside the straits. This Arkona deep water can subsequently spill over to the Bornholm Basin and replace the deep water there, which in turn supplies the southern and eastern parts of the Baltic Proper with salty and dense water. Entrainment of lighter surrounding water results in a continuously decreasing density of the bottom current and finally the inflowing water is interleaved at the depth of neutral buoyancy in the Eastern Gotland Basin. The intrusion depth is determined by the initial volume and density of the inflow, and also the density of the entrained ambient water that dilutes the dense bottom current (cf. Stigebrandt, 2003).

At this point, only one third of the water in the dense current origins from outside the straits (on average), while the remaining two thirds consist of entrained brackish surface water (Stigebrandt and Gustafsson, 2003). The water entering through the straits is already a mixture of typically one third ocean water and two thirds brackish water (cf. section 2.1), and as a long-term mean only about one ninth of the intruding deep water is "new water" whereas the major part is recirculated surface water. From the Baltic Proper, relatively dense deep water spreads to the east and north and thus supplies the deep water in the major gulfs with saline and oxygen-rich water. The brackish surface water on average moves in the opposite direction – from the gulfs and through the central basin, leaving the system through the transition area – completing a Baltic Sea conveyor belt (Reissman et al., 2009).

3.2 Deep water ventilation

The oxygen situation in the deeper parts of the Baltic Sea is on an annual to decadal time-scale strongly dependent on climate variations or in other words on changes in physical forcing. Oxygen is mainly supplied to the deep water by intrusions of dense water originating from the Kattegat. These dense inflows bring not only oxygen but also salt and thereby maintain the vertical stratification. Concerning the oxygen situation the effect of dense inflows is therefore twofold. They do supply oxygen to the deeper layers but simultaneously act to strengthen the stratification and thereby constrain the oxygen exchange between the surface layer and the deep. During climatic periods that are wetter than normal, the freshwater

content in the Kattegat surface layer increases, which may have the effect that inflows of dense water are not as saline as usual. This means that inflowing water finds its depth of neutral buoyancy higher up in the water column, typically in the upper part of the halocline region. Subsequently such less dense inflows may ventilate large portions of the halocline region, especially if the stratification is further broken down by strong winds during the winter season (Gustafsson and Stigebrandt, 2007).

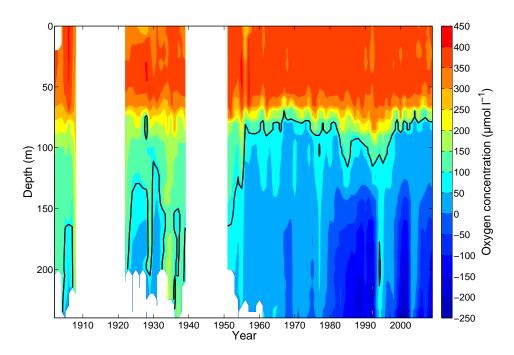


Figure 4. Same as Figure 2, but this time for oxygen concentration (μ mol Γ^1). The black line represents the limit for hypoxia (here defined as 90 μ mol Γ^1). During anoxic conditions, hydrogen sulphide is expressed as negative oxygen equivalents.

As shown by Conley et al. (2002), the ten-year long deep water stagnation period between 1983 and 1993 eventually resulted in comparatively more favourable oxygen conditions within a large part of the water body (cf. Figure 4). Though the deepest parts of the Baltic Proper suffered from severe anoxia, a larger volume than usual of the upper deep water could benefit from a more intense ventilation as the result of a weakened stratification and deepened halocline. Normally, the top of the permanent halocline resides at about 60 meters depth in the Baltic Proper. During the 1983–1993 period, the salinity throughout the water column decreased steadily, especially in the deep water (Figure 2). The density stratification then weakened due to the loss of salt, which in combination with strong winds resulted in that the upper part of the halocline was eroded down to about 90 meters. This increased the volume of the wintertime well mixed layer in the Eastern Gotland Basin from about 4 300 km³ to 5 600 km³. These temporal signs of remediation have now disappeared as saltwater inflows eventually have strengthened the stratification.

On a seasonal scale, oxygen concentration in the surface layer is positively correlated with salinity and negatively correlated with temperature due to the oxygen solubility dependency (Weiss, 1970). To remove the seasonal signal, annual average values were used to calculate cross correlations between temperature, salinity, oxygen and nutrients at BY15 during the period 1970–2009 (Figure 5, left panel). A clear negative correlation between salinity and oxygen is found in the upper deep water whereas the opposite is seen in the lower half of the

water column as well as in the surface layer. The positive correlation between oxygen and salinity in the surface layer is probably an effect of temperature. During the early 1990s when salinity was especially low in the surface layer, oxygen concentrations were comparatively low as well which can be related to high wintertime temperatures. Temperature and oxygen are not correlated in the deeper deep water during this period, whereas a negative correlation is found especially in the surface layer due to the solubility effect.

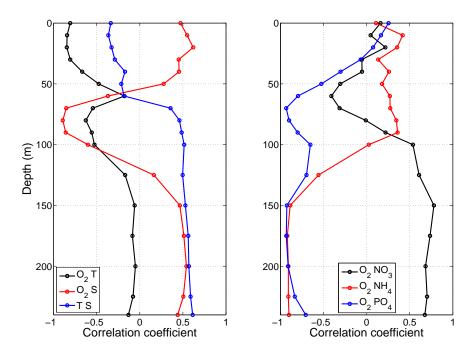


Figure 5. Cross correlations between annually averaged salinity, temperature and oxygen concentrations (left panel) and oxygen, nitrate, ammonium and phosphate concentrations (right panel), based on measurements from BY15 during the period 1970–2009 (from the SHARK database). During anoxic conditions, hydrogen sulphide is expressed as negative oxygen equivalents.

