Records of environmental change and sedimentation processes over the last century in a Baltic coastal inlet

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Contents

Cover Picture: Gropviken, Sweden. Helena Filipsson 2017

Abstract

HANNA NILSSON

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Abstract: The marine ecosystem in the Baltic Sea is affected by multiple stress factors, e.g. eutrophication and deoxygenation, overfishing and anthropogenic pollution. Here we evaluate the short-term trends of dissolved oxygen in bottom waters and changes in the primary productivity within a coastal inlet in the Baltic Sea. Undisturbed sediment cores (mean sedimentation rate 0.5 cm yr^{-1}) were retrieved from the inner and outer part of a coastal inlet, Gropviken, and dated using ^{210}Pb and ^{137}Cs. A multi-proxy approach (grain-size analysis, organic carbon and nitrogen content, biogenic silica and elemental analysis) has been used to provide a better understanding of the environmental change within the inlet. Four significant changes were observed in oxygen deficiency, sedimentation rate and phytoplankton composition during the last century. The deeper area in the inlet has naturally low oxygen conditions due to slow water exchange, but high values of the redox proxies can be observed already in the beginning of the 1930's, with an increase to a maximum in the 1980's. The contributing factor could be an increase of eutrophication from expanded farmland in the area. Signs for increased eutrophication are also seen in higher biogenic silica and organic carbon content beginning in the 1920's . A switch in the phytoplankton composition is observed from the late 1960's onwards and due to the change in nutrient ratios and lower secchi depth. Increased precipitation during this event could have changed the sedimentation rate within the inlet, with a decrease in the shallower area and an increase in the deeper part. As a result of increased precipitation, the riverine input increased and brought more nutrient and weathered particles to the open waters. These four sediment cores will contribute to an increased understanding of short-term environmental changes and sedimentation processes taking place in a coastal inlet of the Baltic Sea.

Keywords: the Baltic Sea, eutrophication, coastal areas, archipelago, laminated sediments, nutrient inputs, carbon and nitrogen content, biogenic silica, sedimentation, environmental impact, marine geology

Supervisor: Helena Filipsson

Subject: Quaternary Geology

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Svensk sammanfattning

HANNA NILSSON

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Sammanfattning: Det marina ekosystemet i Östersjön påverkas av flera olika stressfaktorer, såsom övergödning, förorening, överfiske och syrebrist på havsbottnen. I den här studien utvärderas de kortsiktiga trenderna för syrebrist på havsbottnen samt förändringarna i den primära produktiviteten i fjärden Gropviken i Östersjön. Fyra ostörda sedimentkärnor (med en sedimentationshastighet på 0,5 cm yr^{-1}) hämtades upp från den inre och yttre delen av fjärden Gropviken, och daterades med hjälp utav ^{210}Pb och ^{137}Cs. En multi-proxy studie (kornstorleks-, organiskt kol och kväve-, biogent kisel- och elementanalys) har utförts för att få en tydligare bild av miljöförändringen i Gropviken. Fyra stora förändringar under det senaste århundradet kunde observeras i syrehalten, sedimentationshastigheten och sammansättningen av primärproduktionen. De djupare delarna av inloppet har naturligt låga syrehalter på grund av ett långsamt vattenutbyte, men en ökad syrebrist kunde observeras redan i början av 1930-talet och som fortsatte att öka till 1980-talet. Den bidragande faktorn till ökad syrebrist i området kan ha varit övergödning som har skett genom en ökad näringsämnestillförsel från jordbruket som expanderade i närområdet under denna perioden. Tecken på ökad övergödning kan också observeras i den stigande andelen biogent kisel och organiskt kol som började öka samtidigt som syrehalten förvärrades. En förändring i sammansättningen av primärproduktiviteten i Gropviken observeras i slutet av 1960-talet och framåt. Detta skulle kunna förklaras av en förändring av näringsförhållanden i vattnet samt av en försämring av siktdjupet. Sedimentationshastigheten i inloppet, med en minskning i det grundare området och en ökning i den djupare området, kan ha berott på ökad nederbörd. Ökad nederbörd kan också ha bidragit till en ökad flodinmatning av näringsämnen och lerpartiklar från åar som mynnar ut i Gropviken. Dessa fyra sedimentkärnor skulle kunna bidra till ökad förståelse för kortsiktiga miljöförändringar och sedimentationsprocesser som äger rum i kustnära områden i Östersjön.

Nyckelord: Östersjön, övergödning, kustområden, skärgård, laminerade sediment, näringsämnen, biogent kisel kol och kvävehalt, sedimentering, miljöpåverkan, maringeologi

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1 Introduction

The eutrophication in the Baltic Sea has led to increased algae blooms, increased areas of hypoxia and decreasing populations of fish. A consequence of eutrophication is oxygen depletion of the bottom waters, as organic matter settles and mineralizes on the seafloor. If the bottom water is oxygen depleted the biodiversity is affected negatively as it has to adapt to the new, unfavourable conditions in the aquatic environment (Karlsson et al. 2010).

Hypoxia is defined as dissolved oxygen concentrations of < 2 mg/l (Conley et al. 2011). According to Dìas & Rosenberg (2008), dead zones, areas affected by hypoxia, have grown in both size and number during the last decades. Expansion of hypoxia in the Baltic Sea is well-known (Conley et al 2011), but studies of hypoxia in the coastal zones of the Baltic have been few, even if the input of nutrients from the catchment area is large (Jokinen et al. 2018). The expansion of coastal hypoxia during the last century is forced by anthropogenic activities (Duante et al. 2008; Caballero -Alfonso t al. 2015). This thesis is a part of the *Live2Tell* project, with the aim to reconstruct a Baltic coastal environment which has experienced an increasing anthropogenic impact over the last century and to identify trends of the human-induced pollution at the site.

According to Rabalais et al. (2014) the negative oxygen trends are more widespread in coastal oceans than in open seas. The stratification in Baltic coastal areas is caused by a thermocline rather than a halocline (Conley et al. 2011), which prevents vertical mixing of dissolved oxygen from the surface water to the bottom water. During spring and autumn the water masses mix due to thermal convection (Jokinen et al. 2018). If the delivery of organic input is high, because of seasonal blooms of primary productivity, it may result in seasonal hypoxia (Jokinen et al. 2015). Enrichment of nutrients has led to eutrophication and the preservation of laminated sediments in coastal areas with restricted water exchange since the beginning of the 1950's (Persson & Jonsson 2000). According to Boesch (2002) the main effects of eutrophication are the developments of harmful blooms of toxic algae, hypoxia, loss of benthic fauna (as a consequence of hypoxia) and a general weakening of the ecosystem. Declining dissolved oxygen concentrations in bottom waters interrupt ecosystem functions, such as the biogeochemical cycling of many elements and nutrients. The input of nutrients and elements changes the ecological composition of phytoplankton. (Rabalais et al. 2014).

The Baltic Sea is a naturally vulnerable system influenced by natural and anthropogenic factors. Human activities, leading to pollution, eutrophication, acidification, climate warming and deoxygenation, have a significant negative impact on the Baltic Seas marine environments (Rabalais et al. 2014). Human-induced environmental changes may be rapid and marine organisms must adapt to the new conditions accordingly.

In this study, I compare proxy records (biogenic silica [BSi], C:N ratio, grain-size and heavy metals) of the last century from a coastal inlet in SE Sweden in order to determine if the primary productivity and oxygen levels in the bottom waters changes with an increasing input from the catchment area. The Project *Live2Tell* is a FORMAS-funded research project with the aim to improve the understanding of why certain phytoplankton species are more tolerant to environmental changes, whilst other species disappear. Mining has increased the local metal emissions and the local history of pollutants determines how deep in the sediment the natural background levels of metals are found (SGU 2017). The study site of *Live2Tell* is located in the inlet Gåsfjärden. As a consequence of historical copper mining in the area, which introduced heavy metals to the coastal zone, the site has relatively poor water quality. The copper mine had a waste water outlet into the fjord of Gåsfjärden. The project further includes a control site in Gropviken, 90 km north of Gåsfjärden, in the S:t Anna archipelago, SE Sweden, which has not been exposed to direct metal pollution from a mine. This facilitates a direct comparison of the past environmental conditions with and without the direct influence of mining and will allow us to draw conclusions on the effects of copper mining on ecosystems.

However, Gropviken is affected by human-induced eutrophication and reduced oxygenation. This thesis will focus on Gropviken. The archipelago has a complex topography with many islands and sills, which results in a restricted water exchange between the open sea and the inner archipelago (Jokinen et al. 2018). The area is therefore sensitive to supply of anthropogenic nutrients and pollutants and offers itself as an ideal study regions of the environmental changes caused by those factors.

The aims of the study are:

- To investigate the historical development of organic matter at two locations in the inlet of Gropviken.
- To evaluate and compare the development of the sediments and sedimentation rates within the inlet.
- To investigate potential variability in anthrophonic input of nutrients and pollutants.

1.1 Baltic Sea

The Baltic Sea is a semi-enclosed sea in Northern Europe. It is the world's largest brackish water body with a number of sub-basins. The Baltic Sea is a naturally vulnerable system to hypoxia, characterized by brackish water and a positive estuarine circulation. The beginning of the modern Baltic Sea was typically set around 3000 years ago (Zillén et al. 2008).

The Baltic Sea is surrounded by nine countries and the total drainage area is four times larger than the sea itself. Properties of the straits that separate the sub-basins and large-scale atmospheric circulations are important for the water exchange of the Baltic Sea (Conley et al. 2009). The sea has only narrow connections out to the North Sea, through the Danish Straits. The surface water has a low density due to its low salinity, a consequence of the high riverine runoff, and the deep-water is more saline. (Szymczycha et al.

