

Hypoxia in the Stockholm Archipelago during the last three millennia: natural factors versus human influence

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Abstract

Over the last decades, the coastal areas of the Baltic Sea have been experiencing severe hypoxia, which is related to anthropogenic eutrophication and climate change. In the past three millennia, two other periods of hypoxia in the Baltic Sea have been recognized, coinciding with the Holocene Thermal Maximum and the Medieval Climate Anomaly (MCA). The causes for hypoxia during these periods are still debated, although higher temperatures and stratification seem to have played a role. In order to get a better understanding of the factors that played a role in the development and recovery of hypoxia in the last 3 millennia, the geochemical composition of sediment cores obtained from three different sites in the Stockholm Archipelago, Baggensfjärden, Ingaröfjärden and Erstaviken, was analyzed. Geochemical profiles of redox sensitive elements, total organic carbon (TOC), phosphorus and trace metals were generated and Glycerol Dialkyl Glycerol Tetraether (GDGT) lipids were extracted to reconstruct sea surface temperatures (SSTs) using the TEX₈₆ proxy. Afterwards a combined ²¹⁰Pb and ¹⁴C age model was used to translate depth into calendar years. The generated geochemical data were compared to historical data on population growth and mining activities in the area surrounding the Stockholm Archipelago. The geochemical profiles of redox sensitive elements and TOC confirm the occurrence of hypoxia before and during the MCA while a recovery of oxygen conditions is seen during the Little Ice Age (LIA), a period of cooler climate in northern Europe. TEX₈₆-based SST reconstructions reveal a temperature trend that correlates with the expected temperature change during the MCA and LIA and confirm the change of climate in the transition from the MCA to LIA. This indicates the coupling of temperature and hypoxia. Profiles of copper, lead and zinc, indicate human activity in the form of mining from 1000 AD, which corresponds to the historical data on mining activity in the area surrounding the Stockholm Archipelago. As hypoxia was already present before the onset of the MCA and the estimated start of mining activities, the development of hypoxia before and during the MCA was most likely to a large extent driven by natural factors such as changes in temperature and nutrient availability in the water.

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1. Introduction

1.1 Hypoxia in global perspective

Many coastal areas around the world experience oxygen concentrations below 2 mg/L in the water, a condition referred to as hypoxia. In some systems this is a natural phenomenon, as is the case for upwelling zones, fjords and oxygen minimum zones (OMZs) (Helly and Levin, 2004). However, in many shallow coastal areas, the hypoxic conditions are caused or worsened by human activity. Over the past decades, the extent of coastal hypoxia that is associated with anthropogenic activity has increased significantly (Rabalais et al., 2010).

1.2 Causes of hypoxia

Processes such as degradation of organic matter or the reoxidation of reduced compounds at the sediment-water interface consume oxygen in the bottom waters. Organic material that is present in the bottom water or sediment originates from the photic zone, where it is being produced by phytoplankton. This process, referred to as primary production, requires sufficient nutrients, sunlight and sufficiently high temperatures. Phytoplankton use nutrients such as carbon, phosphorus, nitrogen and trace elements to grow in the surface water. When the organisms die, they sink as organic matter to deeper waters and eventually the sea floor, where it is degraded by microbes. The degradation of organic matter can be carried out with different terminal electron acceptors (TEA) that are present in the water column or are released from the sediment. These are, in the order of decreasing energy yield, oxygen (O_2), nitrate (NO_3^-), Mn-oxides, Fe-oxides and sulfate (SO_4^{2-}), with O_2 oxygen being thermodynamically most favorable (Froelich et al., 1979). If all TEAs are consumed, the degradation of organic material continues through methanogenesis. The organic matter will preferably be degraded with oxygen as a TEA, but if all the oxygen is consumed, other TEAs will be used in order of decreasing energy yield. If the oxygen supply does not meet the oxygen demand, the water will shift from oxic conditions to hypoxia ($[O_2] \leq 2$ mg/L) or even anoxia ($[O_2] = 0$ mg/L) (Carstensen et al., 2014a).

One of the driving factors of high primary productivity and algal blooms is the availability of nutrients in the water. Nutrient enrichment, also referred to as eutrophication, can lead to an increased primary production by phytoplankton in the surface waters (Berner and Berner, 2012). The resulting flux of organic material to the bottom waters leads to an increased oxygen demand, as oxygen is used in the degradation of organic material. Eutrophication stimulates the development of hypoxia in the bottom waters of the Baltic Sea. In spring, primary production is highest due to increased air and water temperatures as well as higher insolation, while during winter months, productivity in the surface waters is low. Also climate warming has an amplifying effect on coastal hypoxia (Rabalais et al., 2010). During summer months, the thermal stratification increases in the water, due to temperature differences between the surface and bottom layers. Also the reduced solubility of O_2 when water temperature rises, contributes to the development of hypoxia (Rabalais et al., 2009). A combination of warming and coastal eutrophication cause increased oxygen depletion in the bottom waters during spring and summer, resulting in hypoxia or in some regions of the Baltic Sea even anoxia.

The most important nutrients that cause coastal eutrophication are nitrogen (N), and phosphorus (P). These are essential nutrients, required for primary production. The preferred ratio in which marine primary producers use these nutrients to grow is on average C:P:N = 106:16:1 (Redfield, 1958). The ratio in which these nutrients are available in the water column determine which of the nutrients is the limiting factor for primary production (Berner and Berner, 2012). As long as the environment is in contact with the atmosphere, C is unlimited available in sea water, as there is a continuous exchange of CO_2 with the atmosphere. In periods of high primary production and fast growth, N can become limiting for primary production, but can always be retrieved from the atmosphere through N-fixation by

cyanobacteria, only maybe not so fast as primary production rates at certain times (Berner and Berner, 2012). Therefore, P might be a limiting nutrient for primary production in estuaries at certain times. Sources of P to the water are terrestrial input and aeolian input. Furthermore, through the recycling of P from the sediment, the water column is provided with P. This recycling process plays an important role in the Baltic Sea, where a lot of P is stored in the sediment, due to the high anthropogenic P load of previous decades (Mort et al., 2010). A large amount of P in the surface water stimulates primary production, which in turn potentially leads to hypoxia in the bottom waters. In low-oxygen waters, P is released from the sediment to the water column (Jilbert and Slomp, 2013a). The released P causes a lower N/P ratio, which stimulates N-fixation by cyanobacteria, as the N-cycle is more adaptable than the P-cycle (Toggweiler, 1999). The availability of both N and P to cyanobacteria in the surface water stimulates primary production again, and thus increases the oxygen consumption in the bottom water, which in return releases P from the sediment (Funkey et al., 2014). This mechanism, referred to as P-recycling, stimulates hypoxia. The main process of P removal from aquatic systems is through burial with sediments, for instance as precipitation of authigenic P minerals or adsorbed onto other elements (Ruttenberg, 2014).

1.3 Consequences of hypoxia

Hypoxic conditions are unfavorable for organisms that live in the affected water layer and need oxygen to sustain (Diaz and Rosenberg, 2008). Levin et al. (2009) found that natural or eutrophication-caused hypoxia lead to a loss of diversity in the coastal benthos, as well as a decline in body size of organisms. Not only ecosystems are affected by severe hypoxia, also the biogeochemical cycles in the water column and sediment are altered due to hypoxia, due to changed redox conditions (Diaz and Rosenberg, 1995; Vahtera et al., 2007).

1.4 Baltic Sea

One of the largest basins worldwide experiencing human-induced hypoxia is the Baltic Sea, a semi-enclosed brackish basin that is located between Sweden, Finland, Poland, Germany, Denmark and the Baltic States. It is connected with the North Sea via narrow straits in the southern part of the basin (Fig. 1.1). Due to the isolated nature of the Baltic Sea, tidal movements are absent. The Baltic Sea is with a surface area of more than 400,000 km² and a volume of more than 20,000 km³ one of the largest estuaries in the world. The surface layer of the Baltic Sea is brackish, with a salinity of approximately 6-8, while the deep water has a salinity of 10-14 (Matthäus, 2006). This large salinity difference, and thus density differences between the surface waters and deep waters has resulted in the presence of a halocline at depths varying between 30m and 80m (Matthäus, 2006). The deepest parts of the basin are permanently hypoxic, while parts of the coastal zones of the Baltic Sea experience episodically occurring hypoxia (Conley et al., 2011; Kemp et al., 2009).



Fig 1. 1 The Baltic Sea with the Stockholm Archipelago (Red); After Harff, 2011

The Baltic Sea formed after the last deglaciation of Scandinavia and evolved from a fresh water lake to the modern-day brackish estuary. Four stages that represent intervals of brackish and freshwater conditions due to changes in the exchange of water with the North Sea, are recognized in the development of the Baltic Sea (Zillén et al., 2008; Conley et al., 2009). The Baltic Sea Ice Lake developed ca. 15 ka before present (BP) as a melt water lake and existed until 11.7 ka BP, when the breaking of a naturally formed dam near Mount Billigen resulted in the drainage of the former ice lake. Subsequently, a partly brackish system developed, the Yoldia Sea, which had a water level equal to the global ocean. Around 10.7 ka BP, the connections with the open sea shallowed due to land-uplift, which resulted in the formation of the Ancylus Lake. Irregular uplift caused the tilting of Lake Ancylus,

restoring the connection with the open ocean through the Kattegat. Eventually, the Öresund strait developed as an inlet of saline water, resulting in the transformation of Lake Ancylus to the Littorina Sea around 10.2 ka BP.

During these four stages, the basin was predominantly fresh. It was during the first Littorina Sea stage, approximately 8.5 ka BP, when a brackish system developed, although the exact timing of this transition is highly debated (Andren et al, 2000; Björck, 1995, Conley et al, 2008). Regardless of the exact timing, it is generally agreed upon that the Baltic Sea system became continuously brackish during the Littorina Sea around 8.5 BP, due to the inlet of salt water through the Öresund Strait. Changes in salinity affected the mixing of the water and contributed to the establishment of a permanent halocline. This transition is often referred to as the 'lake-marine' transition of the Baltic Sea (Björck, 1995).

Hypoxia in the Baltic Sea has occurred during three main periods since the start of the Holocene (11.7 ka BP). During the Holocene Thermal Maximum (ca. 8 - 4 ka BP) hypoxia was widespread in large parts of the Baltic Sea. This hypoxic period coincides with the transition from fresh water to brackish water, and was probably associated with increased salinity and enhanced stratification (Conley et al., 2009; Zillén et al., 2008). The second period of hypoxia occurred before and during the Medieval Climate Anomaly (MCA), which is defined from approximately 950 - 1350 AD (Graham et al., 2011). Currently, the Baltic Sea experiences the third period of hypoxia, likely driven by anthropogenic eutrophication (Conley et al., 2009).

1.5 Modern-day hypoxia of the Baltic Sea

The last decades, large parts of the Baltic Sea experienced hypoxia in the bottom waters below the halocline (Carstensen et al., 2014b). The hypoxic area shows variations over time, but increased especially over the last two decades. In 2014, the hypoxic area in two main, deep basins of the Baltic Sea was approximately 60,000 km², in comparison to the 5000 km² in 1900 AD (Carstensen et al., 2014b). The development of hypoxia over the last decades, has been closely related to human activity in the drainage basin of the Baltic Sea (Carstensen et al., 2014b). Human activity, such as agricultural and industrial practices, contributes heavily to the nutrient input into the Baltic Sea (Ulen et al., 2007; Bonsdorff et al., 1997). This anthropogenic eutrophication has resulted in an increase of algal blooms, hypoxia and anoxia in large areas of the Baltic Sea (Conley et al., 2011). Although the nutrient load from the mainland had decreased due to changed policy, phosphorus that was released from the sediment has increased the dissolved inorganic phosphorus concentrations in the water (Carstensen et al., 2014b).

An important factor that makes the system prone to the development of low-oxygen conditions, is the geographical setting of the Baltic Sea. The only connections with the North Sea are the Skagerrak strait and the Kattegat bay, therefore the exchange of water between the Baltic Sea and the open ocean is limited (Carstensen et al., 2014b). The inflow of dense water in the southern part of the Baltic Sea, results in a bottom layer with saline, dense water (Carstensen et al., 2014b). However, the inflow of oxic water is insufficient to replace the hypoxic deep water masses of the Baltic Sea, and inflow of substantial amounts of oxygenated, saline North Sea water is irregular and sporadic (Zillén et al., 2008).

The drainage basin of the Baltic Sea covers an area four times larger than the surface area of the estuary, leading to a large inflow of fresh water. Therefore, riverine input is a relative important source of water for the Baltic Sea, and reduces the salinity of the surface water. Because of the large density differences between the brackish surface layer and the saline deep waters of the Baltic Sea, the basin is highly stratified. As a result, the oxygen supply to the deep water is limited, which contributes to the development of low-oxygen conditions in the bottom water.