3.3 Biogeochemical feedback processes

Cycling of phosphorus and nitrogen is strongly coupled to oxygen conditions because of the feedback processes arising when oxygen is close to depletion. Oxygen is preferably reduced during remineralization of organic material as this results in the highest energy yield. During oxygen poor conditions however, other agents must be used. The dominant processes taking place can be described as a succession of other oxidants being reduced in an order determined by energy yield (e.g. Jørgensen, 1996). Nitrate is reduced first, resulting in nitrogen gas production due to denitrification. This is followed by the reduction of oxidized forms of manganese and iron. The reduction of metal oxides has very important consequences for the phosphorus cycling as described below. This is followed by sulphate reduction which results in the production of toxic hydrogen sulphide. Finally, organic matter in deep layer sediment can be decomposed by methanogenesis. If oxygen is again supplied to the water, the reduced agents are oxidized again but in the reverse order.

Decomposition of organic material results in the production of e.g. ammonium and phosphate. If oxygen is present in the water, the ammonium is subsequently nitrified to nitrate. If the oxygen concentration on the other hand reaches a critical low level – which it always does at

some depth in the sediments – nitrogen gas is produced due to denitrification (and/or anammox). Denitrification is dependent on nitrate produced by nitrification and there is thus a strong coupling between ammonium production, nitrification and denitrification (e.g. Jørgensen, 1996). If the water turns anoxic, there is an initial large nitrogen sink due to denitrification. Nitrification becomes impeded due to the lack of oxygen and the result can then be a substantial ammonium accumulation. If the anoxic conditions persist after the nitrate has been depleted, further denitrification is impeded because of its dependence on nitrate produced by nitrification. Whether the overall effect of expanding oxygen-poor areas is a sink or a source of bio-available dissolved inorganic nitrogen (DIN) may thus be difficult to predict. In the Baltic Proper, an overall negative correlation between the DIN pool and the volume of hypoxic water has however been shown (Vahtera et al., 2007; Savchuk, 2010). An expansion of oxygen-poor areas thus results in a net DIN sink on basin level in spite of ammonium accumulation.

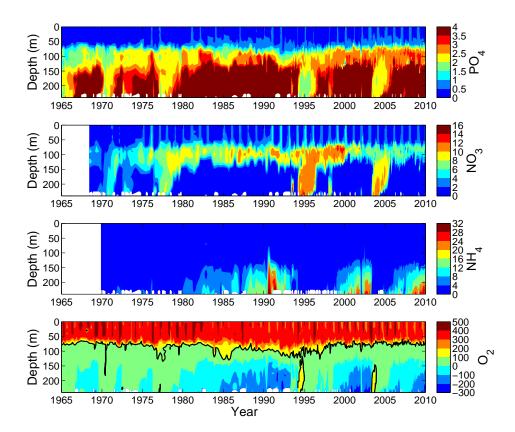


Figure 6. Observations of phosphate, nitrate, ammonium and oxygen (μ mol Γ^1) at BY15 between 1965 and 2009. Black line represents the 90 μ mol Γ^1 limit for hypoxia (lower panel). During anoxic conditions, hydrogen sulphide is expressed as negative oxygen equivalents. White colour represents missing data. Gaps in the measurements were filled by linear interpolation down to 225 metres. Data retrieved from the SHARK database.

In oxygen-rich water, a fraction of the phosphate produced during benthic decomposition is bound to iron oxyhydroxides (and other metal oxides) and deposited at the sediment surface. The remaining part is released to the water. If the oxygen concentration is reduced to a critical low level, there is apart from remineralization an additional rapid release of phosphate from the sediments to the water due to dissolution of e.g. iron-hydroxo phosphates (Fe-P). After all the deposited Fe-P has been dissolved, phosphate release to the overlying water continues but

at the lower rate associated only with remineralization. If an inflow of oxygen-rich water occurs, Fe-P is deposited again. In the Baltic Proper together with the Gulf of Riga and Gulf of Finland, an estimated 100 000 tons of phosphate may on an annual basis be released to the water or deposited at the sediments depending on oxygen conditions (Savchuk, 2010).

The connections between oxygen concentration and the concentrations of phosphate, nitrate, ammonium respectively are very clear in the Eastern Gotland Basin deep water. During extended periods of anoxia in the deep water, the corresponding phosphate concentrations reach high levels as expected (Figure 6, panel 1). Inflows of oxygen-rich water can on the other hand temporarily reduce the deep water phosphate concentrations substantially, as for example seen after the 1977, 1993 and 2003 major deep water inflows. During oxic conditions, deep water ammonium concentrations are low, whereas nitrate is abundant. The opposite is seen during anoxic conditions, when ammonium concentrations can be very high while nitrate is depleted (Figure 6, panel 2 and 3). A correlation analysis further reveals the oxygen control on nutrients (Figure 5, right panel). A very strong negative correlation between oxygen and phosphate is seen in the deep water, which again is the result of dissolution and precipitation of Fe-P during anoxic and oxic conditions respectively. During oxic conditions the ammonium produced in the deep water as organic matter decompose is oxidized into nitrate, whereas nitrate is reduced during oxygen depleted conditions. In the lower half of the water column, ammonium is thus negatively correlated and nitrate positively correlated with oxygen.