2019). The inflow of denser oxygen-rich saline water from the North Sea is the most effective way of oxygenation of the bottom water in the Baltic Sea. This occurs mainly during autumn storm events (Bernes 2005). However, these events lead to a strengthening of the stratification, as they introduce more saline water masses and thereby, in time, enlarge the area of oxygen depletion in the bottom waters. The supply of oxygen to the bottom of the Baltic Sea is otherwise limited due to the strong halocline between the upper water masses and the denser bottom waters (Rabalais et al. 2007). Sediments in the deepest areas are only populated by bacteria.

Over the past 100 years the sea has endured an increase of multiple stressors, such as eutrophication, ocean acidification and climate change, due to human impacts. As a result the Baltic has become one of the world's most polluted seas. A decline in dissolved oxygen concentration [O_2] in the Baltic has been known since the 1930s (Vlasov et al. 2010). The marine environment has been contaminated for over a decade and pollutants have accumulated in the food-web reaching levels toxic for marine organisms (FEHY 2013). Leakage of untreated sewage water, industrial fertilizers, agricultural practices, diffuse runoff from land and atmospheric deposition are direct threats to the marine ecosystems in the Baltic Sea (Szymczycha et al. 2019).

2 Study area and site description

Gropviken is a coastal inlet in S:t Anna archipelago (Östergötland, SE Sweden) in the southern part of the Baltic Sea (Fig.1). S:t Anna archipelago covers approximately 300 km^2 and is characterized by narrow fjord-like inlets and small islands. The archipelago consists of a network of bays and sill basins (Jonsson et al. 2003). Faults in NW/SE directions are intersecting the area. The archipelago has no distinct halocline because it is relatively shallow. The thermocline is usually around 10 meters water depth during summer (Persson & Jonsson 2000). In inlets like this one, the water exchange under the halocline is often limited, which can lead to the accumulation of nutrients in the bottom water and oxygen deficiency as a consequence (Jonsson et al. 2003).

Gropviken is approximately 4.3 km^2 in area, six km long and 500 m wide, and has a maximum water depth of 39 m. Deep water exchange occurs every 100 days when there is a weakening of the thermocline caused by the season variations during spring and autumn (Jonsson et al. 2003). Oxygen deficiency at the bottom should therefore increase during the stagnation periods. The area is relatively unexploited and sporadically populated. Gropviken has small marinas and is a popular location for tourists during summer. Two locations in Gropviken have been studied, Gp1, in the inner part of the coastal inlet and Gp2 in the outer part of the coastal inlet (Fig. 1).

The sampling locations in Gropviken were chosen to target waters not affected by any known local emissions of metal pollutants. The sediments at Gp1 and Gp2 are not affected by any large wave activity or bottom currents and can therefore act as a trap for metals and persistent organic compounds from emissions of various kinds. Sea beds without strong bottom currents and with oxygen-poor bottom water are ideal for environmental sampling due to the fact that sediments are deposited undisturbed year after year. The data from the sequences can provide information about the variation though time of both elemental content, organic matter and grain size distribution. This allows determining changes in the environment over time.

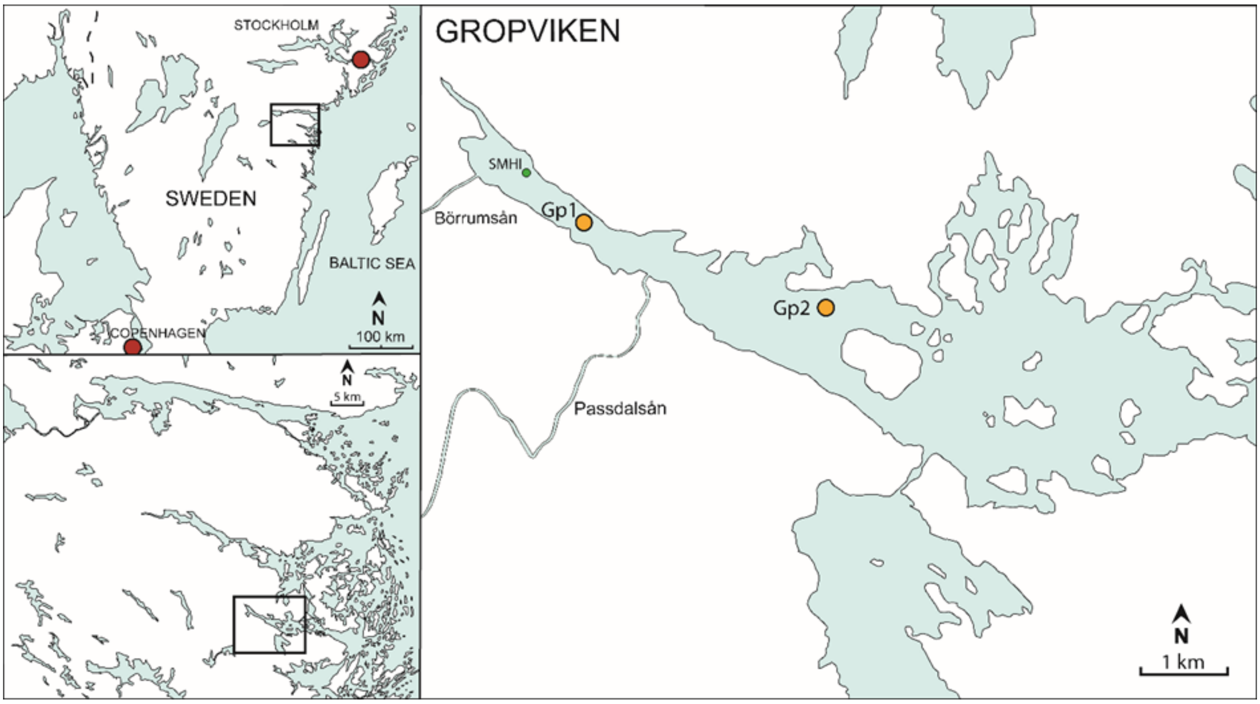

Fig. 1 Map over Gropviken with sampling site of Gp1 and Gp2. The measurements from SMHI station GROPVIKEN is in the inner part of the inlet. The streams, Passdalsån and Börrumsån, have their outlets in Gropviken.

Farthest into the western part of the bay two smaller rivers open, which, under high water flows, are likely to transport and introduce nutrients from the surrounding farmland. Results from Jonsson et al. (2003) show that the seafloor consist mostly of accumulation bottoms and the majority of these are hydrogen-sulfide rich. Accumulation bottoms is where fine material (<0.6 µm) is continuously deposited and which is defined by a high water content, has high organic carbon content. Since organic matter consumes oxygen in the decomposition processes, such areas are more sensitive to an extra load of organic matter input with regards to their oxygen conditions. The accumulation bottoms can bind different types of metals and pollutants due to the clays it contains (Jonsson et al. 2003). The hydrogen sulfide rich bottom sediments indicate that large parts of Gropviken have oxygen depletion in the bottom waters.

2.1 Geology

S:t Anna archipelago was submerged around 10 000 years ago and during a slow land uplift waves have washed away loose sedimentary deposits of the bedrock. Today, the area is still rising with 2-3 mm per year (Gezelius et al. 2011). Through a rise in sea level around 6000 years ago, former valleys are now long narrow inlets, such as Gropviken (Persson & Jonsson 2000; SGU n.d.b).

Sandy moraines can be found on higher areas and finer sediment is deposited in valleys within the Gropviken area (SGU n.d.a). The soil consists of glacial silt and clay, and in a few places around the inlet postglacial clay is found. Near the stream outlets young fluvial sediments have been deposited. The thickness of unconsolidated sediment layers in the area varies, but generally it is 0-1 m thick. Bedrock is exposed at various places around the inlet and it is mainly gneissic rock from the Svecokarelian orogeny, 2850 -1870 Ma. A brittle shear zone in the bedrock follows the inlet (SGU n.d.c).

2.2 Climate and ecosystem

Gropviken is a mild temperate coastal area with a mean annual air temperature of 6.5-7 °C. The coastal climate is characterized by cold springs and mild autumns (Gezelius et al. 2011). The annual average precipitation is 500 mm/year and W-S winds dominate (SMHI 2017a).

The adjacent terrestrial area has open meadows with low vegetation, open fields of farmland and a few light open coniferous forests dominated by *Pinus spp*. The coastline consists of exposed bedrock vegetated with *Pinus spp*. and lower vegetation. (Edlund 2011)

Two streams have their outlets into the inner part of Gropviken. Börrumsån is an 8.4 km long stream with meandering stretches, which runs mostly through agricultural landscapes. The water is affected by the surrounding farmlands and has low transparency. The catchment area is dried out during longer dry periods due to trenching. Passdalsån is 4.2 km long and has eroded down into fine grained sediment. Parts of the stream run through agricultural land. The lowest section of Passdalsån, near the outlet to Gropviken, is protected as part of the Passdalsån Natura 2000-area (European network of protected areas) (Edlund 2011).

The water column is vertically stratified in Gropviken. Depending on season the salinity in the surface water varies between 5-7. The salinity gets lower with increasing precipitation and increased riverine input. The salinity in bottom water is stable throughout the year (Fig. 2). The water exchange occurs every 10-39 days in the surface water. Gropviken is ice covered around 90 days per year. Deep water exchange occurs every 100 days when there is a breakdown of the thermocline (Persson & Jonsson 2000).

2.3 Eutrophication and environmental toxins in Gropviken

The area is relatively unexploited and sparsely populated. Gropviken has a couple of small marinas and is a popular location for tourists during summer. The anthropogenic nutrients are introduced by the two streams, Börrumsån and Passdalsån, which transport nutrients from forestry, agriculture, lakes and sewers. The marinas are additional sources of pollutants.