As a result of hypoxia in large parts of the Baltic Sea, benthic organisms experience stress (Carstensen et al., 2014a). If hypoxia is only periodic and recovers after some time, populations of organisms may recover. However, if hypoxia endures, populations may suffer (Diaz and Rosenberg, 2008). The effects of hypoxia are not limited to the biota, the low-oxygen conditions affect the geochemistry of the bottom and surface waters to a great extent. Depending on element specific characteristics, a number of elements behave differently under hypoxic conditions and oxic conditions (Kemp et al., 2009). The chemistry of the system in turn influences the oxygen conditions in the water. An example of this is the feedback mechanism of P, that sustains hypoxia through recycling of sedimentary P (Mort et al., 2010).

1.6 Medieval Climate Anomaly and Little Ice Age

The MCA was a warm period in the North Atlantic region between 950-1350 AD. The sea surface temperatures of the Baltic Sea were comparable to modern day temperatures (Kabel et al., 2012). Although the exact causes for this period of warm climate are not known, proxies indicate a shift in global circulation patterns that could be partly responsible for the climate change at that time (Diaz et al., 2011; Graham et al., 2010). Large areas in the Baltic Sea experienced low-oxygen conditions during the MCA (Zillén et al., 2008). The changes in climate were accompanied by large-scale changes in population and agricultural practices. Traces of agricultural activity in the form of pastures and small-scale cultivation dating back to the Iron Age (650 BC to 1150 AD), have been found in parts of Sweden (Skold et al., 2010). These forms of deforestation, agriculture and other human activity have most likely affected the local environment and surrounding aquatic systems. In Denmark it has been shown that nutrient enrichment from agricultural activity has had influence on lakes from the Iron Age and even earlier (Bradshaw et al., 2005). It is therefore not unlikely that the coastal areas of the Baltic Sea have been affected by this early human activity as well. During the early medieval period from approximately 1050 AD, population growth caused large-scale expansion of agricultural area and human settlements (Skold et al., 2010; Zillén et al., 2008).

The MCA was followed by a period characterized by lower temperatures, referred to as the Little Ice Age (LIA), a period in which the SSTs of the Baltic Sea were ca. 2°C below modern day temperatures (Kabel et al., 2012). There is no consensus on the beginning of the LIA, but its start is estimated in the 14th century, after which it intensified and persisted to 1800 AD (Zillén et al., 2008). A number of causes are suggested to be responsible for the cooling of the climate such as a decrease in solar activity, volcanic activity and changed ocean circulations (Bradley et al., 2003). The changed climate during the LIA has likely had an effect on the hypoxia in the Baltic Sea. However, also anthropogenic factors could have influenced the oxygen availability in the deep waters. Another factor that has been suggested as a possible cause for the recovery of the hypoxic areas in the Baltic Sea is the population decrease resulting from the Plague. It has been estimated, that over 60% of the Swedish population was killed by the Plague during 1300 AD and 1413 AD (Zillén and Conley, 2010). The decline of the population has led to what is referred to as the agricultural crisis: the decline of agricultural area and the abandonment of farms (Funkey., 2014; Zillén and Conley, 2010; Skold et al., 2010). The decline of settlements and agricultural activity lead to a decline in nutrient runoff to the Baltic Sea, which could have resulted in a lowered nutrient supply to the Baltic Sea and thus affected the oxygen balance of the Baltic Sea (Zillén and Conley, 2010).

1.7 Relevance of study

While the dynamics of hypoxia in the open basin have been studied extensively, little is known about the driving factors of hypoxia in the coastal waters of the Baltic Sea (Conley et al., 2011). Knowledge about hypoxia in the past is essential to understand the current episodes of hypoxia and to predict the evolution of hypoxia in the future. The MCA forms an excellent period to study the influence of both natural and anthropogenic factors on hypoxia, as it is thought that humans already influenced the system at that time (Zillén and Conley, 2010). As large parts of the coastal areas in the Baltic Sea are currently experiencing hypoxia, we want to investigate if this was also the case during the MCA. This study uses sediment records of three locations in the Stockholm Archipelago to reconstruct the oxygen conditions over the Holocene, with a focus on the MCA. Furthermore, if hypoxia was present in the coastal waters around Stockholm during this time, we will identify the factors that contributed to the development of hypoxia during the MCA and the factors that have led to the recovery of the oxygen conditions. In order to do so, we use geochemical profiles of redox sensitive elements, total organic carbon (TOC), phosphorus and trace metals, together with extraction of Glycerol Dialkyl Glycerol Tetraether (GDGT) lipids that are used to reconstruct sea surface temperatures (SSTs) using the TEX₈₆ proxy. Trace metals are used to date the emergence of mining activity in the region surrounding the Stockholm Archipelago. A combined ²¹⁰Pb and ¹⁴C age model is used to translate depth into calendar years. The generated geochemical data are compared to historical data on population growth and mining activities in the area surrounding the Stockholm Archipelago.

2. Methods

2.1 Site description

The sampling sites are located in the Stockholm Archipelago, the second-largest archipelago in the Baltic Sea. It covers an area of approximately 35000 km² and is formed by approximately 30000 small islands (Eriksson et al., 2004). The area around Stockholm has been and is still being affected by postglacial rebound, which has resulted in the current landscape with small islands (Eriksson et al., 2004). Already during the 9th and 10th centuries, the area around present-day Stockholm emerged as an important trading city and center of economic activity (Scott, 1988). Therefore, the Stockholm Archipelago has likely been affected by human influence since that time. This makes the Stockholm Archipelago an interesting area, as it provides opportunities to study the dynamics of hypoxia and the effects of both anthropogenic and natural influences on the coastal waters of the Baltic Sea during the MCA and the LIA. Today the coastal area around Stockholm is still intensively used for recreation and boating (Eriksson et al., 2004).

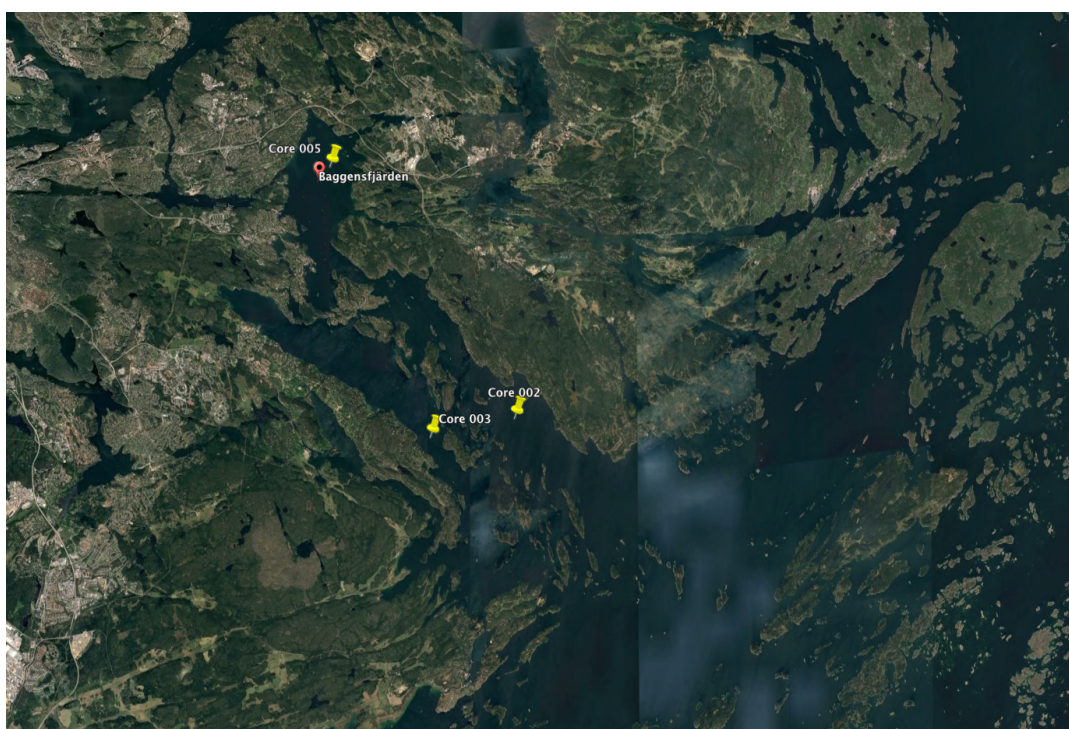


Fig. 2 1 Sampling sites in the Stockholm Archipelago with the locations of core 002 (Ingaröfjärden); core 003 (Erstaviken) and core 005 (Baggensfjärden). Google Earth, 2017

2.2 Preparation of samples

Three sediment cores (all piston cores with a length of ca. 6 m) were obtained from three different locations in the Stockholm Archipelago. (Fig. 2.1) Core 002 was obtained from Ingaröfjärden at a water depth of 37.4 m. Core 003 was obtained from Erstaviken at a water depth of 68.8 m. Core 005 was obtained from Baggensfjärden at a water depth of 57 m. After retrieval, the cores were separated in a working half and an archive half. The working half was then sampled for further analyses at a resolution of 10 cm for core 002 and core 005, and a resolution of 0.5 for core 003. The samples were freeze-dried, and crushed afterwards using an agate mortar and pestle.

Due to expansion of the sediment upon retrieval of the cores, approximately 20-30 cm of the top was lost. As a consequence, the depths that were assigned to the measured data in the upper meter of the core are likely to deviate from the true depths. To correct for this, short cores (60-65 cm) were obtained during the same cruise. The samples of the short cores were analyzed in a different batch (Van Aartrijk, BSc thesis UU, 2016), using identical methods. In order to get a complete overview of the system, the geochemical profiles of the short cores were connected to the profiles of the long cores. This was only done for the measured inorganic chemical components, as GDGTs were not measured for the short cores. This connection was made by using the organic carbon (TOC) profiles of both cores, as the estimated error of TOC is smallest of all measured elements. The profiles were matched based on the TOC content, using the depths of the short core as leading. Consequently, the depths of the upper meter of the long core were adjusted to correctly overlap with the profiles of the short core.

2.3 Analyses

2.3.1 Age model

In order to convert the measured depths to age, an age model based on data provided by Daniel Conley (Conley, 2016, personal comm.) was used (Fig. 2.2). Conversion of depth to age was only performed for core 003.

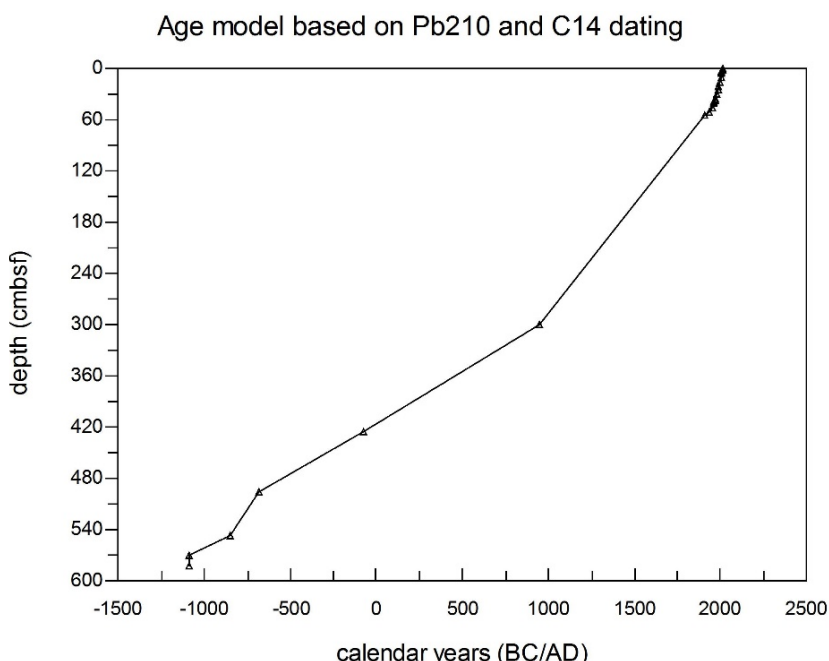


Fig. 2.2 Age model for core 003, obtained at Erstaviken, based on ^{210}Pb and ^{14}C dating. Data provided by Conley (2016, personal comm.)

Subsamples from each core were taken for analysis of the chemical composition of the sediment. All samples from Core 002 and Core 005 were analyzed. Core 003 was first analyzed at a 10 cm resolution as a pilot study. Based on ^{14}C dating it was clear that core 003 had the highest sedimentation rates and was thus most suitable for detailed analyses of the MCA hypoxic interval. The focus of this detailed analysis was on the interval of 1.5 to 4 m depth, as this depth interval likely comprised the Medieval Climate Anomaly (MCA) and because the results of the pilot study showed the highest variety over this interval. A selection was made from the samples from core 003. For the analysis of GDGTs in the sediment, 48 samples were selected from core 003.