3.4 Plankton dynamics

Diatoms that are normally abundant during spring may have relatively high sinking speeds. A large fraction of the particulate organic carbon produced early in the season may thus be lost from the surface layer and mainly remineralized in the deep (Blomqvist and Heiskanen, 2001). Dinoflagellates, which sometimes dominate the spring bloom are associated with lower sedimentation rates. Nutrients can thus be more effectively recycled in the upper part of the water column. During the spring bloom, nitrate is almost depleted down to the top of the permanent halocline, whereas phosphate is still abundant in the surface layer at the collapse of the bloom. Nitrogen fixing cyanobacteria are thus favoured and can indeed be observed in massive surface accumulations during calm summer conditions. Because of the buoyancy of cyanobacteria, their direct contribution to the oxygen demand in the deep water is often assumed to be small (e.g. Blomqvist and Heiskanen, 2001; Vahtera et al., 2007). Based on nitrogen isotopes, Voss et al. (2005) however found that at least 50 percent of the nitrogen in the central Baltic Sea sediment pool originated from fixation of atmospheric nitrogen. Whether directly, or indirectly by fuelling the next season's spring bloom, cyanobacteria are thus important contributors to the deep water oxygen demand.

Observations of CO₂ partial pressure (pCO₂) indicate that an additional source of nitrogen in the Baltic Proper is utilized during spring and early summer, apart from the surface layer nitrate pool that is replenished during winter (Schneider et al., 2009). After the collapse of the spring bloom which occurs as the nitrate pool in the surface layer is exhausted, pCO₂ remains at a low level despite the solubility effect that tends to increase pCO₂ as temperature increases. It is not yet clear what the origin of this extra source is. Fixation of atmospheric nitrogen during spring has been suggested as the main source (e.g. Schneider et al., 2009) and this assumption has also been used in model parameterizations (e.g. Omstedt et al., 2009). Sufficiently large blooms of cyanobacteria to explain the suppressed pCO₂ after the spring bloom have however as yet not been observed. Another possibility is that phytoplankton to

some extent are able to use the large pool of dissolved organic nitrogen (cf. Eilola, 2009). Vertically migrating species can to some extent play a role as well (Höglander et al., 2004), enabling an additional supply of nitrogen from below the photic zone. The overconsumption of carbon and associated increased transport of organic carbon out of the productive layer that has been observed in some systems may also contribute (Schartau et al., 2008).

3.5 Nutrient supply

Waterborne nitrogen input (riverine input, direct point and diffuse sources) and atmospheric nitrogen deposition to the Baltic Sea during the period 2001–2006 have been estimated to be about 640 000 and 200 000 t yr⁻¹ respectively (HELCOM, 2009). In addition, cyanobacteria can through fixation of atmospheric nitrogen gas import a large amount of nitrogen to the system. Estimations of nitrogen fixation in the Baltic Proper vary between 200 000–800 000 t yr⁻¹ (e.g. Larsson et al., 2001; Wasmund et al., 2005). Inter-annual variability is substantial, which partly explains this very large range, but estimations also depend on method. Comparing these numbers to the contemporary waterborne loads and atmospheric deposition, nitrogen fixation can supply some 20–50 percent of the total nitrogen input to the system. The waterborne input of total phosphorus during the period 2001–2006 was on average about 30 000 t yr⁻¹ whereas the atmospheric contribution was only 1–5 percent of the total input (HELCOM, 2009). However, the external load of phosphorus represents only a small part of the phosphorus available for plankton production. Remineralization in the upper water column and entrained deep water contribute with the major fractions (Vahtera et al., 2007).

Temporal and spatial changes in nutrient concentrations observed since 1970 depend more on internal nutrient feedback processes (cf. Section 3.4) than they depend on the variable external loads. Magnitudes of plankton blooms are as a consequence not directly determinable from the magnitudes of the external loads. External nitrogen loads can be counteracted by sinks related to biogeochemical feedback processes together with permanent burial. The large supply of phosphorus since the 1960s has however not been balanced by sinks, resulting in a large long-term accumulation amounting to 200 000–300 000 tons during the last five decades (Savchuk, 2010).

3.6 Nutrient load reductions and large-scale engineering

If the contemporary high nutrient loads are allowed to continue and if the atmospheric circulation essentially remains the same, the large hypoxic areas and other signs of eutrophication in the Baltic Sea will persist. Only limited periods of system self remediation such as during the 1990s can be expected. In the eutrophication segment of the HELCOM Baltic Sea Action Plan (BSAP), the overall future goal is a Baltic Sea unaffected by eutrophication (HELCOM, 2007). In order to reach this goal, maximum allowable annual inputs of nutrients to the entire system have been estimated to 21 000 tonnes of phosphorus and 600 000 tonnes of nitrogen from waterborne and airborne sources combined. Because of the nutrient feedback processes in response to oxygen conditions, management is however complicated. If an improved oxygen situation is achieved, the internal phosphate load is expected to decrease as the sediment leakage diminishes. The long-term effect of improved oxygen conditions on the phosphorus retention is however not clear. Concerning DIN on the other hand, observations reveal an overall negative correlation between hypoxic water volume and DIN pool size, i.e., the DIN pool increases during improved oxygen conditions (e.g. Savchuk, 2010).