Iron ore mines in Nartorp were active between 1817 and 1927 (Nartorpsbygden n.d.), 5 km NE of Gropviken. Over 300,000 tonnes of iron was shipped to Germany (Blåkusten n.d.a) from two small cargo ports, Fruglots and Björkvik, in Gropviken. Fruglots harbor is located in the inner part of Gropviken and was also used for steamboats in the 1800's to early 1900's (Blåkusten n.d.b). From 1912 to 1917 was iron ores only shipped from Björkvik harbor in the northern shore of Gropviken (Blåkusten n.d.a).

According to the EU Water frame works classification, the ecological status is assessed as insufficient in Gropviken (EEA 2018). The biological quality factor for bottom fauna and phytoplankton is poor. Furthermore, the nutrient levels and water transparency is, according to the quality factors, unacceptable. As a result of a high level of phosphorus and nitrogen the amount of phytoplankton increases and the transparency of the water decreases. The quality factor for chlorophyll and biovolume have an insufficient to moderate status. Oxygen conditions are changed seasonally due to high organic load, which affects the bottom fauna (VISS 2019).

The station GROPVIKEN was measured by the SMHI (Swedish Metrological and Hydrological Institute) for physical and chemical parameters five times during 2017 and 2018 close to Gp1 (Fig.1). Salinity, temperature, secchi depth and nutrients are seasonally variable in the surface water. In the bottom water the salinity is stable, and temperature and nutrients are fluctuating throughout the seasons (Fig. 2). Even if previous studies have shown oxygen depletion in the bottom water, this was not the case in 2017, at least at the station the bottom water was fully oxygenated at 15 meters depth.

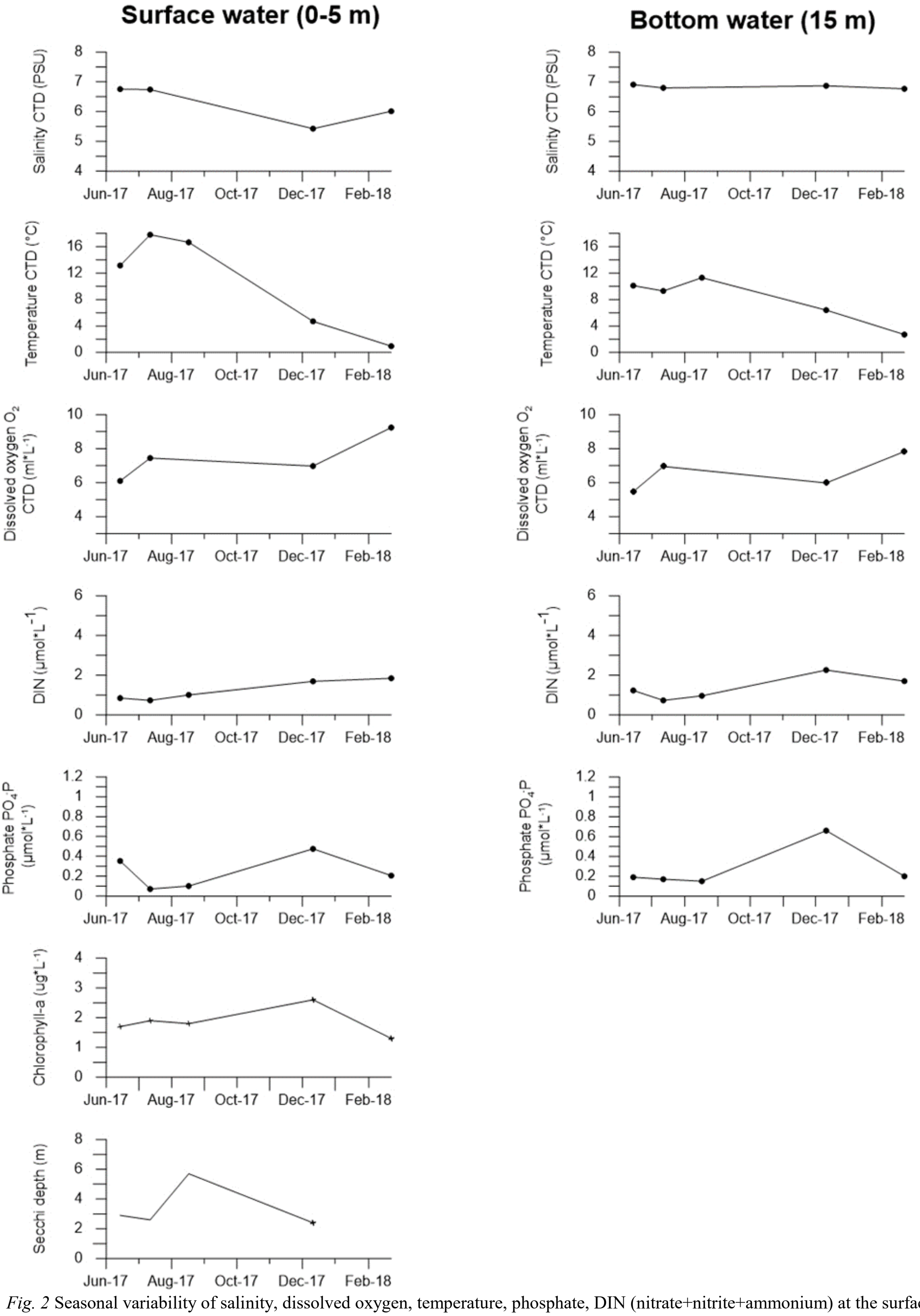

Fig. 2 Seasonal variability of salinity, dissolved oxygen, temperature, phosphate, DIN (nitrate+nitrite+ammonium) at the surface and bottom waters in Gropviken. Variations in secchi depth and Chlorophyll-a is measured in the surface water. The data was measured between 2017 and 2018 by SMHI at the station GROPVIKEN.

3 Descriptions of proxies

3.1 Grain-size analysis

Grain-size analysis is a laboratory study to determine distribution of different sediment particle sizes, and by that determine the environment conditions at the time of the deposition. The main purpose of grain-size analysis is to obtain a deeper understanding of the paleo-environment and environmental changes, but also to reconstruct past sedimentary transports, depositional conditions and sediment origin. The grain size distribution depends on the sediment input and hydrodynamic conditions as well as the bathymetry of the basin in coastal zones (López 2017). If the sediment provenance is fixed, the temporal variations will be shown due to energy and transport mechanism by riverine inputs, changes in wind pattern (waves and currents) which change the bottom water energy (Ning et al. 2016; McCave et al. 2006). Periods with substantial higher energy in the bottom water will deposit coarser grains.

3.2 Carbon and Nitrogen content

The organic matter content in a sediment core provides proxies to reconstruct paleoenvironmental and regional climatic changes. Organic matter is only a minor fraction of the sediment but allows insights into the complex mixture of organisms that have lived in the environment during deposition (Meyers & Ischiwatari 1993).

The organic matter in coastal sediments originates from both terrestrial and aquatic sources, which makes it possible to draw conclusion regarding the origin of the sediments. Vascular plants are rich in cellulose and algae are rich in proteins instead. Aquatic materials, e.g. phytoplankton, contain more nitrogen in the proteins, while in terrestrial materials, e.g. grass or vascular plants, carbon is dominant and almost no nitrogen present. Therefore, an analysis of the carbon-to-nitrogen ratio gives information about the dominance of aquatic versus terrestrial biomass in the sediment (C/N ratio between 3 and 9: organic matter dominated by aquatic biomass (protein-rich and lignin-poor); C/N ratio over 20: terrestrial biomasses are dominant (protein- poor and lignin-rich) (Brodie et al. 2011).#

3.3 Biogenic Silica analysis

The determination of biogenic silica (BSi) is an important method to estimate changes of past diatom productivity and thereby the aquatic productivity in coastal areas. This is based on the assumption, that the measurements of BSi estimate past diatom blooms. Silicon is an essential nutrient for diatoms and availability of silicon in oceans depends on weathering processes and riverine inputv (DeMaster 1981).

In combination with other methods BSi is used as a proxy for environmental changes, and to understand the biological effect on the silica cycle in both terrestrial and aquatic environments (Clymans et al. 2015).

Diatoms are one of the largest groups of primary producers and a component of the aquatic food web. The availability of silicon in the oceans is influenced by the growths and formation of skeletal materials of diatoms. Diatoms take up dissolved silica (DSi) in water to build their frustules and thereby produce BSi (Ragueneau et al. 2006).

3.4 Elemental analysis

Sediment at a specific site has a unique transportational and depositional history. It is therefore important to have knowledge of the accumulation rate in order to understand how the concentrations of organic matter and pollutants, as well as the environment, as a whole have varied. The chemical and biological analysis of sediment sequences can therefore be used to track environmental change.

The redox conditions on the site are important for the mobility of the metals in the bottom waters and sediments. Manganese (Mn), iron (Fe), arsenic (As) and phosphorous (P) migrate upward in the sediment towards the sediment-water interface and enrich in the sediment surface where they are adsorbed to iron oxides. Heavy metals (Hg, Pb, Zn, Cu and Ni) participate with sulfides forming soluble compounds and are therefore stable under reduced conditions (Farmer 1991).

Changes in the supply of minerogenic material (riverine input and/or sediment focusing), leave an imprint in the grain size and possibly also the Ti/K and Ti/Al profiles. Seafloor with declined dissolved oxygen levels in the overlying water column are often enriched in trace metals. Molybdenum (Mo) is commonly normalized to aluminum (Al), is an indicator of anoxic and sulfidic bottom conditions (Rabalais et al. 2014) and has previous been applied as a proxy for redox fluctuations in bottom waters in the deep areas of the Baltic Sea (Jokinen et al. 2018). Mo/Al ratios have been used in previously studies of Jilbert and Slomp (2013) and Zillén et al. (2008) to document human-induced hypoxia in bottom waters. The variations in C_{org}/P_{tot} can also be used as a proxy, because phosphorus is stored in the seabed as Fe-P between hypoxic events when the productivity is high (Conley et al. 2002).