2.3.2 Inorganic analyses

Analysis of organic carbon and nitrogen

Subsamples of powdered and freeze dried sediment (0.3 g) were weighed into a 15 ml centrifuge tube and acidified with 7.5 ml 1M HCL, in order to remove the carbonates. After addition of the acid, the samples were being shaken for 4 hours at 125 rpm. For the second acidification step, the samples were centrifuged for 7 min (2800g), decanted and acidified with another 7.5 ml 1M HCL and put on the shaker for another 12 hours. After 12 hours, the samples were centrifuged, decanted and washed with UHQ to get rid of the remaining acid in the sediment. Subsequently, the decalcified samples were dried in the oven at 60°C for 3 days. Then the samples were weighed again to determine the amount of weight loss through carbonate removal.

For the analysis of C and N, approximately 10 to 20 µg of each dry decalcified sample was weighed into a tin cup, after which the tin cups with sediment were analyzed for organic N and C by a Fisons Instruments NA 1500 NCS analyzer.

Total elemental composition using ICP-OES

Approximately 125 mg of powdered and freeze dried sediment was weighed into a teflon destruction vessel and acidified with a mix of 2.5 ml HClO₄:HNO₃=3:2, and 2.5 ml HF (Fig.2.3). The teflon vessels were placed overnight on a hot plate at 90°C. The next day, the caps of the teflon vessels were opened and the vessels were placed on a hot plate at 140°C, until the acid was evaporated and a gel was formed. After this, 25 ml of 1M HNO₃ was added and the closed vessels were placed on a hot plate at 90°C. After 1 night, the vessels were weighed again to determine the dilution factor, and were subsequently analyzed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES; SPECTRO ARCOS) to determine the total elemental composition. As the first diluted samples contained dark suspended particles, presumably organic material, the samples of the pilot study of core 003 were treated with concentrated perchloric acid 30% (H₂O₂) after evaporation of the acids used for the destruction. Comparison between the samples of the different batches afterwards,

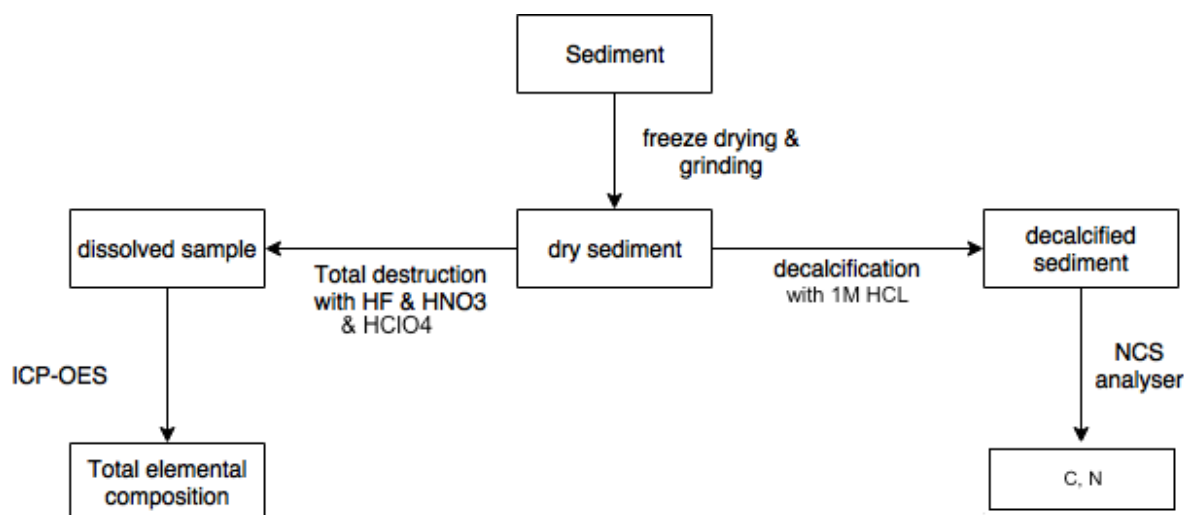


Fig. 2.3 Schematic overview of methods for inorganic analyses

showed no significant differences in the inorganic composition between the samples treated with H₂O₂ and the ones that were not. Therefore, we concluded that the dark particles did not have a significant effect on the measured inorganic composition of the samples. Due to contamination during the dilution, the samples in the pilot study for core 003 were contaminated with phosphorus (P). However, as the amount of contamination was known, based on blanks and internal standards, we were able to manually correct the results for this contamination.

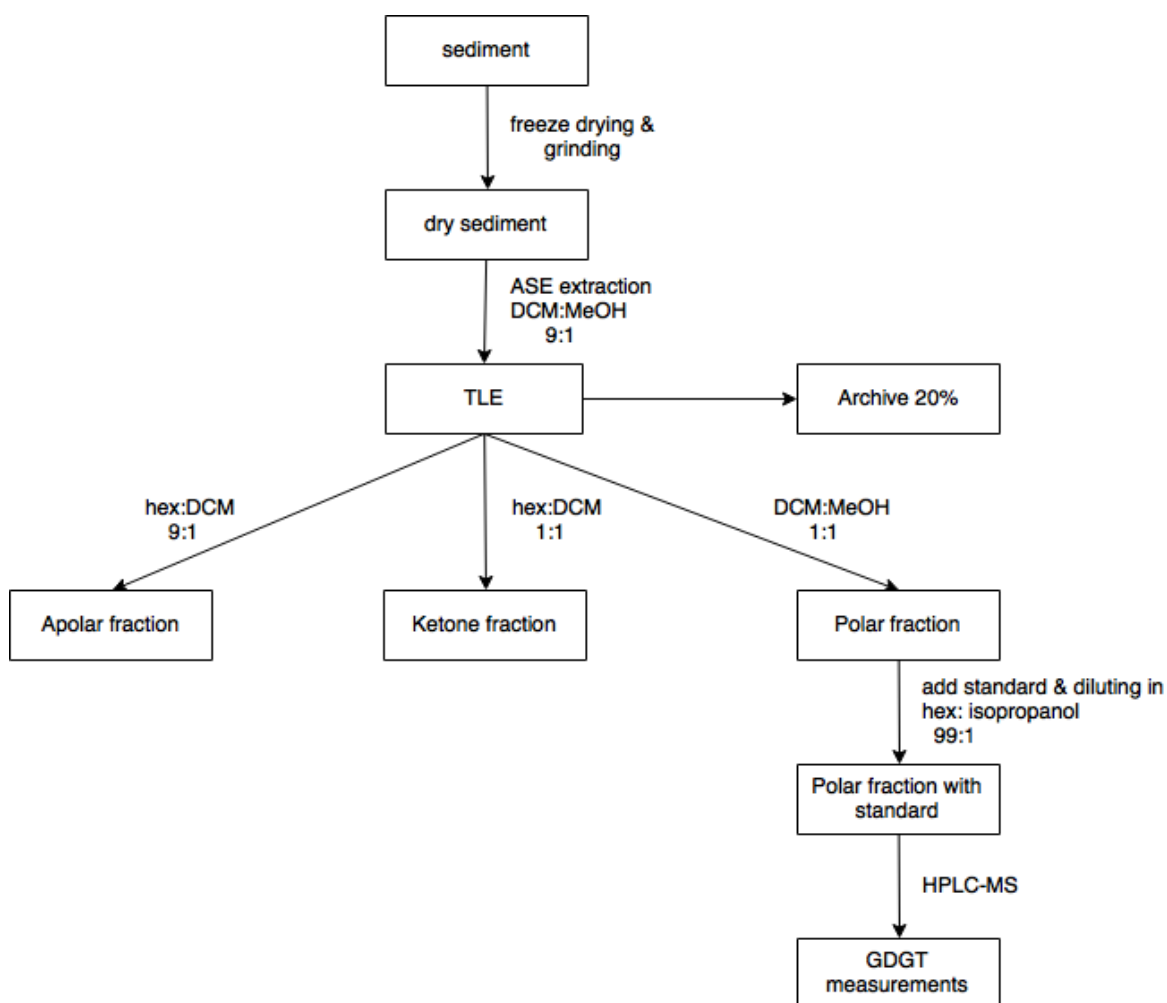


Fig. 2.4 Schematic overview of methods for analysis of GDGTs

2.3.3 Organic geochemistry- GDGT analysis

For the analysis of the organic compounds of the samples, the total lipid extract (TLE) was extracted from the sediment with Dichloromethane (DCM): Methanol (MeOH) (9:1; v/v) solvent mixture, using an Accelerated Solvent Extractor (ASE350, DIONEX) (Fig. 2.4). To extract the TLE, approximately 1 g of powdered and freeze dried sediment of each sample was mixed with diatomaceous earth and weighed into cells, after which they were extracted using the ASE. To exclude contamination artefacts, blanks were added. After extraction, the TLEs of all samples and blanks were dried to near dryness under a N₂ flow using a turbovap. Afterwards the dried TLEs were weighed, and dissolved in a MeOH:DCM (1:1; v/v) solvent mixture. Of the total amount of TLE, 20% was archived. The remaining 80% was separated in different fractions with manual small column chromatography, using activated aluminium oxide powder in pasteur pipettes and different solvents as carriers for the samples. The TLEs were separated into three different fractions, the apolar fraction, the ketone fraction and the polar fraction, using hexane:DCM (9:1, v/v) hexane:DCM (1:1, v/v) and MeOH:DCM (1:1, v/v), respectively. The apolar and ketone fractions were dried under a N₂ flow and weighed, to determine the total amount of the fraction extracted per sample. The dried apolar and ketone fractions were stored and not further analyzed. The GDGT fractions were dried under a N₂ flow after which 99 ng of the C46 GDGT internal standard was added for quantification. Subsequently GDGT fractions were dissolved in

hexane:propanol (99:1, v/v) and filtered over a 0.45 µm mesh PTFE filter (ø 4mm) prior to analysis. Analysis of GDGTs was performed by ultra-high performance liquid chromatography-mass spectrometry (UHPLC -MS) on an Agilent 1290 infinity series coupled to a 6130 single quadrupole MSD, equipped with auto-injection system and HP-Chemstation, following the setup described in Hopmans et al. (2016). TEX₈₆ values (Kim et al., 2010;

1) were used to estimate mean annual sea surface temperatures (SSTs) using the TEX₈₆ calibration by Kabel et al. (2012) (eq. 1 & 2)

$$TEX_{86L} = \frac{[GDGT-2]}{[GDGT1]+[GDGT-2]+GDGT-3]} \quad (\text{Eq. 1; Kim et al., 2010})$$

$$SST = 34.03 * TEX_{86L} + 36,73 \quad (\text{Eq. 2; Kabel et al., 2012})$$

The soil pH and mean annual air temperature (MAAT) were calculated using the calculations described by De Jonge et al. (2014).

2.4 Sediment as a chemical tool to reconstruct hypoxia

As conditions in the bottom waters affect the chemistry of the seafloor, the sediment can be a useful tool to examine (past) redox conditions in the water. Based on sediment composition, conclusions can be drawn about the conditions in the system at the time of deposition. Sediments in hypoxic or anoxic conditions generally have a high organic matter content, a combined effect of a high organic matter supply from the photic zone and the reduced degradation of this organic matter due to the lack of oxygen (Reed et al., 2011). Also, bulk nutrients P and N can be used to reveal information about the redox conditions during deposition, as both are affected by the organic matter supply and by redox conditions in the water. Furthermore, the content of trace elements such as Molybdenum (Mo) and Iron (Fe) can be used as proxies for past redox conditions.

2.4.1 Mn

The dominant manganese (Mn) species in sea water are Mn²⁺ and MnCl⁺, but both are thermodynamically unstable in oxic waters. The unstable Mn(II) species are oxidized to insoluble Mn(III) and Mn(IV) solid phases. Mn(IV) solid phases, also known as Mn-oxides, are formed in the oxic water layers and sink to the bottom waters (Slomp et al., 1997). If the bottom waters are oxygen depleted, the Mn-oxides will be reduced and dissolved below the oxic-anoxic boundary of the water. Mn(II) is then released to the water and diffuses upward or downward, where it is either released to the water column or precipitates as Mn oxides in case the pore water contains oxygen (Lenz et al., 2015) However, in anoxic environments with a sufficiently high alkalinity, authigenic Mn-carbonates can form, often associated with calcium (Lepland and Stevens, 1998; Jakobsen and Postma, 1989). Although these Mn-carbonates are formed under anoxic conditions, oxic conditions are required beforehand to transport the Mn to the sediment water interface, as Mn carbonates do not form in the water column but on the sediment (Calvert and Pedersen, 1996). The presence of Mn-carbonates, often in the form of Ca-rhodochrosites, has been shown in deeper parts of the Baltic Sea, such as the Gotland Deep (Heiser et al., 2001).