Future scenarios concerning the response of nutrient cycles to external load reductions have been simulated in different studies. Neumann and Schernewski (2005) modelled the possible future effects if both phosphorus and nitrogen loads to the Baltic Sea were to be reduced by fifty percent. According to their results, several decades would pass before an overall positive effect of such large nutrient reductions could be expected. Similarly, but with different model parameterizations, Savchuk and Wulff (2009) modelled the future evolution if the external loads instantly were to be reduced to the levels that probably prevailed at the beginning of the twentieth century. Their results suggest an initial rapid positive effect followed by a century-long decrease slowly going towards a new balance. Even if the HELCOM nutrient reduction goals were to be reached overnight, one would have to wait to see positive responses. One reason is the long residence times in the deep water. The large internal supply of phosphate compared to external loads (e.g. Vahtera et al., 2007) can continue to fuel cyanobacteria blooms and thus a large nitrogen fixation even if external phosphorus loads are reduced.

There are currently several different projects running with the aim to artificially force a rapid improvement of the Baltic Sea ecosystem state. Three major tracks can be distinguished, all with the main goal to reduce phytoplankton abundance and deep water oxygen demand (cf. Conley et al. 2009b). These can be classed as physical, chemical and biological manipulation strategies. Physical manipulations include different methods to artificially oxygenate the deep water and also alterations of the flows through the Danish Straits (cf. Gustafsson et al., 2008). Another possibility to reduce phosphate concentrations and productivity is to add chemicals to the water in order to bind and precipitate phosphate. The third main track is ecosystem remediation by biomanipualtion. This could possibly be achieved by for example removing planktivorous fish in order to increase the grazing pressure on phytoplankton. There are uncertainties concerning the overall effects on the ecosystem associated with all three methods (Conley et al. 2009b). Regardless of method performed on a large scale (if any of the above), this must be done together with a reduction of external nutrient loads. At the moment, phosphorus load reductions seem most crucial in the Baltic Proper since nitrogen fixation may counteract reductions in nitrogen loads. But, model studies (e.g. Wulff et al., 2007), suggest that the largest positive long-term effects concerning e.g. oxygen conditions result from simultaneous reductions of both nitrogen and phosphorus loads.

3.7 Future climate change

Another concern is the future impact on the Baltic Sea ecosystem following a continuous warming. Model studies indicate a 3-5 °C air temperature increase in the region during this century (BACC, 2008). Apart from the temperature effect on oxygen solubility, changes in net precipitation and thus freshwater load to the Baltic Sea are to be expected. Warming is probable to have the effect that runoff increases in the north and decreases in the south (Graham, 2004; Hansson et al., 2010). There are however different views concerning the overall effect. Graham (2004) suggests an overall increased freshwater input of up to 15 percent depending on climate change scenario. On the contrary, Hansson et al. (2010) could from a reconstruction of the past 500 years in the Baltic Sea draw the conclusion that warmer periods were generally associated with an overall decreased runoff. If the total runoff increases, so will the nutrient loads. But at the same time, periods of low salinity are normally associated with improved oxygen conditions. If the overall effect on the other hand is a decreased runoff, we could expect a decreased external nutrient load but simultaneously a stronger stratification. A strong stratification is normally associated with large hypoxic areas and also a large internal phosphate load. This could possibly to some extent counteract the effects of a reduced external phosphorus load.

4 Modelling

In the Baltic Sea system, the physical response to changes in the external forcing, such as freshwater supply and large-scale atmospheric circulation, is rather well understood as shown by hindcast model simulations. The biogeochemical responses to changes in climate and external nutrient loads are not equally well understood at the moment. But, coupled physicalbiogeochemical models are under strong development and a basic understanding of the cycling of nutrients and other dissolved substances has evolved despite uncertainties and gaps in our knowledge. Using the best available estimations of the evolution of climate and nutrient loads in the region, models are the only tools capable of making predictions of future changes in the Baltic Sea. The future development is however inherently unpredictable due to for example economical priorities and technological advances. But at the same time, these factors may to some extent be manipulated and adapted in order to avoid an undesired future course of the Baltic Sea environmental state. Many different processes simultaneously influence the ongoing variations and changes in the system and models are indispensable tools to identify the relative importance of different phenomena. Without a correct first-order understanding of this complex system the impact of different system management options cannot be evaluated. A short description of the model used in this work is outlined in the following sections.

4.1 Mathematical background

Throughout this thesis the PROBE-Baltic model setup as described by Omstedt (1990) is used. The Baltic Sea system is divided into thirteen coupled sub-basins determined from topography (Figure 1 and Table 1). Using a one-dimensional model formulation, it is assumed that these basins are horizontally homogeneous, whereas the vertical resolution is on the order of one meter. In order to describe the system's physical conditions, six state variables are handled. These are summarized in Table 2.

Table 2. State variables in the physical compartment of the PROBE-Baltic model.

State variable (φ)	Description	Unit
ρU	Momentum in the <i>x</i> -direction	kg m ⁻² s ⁻¹
ho V	Momentum in the <i>y</i> -direction	$kg m^{-2} s^{-1}$
H	Heat content	$\mathrm{J}~\mathrm{m}^{-3}$
S	Salinity	-
k	Turbulent kinetic energy	$m^2 s^{-2}$
3	Dissipation of turbulent kinetic energy	$\mathrm{m}^2\mathrm{s}^{-3}$

Salinity and temperature⁵ together determine the density stratification. Boundary conditions for the state variables must be defined as well, and the success of the model relies on the quality of the meteorological forcing that is used to calculate the boundary conditions. Wind speed is for example required to specify the boundary conditions for momentum, turbulent kinetic energy and dissipation. To determine the different components in the net heat exchange between ocean and atmosphere, air temperature, relative humidity and cloudiness (which reflects solar insolation and traps long wave radiation) must be known in addition to wind speed. Furthermore, river runoff and net precipitation (precipitation minus evaporation) must be provided for each basin. The model is in addition fed with daily values of the

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⁵ Temperature is derived from the heat variable; $H = \rho c_p T$, where H is heat, ρ density, c_p specific heat capacity and T temperature.