4 Methods

4.1 Core collection, subsampling & hydrographic profiling

Undisturbed sediment cores were collected by the *Live2Tell* team on the 27th and 28th of June 2017 during an expedition cruise with *R/V Electra* (Table 1). The sites were chosen after a study of Jonsson et al. (2003) and the seafloor was surveyed with a sediment echo sounder in order to collect samples from both accumulation bottoms and, if possible, avoid gas rich sediments. A GEMAX corer was used to collect the sediment cores. The GEMAX corer has two translucent plastic tubes, with a diameter of 90 mm and max length of 80 cm, that allow free water passage until the corer reaches the seafloor. Down at the seafloor two arms act as a locking mechanism to trap the sediments into the tubes. The GEMAX corer collects two parallel cores simultaneously, in this case named A and B. Lead weights were used in Gp1, but in Gp2 all weights had to be removed due to the softness of the sediments.

Fig. 3 Laminated sediment collected at the site Gp2. 0-20 cm has distinct laminated layers. Photo credit: Kotaro Hirose 2017

Four sediment cores were sampled from two sites in Gropviken. Gp1A and Gp1B were collected at the inner part of the coastal inlet, at position N 58° 20.44'/E 016° 39.37'. The water depth at the site was 19 m. Gp2A and Gp2B were collected at the outer part of the coastal inlet at position N 58° 19.92'/E 016° 42.35', with a water depth of 30 m (Fig. 1). The cores were sliced immediately on board into 1 cm thick sections and the samples kept cold in plastic containers. An additional core was collected close by Gp2AB and was divided in half along its length (Fig. 3). The cores at Gp1 was 45 cm long and at Gp2 50 cm. The sediment smelled of H_2S.

Table 1. Contributions for this project.

Contributions		
CTD profiling Sediment core sampling with r/v Electra	Helena Filipsson, Kotaro Hirose, Anna Godhe, Johan Burman	Geology Department, Lund University. 2017
C_{org} and N_{tot}	Hanna Nilsson, (with help from Karl Ljung)	Geology Department, Lund University. 2018
Biogenic Silica	Hanna Nilsson with help from Petra Zahajská and Carla Nantke	Geology Department, Lund University. 2018
ICP-OES	Sofia B. Wisén	Dept. of Biology, Lund University. 2018
Grain size analysis	Hanna Nilsson (with initial help from Åsa Wallin)	Geology Department, Lund University. 2018
Chronology	Rosine Cartier & Guillaume Frontorbe. Age-model and subsequent discussions H. Nilsson/H Filipsson	Geology Department, Lund University. 2018
Hydrographic data	SHARK	SMHI-Swedish environmental monitoring program

All samples from cores Gp1A, B and Gp2A, B were weighed and frozen. Once the samples were frozen they were freeze-dried for 72 hours. After the process, the samples were weighed again, and the water-content was determined. Hydrographic data was collected using a Seabird 911+ CTD (Conductivity, Temperature & Depth (pressure of seawater). A sonde was attached to the CTD to measure dissolved oxygen concentrations.

4.2 Chronology and elemental analysis

The sediment cores Gp1A (inner part of inlet) and Gp2B (outer part) have been dated using ^{210}Pb and ^{137}Cs dating methods at the Department of Geology at Lund University (Table 1). By observing the distribution of different substances with known emission history and the activity of radioactive substances (Bq/kg sediment), such as ^{210}Pb and ^{137}Cs, sediment accumulation rates can be determined. An age-depth model was established based on the combination of ^{210}Pb and ^{137}Cs. ^{137}Cs began to appear in the environment after the atomic bomb tests in the atmosphere and reached a first peak around 1963/64. The peak of ^{137}Cs has been used as a marker for Chernobyl, a reactor accident in 1986 (Appelby 2001).

Recognizable features in the measured atmospheric lead isotope data (^{210}Pb) were compared with ^{137}Cs Constant Rate of Supply (CRS) and Constant Initial Concentration (CIC). For the ^{137}Cs dating, the CRS model was constrained for accumulation rates and age models (Appelby 2001), because it was considered more reliable due to the non-constant sedimentation rate at both sites. We applied a model of total supported and unsupported ^{210}Pb activity to see recognizable features correlate the ^{137}Cs activity. The sedimentation rate and an age-model were constrained by a CRS model of the ^{137}Cs activity. The ages of the lower part of the sequences were deduced by linear extrapolation based on the sedimentation rate of the last six samples (for Gp1:15-16 to 38-39 cm; Gp2: from 40-41 to 34 -35 cm).

Elemental analysis of Gp2A with ICP-OES (inductively-coupled plasma optical emission spectrometry) was performed at the Biology Department at Lund University, 2018. Measured elements (Ag, Al, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mo, P, Pb, S, Sc, Sr, Ti, V, Y, Zn, Zr) were summarized and normalized to aluminum. Al is an indicator for the proportion of detrital particles in the samples. Elements originating from non-detrital particles can be calculated using the ratio between the total element content to Al (Farmer 1991). Before the measurements the samples were soaked in a mixture of 10 ml of HNO_3 and 10 ml of ionized H_20 to digest for 45 min. The dilution factor was 100 ml. The elements were measured in ppm. The measurements were corrected for the weight of salt in the pore water following

$$\text{Salt content of dry sample \%} = \frac{\text{salt content \%}}{\text{salt content \%} - \text{sediment content \%}} x\ 100$$

4.3 Grain-size analysis

Organic matter, calcium carbonate and opal minerals (BSi) had to be removed, so only the minerogenic material would be left for the analyses. A modified cleaning protocol of Van Hengstum et al. (2007) was used. Each sample of Gp1B (44 samples) and Gp2B (45 samples) was analyzed. The sediment particles are classified based on their nominal diameter (in µm). The grain size fractions by Udden-Wentworth (1922) are modified and used as following: sand (>63 µm), coarse to medium silt (16-63 µm), very fine to fine silt (4-16 µm) and clay (<1 -4 µm).

A homogenized subsample of 10 g was weighed from each sample and put into 800 ml beakers. To remove organic matter, the subsamples were treated with a mixture of 300 ml de-ionized water and 45 ml hydrogen peroxide (H_2O_2) (33 % concentration). The beaker was placed on a heating plate until reaction ceased. The mixture had to cool to ca. 40°C. To remove calcium carbonate 45 ml hydrochloric acid (HCl) (10 % concentration) was added to the mixture and the beaker was heated again on a hot plate for two minutes. To dilute and remove the chemicals 400 ml de-ionized water was added. The sediment had to settle before siphoning off water. The procedure was repeated three to five times until the mixture had a neutral pH. If the mixture didn't settle, the sample was centrifuged in tubes with deionized water until a neutral pH level was reached.

To remove opal minerals the material was heated in a 200 ml solution of sodium hydroxide (NaOH) (8 % concentration) until the reaction ceased. 300 ml deionized water was added to dilute the mixture. The sample was centrifuged and washed until a neutral pH was achieved. After the chemical treatment a few drops of each sample were inspected under a microscope to determine whether all opal minerals were removed.

By adding 100 ml of 0.05 % Calgon ($Na_4P_2O_7$) to each sample and then heating it up to boiling point, the grains were dispersing. Afterwards the samples were sieved with a >63 µm fraction sieve. The sediment residue of >63 µm was transferred from the sieve to a weighing boat and dried at 60°C in an oven over night and each sample was weighed afterwards. The sand fraction was calculated by dividing the dry weight of the >63µm fraction with the original sample weight of the whole sample.

The rest of the sample (<63 µm) was centrifuged until 50-80 ml were reached and then analyzed in a Micromeritics Sedigraph III Particle Size Analyzer. The sedigraph measures the relative mass concentration of sediment particles in a liquid medium. The method is based on Stoke's law under the known conditions of density and velocity of a liquid and the particles density (McCave et al. 2006).

4.4 Carbon and Nitrogen content

The sediment cores Gp1B and Gp2A were analyzed for inorganic and organic carbon (total carbon (C_{tot}) and organic carbon (C_{org})) and nitrogen content following the method of Brodie et al. (2011). To obtain both the inorganic - and organic content each sample needs to be analysed with respect to one untreated and one acid treated subsampling. The acid removes calcium carbonates and the difference between these two samples is inorganic carbon.

The untreated samples were analysed for their total carbon and total nitrogen content. 5-10 mg of the samples were homogenized and placed into tin (Sn) capsules. The capsules were closed and folded into small spheres before analyzing in a Costech ECS 4010 Elemental Analyzer.

The treated samples were analysed for their total organic carbon and total organic nitrogen content. 5-10 mg of sediment were homogenized and placed into silver (Ag) capsules. The capsules were placed into a glass tray and onto a cold hotplate. 10 µl deionized water were added with a pipette to moisten the samples and to avoid a powerful reaction before adding hydrochloric acid. 10 µl of 2 M hydrochloric acid (HCl) were added to each sample to get rid of carbonates. The hotplate was slowly warmed up to ~50° C. Additional 20, 30, 6x50 µl of 2 M hydrochloric acid (HCl) were added to the samples one after another. After each addition of hydrochloric acid, the samples had to settle and some of the liquid had to evaporate, for the sample not to spill over. This is because samples with high carbonate content tend to react strongly with hydrochloric acid causing bubbling. The prepared Ag capsules are placed on a hotplate for 24 hours to let the liquid evaporate. When the samples were dried, the Ag capsules were folded and wrapped in tin capsules.

Afterwards the samples were analyzed with the elemental analyzer Costech ECS 4010. When the measurements were done inorganic carbon (IC) and C/ N was calculated.

$$IC = (C_{tot} – C_{org}) *8.3$$

*8.3 = molecular weight difference between $CaCO_3$ and C

The carbon mass accumulation rate was calculated as the percentage of carbon content multiplied by the sedimentation rate and the dry bulk density of the sample. The measurements were corrected for salt content (7 PSU).