2.4.2 Mo

Mo is a redox-sensitive transition element that is present in seawater and can be used to reconstruct paleoredox conditions in marine systems (Tribovillard et al., 2006; Scott and Lyons, 2012). Mo behaves relatively conservative in oxic water, but oxygen-depleted bottom waters affect the reactivity of Mo. Research has shown that Mo is trapped in the sediment under low-oxygen conditions, through which it is removed from the water column (Emerson and Husted, 1991). Sediment enrichments of Mo thus indicate low-oxygen conditions at the time of deposition or during early diagenesis. However, a complicating factor for the use of Mo as a proxy for paleoredox conditions is the so-called '*basin reservoir effect*'. In restricted basins, the supply of Mo might become insufficient and results in lower Mo fixation in the sediment, even in strongly reducing sediments (Algeo, 2004; Algeo and Lyons, 2006; Tribovillard et al., 2006)

2.4.3 Pb, Zn and Cu

Trace metals such as lead, copper and zinc can be used as a measure for human activity, as they have been exploited by mankind for a long time. Furthermore, Pb concentrations can be used as an independent age constrain in the Baltic Sea, as three peaks of Pb pollution have been dated and can be used as reference data (Zillén et al., 2012).

The area north-west of Stockholm was known for mining activities, especially around the cities of Norberg and Falun, that are estimated to have been exploited from the late 10th century (Bindler et al., 2011; Bindler and Rydberg, 2015). The mining flourished during the medieval period and continued until the 20th century. This makes the profiles of Cu and Pb, which are among the metals that were mined, especially interesting in the study of hypoxia and anthropogenic influence, as Cu and Pb can be used as a measure for human activity. Unlike Pb and Cu, Zinc (Zn) exploitation did not start before the 16th century, as no method for separating metallic Zn from the ore seems to have been known in Europe before that time. Commercial production of Zn did not start until the 18th century (Blair and Ramsay, 1991).

2.4.4 GDGT proxies

As temperature is an important factor influencing stratification and hypoxia in the bottom water, it is useful to obtain insight in the temperature evolution in this area in the past. To reconstruct paleotemperatures, several proxies based on biomarkers are available. These proxies are based on the fact that the biosynthesis of specific organic compounds by certain micro-organisms depends on the temperature of the water at the time of production. For example, archaea and bacteria produce Glycerol Dialkyl Glycerol Tetraethers (GDGTs) as membrane lipids. The molecular structure of these GDGTs varies with different environmental conditions that prevailed at the time of their production, such as SST, MAAT and pH (Schouten et al., 2002; Weijers et al., 2007). A division is made between GDGTs based on their structure, separating them in isoprenoid GDGTs and branched GDGTs. Isoprenoid GDGTs are produced by marine planktonic archaea, as part of their membrane lipid, and are mainly produced in marine environments (Schouten et al., 2013). Branched GDGTs are primarily produced by bacteria in terrestrial environments such as soils, but have recently also found to be produced in lakes or deltaic waters (Schouten et al., 2013). By calculating the relative abundance of the specific isoprenoid GDGT crenarchaeol, compared to branched GDGTs in sediments, an estimate can be made of the relative input of soil organic matter into marine systems, and is expressed as the Branched and Isoprenoid Tetraether (BIT) index. BIT values (< 0.3) indicate the dominance of marine organic matter, whereas high BIT (> 0.7) values indicate that the input of terrestrial organic matter was relatively high at the time of deposition (Hopmans et al., 2004). Another proxy that is used, TEX_{86} , is used to reconstruct paleo-SSTs. TEX_{86} is based on the number of cyclopentane rings that are incorporated in the GDGT of membrane lipids of archaea (Schouten et al., 2002; Kim et al., 2010). As temperature increases, the number of cyclopentane rings in the isoprenoid GDGT molecules increases as well. Incubation experiments showed that TEX_{86} index has a significant linear correlation with growth temperature and can thus be used as proxy to reconstruct the annual sea surface temperatures (Wuchter et al., 2004).

3. Results

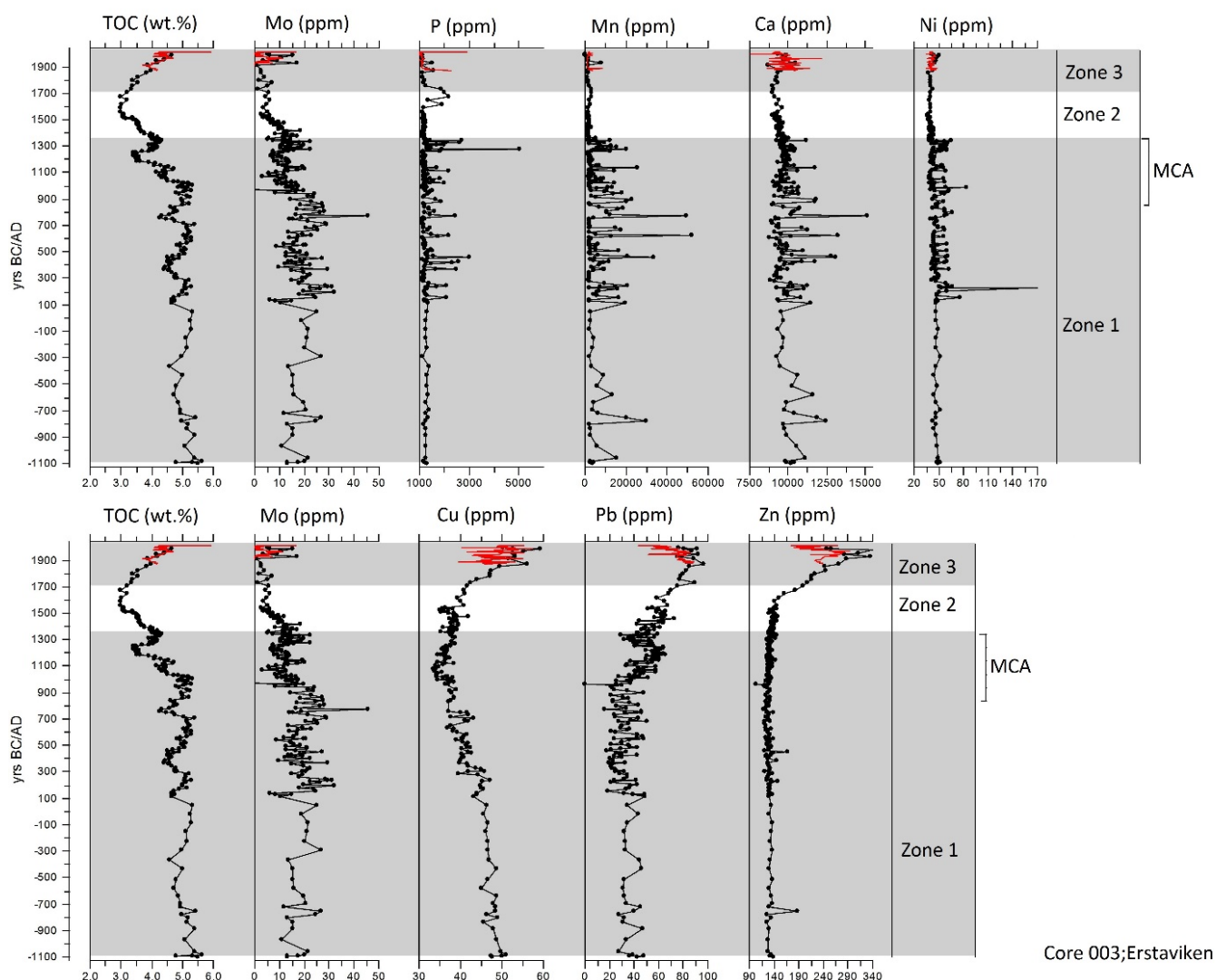


Fig. 3.1 Sediment profiles of redox sensitive elements and trace metals, obtained at Erstaviken. The grey bands were based on Mo and indicate zones of different oxygen conditions. The age of the sediments was determined using an age model based on data of Conley (2016, personal comm.)

3.1 Erstaviken

3.1.1 Redox sensitive proxies and trace metals

The TOC contents of core 003 vary between 3.0 wt.% and 5.7 wt.% (± 0.07 wt.%) (Fig. 3.1a). TOC remains relatively constant from 1150 BC to 900 AD with values around 5 wt.%, and gradually decreases to a minimum value of ca. 3 wt.% around 1500 AD. From 1600 AD, TOC values increase again to 5 wt.% at the top of the core. In the period from 350 AD to 1350 AD, four phases of higher values appear in the TOC profile. From 110-370 AD, the first phase is seen, followed by a second between 460-760 AD. The third phase is seen from 840-1190 AD, rapidly followed by the fourth and last phase between 1240-1400 AD. The Mo content is ca. 20 ppm (± 2.95 ppm) in the interval corresponding to the time between 1150 BC and 900 AD. From 900 AD, Mo content decreases to 4 ppm in 1500, after which it remains below 5 ppm in the remaining record, with a slight increase 15 ppm from 1800 AD. In the interval between

350-1500 AD, phases similar to those of TOC were seen. The P signal shows a background of 1000 ppm (± 325 ppm) over the entire record, with sharp peaks with values up to 5000 ppm from 150 AD to 1350 AD. In the interval from 1600 AD to 1950 AD, four small peaks appear in the P signal. Also for Mn, large peaks appear from 1150 BC to 1350 AD, with values up to 50000 ppm (± 1310 ppm), against a background value of ca. 2000 ppm. The clusters of peaks in Mn coincide with the four phases of high TOC and Mo. Similar trends are seen for Ca, with peaks of Ca up to 15000 ppm (± 228 ppm), against an apparent background value of 9000 ppm. The peaks of Ca coincide with the Mn peaks and with the phases in TOC and Mo. The profile of Nickel (Ni) shows a background value of 40 ppm (± 3.53 ppm), with sharp peaks that coincide with a part of the P, Mn and Ca peaks.

From 1150 BC - 900 AD, Pb content of the sediment is relatively stable around 30 ppm (± 14.8 ppm) (Fig. 3.1b). From 900 AD, Pb content starts increasing until it reaches a value of ca. 90 ppm around the start of the 20th century. Remarkably, the Pb content of the sediment decreases in the last decades of the 20th century. The profile of Cu shows a different profile. From ca. 1150 BC to 1100 AD, the Cu content decreases from 50 ppm to 35 ppm (± 1.4 ppm), after which it increases to 40 ppm in 1480 AD. From ca. 1500 AD, Cu increases rapidly to 60 ppm around 1980 AD. In the last two decades of the 20th century, Cu content decreases rapidly. Zn shows a trend unlike the trends seen in the other elements. The content of Zn in the sediment is with 150 ppm (± 14.5 ppm) remarkably stable from 1150 BC to 1575 AD. However, from 1575 AD, Zn increases rapidly to 350 ppm in 1928 AD. Like Pb and Cu, the content of Zn decreases rapidly to ca. 200 ppm in the last two decades of the 20th century.

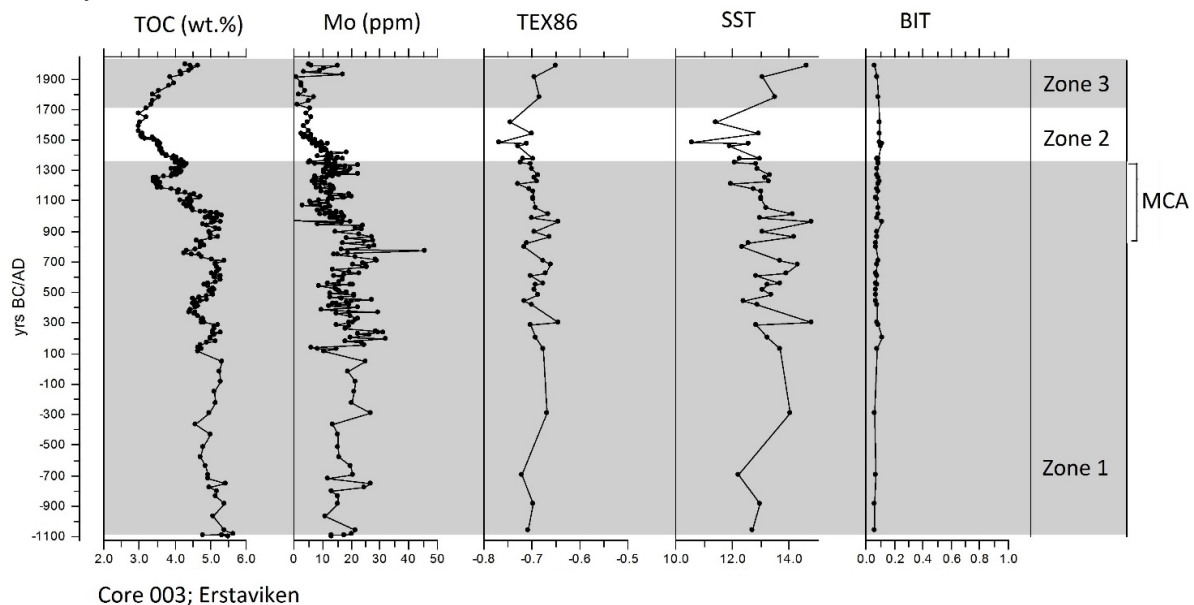


Fig. 3.2. Sediment profiles of GDGT proxies, obtained at Erstaviken. The grey bands were based on Mo and indicate zones of different oxygen conditions. The age of the sediments was determined using an age model based on data of Conley (2016, personal comm.)