Kattegat water level which is necessary to calculate the barotropic exchange through the Danish Straits.

All state variables (φ) are described by the following conservation equation:

$$\frac{\partial \varphi}{\partial t} + W \frac{\partial \varphi}{\partial z} = \frac{\partial}{\partial z} \left(\Gamma_{\varphi} \frac{\partial \varphi}{\partial z} \right) + S_{\varphi} \tag{1}$$

The first term is the local change in time, the second term vertical advection, the third is turbulent diffusion and the fourth, S_{φ} , symbolizes source and sink terms. W is vertical velocity, v_t the coefficient for turbulent diffusion of momentum or in other words kinematic eddy viscosity and σ_{φ} a Prandtl-Schmidt number which expresses the ratio between momentum diffusion and diffusion of variable φ . The vertical velocity W depends on the horizontal area as well as in- and outflows at a certain depth z:

$$W(z) = \frac{Q_{in}(z) - Q_{out}(z)}{area(z)}$$
(2)

The boundary conditions for the different variables couple the diffusion term to fluxes across the boundaries,

$$\frac{\partial}{\partial z} \left(\Gamma_{\varphi} \frac{\partial \varphi}{\partial z} \right)^{sur,bot} = F_{\varphi}^{sur,bot} \tag{3}$$

Here, $F_{\varphi}^{sur,bot}$ represents the fluxes of variable φ at the air-water and sediment-water interfaces respectively.

A complete description of boundary conditions as well as source and sink terms for the six physical state variables in Table 2 are given by Omstedt and Axell (2003).

4.2 Biogeochemical source and sink terms

In Paper IV (which contains the most detailed biogeochemical model description), thirteen biogeochemical state variables are included and coupled to the physical model (Table 3). These are written as conservation equations as described by Equation 1, with boundary conditions determined according to Equation 3. There are three phytoplankton groups. The first represents fast growing and relatively fast sinking species typical for spring and autumn bloom conditions. The second group represents nitrogen fixing cyanobacteria, which are not limited by low DIN concentrations. Furthermore there is one group representing species more typical for summer conditions; slowly sinking species that are favoured when nutrients are scarce. Zooplankton are described by one bulk equation that also constitutes a closure term for the biogeochemical model. That is, none of the processes higher up in the ecosystem are explicitly modelled, but instead implicitly included in this equation. Detritus is divided into three separate equations, allowing a description of the specific fluxes of organic carbon, nitrogen and phosphorus associated with different processes. The carbonate system is represented by two equations termed acid and basic carbon. From these two equations, pH, total inorganic carbon, CO₂ partial pressure and total alkalinity can be calculated (cf. Omstedt et al., 2009). Three inorganic nutrients are included; nitrate, ammonium and phosphate. These

are largely controlled by the oxygen concentration which is represented by one equation. In many aspects, the biogeochemical model formulation follows the parameterizations described by e.g. Savchuk and Wulff (1996) and Savchuk (2002). A short overview of the source and sink terms associated with the different variables is outlined below. Detailed descriptions of the parameterizations are presented in the appendix belonging to Paper IV.

Table 3. Biogeochemical state variables.

State variable	Definition	Unit
PC_1	Phytoplankton group 1	mol P kg ⁻¹
PC_2	Phytoplankton group 2	mol P kg ⁻¹
PC_3	Phytoplankton group 3	mol P kg ⁻¹
ZOO	Zooplankton	mol P kg ⁻¹
DETC	Detritus, carbon	mol C kg ⁻¹
DETN	Detritus, nitrogen	mol N kg ⁻¹
DETP	Detritus, phosphorus	mol P kg ⁻¹
AC	Acid carbon	mol C kg ⁻¹
BC	Basic Carbon	mol C kg ⁻¹
NO_3	Nitrate	mol N kg ⁻¹
NH_4	Ammonium	mol N kg ⁻¹
PO_4	Phosphate	mol P kg ⁻¹
O_2	Dissolved oxygen	mol O ₂ kg ⁻¹

Phytoplankton

The temporal and spatial appearance of phytoplankton groups is primarily determined by the availability of light and nutrients. In the case of cyanobacteria, an upper salinity limit for blooms to develop is included as well. The first group settles through the water column at a constant rate, whereas the other two are assumed to be able to control their vertical displacement, resulting in zero net sedimentation rate for living plankton from these groups. Growth and mortality rates are temperature dependent, and dead organisms enter the detritus pools. The magnitudes of blooms are furthermore controlled by zooplankton grazing. The first and third groups assimilate carbon dioxide, nitrate + ammonium and phosphate according to Redfield ratios (C:N:P = 106:16:1). Cyanobacteria on the on the other hand have a variable phosphate demand which in the model depends on the phosphate concentration in the ambient water. The C:P and N:P ratios are allowed to vary between 42–420:1 and 6–64:1 respectively, whereas the ratio of C:N = 106:16 is held constant.