The contribution of the terrestrial plant derived organic carbon ($\%OC_{terr}$) and phytoplankton organic carbon ($\%OC_{phy}$) of total organic carbon (C_{org}) were estimated with the N/C ratio with end-member values of $(N/C)_{terr} = 0.04$ and $(N/C)_{phy}= 0.13$ following Jokinen et al. (2018) and Jilbert et al. (2018).

$$\%OCterr = \frac{(N/C)sample - (N/C)phy}{(N/C)terr - (N/C)phy} x\ 100$$

and $\%OC_{phy} = 100 - \%OC_{terr}$

4.5 Biogenic silica

The BSi method is a modification of the protocols by Stickland & Parson (1968) and Clymans et al. (2015) and used to determine the content of BSi in aquatic sediment cores. The BSi was measured in every sample of Gp1B and Gp2A.

Ca. 30 mg of freeze-dried homogenized sample was weighed in 15 ml plastic bottles. The sample was dissolved in a weak base of 40 ml 0.1 M sodium carbonate (Na_2CO_3) to dissolve the BSi. A shaking bath was heated up to 85°C and the bottles were placed in 3 bottle racks into the bath for three, four and five hours to let the samples digest.

After for three, four and five hours, respectively, with ten minutes delay between each rack, the samples were put into a cold bath for three minutes to stop the digestion processes. 20 ml plastic bottles were filled with 9 ml of 0.1 M hydrochloric acid (HCl) and 1 ml of the extraction solution was added. Hydrochloric acid is neutralizing and dissolves soluble inorganic carbonates. One pipette was used for every 10 samples and washed 3 times between each subsampling.

Smart Chem 200 (AMS Systea) determines the dissolved silica concentrations of the sample based on the automated molybdate blue method (Stickland & Parson 1968). The weight percent of BSi after three, four and five hours was plotted versus time. The mass accumulation rate was calculated as the percentage of BSi multiplied by the sedimentation rate and the dry density of the sample. BSi MAR was calculated by using the BSi content % x Sediment Rates (SR) x dry bulk density (DBD).

5 Results

According to the trends that the environmental proxies show for Gropviken, the sequences can be divided into four zones (Fig. 8, 9, 10, 11 & 12). The zones are based on the multiple proxies that vary concurrently.

5.1 Age model

At Gp1 (inner site) the ^{137}Cs increase from 15 to 5 cm, the rapid increase at 13 cm depicting the Chernobyl accident in 1986 (Fig. 4C). To establish the age-depth model, ^{137}Cs activity was compared to the content of radioactive substance of ^{210}Pb in the sediment with the CRS dating model (Appelby 2001). Total and unsupportive ^{210}Pb show a decreasing trend with depth over the uppermost 15 cm.

The results of the age model and the calculated sedimentation rate are shown in Fig. 4. The sediment sequence is 45 cm long and represents the timespan from 1896 to 2017. The average sedimentation rate (SR cm year^{-1}) is 0.32 cm year^{-1}. The sedimentation rate has three distinct stages. In the deepest part of the sequence (39 to 16 cm) the sedimentation rate is 0.39 cm year^{-1}. After 15.5 cm the sedimentation rate decrease to 0.15 cm year^{-1}, and remains stable until 10.5 cm, where the sedimentation rate increase to a maximum of 0.67 cm year^{-1}.

In the sequence of Gp2 the rapid increse of ^{137}Cs is observed around 21 cm depth and corresponds to the Chernobyl accident in 1986 (Fig. 5C). Total and unsupportive ^{210}Pb show a decreasing trend with depth in the uppermost 25 cm.

The core represents the time interval from 1880 and 2017 and the average sedimentation rate at Gp2 is 50 mm per year. The sedimentation rate follows a step -wise decreasing trend down the core and the section can be divided into three subsections accordingly. In the lower part of the sequence (40.5 to 34.5 cm) the sedimentation rate is 0.20 cm year^{-1}, between 34.5 to 14.5 cm the sedimentation rate is 0.50 cm year^{-1} and in the upper part, 14 to 0 cm, of the core the sedimentation rate is 0.77 cm year^{-1} (Fig. 5D).

5.2 Hydrographic results

The inner station, Gp1, had two different water masses; one surface water mass and a bottom layer. The outer station, Gp2, had a surface layer, an intermediate layer and a bottom layer. The measurements are equivalent for the two stations with a thermocline at 6-8 meter (Fig. 6). The temperature in the surface water is around 12-13 °C and drops to 9-10 °C at the thermocline at 8 meters water depth. Dissolved oxygen concentration follows the temperature with concentrations of 6 ml/l in the surface water and a drop to 5.3 ml/l at 8-meter water depth. The bottom waters at the two locations have dissolved oxygen levels of 4-5 ml/l.

The salinity profile is stable throughout the water column. At the Gp2 location two thermoclines were found, one at 8 meters water depth and another around 22-meter water depth (Fig. 7). The dissolved oxygen levels decrease at 8 meters but followed the temperature with an abrupt decrease at 20 meters water depth.

5.3 Grain-size analysis

Both stations are characterized as accumulation bottoms for fine material with a dominance of the clay fraction (Fig. 8 & 9).

The grain size distribution at Gp1 is presented in Fig. 8. The fraction of clay, coarse to medium silt and very-fine to fine silt are represented as %. In zone 1 the lowest content of clay (90 %) is measured. An increase of clay occurs in zone 2 (up to 95 %). After this period the relative contribution of each size fraction remained stable until the uppermost part of the core (zone 3-4). The sand fraction is small, with an average of 0.001 % of the sediment.

At Gp2 the clay particles show a general de-

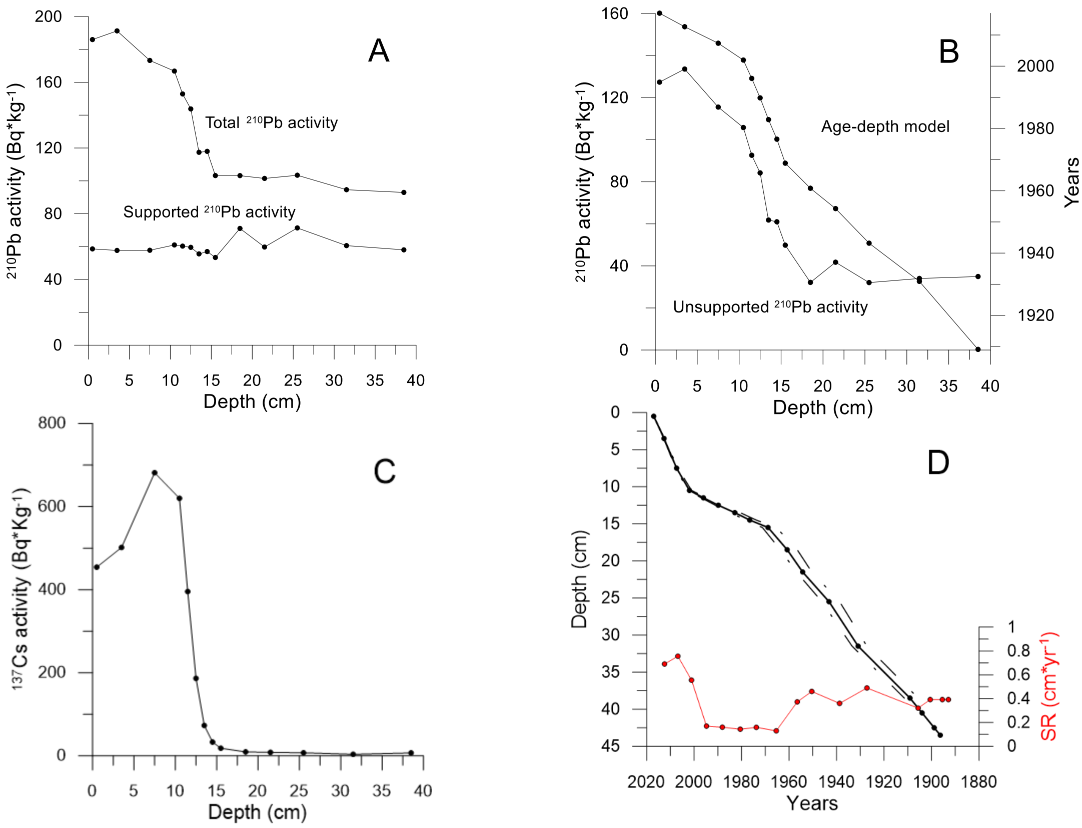

Fig. 4 Age-depth calibration for the sediment sequence of Gp1. A) Total and supported ^{210}Pb activity B) Unsupported ^{210}Pb activity and associated age-model C) ^{137}Cs activity 1986 D) Age-depth model for the whole sequence based on the CRS model of ^{137}Cs activity and calculated sedimentation rates (SR)