3.1.2 GDGT Proxies

The calculated values for the BIT index are very low through the entire core, with values not exceeding 0.11 (Fig 3.2). The SST curve derived from TEX_{86L} indicates sea surface temperatures that varied between 10°C and 14.8°C. SST decrease rapidly in the upper 1.5 m of the core, from almost 15°C to 10.6°C. Further down, SST increase to an optimum of almost 15°C between 3 and 4 m depth. Below 4 m, SST decrease to 13°C. As the BIT index reveals the domination of isoprenoid GDGTs over branched GDGTs, calculation of pH and MAAT is not relevant.

3.2 Ingaröfjärden and Baggensfjärden

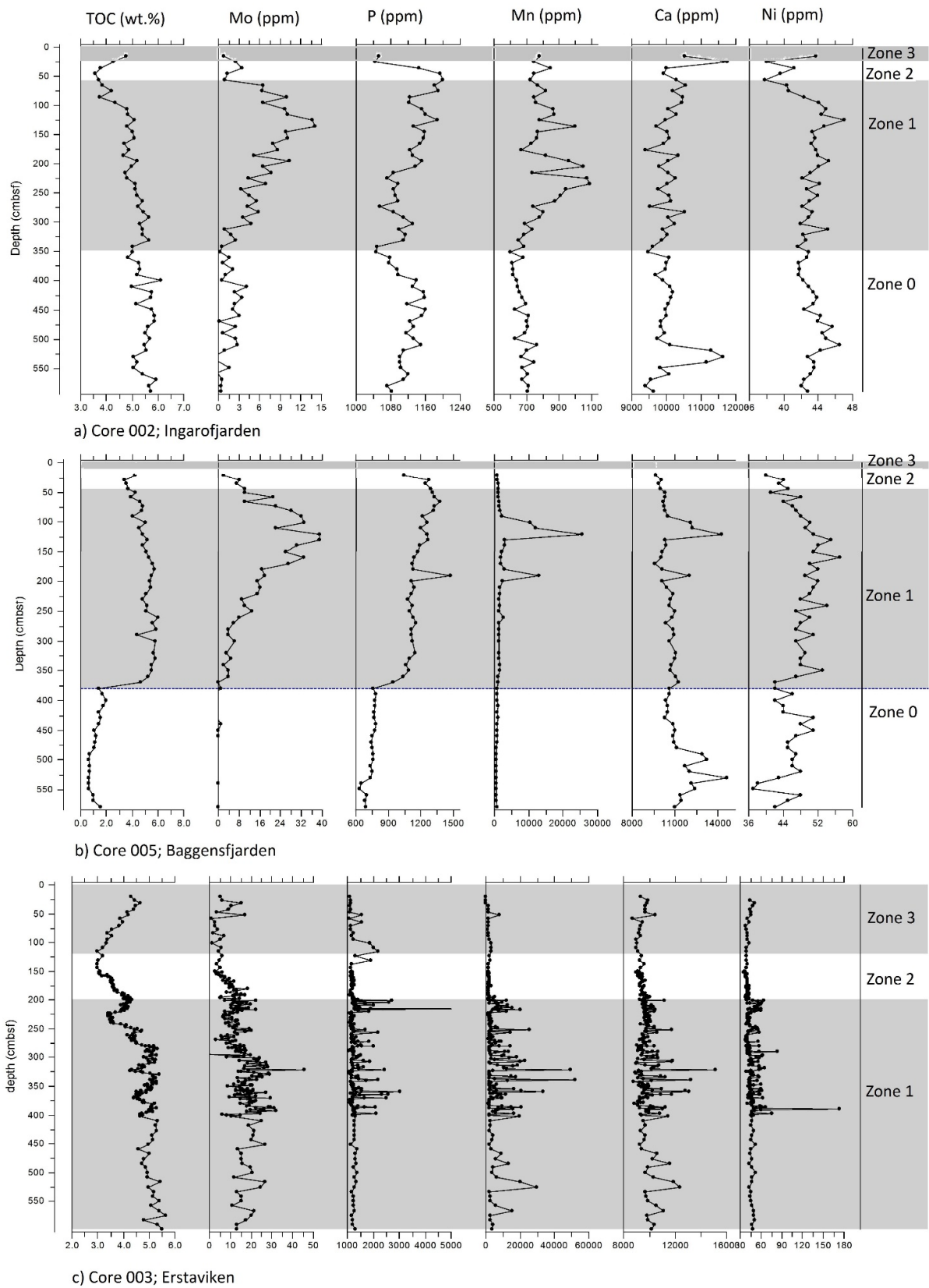
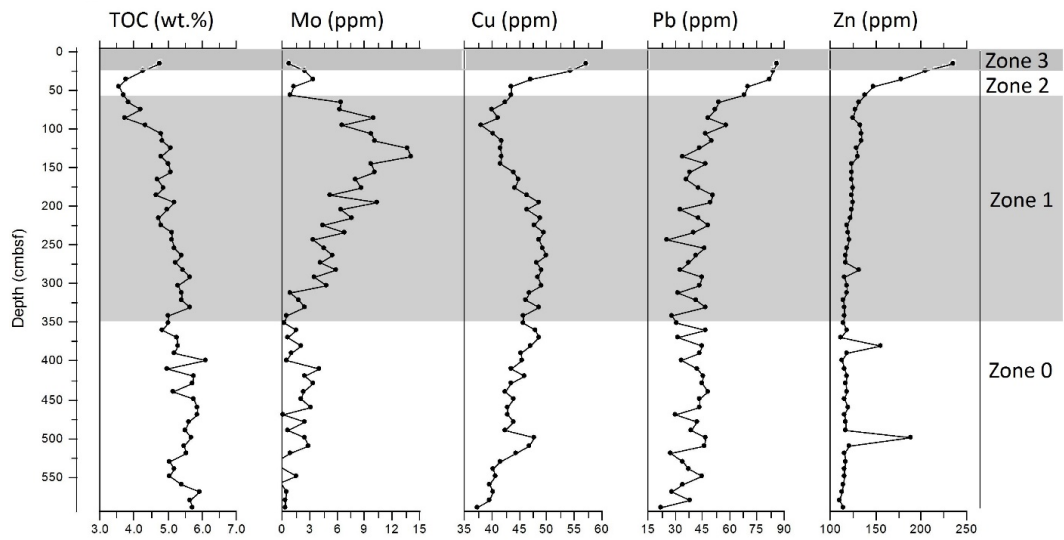


Fig. 3.3 Sediment profiles of redox-sensitive elements obtained at Ingaröfjärden, Baggensfjärden and Erstaviken. The grey bands were based on Mo and indicate zones of different oxygen conditions.

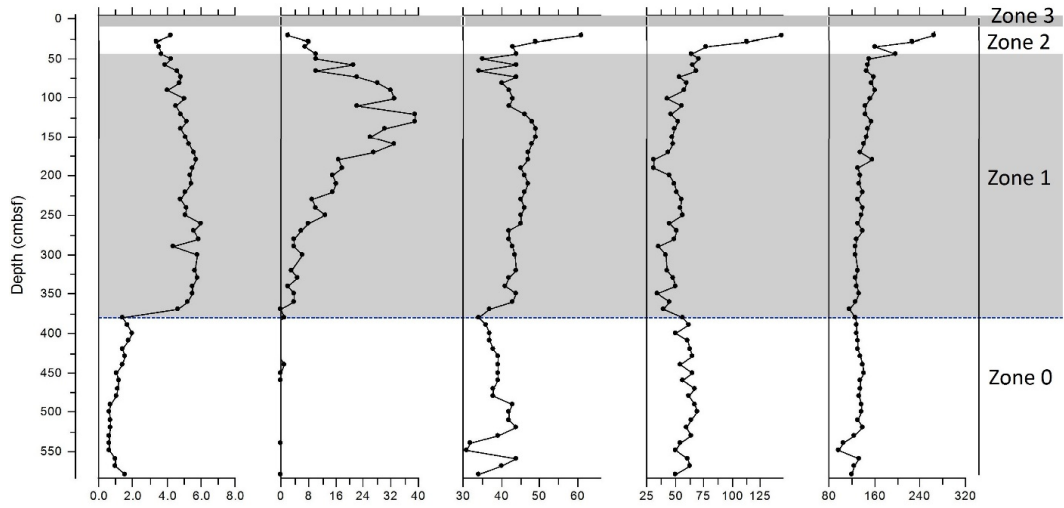
3.2.1 Redox-sensitive elements and trace metals

The TOC contents of the sediment of core 002 are around 6 wt.% (± 0.13 wt.%) at the base of the core and gradually decrease to 5 wt.% at a depth of 125 cmbsf, after which they rapidly decrease to minimum values of 3.5 wt.% (Fig. 3.3a). TOC values increase again to 5 wt.% in the upper 50 cm of the record. The content of Mo at the base of the core is negligibly low, and increases from 350 cmbsf to a maximum value of 15 ppm at 125 ppm (± 1.48 ppm), after which it gradually decreases to 1 ppm at 50 cmbsf. The content of P at the base of the core lies around 1100 ppm (± 159 ppm) and fluctuates around a generally increasing trend until ca. 1200 ppm is reached around 50 cmbsf. Decreases in the general trend of P are seen between 400 and 350 cmbsf and above 50 cmbsf. Mn content is ca. 700 ppm (± 15.8 ppm) at the base of the core and remains constant to 350 cmbsf, after which it rapidly increases to two peaks of 1100 ppm at 250 and 200 cmbsf. From 200 cmbsf and above, Mn content of the sediment remains constant around 750 ppm. The peaks of Mn and P show some similarities. The Ca content of the sediment varies between 9500 and 10500 ppm (± 260 ppm), with two major peaks of approximately 11500 ppm at 30 cm and 525 cm depth. The two peaks of Ca do not seem to coincide with peaks in Mn or P. Ni in core 002 is relatively stable with values between 40 and 45 ppm (± 1.19 ppm). In the upper 150 cm of the core, the Ni content is lower and lies slightly below 40 ppm.

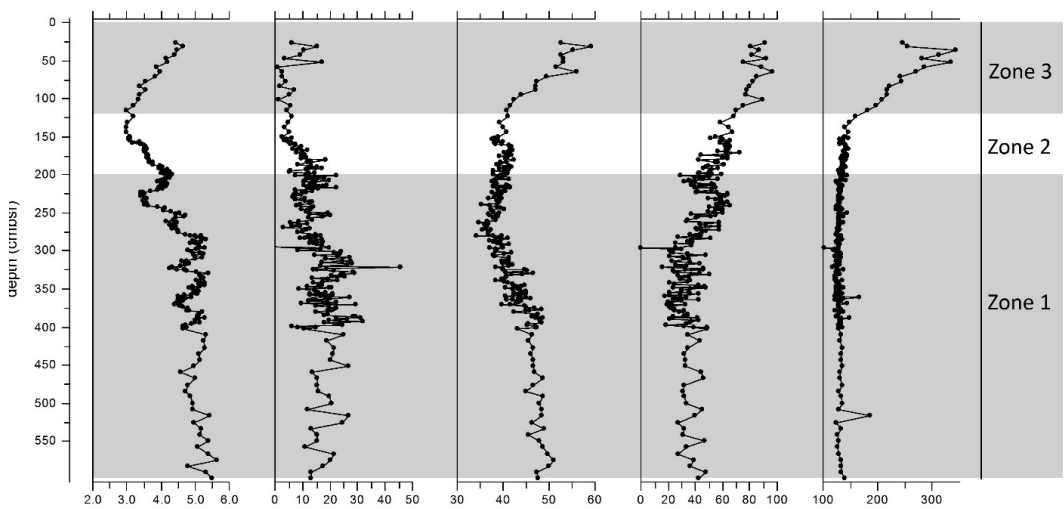
The TOC signal of core 005 appears to differ from core 002 (Fig. 3.3b) At the base of the core, TOC values are around 1 wt.% (± 0.05 wt.%) and gradually increase to 1.5 wt.% at 375 cmbsf, after which the TOC content abruptly increases to 6 wt.%. Throughout the remaining part of the core, TOC values gradually decrease to 4 wt.% at the top of the core. Mo in core 005 shows a similar trend as core 002, with only higher values. Mo is absent at the base of the core and reached detectable concentrations at 375 cmbsf. It then rapidly increases and reaches a maximum value of 4 ppm (± 1.23 ppm) at 175 cmbsf, after which it decreases to values below 5 ppm in the top of the record. The P content of core 005 is approximately 600 ppm (± 192 ppm) at the base of the core and gradually increases to 700 ppm at a depth of 375 cmbsf, after which it abruptly shifts to 1000 ppm. From 350 to 50 cmbsf, the P content gradually increases to 1200 ppm, with one positive excursion around 200 cmbsf. In the top 50 cm of the core, a sharp decline is revealed. Mn content of core 005 is remarkably higher than the Mn content of core 002, with values between 600 ppm and 37000 ppm (± 36 ppm), and most measured values higher than 1000 ppm. The Mn profile of core 005 shows a relatively stable signal, with excursions around 130, 200 and 270 cmbsf. Ca content of the sediment is ca. 11000 ppm (± 206 ppm) at the base of the core and show an overall decreasing trend towards minimum values of 9500 ppm at the top of the core, with positive excursions at the depths of 525, 500, 200 and 125 cmbsf. Ni content varies between approximately 37 and 55 ppm (± 0.54 ppm), and shows a similar trend as seen in core 002. The Ni content at the base of the core is ca 40 ppm and increases to 55 ppm at 150 cmbsf, after which it decreases to ca 37 ppm in the top of the core.



a) Core 002; Ingaröfjärden



b) Core 005; Baggensfjärden



c) Core 003; Erstaviken

Fig. 3.4 Sediment profiles of trace metals obtained at Ingaröfjärden, Baggensfjärden and Erstaviken. The grey bands were based on Mo and indicate zones of different oxygen conditions.