Zooplankton

Living organisms from all three plankton groups as well as detritus are consumed by the zooplankton group. Preferential feeding separates the relative grazing pressure on different food sources. A temperature dependence delays the appearance of zooplankton, resulting in a small grazing pressure on spring bloom species. The zooplankton cell stoichiometry is prescribed to be C:N:P = 100:20:1. It is assumed that food is assimilated according to these ratios whereas the residues from food having a different composition are excreted. Excretions of carbon and nutrients directly enter the acid carbon, ammonium and phosphate pools in ratios determined by both the zooplankton stoichiometry and the variable food composition. Natural mortality and predation on zooplankton is described by one loss term, which is assumed to partly fuel the detritus pools and partly enter the nutrient and acid carbon pools. This last division is related to the model closure function of the zooplankton group. All processes higher up in the ecosystem are implicitly included in this bulk equation and in the end one fraction of the organic matter is remineralized due to excretion by predators and

another fraction enters the detritus pool in the form of for example faecal pellets and dead predators.

Detritus

The detritus pools are fuelled by dead organisms and faecal pellets. As the zooplankton cell stoichiometry differ from that of phytoplankton, and as cyanobacteria have a variable cell stoichiometry in this model, detritus is split into three different pools accounting for organic carbon, nitrogen and phosphorus respectively. In addition, nitrogen and phosphorus are assumed to be preferentially recycled compared to carbon. There is a further input associated with resuspension of organic material settled at the sediment surface. A general transport of organic material from shallow depths to the deepwater sediments arises from this resuspension. The loss terms include sinking, remineralization and grazing by zooplankton.

Acid and basic carbon

Sources to the acid carbon pool are remineralization of organic carbon from the detritus pool and in the sediments, zooplankton excretions and also the fraction of the zooplankton loss term associated with mortality and predation described above. The sink term depends on assimilation of carbon dioxide related to phytoplankton production. The acid carbon pool is further altered by the boundary condition at the air-sea interface, which determines the net loss of carbon dioxide to the atmosphere. The abundance of calcifying plankton is assumed to be negligible in the Baltic Sea, and there are as a consequence no sources or sinks in the basic carbon conservation equation.

Nutrients

Inorganic nutrients are assimilated during phytoplankton production and again supplied to the water due to remineralization of organic matter, both in the water column and in the sediments. During oxic conditions, a fraction of the remineralized phosphorus is implicitly assumed to be adsorbed to metal oxides and precipitated. In addition, ammonium is oxidized and enters the nitrate pool. During oxygen poor conditions on the other hand, there is an increased leakage of phosphate from the sediments as the metal oxides are reduced and no longer able to bind phosphate. Nitrogen is on the contrary permanently lost from the bioavailable pool due to denitrification.

Oxvgen

The amount of oxygen produced due to photosynthesis depends on the ratios of nitrate and ammonium assimilated. Sink terms for oxygen are remineralization, nitrification and zooplankton excretion. During oxygen poor conditions, nitrate is primarily used to oxidize organic matter. When nitrate is depleted the reduction of other oxidants such as sulphate, and the associated production of hydrogen sulphide is expressed as negative oxygen equivalents. The decomposition rate is assumed to be independent of oxidant. Oxygen concentration in the surface layer is in addition controlled by the air-sea exchange boundary condition, depending on solubility and wind speed.

Sediment variables

In addition to the thirteen biogeochemical state variables, the depth dependent sediment pools of organic carbon, nitrogen and phosphorus are calculated. Settling phytoplankton and detritus fuel the sediment pools, but depending on the bottom stress, organic material may be resuspended again and enter the detritus pools. A fraction of the settled material is permanently buried whereas the rest is decomposed, resulting in a leakage of acid carbon and inorganic nutrients to the water. Remineralization in the sediments during oxic conditions is

always associated with a denitrification loss, the rate depending on the oxygen concentration in the overlying water. During anoxic conditions, a fraction of the ammonium is adsorbed to the sediments.

5 Summary of papers

All papers in this thesis are model based studies, and the modelling of physical and biogeochemical processes is made from a holistic point of view. The main purpose is to describe large-scale and long-term evolution of physical and biogeochemical properties rather than a detailed analysis of local and temporal phenomena. The approach of the biogeochemical study is to determine the control of nutrient fluxes and large scale budgets rather than a full resolution of all the possible pathways in for example the sediments or at the oxycline in the water column. Oxygen is a key parameter because of the strong nutrient dependence on oxygen concentration, and oxygen is in turn largely affected by the physical circulation. Plankton dynamics is in this work critical to determine the effects on e.g. deep water oxygen demand or surface layer pH, but it is not of so much interest to study the different plankton groups themselves in detail.

5.1 Paper I

Here, the effect of all biogeochemical interactions on the oxygen conditions are highly simplified and described only by long-term average oxygen removal rates. Despite this simplistic model approach, modelled oxygen concentrations agree well with observations during the period 1958–2006 (Figure 7). One implication is that when modelling the long term evolution of oxygen as well as other dissolved substances, an accurate description of the physical circulation is of great importance. It is shown that the volume of well ventilated water increases considerably during periods with wetter and windier conditions than normal. If the climate on the other hand is drier than normal, this may result in spreading hypoxic bottoms areas due to a strengthened stratification that inhibits vertical mixing.