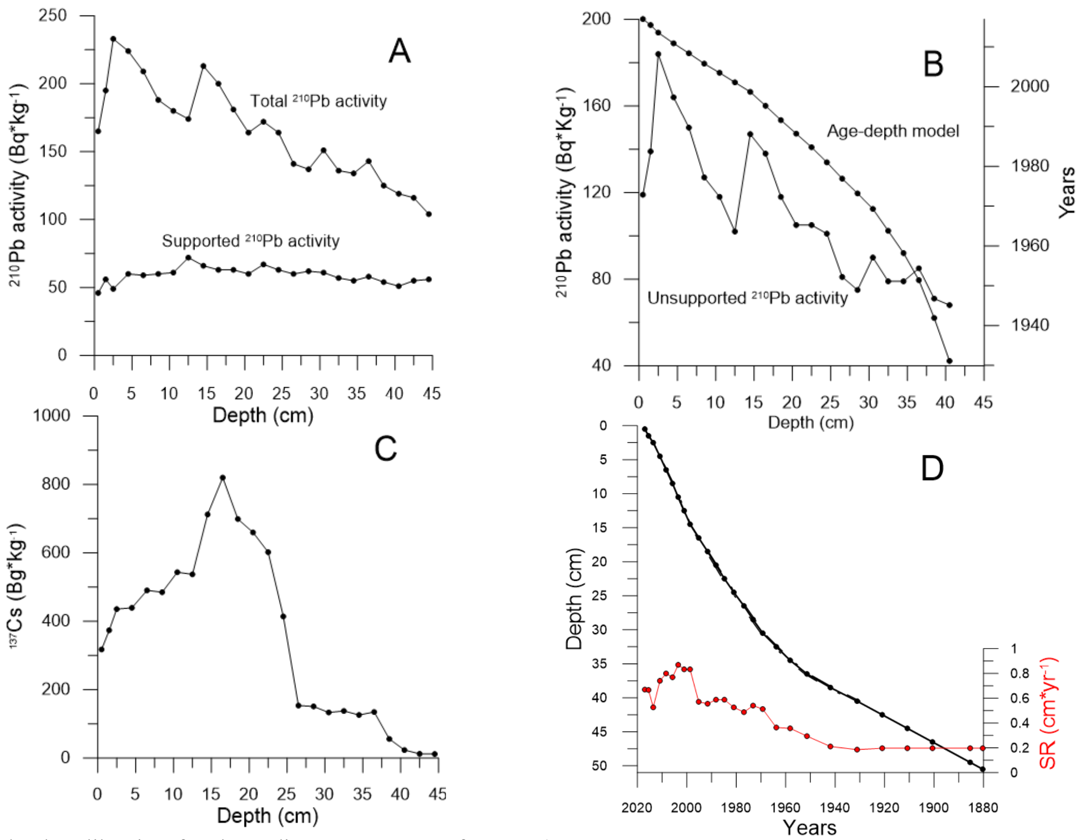

Fig. 5 Age-depth calibration for the sediment sequence of Gp2. A) Total and supported ^{210}Pb activity B) Unsupported ^{210}Pb activity and associated age-model C) ^{137}Cs activity D) Age-depth model for the whole sequences based on the CRS model of ^{137}Cs activity and calculated sedimentation rates (SR)

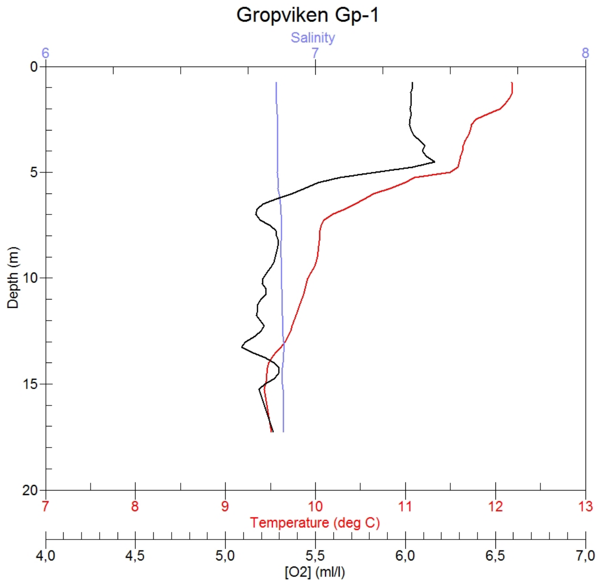

Fig. 6 Water column parameters measured at the sampling location Gp1 during the *Livetotell* cruise in June 2017. CTD measurements (conductivity, temperature, depth). The Stratification is visible between 5-7 meters in temperature and dissolved oxygen**.**

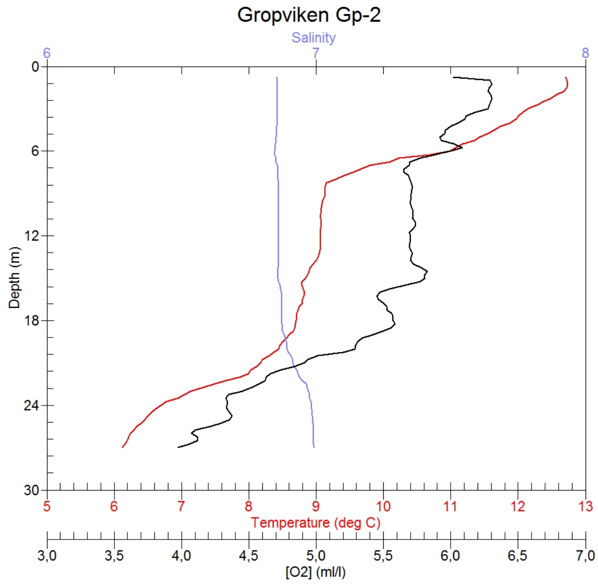

Fig. 7 Water coulumn parameters measured at the sampling location Gp2 during the *Livetotell* cruise in June 2017. The Stratification is visible between 5-7 meters and 20- 22 meters in temperature and dissolved oxygen.

creasing trend towards the top (Fig. 9). Clay particles (<4µm) are dominating throughout Gp2, with an average content of 95 %. The clay content varies by 2 % throughout the core with a slight decrease from 97 % in the bottom of the core (zone 1) to 94 % in the upper part (zone 4). The lowest value is 92 % at 5 cm depth. The silt fraction has the same pattern, with an increase of 1.5 % from the bottom (zone 1) to the upper part of the core (zone 4). The fraction >63 µm has a stable gradient with an offset at 42 cm (transit between zone 1 and zone 2), where it contains charcoal.

5.4 Organic components

The results of the geochemical analyses of biogenic components in Gropviken station cores Gp1 and Gp2 (C_{org}, C_{org} Mar, C_{org}/N_{tot}, BSi, BSi MAR) are summarized in Fig. 8 for Gp1 and in Fig. 9 for Gp2.

5.4.1 Organic carbon content

C/N values are stable throughout the core and this is a consequence of the organic carbon (C_{org}) and total nitrogen are following the same trend throughout the core. C/N has a slight negative trend from 9 % in zone 1 to 8.5 % in zone 4 at Gp1. Whereas Gp2 has a slightly positive trend through the whole sequence with an increase from 7.5 to 8 %.

A decrease in C_{org} content from 4 % to 2 % is recorded through zone 1 and zone 2 at Gp1. In zone 3 an increasing trend is recorded, going from 2 % to 4 % (Fig. 7). The C_{terr} is stable through the sequence and C_{phy} shows a decreasing trend from zone 1 to the bottom of zone 3 where it starts to increase until the top of the core. C_{org} MAR is rapidly increasing in the end of zone 1 at the same time as the sedimentation rate is increasing (Fig. 8). In zone 3 C_{org} MAR is decreasing when the C_{org} content increases. In the top 3 cm the C_{org} MAR is decresing.

At Gp2 the C_{org} percentage increases from the bottom of the sequence to the top (Fig. 9). C_{terr} has a decreasing trend from 2% at the beginning of zone 1 to almost 0 % in end of zone 4 (Fig. 8). The opposite occurs to C_{phy} where it increases from 0 % in the beginning of zone 1 to 5 % in zone 4. C_{org} MAR is increasing from the bottom of the core to the top, with a larger increase at the transit between zone 1 and zone 2 as well in the transit of zone 3 to zone 4. This corresponds to depth as the sedimentation rate is increasing (Fig. 9). The increase of C_{org} MAR have a similar trend as C_{org}.. A decrease of C_{org} MAR is showing in the top 5 cm .

5.4.2 Biogenic silica

Records in Gp1 present a decrease of BSi content in zone 1. BSi content is between 5.5-6% in zone 2. In zone 3 BSi content is lower (4%), and in the beginning of zone 4 the content increases to 7,2 %. In the end of zone 4 BSi decreases to 4 % (Fig. 8). BSi MAR is following the trend of sedimentation rate (Fig. 8). In zone 3 the lowest BSI MAR is measured, with only 0.3 g/cm^2/yr, while in the beginning of zone 4 it rapidly increases to 1.9 g/cm^2/yr. In the end of zone 4 the BSi MAR decreses down to 0.5 g/cm^2/yr.

Larger variations are recorded at Gp2, but the trend is slightly decreasing from the bottom to the upper part of the sequence (Fig. 9). BSi MAR is following the sedimentation rate trend. In zone 2 the BSi increases from 0.27 to 0.62 g/cm^2/yr. A rapid increase occurs in the beginning of zone 3 from 0.62 to 0.91 g/cm^2/yr and after wards the BSi MAR stays relatively stable through the zone. In zone 4 the BSi following zone 3 until the top 5 cm where it decreses from 0.9 to 0.07 g/cm^2/yr.

5.5 Redox proxies

Redox proxies were analysed at the outer station (Gp2). Molybdenum (Mo) content and Mo MAR (Fig.