In the lower 400 cm of the core, the Pb content is stable with values around 40 ppm (± 6.10 ppm), after which it gradually increases to 90 ppm at the top of the core (Fig. 3.4a). The Cu content at the base of the core is below 40 ppm (± 0.69 ppm) and increases to 50 ppm at a depth of 250 cmbsf, after which it decreases to values below 40 ppm at a depth of 100 cmbsf. Above 100 cmbsf, the Cu content increases to 55 at the top of the core. A small peak of 50 ppm is seen around 500 cm depth. The Zn profiles are relatively stable with values around 120 ppm (± 7.78 ppm) in the bottom part of the core, and rapidly increases in the upper meter to ca. 230 ppm.

Core 005 reveals a more complicated pattern than core 002 with regard to the Cu content of the sediment (Fig.3.4b). The profile of Cu shows an overall increasing trend from values of 35 ppm (± 0.46 ppm) at the base of the core towards values around 50 ppm at a depth of 125 cmbsf, after which the signal reveals two negative excursions. From 50 cmbsf, Cu content rapidly increases to 60 ppm at the top of the core. The signal of Pb is shows a decreasing trend from the base of the core, where Pb values are around 60 ppm (± 7.62 ppm) to 200 cmbsf, where values are around 40 ppm. From 200 cmbsf to 50 cmbsf, the Pb content of the sediment increases to 60 ppm, after which it rapidly increases to 140 ppm at the top of the core. For Zn, a similar trend appears, with a stable Zn content around 130 ppm (± 3.08 ppm) in the lower 550 cm of the core, and a rapid increase to 280 ppm in the upper 50 cm of the core.

4. Discussion

4.1 Indications of hypoxia in the past three millennia

Although the three cores were obtained from the same area, they were taken at different locations with different water depths and sedimentation rates. Despite these differences the cores can be correlated to each other based on the profiles of for example TOC and Mo (Fig.4.1). Comparison of the cores reveals that the sedimentation rate of core 003 was much higher than for core 002, implying that core 002 covers a much longer period of time than core 003. The sudden shift around 400 cm in core 005, indicates a hiatus, making it difficult to estimate the time span of this core.

The profiles of Mo in the three cores reveal that the coastal waters of the Stockholm Archipelago experienced hypoxia during the MCA. From our data of Mo and TOC, four zones can be distinguished in the records. Zone 0 is only recorded in core 002 and core 005, a period of low Mo, indicating oxic conditions. Zone 1 is recorded in all three cores, a period of high Mo, indicating hypoxic or even anoxic conditions. In zone 2, Mo decreases and indicated oxic conditions at the sediment-water interface, this zone can be correlated to the onset of the LIA (Zillén et al., 2008). In zone 3, the modern zone, conditions in the water return to hypoxic. TOC was high in all zones, except for zone 2, when Mo decreased and conditions became oxic. Whether TOC is high as a result of high primary productivity or due to high preservation cannot be determined based on the data that is currently available.

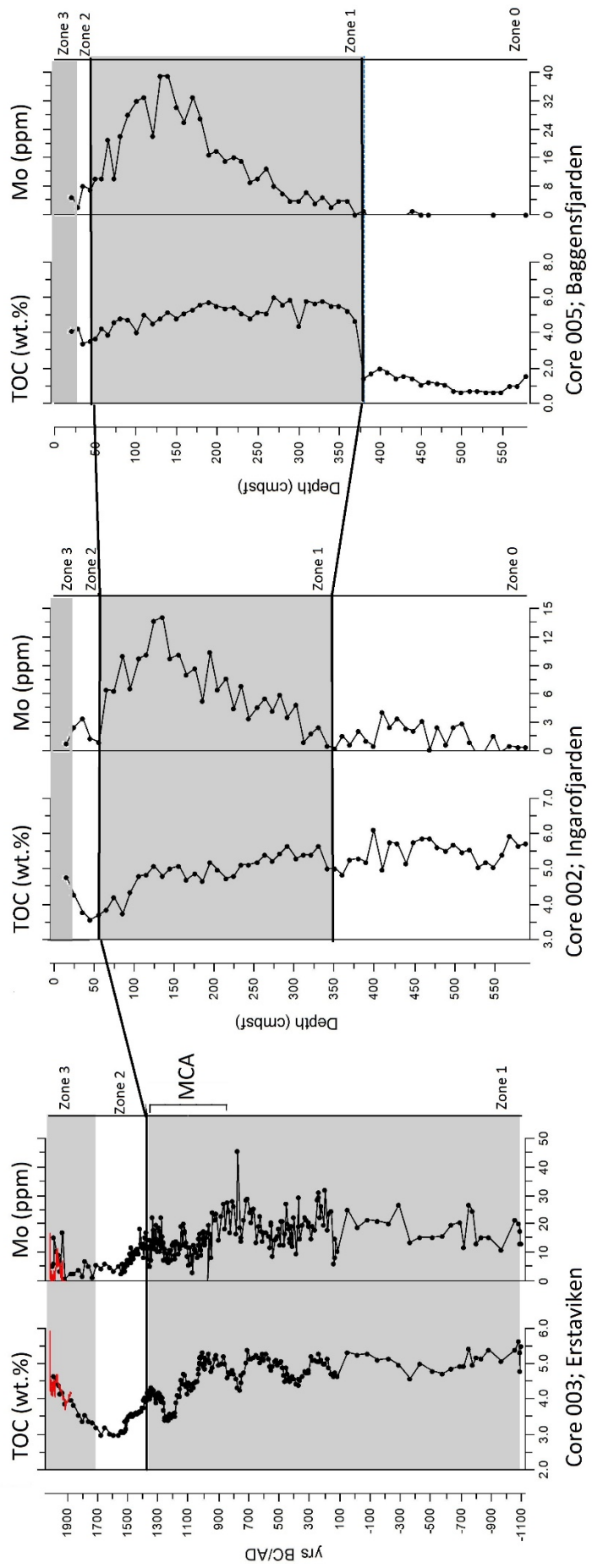


Fig.4.1 Correlation of core 003, Erstaviken; core 002, Ingaröfjärden and core 005, Baggensfjärden, based on Mo data.

4.2 Dynamics of hypoxia in the past three millennia

Core 003 covers three of the four aforementioned periods, with a period of high Mo at the bottom and the top of the core, and a period of low Mo in between. The TOC content of the sediment shows a similar trend and is high in the top and base of the core, but decreases in zone 2. The high Mo content indicates that the system already experienced hypoxia around 1150 BC, a condition that lasted until approximately 1350 AD. The periodic shifts that are seen in the profiles of Mo and TOC reveal the presence of phases within the hypoxic period from 1150 BC -1350 AD. In this period, also sharp peaks in the profile of Ca that coincide with peaks in Mn, can be seen. The large decrease in TOC and Mo from 1350 AD onwards indicates a shift from generally (seasonally) hypoxic conditions to more oxygenated conditions. Around 1700 AD, TOC increases and is followed by an increase of Mo around 1900 AD. Laminated sediments in the deep basins of the Baltic Sea, i.e. the Baltic Proper, Landsort Deep and the Gotland Basin, confirm the presence of hypoxia already before the start of the MCA (Zillén et al., 2008). Similar to the sediments of the Stockholm Archipelago, the laminated sediments disappear from the records of the deep basins around 1300 AD, marking the onset of the LIA. Comparison of the TOC and Mo content with records of the Landsort Deep shows that the TOC content of the Landsort Deep is 2-3 wt.% higher than in the records of the Stockholm Archipelago before and during the MCA. Also, the Mo content of the Landsort Deep in the same interval is twice as high as in the Erstaviken and Baggensfjärden and a fourfold of Ingaröfjärden (Dijkstra et al., 2016). This indicates that, although hypoxia was present in the waters of the Stockholm Archipelago before and during the MCA, it was less severe than in the deep basins of the Baltic Sea. This could be due to the limited water depth of the Stockholm Archipelago compared to the deep basins, resulting in a better mixing of the water. However, coastal sediments from the Gåsfjärden, part of an archipelago south of Stockholm reveal TOC contents that are ca. 2-3 wt.% higher than the records of the Stockholm Archipelago before and during the interval of the MCA (Ning et al., 2016). A possible explanation for this could be the location of the Gåsfjärden, as it is located 200 km south of the Stockholm Archipelago and thus has a higher insolation, which could be a stimulating factor for primary productivity.

4.3 Formation of Ca-rhodochrosites

The hypoxic period of zone 1 coincides with the large peaks of Mn that appear in the sediment. The peaks of Mn correspond to peaks in the profile of Ca, indicating the presence of Ca-rhodochrosites. Ca-rhodochrosites have been found in the deep basins of the Baltic Sea and are thought to be formed after inflows of North Sea water (Jakobsen and Postma, 1989). During these inflows of oxygenated water, Mn-oxides form from Mn^{2+} that is already present in the water column, and sink to the sediment-water interface (SWI). Once the bottom waters return to hypoxic conditions, the Mn-oxides are reduced and Mn is incorporated into Mn-carbonates such as Ca-rhodochrosites (Fig. 4.2) (Jilbert and Slomp, 2013b). Together with the decrease of TOC and Mo, marking the onset of the LIA, the peaks of Mn and Ca disappear. The presence of Ca-rhodochrosites in the sediments of the Stockholm Archipelago before and around the MCA, and the absence of the Ca-rhodochrosites with the onset of the LIA, confirms the hypothesis that the Stockholm Archipelago experienced hypoxic conditions before and during the MCA, that recovered during the LIA. As well as in core 003, peaks of Mn and Ca appear in core 002 and core 005 in the interval that is linked to the MCA, although the lower resolution of the analyses makes it difficult to identify the presence of individual peaks. The two large peaks of Mn and Ca around 100 and 200 cmbsf in core 005 coincide and could indicate the presence of Ca-rhodochrosites, although there seems no direct link to the P profile. The peaks of Mn and Ca in core 002 cannot be related, which implies that Ca-rhodochrosites were not formed at that site. This can be attributed to the differences in water depths at the sampling sites, as core 002 was obtained in shallower water than core 003 and core 005, as shallower water has better mixing and will therefore be less sensitive to the effects of inflow events.

From 130 AD, peaks of P appear in the sediment of core 003, that coincide with peaks in the profiles of Ca and Mn. The association of P with Ca-rhodochrosites is likely, as part of the Ca-Mn peaks coincide with peaks in P. It is however unknown why the peaks of P are not present before 130 AD. Association of P with Ca-rhodochrosites is thought to be related to inflow events (Jilbert and Slomp, 2013b), which suggest that a change in the inflow events occurred around 150 AD. As indicators of hypoxia are clearly present in the third zone, indicating the occurrence of inflow events, the absence of P bound to Mn-carbonates is remarkable. These observations indicate a change in the reaction of Mn to inflow events and hypoxia, as they show that Mn-carbonates are no longer formed after inflow events. This is consistent with the findings of Lenz et al. (2015), who show that Mn-carbonates are less likely to be formed in the Gotland Deep after inflow events. Their explanation is that the Mn-oxides that are formed in oxic conditions during inflow events, are reductively dissolved faster than earlier. As a consequence, Mn that is released in the reductive dissolution of Mn-oxides can more easily escape to the overlying water column and will not precipitate as Mn-carbonates.

Remarkable as well are the peaks of Ni in the interval from 150 AD to 1350 AD, largely coinciding with the peaks of P, Mn and Ca. An explanation for this could be the association of Ni with MnO₂, as described by Canavan et al. (2007). They show that Mn-oxides in the water column can scavenge Ni²⁺. Although their conclusions were based on a freshwater environment, the same could hold true for the situation in the brackish coastal waters of the Stockholm Archipelago. If this is the case and Mn-oxides are subsequently deposited on the sediment-water interface and reduced when conditions become hypoxic, Ni could be left in the sediment. This would explain the peaks of Ni coinciding with peaks of Mn, Ca and P, as Ni is deposited together with Mn. This also supports the theory of a change of inflow events around 150 AD, as MnO₂ is formed during inflow events (Lenz et al., 2015).