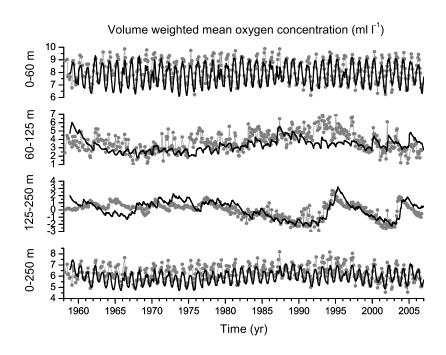


Figure 7. Comparison of modelled (black lines) and observed (gray dots) oxygen concentrations (ml Γ^1) in the surface layer, upper deep water, deeper deep water and total water column. From Paper I.

5.2 Paper II

In this study, the model is forced by reconstructed climatic forcing covering the last half millennium. Among other things it is shown how the correlation between modelled oxygen and salinity in the Eastern Gotland Basin differ depending on depth interval. In the upper deep water (defined as the water between 60–125 meters), a clear negative correlation is found for the period 1500–1950. In the deeper deep water (125–240 meters) however, the correlation is positive (Figure 8). The reason is that below 125 meters, oxygen is supplied by large intrusions of salt water, whereas the upper deep water benefits more from periods of weak stratification and low salinity as discussed in Section 3.2. It is suggested that long stagnation periods lasting up to a decade in the Baltic Sea deep water – though uncommon – probably have occurred at least one time per century since 1500. It is also deemed highly unlikely that the last fifty years of impoverished oxygen conditions primarily can be coupled to the climate change.

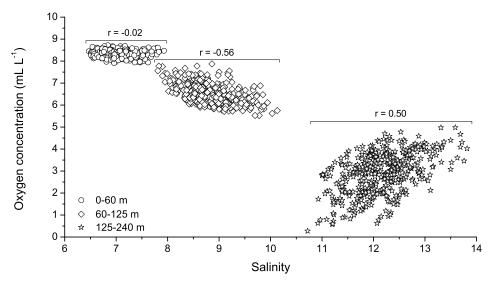


Figure 8. Correlation between salinity and oxygen in the surface layer, upper deep water and deeper deep water. From Paper II.

5.3 Paper III

Here, a complete but comparatively simple system of biogeochemical model equations is coupled to the physical model with the main purpose to describe the carbonate system in the Baltic Sea surface layer. The result is a tool that can be used to examine the ocean-atmosphere exchange of carbon dioxide and also the effect of acidification associated with increasing atmospheric carbon dioxide levels. It is suggested that before 1950 (when the effects of eutrophication are prescribed to start), the Baltic Sea mainly acted as a source of CO_2 to the atmosphere, whereas the effects of eutrophication altered this picture as a consequence of the increased production of organic carbon.

It is also implied that eutrophication to some degree may have counteracted the acidification of the sea associated with increasing atmospheric pCO₂. The development of surface water pH since 1750 is modelled for two different hindcast scenarios. One model run is performed where external nutrient loads were low throughout the run (Figure 9a) and another run where the nutrient loads increased largely the year 1950 (Figure 9b). An increased availability of nutrients results in a larger phytoplankton production and thus a larger assimilation of

dissolved inorganic carbon. This means that the acidification of the sea due to increasing atmospheric pCO₂ can partly be counteracted. It is thus implied that the Baltic Sea surface water pH has probably decreased less than it would have if it were not for eutrophication.

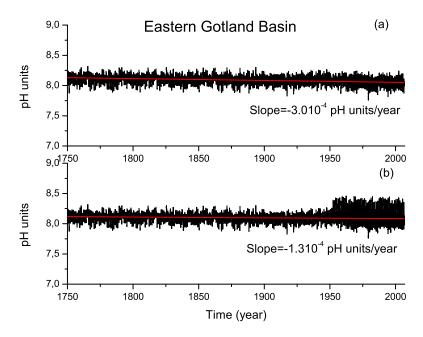


Figure 9. Modelled surface water pH (black lines) and linear fit (red lines) since 1750. The external nutrient loads were assumed to remain at the low levels estimated for the beginning of the twentieth century (a), or increased suddenly the year 1950 to contemporary values (b). From Paper III.

5.4 Paper IV

In the final paper, an expanded and refined biogeochemical module is presented. Here, the vertical flux of particulate organic carbon (POC) to the deep water since 1900 is studied. This flux determines the deep water oxygen demand and ultimately the nutrient feedback processes associated with low oxygen concentrations. Reconstructed climatic forcing is used before the availability of direct observations. Concerning nutrient loads, it is assumed that low preindustrial loads are valid until 1950. The loads then increase substantially during the 1950s due to human activities. In addition, hindcast simulations are performed where the external loads of either dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP) or both DIN and DIP are kept at the low pre-industrial levels throughout the model run.

On average, the contemporary POC flux is found to be two times larger than the flux during the first half of the twentieth century (Figure 10, standard run). If both DIN and DIP loads remain low however, only a very slight POC flux increase of about 1 g C m⁻² per century is found (Figure 10, lower panel). It is thus suggested that the doubled vertical transport of POC during the last century cannot primarily be related to longer-term climate trends. The increased POC flux is instead found to almost completely depend on the increased external nutrient loads from 1950, and also on the nutrient feedback effects following an increased deep water oxygen demand.

Compared to the scenario were both the DIN and DIP loads are low, the POC flux increases in the scenario were only the DIP load is kept low (Figure 10). As the DIN load increases from 1950 and onwards, so does the spring bloom magnitude. Less DIP however remain after the spring bloom, resulting in reduced cyanobacteria blooms. Compared to the standard run, the overall effect is nevertheless a decreased POC flux.