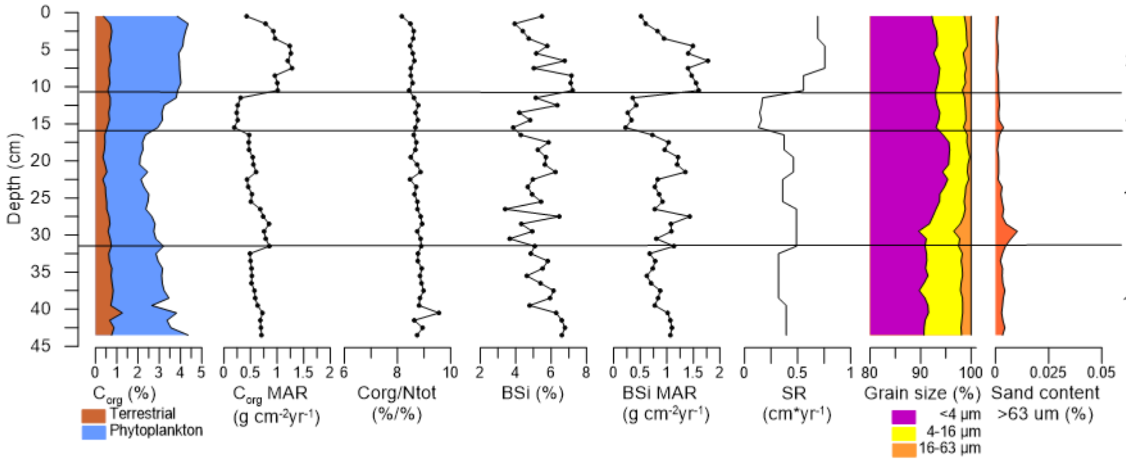

Fig. 8 Records of total organic carbon (C_{org} %) divided into terrestrial and phytoplanktonic (C_{terr} vs. C_{phy}), C_{org} MAR, C_{org} / N_{tot} ratio, biogenic silica (BSi %), BSi MAR, grain-size distribution and sedimentation rate (SR, cm year^{-1}) with results from the Gp1. The mass accumulation rate (MAR) for BSi and C_{org} is represented in cm-2 year-1). The data is taken from Gp1A and Gp1B which can explain the small deviation between grain size and SR. All records are plotted against depth and divided into four zones based on the changes in the SR and organic matter.

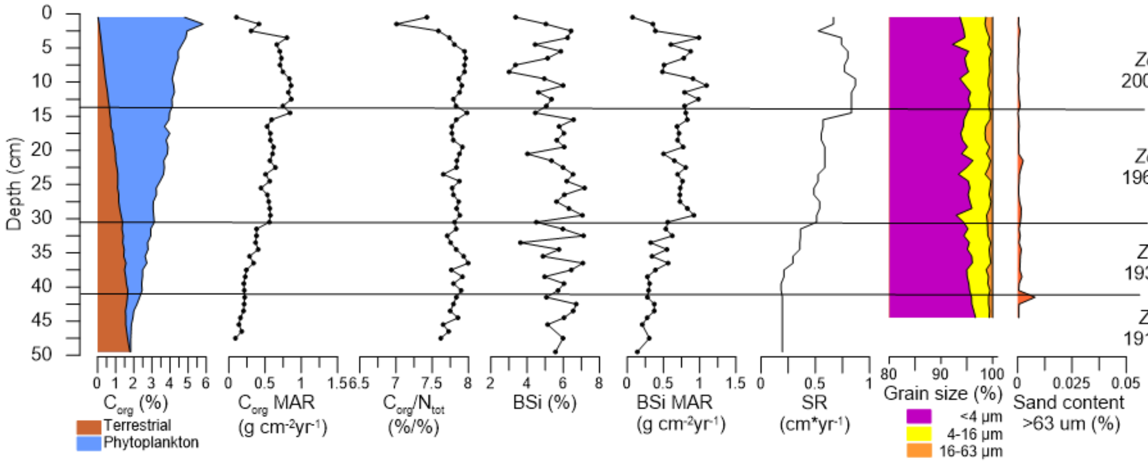

Fig. 9 Records of total organic carbon (C_{org} %) divided into terrestrial and phytoplanktonic (C_{terr} vs. C_{phy}), C_{org} MAR, C_{org} / N_{tot} ratio, biogenic silica (BSi %), BSi MAR, grain-size distribution and sedimentation rate (SR, cm year^{-1}) with results from the Gp2. The mass accumulation rate (MAR) for BSi and C_{org} is represented in cm-2 year-1). The data is taken from Gp2A and Gp2B which can explain the small deviation between grain size and SR. All records are plotted against depth and divided into four zones based on the changes in the SR and organic matter.

10) displays negligible changes through the sequences of Gp2 with a slight increase from zone 1 to zone 2. In zone 3 Mo MAR is stable at 0.29 umol/m^2/yr. Mo MAR decreases from the beginning of zone 4 to the top. C_{org}/P_{tot} increases from 150 molar/molar in zone 1 to 230 at 15 cm in zone 3, where it starts to decrease again from 230 to 175 in zone 4 (Fig. 10).

5.6 Geochemistry trace elements concentrations and ratios

During the ICP-EOS analyses a total digestion (HF + $HClO_4$ + HNO_3) was not conducted and therefore normalizations against Al are most likely not correct. Because of the lacking total digestion only the trend has been used as an indicator of the variations in concentration of the various elements. The Ti/K ratio is not reliable because of the "signal to noise ratio" and will therefore not be further regarded in the study. C_{org}/P_{tot} is a better proxy for hypoxia in Gp2.

The element ratios in Fig. 11 and concentration in Fig. 12 show similar distribution patterns throughout the sequence. A rapid increase of all Al-normalized elements is recorded between 40 and 35 cm in zone 2 (Fig. 12). P, Pb/Al, Zn and Zn/Al decrease from in zone 3 to the top of the sequence. Ca, Ca/Al, Ni, Ni/Al, Cu and Cu/Al are stable after 35 cm to the top and Co, Co/Al, Cr and Cr/Al are slightly increasing towards the top.

6 Discussion

The data from Gropviken is demonstrating that the coastal inlet has received industrial and agricultural runoffs and atmospheric deposition, which are high in plant nutrients and increase the abundance and change the composition of phytoplankton. The major climate states of the 100 years are characterized by different

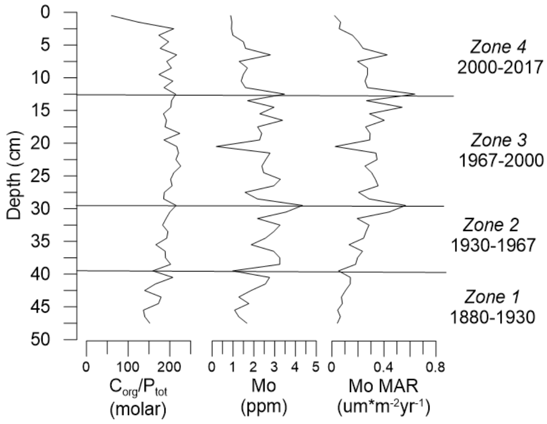

Fig. 10 Records of redox proxies for Gp2. C_{org}/P_{tot} ratio (<75=oxic, >200=hypoxic), Mo (ppm) and Mo MAR. All records are plotted against depth and divided into four zones based on the changes in the SR and organic matter seen in Fig 9.

biogeochemical regimes observed in four time zones, with a distinct transitional state occurring in between. I will discuss the interpretations for each zone, and then have a general discussion about the short-term changes within the inlet.

6.1 Zone 1 1880-1930

6.1.1 Water energy

The first zone in Gp1 has a low clay content compared to the other zones, which indicates higher water energy during that time (Fig. 13). A slight decrease in the sedimentation rate is occurring from 1910 onwards at Gp1 which could be explained by more vertical mixing due to increased wind energy or more riverine input. Another explanation could be increased boat traffic in the inlet when the new cargo port to the mine was built in 1912 (Blåkusten n.d.a). In 1915 the grain size fraction >63µm increased at Gp2 due to increased amounts of charcoal, which could be traces of marine traffic and steamboats (Blåkusten n.d.b). Zone 1 is also characterized by a lower sedimentation rate compared to the other zones in the outer site, Gp2 (Fig.14). The clay content at Gp2 was at its maximum during this period and this indicates rather low water-energy conditions. The differences in the sedimentation rate at the two sites may be explained by most particles only accumulating close to the river mouth because of low energy conditions. This would have hindered the input of larger grain sizes due to too little water energy for transportation of those fractions (McCave 1995).

6.1.2Organic matter and primary productivity

Both locations have low C_{org}/N_{tot} ratios and this indicates that the organic matter in the sequences originates from aquatic biomass rather than terrestrial sources (Brodie et al. 2011). Findings from similar settings in archipelagos in the Baltic Sea region show comparable results in the C/N ratios (Ning et al. 2018; Jokinen et al. 2018). The C_{phy} in Gp1 is generally at a high level, compared to Gp2, due to a high phytoplankton content. Overall the BSi and C_{phy} contents have a decreasing trend during zone 1, mainly due to a decrease in primary productivity by phytoplankton. C_{org} MAR values during this time remain low at Gp2 because of the low sedimentation rate. Gp1 and Gp2 have different trends, with a decrease in Gp1, that correlates with the decrease in sedimentation rate in Gp1, and an increase in Gp2 (Fig. 15 & 16).

The C_{terr} had its peak in the beginning of zone 1 and exhibits a decreasing trend throughout

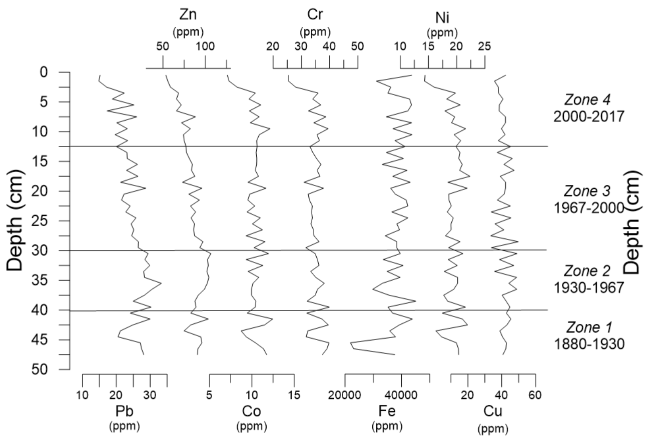

Fig. 11 Records of various metals potentially linked with anthropogenic activities, measured in ppm from Site Gp2. All records are plotted against depth and divided into four zones based on the changes in the SR and organic matter seen in Fig. 9.