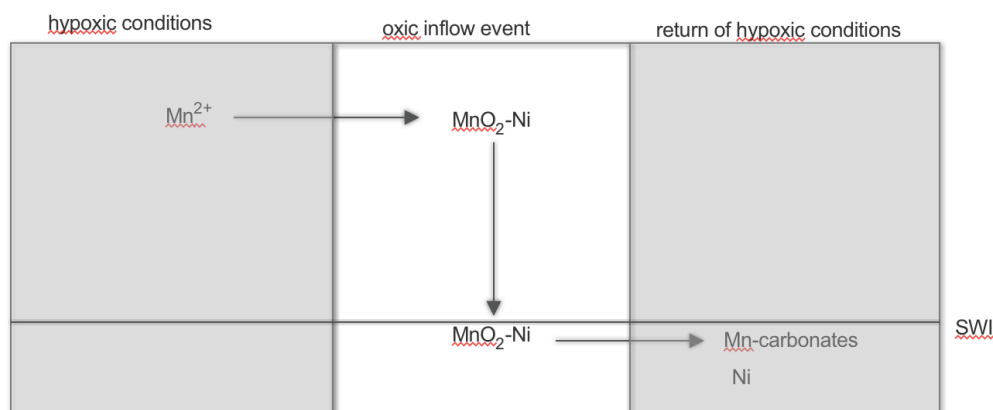


Fig. 4.2 Schematic overview of formation of Mn-carbonates with scavenging of Ni after inflow event

4.4 Relationship between SST and hypoxia

As temperature can be an important factor in the development of hypoxia, reconstruction of paleo-SSTs can reveal an eventual link between SST and hypoxia over the past three millennia. The BIT index that was calculated from GDGT analysis, was very low for the entire core, indicating that the organic material was mostly from marine origin. As the sampling sites are located in coastal waters where terrestrial input is expected to be high, it is most likely that this is due to a high marine productivity. This makes TEX₈₆ a suitable proxy to calculate SST. The SST that has been reconstructed for core 003, show that around 650 BC, temperature of the surface water is around 12°C. Before and during the MCA, from 300 AD until 1300 AD, SST has increased to 14°C. The decrease of the SST with 3.5°C around 1300 AD can be directly related to the changing climate and the onset of the LIA. Kabel et al. (2012) report a 2-3°C difference of SST between the MCA and the

LIA for the deeper parts of the Baltic Sea, which is lower than the difference found based on our data. The changing climate after the LIA is reflected in the SST record as well, as temperatures rise from 1600 AD to 14.5°C in modern time. The SSTs reconstructed for the Baltic Sea by Kabel et al. (2012) are ca. 2°C higher than the SSTs that were calculated based on our data, this could be due to the differences between the different sub basins that were sampled. The dynamics of hypoxia seem to be directly linked to the changes in SST. The phases of stronger hypoxia are accompanied by higher SST of approximately 14°C, while the moments of weaker hypoxia coincide with slightly lower SST of 12.5°C. The changes in SST from 350 AD however, seem to have affected either the production or the preservation of organic carbon, as the profiles of SST and TOC show a similar trend in the interval between 350 AD and 1350.

Although SST of modern day is comparable to the highest SST during the MCA, the Mo content of the top sediment is much lower than it was during the MCA. An explanation for this could be the limited availability of Mo, resulting in the reservoir effect that was described earlier. This could be the result of differences in hypoxic area between the MCA and modern conditions. Furthermore, the concentration of TOC in modern sediments is higher than it was during the LIA, but it is lower than it was during the MCA. This could explain why primary production and algal blooms in the current situation are stimulated by anthropogenic nutrient input (Conley et al., 2011). If an upper limit of primary production was reached during the first hypoxic period of core 003, extra nutrient input would not have stimulated primary production, as nutrients were not the limiting factor. In the modern day situation, nutrients are limiting for primary production in the Baltic Sea, which implies that the upper limit of primary production has not yet been reached.

4.5 Human activity and hypoxia

In the situation of the Stockholm Archipelago, the profiles of Pb, Cu and Zn are strongly influenced by human activity, which makes these elements useless as proxies for redox conditions. The elements have however shown to be useful as indicators of human activity, as they mark the start of mining activities in the region. The timing of the rapid increases in the profiles of Pb and Zn correlates to the rising industries of mining in the area NW of Stockholm. The three records show that zone 1 is hypoxic, as Mo values are high, but no signs of human influence are seen, based on the absence of enrichments in Cu, Pb and Zn in this zone. However, at the end of zone 1, from the 10th century, the mining of Cu and Pb started, which is reflected in the increase of Pb around 900 AD (Bindler et al., 2011; Bindler and Rydberg, 2015). The enrichments of Cu and Pb continue in zone 2, which corresponds with the onset of the LIA. Although human activity is still reflected in the profiles of Cu and Pb, the Mo profile of the records indicates a recovery of hypoxia in this period. This suggests that the recovery of hypoxia is independent of the human activity at that time. At the end of zone 2, in the 16th century, an increase of Zn appears, which is consistent with the literature, that reports the start of Zn mining in the 16th century (Blair and Ramsay, 1991).

The profiles of Zn and Pb provide evidence of human activity in the area around Stockholm from the 10th century, and can therefore be used as an indication that anthropogenic influence might have played a role in the biogeochemistry of the system, at least from the 10th century. Traces of human activity and agricultural practices during the Iron Age have been found in other parts of the Baltic region. This implies that human activity was also present in the Stockholm Archipelago before the 10th century, but this is not reflected in the profiles of Cu, Pb and Zn, as mining activities only started from the 10th century. The potential influence of human activity on the development of hypoxia in the earliest period of zone 1, from 1100 BC to 900 AD can therefore not be excluded.

The three major periods that are visible in core 003, show that the system has been hypoxic for a long time. The Mo profiles of core 002 and core 005 show that before the hypoxic period, the system was oxic. However, also during the oxic period that is visible in core 002, TOC was high. This suggests that

the high TOC is the result of high primary productivity and is not solely the effect of high preservation. The increase of SST around 300 BC, seems to have had no significant effect on the productivity, as TOC does not increase accordingly. This could indicate the presence of an upper limit for primary production, caused by light-limitation of algal blooms (Cloern, 1999). Unlike what was expected, human activity from the 10th century appears to coincide with the decrease in TOC and Mo that is seen around 900 AD. It is therefore unlikely, that human activity and anthropogenic eutrophication has been the driver of hypoxia during the MCA.

5. Conclusion

We conclude that hypoxia was indeed present in the coastal waters of the Stockholm Archipelago during the MCA. Our observations however, indicate that the onset of this hypoxia did not coincide with the start of the MCA, as the bottom water of the Stockholm Archipelago had already experienced hypoxia before the onset of the MCA. Based on Mo and TOC, the time interval from 1100 BC to 1900 AD can be divided in three periods. The period from ca. 1100 BC to 1350 AD, is characterized by high TOC and Mo content, indicating hypoxic conditions. Sharp peaks of Ca and Mn, likely related to Ca-rhodochrosites, indicate the occurrence of inflow events during the entire interval from 1100 BC to 1350 AD and sustain the conclusion that the waters of the Stockholm Archipelago were hypoxic before and during the MCA. The period between ca. 1350 AD to 1800 AD, has lower TOC and Mo values and was most likely oxic. The period from 1800 AD to modern day, is characterized by high TOC and Mo, again pointing to hypoxic conditions. The profiles of TOC and Mo of core 002 reveal that the first period of hypoxia was preceded by a period with oxic conditions, the timing of this transition is however unknown.

The low BIT values indicate that the waters of the Stockholm Archipelago were dominated by marine productivity over terrestrial input of organic material throughout the entire interval. SST that was calculated for core 003, using TEX_{86L} , shows that the temperature of the coastal water increased between 700 BC and 300 BC, which has had no measurable effect on the concentration of TOC and Mo in the sediment. As hypoxia was already present and remained at a constant level from 1100 BC until 900 AD and did not respond to the increased SST. Around 1400 AD, SST decreased again, which corresponds to the decrease of TOC and Mo in the period from 1350-1800 AD, and coincides with the onset of the LIA.

The role of anthropogenic activity in the development of hypoxia in the Stockholm Archipelago during the MCA and before was limited, as hypoxia was already present before the large population growth that occurred during early medieval time. As the hypoxia seems to remain at a constant level until 900 AD, we suspect primary production was limited by another factor than nutrient supply during that period, this could likely be contributed to the light-limitation of algal blooms. This indicated that nutrient levels were already high during this period, which explains why anthropogenic eutrophication in early medieval time seems to have had no effect on hypoxia. The profiles of TOC and Mo of core 003 sustains this conclusion, as they show that the strongest hypoxia was already on its return when population growth became significant. This indicates that the development of hypoxia was most likely due to natural causes. Unlike the modern day coastal hypoxia, anthropogenic eutrophication seems to have had limited effect on the development of low-oxygen conditions in the bottom waters around Stockholm.

There is still a limited understanding of the consequences of current climate warming for the development of hypoxia in vulnerable systems such as the Baltic Sea. This study shows the importance of temperature on the development of hypoxia and based on our findings, we expect that rising temperatures in the future will negatively affect the oxygen conditions in the coastal waters of the Baltic Sea. Obtaining a better understanding of the combined effects of human-induced eutrophication and rising temperatures in the Baltic Sea will hopefully allow us to make accurate predictions about the development of hypoxia in the years that are to come.

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7. References

- Algeo, T.J. (2004) *Can marine anoxic events draw down the trace- element inventory of seawater?* *Geology* 32, pp. 1057–1060
- Algeo, T. J., and Lyons, T. W. (2006). *Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions.* *Paleoceanography* 21, pp. 1-23
- Berner, A.K. and Berner, R.A. (2012) *Global environment: water, air and geochemical cycles.* Princeton, New Jersey, Princeton University Press.
- Bindler, R. Segerström, U., Pettersson-Jensen, I., Berg, A., Hansson, S., Holmström, H, Olsson, K. and Renberg, I. (2011) *Early medieval origins of iron mining and settlement in central Sweden: multiproxy analysis of sediment and peat records from the Norberg mining district.* *Journal of Archaeological Science* 38, pp. 291-300
- Bindler, R. and Rydberg, J. (2015) *Revisiting key sedimentary archives yields evidence of a rapid onset of mining in the mid-13th century at the great copper mountain, Falun, Sweden.* *Archaeometry* 58, pp. 642–658
- Björck, S. (1995) *A review of the history of the Baltic Sea, 13.0-8.0 ka BP.* *Quaternary International* 27, pp. 19-40
- Blair, J. and Ramsay, N. (1991) *English Medieval Industries: craftsmen, techniques, products.* London and Rio Grande, Ohio. The Hambledon Press
- Bonsdorff, E., Blomqvist, E.M., Matilla, J. and Norkko, A. (1997) *Coastal Eutrophication: Causes, Consequences and Perspectives in the Archipelago Areas of the Northern Baltic Sea.* *Estuarine, Coastal and Shelf Science* 44, pp. 63-72
- Bradley, S.R., Hughes, M.K. and Diaz, H.F. (2003) *Climate in Medieval time.* *Science* 302, pp. 404-405
- Bradshaw, E.G., Rasmussen, P., Nielsen, H. and Anderson, N.J. (2005) *Mid- to late- Holocene land use change and lake development at Dallund Sø, Denmark: trends in lake primary production as reflected by algal and macrophyte remains.* *The Holocene* 15, pp. 1130-1142
- Calvert, S.E., Pedersen, T.F. (1996) *Sedimentary geochemistry of manganese: implications for the environment of formation of manganiferous black shales.* *Economic Geology* 91, pp. 36–47
- Canavan, R.W., Van Cappellen, P., Zwolsman, J.J.G., Van den Berg, G.A. and Slomp, C.P. (2007) *Geochemistry of trace metals in a fresh water sediment: field results and diagenetic modeling.* *Science of the Total Environment* 381, pp. 263-279
- Carstensen, J. Conley, D.J., Bonsdorff, E., Gustafsson, B.G., Hietanen, S., Janas, U., Jilbert, T., Maximov, A., Norkko, A., Norkko, J., Reed, D.C., Slomp, C.P., Timmermann, K. and Voss, M. (2014a) *Hypoxia in the Baltic Sea: Biogeochemical Cycles, Benthic Fauna, and Management.* *Ambio* 43, pp. 26-36
- Carstensen, J., Andersen, J.H., Gustafsson, B.G., Conley, D.J. (2014b) *Deoxygenation of the Baltic Sea during the last century.* *Proceedings of the National Academy of Sciences of the United States of America* 111, pp. 5628–5633