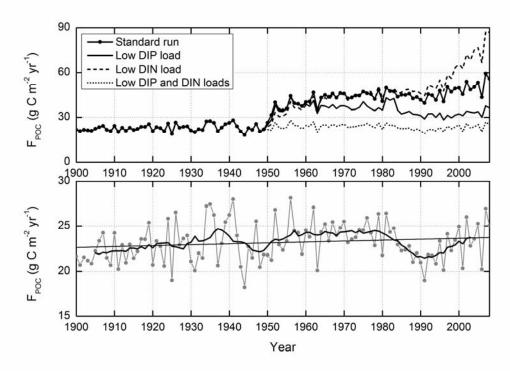


Figure 10. Upper panel: POC flux through the 60 metres horizon resulting from different nutrient load simulations; the standard case and three hindcast scenarios. Lower panel: Close-up of the POC flux where DIN and DIP loads were low (full circles), including a 10-year running mean (thick line) and linear fit: slope = $0.01 \text{ g C m}^{-2} \text{ yr}^{-1}$ (thin line). From Paper IV.

If only the DIN load is kept low, the DIN:DIP ratio in the surface layer decreases following the increased DIP load from 1950. Nitrogen fixing cyanobacteria are thus favoured. In the long run, the increased cyanobacteria production results in an increased POC flux compared to the standard run (Figure 10). This is a consequence of the ability of cyanobacteria in the model to over-consume carbon compared to classical Redfield ratios. The deep water oxygen demand thus slowly increases and ultimately results in an increased internal phosphate load that further amplifies cyanobacteria production.

6 Future outlook

Regarding the future environmental state of the Baltic Sea system, there are several concerns associated with human activities in the catchment area. Major issues are e.g. the large hypoxic areas, potentially harmful algal blooms, and also the effect of the system's acid-base balance related to increasing levels of atmospheric CO₂. Despite the extensive research that has been done concerning e.g. nutrient cycling, sediment-water interactions and plankton dynamics, many questions remain unanswered. Ecosystem models can suggest what impact different management options might have, but gaps in our knowledge limit their predictability. One research challenge is to parameterize poorly known processes and incorporate these parameterizations in the models.

During the course of this thesis, several aspects of the model formulations used in the studies have been identified where improvements and future research appear essential. Mostly, this concerns the biogeochemical modelling. In Paper IV, a missing nitrogen source in connection to the collapse of the spring bloom is discussed. Identification of this source should have important consequences for the plankton dynamics and possibly the deep water oxygen demand and nutrient cycling in the long run. This is thus an interesting and important question for future research.

The number of state variables in the biogeochemical model is limited. It is easy to identify other variables that could be included in the future. One example is silica, which at times can limit diatom growth and thus favour other species during the spring bloom. Other substances that could be important to include in the model are iron and manganese. One reason to include them is that oxidized forms of iron and manganese are reduced during decomposition in anoxic water and thus delay the production of hydrogen sulphide. Another reason is that especially iron oxyhydroxides are tightly coupled to the adsorption of phosphate to the sediment surface.

Throughout this thesis, the work is focused on the Eastern Gotland Basin. This is the largest sub-basin in the system, and it is likely to be representative for the entire Baltic Proper. But, at least some of the parameterizations used are not necessarily valid in the entire system. One example is the assumption that calcifying plankton species can be neglected. This assumption is probably correct east of the Danish Straits, but blooms of calcifying plankton species are known to develop in the Kattegat-Skagerrak area (Tyrrell et al., 2007). A local study focused on the carbonate system in the Kattegat basin should reveal shortcomings in the present model formulation.

Finally, it would be most interesting to test the performance of the model in a different system. The system closest at hand is the Black Sea, since it shares many general properties with the Baltic Sea: It has a rather limited water exchange with the ocean (the Mediterranean) through the transition area (the Marmara Sea and the Bosporus and Dardanelles straits). The surface layer is largely influenced by river runoff and the deep water is permanently anoxic. A study of the Black Sea would show whether the model parameterizations are globally valid, or if they because of substantial trimming only fit the local conditions in the Baltic Sea.

Acknowledgments

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Mostly by accident, I started my studies in oceanography during fall 2002. As surely is the case for many students who choose to remain in this field, I probably would have ended up somewhere else if not for the amazingly interesting and inspiring lessons held by Leif Djurfeldt during the introductory course. The opportunity to later on spend half a year in Chile and especially the weeks in the archipelago among dolphins, pelicans and penguins – and with the seven metres tidal range – had a huge impact as well.

With his optimism, enthusiasm and endless supply of new ideas and perspectives, Anders Omstedt is a role model for supervisors. The support whenever needed and also the great patience throughout the years have been invaluable. I look forward to a continued cooperation in the years to come and I rest assured that many interesting research results will come from this. I would also like to thank Göran Björk and Anders Stigebrandt for their valuable comments on the thesis summary. The colleagues and especially my fellow Ph. D. students have made this period memorable and enjoyable. Something that has become even more obvious after a summer spent in an office at the end of a deserted hallway.

To my friends, family and extended family – who wisely have deemed it preferable not to spend too much time trying to figure out what I have actually been doing for the last five years – I am grateful for not having to dwell upon work issues on my spare time. To my father and sister I am grateful for their unlimited faith in my capacity. To Annie I am grateful for everything else.

My thoughts are with my mother when I watch the sea.

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