Cloern, J.L. (1999) *The relative importance of light and nutrient limitation of phytoplankton growth: a simple index of coastal ecosystem sensitivity to nutrient enrichment*. *Aquatic Ecology* 33, pp. 3-16

Conley, D.J., Björck, S., Bonsdorff, E., Carstensen, J., Destouni, G., Gustafsson, B.G., Hietanen, S., Kortekaas, M., Kuosa, H., Markus Meier, H.E., Muller- Karulis, B., Nordberg, K., Norkko, A., Nurnberg, G., Pitkanen, H., Rabalais, N.N., Rosenberg, R., Savchuk, O.P., Slomp, C.P., Voss, M., Wulff, F. and Zillén, L. (2009) *Hypoxia related processes in the Baltic Sea*. *Environmental Science & Technology* 43, pp. 3412-3420

Conley, D.J., Carstensen, J., Aigars, J., Axe, P., Bonsdorff, E., Eremina, T., Haahti, B., Humborg, C., Jonsson, P., Kotta, J., Lannegren, C., Larsson, U., Maximov, A., Rodriguez Medina, M., Lysiak-Pastuszek, E., Remeikaite-Nikiene, N., Waive, J., Wilhelms, S. and Zillén, L. (2011) *Hypoxia is increasing in the coastal zone of the Baltic Sea*. *Environmental Science & Technology* 45, pp. 6777–6783

Diaz, R.J. and Rosenberg, R. (1995) *Marine benthic hypoxia: a review of its ecological effects and behavioural responses of marine macrofauna*. *Oceanography and Marine Biology Annual Reviews* 33, pp. 245–303

Diaz, R.J. and Rosenberg, R. (2008) *Spreading dead zones and consequences for marine ecosystems*. *Science* 321, pp. 926-929

Diaz, H.F., Trigo, R., Hughes, M.K., Mann, M.E., Xoplaki, E. and Barriopedro, D. (2011) *Spatial and temporal characteristics of climate in medieval times revisited*. *American Meteorological Society* 92, pp. 1487-1500

Dijkstra, N., Slomp, C.P. and Behrends, T. (2016) *Vivianite is a key sink for phosphorus in sediments of the Landsort Deep, an intermittently anoxic deep basin in the Baltic Sea*. *Chemical Geology* 438, pp. 58-72

Emerson, S.R. and Husted, S.S. (1991) *Ocean anoxia and the concentrations of molybdenum and vanadium in seawater*. *Marine Chemistry* 34, pp. 177-196

Eriksson, B.K., Sandström, A., Isaeus, M., Schreiber, H. and Karas, P. (2004) *Effects of boating activities on aquatic vegetation in the Stockholm Archipelago, Baltic Sea*. *Estuarine, Coastal and Shelf Science* 61, pp. 339-349

Froelich, P. N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D. Hartman, B. and Maynard, V. (1979) *Early Oxidation of Organic-Matter in Pelagic Sediments of the Eastern Equatorial Atlantic - Suboxic Diagenesis*. *Geochimica Et Cosmochimica Acta* 43, pp. 1075-1090

Funkey, C.P., Conley, D.J., Reuss, N.S., Humborg, C., Jilbert, T. and Slomp, C.P. (2014) *Hypoxia sustains cyanobacteria blooms in the Baltic Sea*. *Environmental Science & Technology* 48, pp. 2598-2602

Graham, N.E., Ammann, C.M., Fleitmann, D., Cobb, K.M. and Luterbach, J. (2011) *Support for global climate reorganisation during the Medieval Climate Anomaly*. *Climate Dynamics* 37, pp. 1217-1245

Harff, J., Björck, S. and Hoth, P. (2011) *The Baltic Sea Basin*. Springer Berlin

Heiser, U., Neumann, T., Scholten, J. and Stuben, D. (2001) *Recycling of manganese from anoxic sediments in stagnant basins by seawater inflow: a study of surface sediments from the Gotland Basin, Baltic Sea*. *Marine Geology* 177, pp. 151-166

- Helly, J. J. and Levin, L. A. (2004) *Global distribution of naturally occurring marine hypoxia on continental margins*. Deep-Sea Research 51, pp. 1159–1168
- Hopmans, E.C., Weijers, J.W.H., Schefuss, E., Herfort, L., Sinninghe Damsté, J.S. and Schouten, S. (2004) *A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids*. Earth and Planetary Science Letters 24, pp. 107–116
- Hopmans, E. C., Schouten, S., & Damsté, J. S. S. (2016). *The effect of improved chromatography on GDGT-based palaeoproxies*. Organic Geochemistry 93, pp. 1-6
- Jakobsen, R. and Postma, D. (1989) *Formation and solid solution behavior of Ca-rhodochrosites in marine muds of the Baltic deep*s. Geochimica et Cosmochimica Acta 53, pp. 2639–2648
- Jilbert, T. and Slomp, C.P. (2013a) *Rapid high-amplitude variability in Baltic Sea hypoxia during the Holocene*. Geology 41, pp. 1183-1186
- Jilbert, T. and Slomp, C.P. (2013b) *Iron and manganese shuttles control the formation of authigenic phosphorus mineral in the euxinic basins of the Baltic Sea*. Geochimica et Cosmochimica Acta 107, pp. 155-169
- Jonge, de, C., Hopmans, E.C., Zell, C.I. Kim, J-H., Schouten, S. and Sinninghe Damsté (2014) *Occurrence and abundance of 6-methyl branched glycerol dialkyl glycerol tetraethers in soils: Implications for palaeoclimate reconstruction*. Geochimica et Cosmochimica Acta 141, pp. 97–112
- Kabel, K., Moros, M., Porsche, C., Neumann, T., Adolphi, F., Andersen, T.J., Siegel, H., Gerth, M., Leipe, T., Jansen, E. and Sinninghe Samsté, J.S. (2012) *Impact of climate change on the Baltic Sea ecosystem over the past 1000 years*. Nature Climate Change 2, pp. 871-874
- Kemp, W.M., Testa, J.M., Conley, D.J., Gilbert, D. and Hagy, J.D. (2009) *Temporal responses of coastal hypoxia to nutrient loading and physical controls*. Biogeosciences 6, pp. 2985–3008
- Kim, J., Van der Meer, J., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koc, N, Hopmans, E.C. and Sinninghe Samsté, J.S. (2010) *New indices and calibrations derived from the distribution of crenarchaeal isoprenoid tetraether lipids: Implications for past sea surface temperature reconstructions*. Geochimica et Cosmochimica Acta 74, pp. 4639-4654
- Lenz, C., Jilbert, T., Conley, D.J., Wolthers, M. and Slomp, C.P. (2015) *Are recent changes in sediment manganese sequestration in the euxinic basins of the Baltic Sea linked to the expansion of hypoxia?* Biogeosciences 12, pp. 4875-4894
- Lepland, A. and Stevens, R.L. (1998) *Manganese authigenesis in the Landsort Deep, Baltic Sea*. Marine geology 151, pp. 1-25
- Levin, L.A., Ekau, W., Gooday, A.J., Jorissen, F., Middelburg, J.J., Naqvi, S.W.A., Neira, C., Rabalais, N.N. and Zhang, J. (2009) *Effects of natural and human-induced hypoxia on coastal benthos*. Biogeosciences 6, pp. 2063-2098
- Matthäus, W. (2006) *The history of investigation of salt water inflow into the Baltic Sea from the early beginning to recent results*. Marine Science Reports 65, pp. 1–74
- Mort, H.P., Slomp, C.P., Gustafsson, B.G. and Andersen, T.J. (2010) *Phosphorus recycling and burial in Baltic Sea sediments with contrasting redox conditions*. Geochimica et Cosmochimica Acta 74, pp. 1350-1362

- Ning, W., Ghosh, A., Jilbert, T., Slomp, C.P., Khan, M., Nyberg, J., Conley, D.J. and Filipsson, H.L. (2016) *Evolving coastal character of a Baltic Sea inlet during the Holocene shoreline regression: impact on coastal zone hypoxia*. *Journal of Paleolimnology* 55, pp. 319-338
- Rabalais, N.N., Turner, R.E., Diaz R.J. and Justic, D. (2009) *Global change and eutrophication of coastal waters*. *ICES Journal of Marine Science* 66, pp. 1528–1537
- Rabalais, N. N., Diaz, R.J., Levin, L.A., Turner, R.E. , Gilbert, D. and Zhang, J. (2010) *Dynamics and distribution of natural and human-caused hypoxia*. *Biogeosciences* 7, pp. 585–619
- Redfield, A.C. (1958) *The biological control of chemical factors in the environment*. *American Scientist* 46, pp. 206-226
- Reed, D.C., Slomp, C.P., de Lange, G.J. (2011) *A quantitative reconstruction of organic matter and nutrient diagenesis in Mediterranean Sea sediments over the Holocene*. *Geochimica Cosmochimica et Acta*, 75, pp. 5540–5558
- Ruttenberg, K.C. (2014) *The global phosphorus cycle*. In: Holland H.D. and Turekian, K.K, editors. *Treatise on Geochemistry*, 2nd ed. Elsevier, Oxford.
- Schouten, S., Hopmans, E. C., Schefuß, E., and Sinninghe Damste, J. S. (2002). *Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures?* *Earth and Planetary Science Letters* 204, pp. 265-274
- Schouten, S., Hopmans, E.C. and Sinninghe Damsté, J.S. (2013) *The organic geochemistry of glycerol dialkyl glycerol tetraether lipids: A review*. *Organic geochemistry* 54, pp. 19-61
- Scott, F.D. (1998) *Sweden, the nation's history*. Southern Illinois University Press, Carbondale and Edwardsville.
- Scott, C., & Lyons, T. W. (2012) *Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: refining the paleoproxies*. *Chemical Geology*, 324, pp.19-27
- Sinninghe Damsté, J.S. (2016) *Spatial heterogeneity of sources of branched tetraethers in shelf systems: The geochemistry of tetraethers in the Berau River delta (Kalimantan, Indonesia)*. *Geochimica et Cosmochimica Acta* 186, pp. 13-31
- Skold, E., Lageras, P. and Berglund, B.E. (2010) *Temporal cultural landscape dynamics in a marginal upland area: agricultural expansions and contractions inferred from palynological evidence at Yttra Berg, southern Sweden*. *Vegetation History Archaeobotany* 19, pp. 121-136
- Slomp, C.P., Malschaert, J.F.P., Lohse, L. and Van Raaphorst, W. (1997) *Iron and manganese cycles in different sedimentary environments on the North Sea continental margin*. *Continental Shelf Research* 17, pp. 1083-1117
- Toggweiler, J.R. (1999) *An ultimate limiting nutrient*. *Nature* 400, pp. 511-512
- Tribouillard, N., Algeo, T.J., Lyons, T. and Riboulleau, A. (2006) *Trace metals as paleoredox and paleoproductivity proxies: an update*. *Chemical Geology* 232, pp. 12-32
- Ulen, B., Bechmann, M., Föster, J., Jarvie, H.P. and Tunney, H. (2007) *Agriculture as a phosphorus source for eutrophication in the north-west European countries, Norway, Sweden, United Kingdom and Ireland: a review*. *Soil Use and Management* 23, pp. 5-15

Vahtera, E., Conley, D.J., Gustaffson, B., Kuosa, H., Pitkanen, H., Savchuk, O., Tamminen, T., Wasmund, N., Viitasalo, M., Voss, M. and Wulff, F. (2007) *Internal ecosystem feedbacks enhance nitrogen-fixing cyanobacteria blooms and complicate management in the Baltic Sea*. *Ambio* 36, pp.186–194

Weijers, J. W., Schouten, S., van den Donker, J. C., Hopmans, E. C., and Sinninghe Damsté, J. S. (2007). *Environmental controls on bacterial tetraether membrane lipid distribution in soils*. *Geochimica et Cosmochimica Acta*, 71, pp. 703-713

Wuchter, C., Schouten, S., Coolen, M.J.L. and Sinninghe Damsté, J.S. (2004) *Temperature dependent variation in the distribution of tetraether membrane lipids of marine Crenarchaeota: implications for TEX86 paleothermometry*. *Paleoceanography* 19, pp. 4028.

Zillén, L., Conley, D.J., Andrén, T., Andrén, E. and Björck, S. (2008) *Past occurrences of hypoxia in the Baltic Sea and the role of climate variability, environmental change and human impact*. *Earth-Science Reviews* 91, pp. 77–92

Zillén, L. and Conley, D.J. (2010) *Hypoxia and cyanobacteria blooms - are they really natural features of the late Holocene history of the Baltic Sea?* *Biogeosciences* 7, pp. 2567-2580

Zillén, L., Lenz, C., & Jilbert, T. (2012) *Stable lead (Pb) isotopes and concentrations—A useful independent dating tool for Baltic Sea sediments*. *Quaternary Geochronology* 8, pp. 41-45