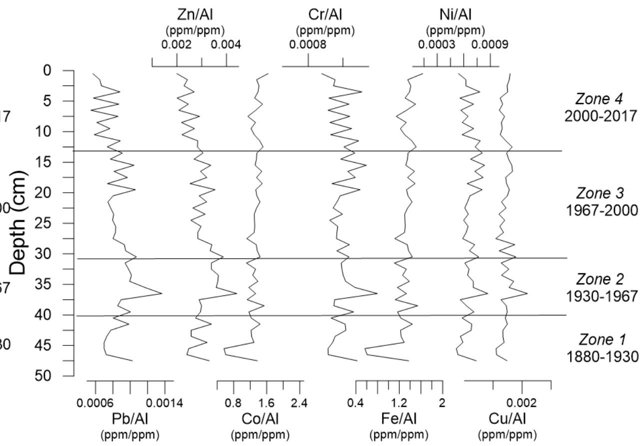

Fig. 12 Measured trace elements normalized to Al at Gp2. All records are plotted against depth and divided into four zones based on the changes in the SR and organic matter seen in Fig 9.

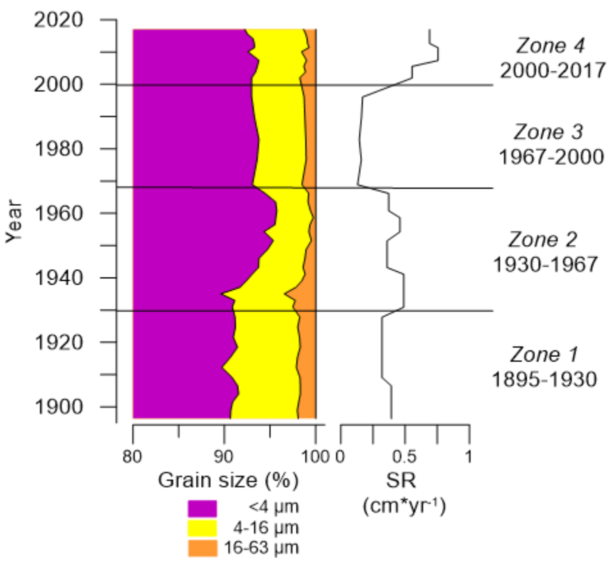

Fig. 13 Gp1: Grain-size distribution and sedimentation rate. All records are plotted against age and divided into four zones based on the changes in the grain-size distribution, SR and organic matter seen in Fig 8

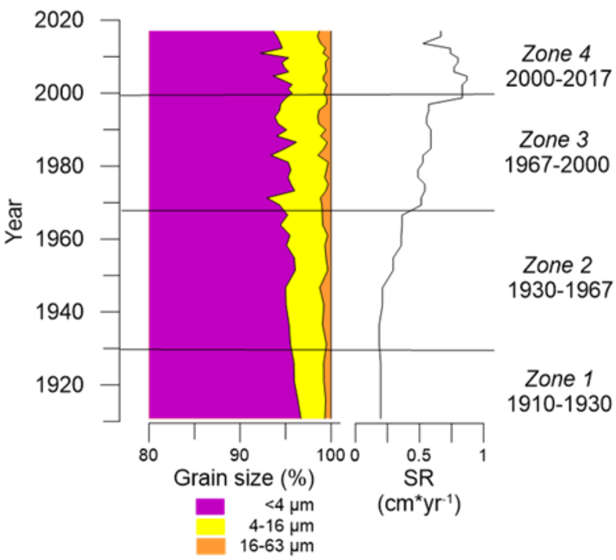

Fig. 14 Grain-size distribution and sedimentation rate variations measured at Gp2. All records are plotted against age and divided into four zones based on the changes in grain-size distribution, the SR and organic matter seen in Fig 9.

the studied sections (Fig. 15), whereas the concentration of C_{phy} increased steadily throughout the century at Gp2. The terrestrial input is stable whereas the productivity increases due to anthropogenic input of nutrients. Not only major nutrients, such as nitrogen and phosphorus, can change the phytoplankton composition, but also trace metals (National Research Council 2000). Some species can tolerate toxic metals, such as copper, as seen in Gåsfjärden, where the diatom species composition changed due to a leakage from copper mining spoil heaps close to the inlet (Ning et al. 2018). A change in C_{org} and BSi, that could indicate a switch in the primary productivity, is not seen in Gropviken during zone 1.

6.1.3 Hypoxia

The outer site, Gp2, has an increase of C_{org}/P_{tot}, which indicates hypoxic conditions (values over 200 indicate hypoxia, whereas values below 75 mark oxic periods; Jilbert & Slomp 2013) (Fig. 16). The Mo and Mo MAR are also increasing, which is indicative of increasing redox conditions (Jilbert & Slomp 2013). The increase could be the result of an extended period of no water exchange of the bottom waters combined with an increase of organic matter input to the inlet, which increased the consumption of oxygen during remineralization.

6.1.4 Pollutants

S:t Anna archipelago underwent a building boom as work opportunities expanded in the area from the end of 1800 until 1920 (Gezelius et al. 2011). The Nartorps mine was located 5 km northeast of Gropviken and was operating between 1880 and 1927 (Nartorp n.d.). Frugelots and Björnvik, harbors located in the inner part of Gropviken, were operating as the cargo sites for shipping the ore to Germany during these years (Blåkusten n.d.). There is no evidence for leakage from any spoil heap at the cargo sites in the results of the elemental analysis, except for a slight increase in Zn/Al and Cr/Al ratio around that time which could be due to an increase in population size and pollution, but not from any iron ore spoil heaps (Fig 18).

6.2 Zone 2 1930- 1967

6.2.1 Water energy

During the beginning of zone 2 the content of clay was increasing to its maximum at Gp1, as well as the sedimentation rate, which might be a sign for more input of inorganic matter from the two streams Passdalsån and Börrumsån (Fig 1), possibly resulting from increased precipitation and runoff from land. Börrumsåns water became less transparent because of high amounts of suspended matter due to erosion and organic matter input from agricultural runoffs (Länsstyrelsen 2018). Positive changes in the precipitation would increase the fluvial input, because it could cause more runoff from land. On the other hand, the increase in finer sediment components could also be an indication of progressively calmer conditions in the area (McCave 1995). The outer part of the basin, at Gp2, demonstrated an increasing trend in sedimentation rate in the same period as grain particles >4µm slightly increased. This indicates an increase of particle input from the catchment area and a higher water energy. However, the increase of the sedimentation rate in the two sites is not large and probably an outcome of more input of both organic and inorganic matter to the inlet.

6.2.2 Organic matter & primary productivity

Increasing BSi content is an indicator for an increase in primary productivity in the surface water (Ning et al. 2018). Occurrences of spring blooms can leave a massive signal in the BSi content in sediment cores (Jokinen et al. 2015). The one-centimeter resolution of our analyses, however, may not be high enough to

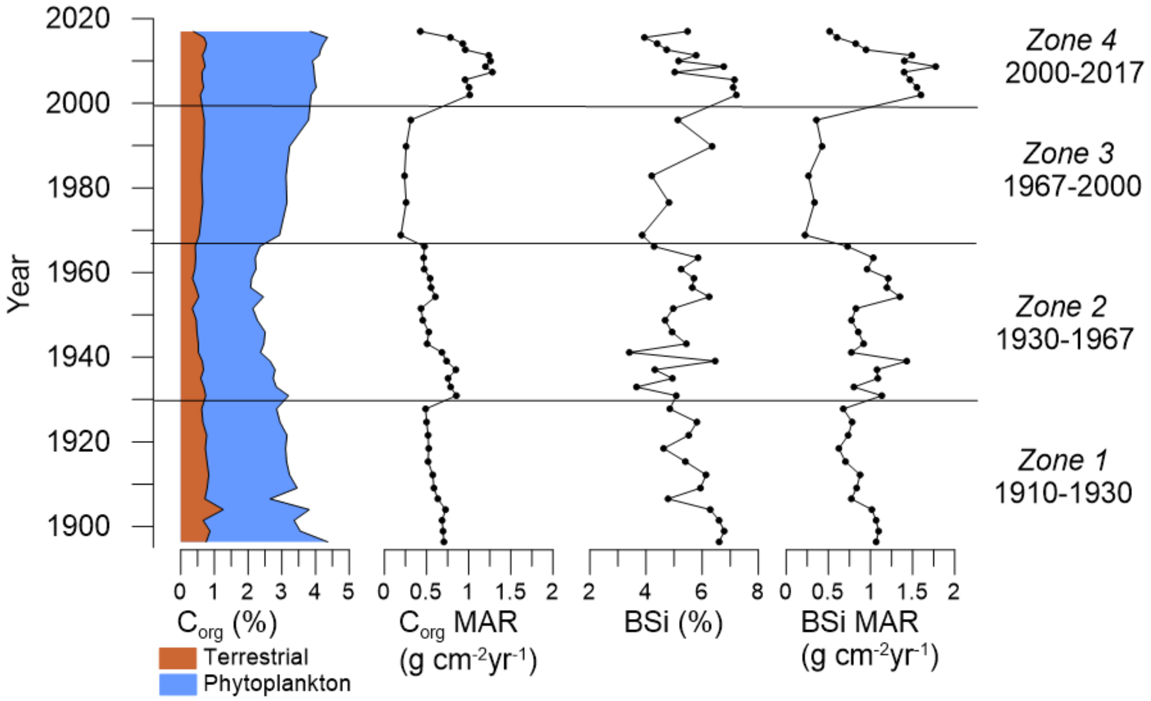

Fig. 15 Records of total organic carbon (C_{org} %) divided into terrestrial and phytoplanktonic (C_{terr} vs. C_{phy}), C_{org} MAR, C_{org} / N_{tot} ratio, biogenic silica (BSi %), and BSi MAR with results from the Gp1. The mass accumulation rate (MAR) for BSi and C_{org} is represented in cm-2 year-1). All records are plotted against age and divided into four zones based on the changes in the SR and organic matter in Fig. 8.

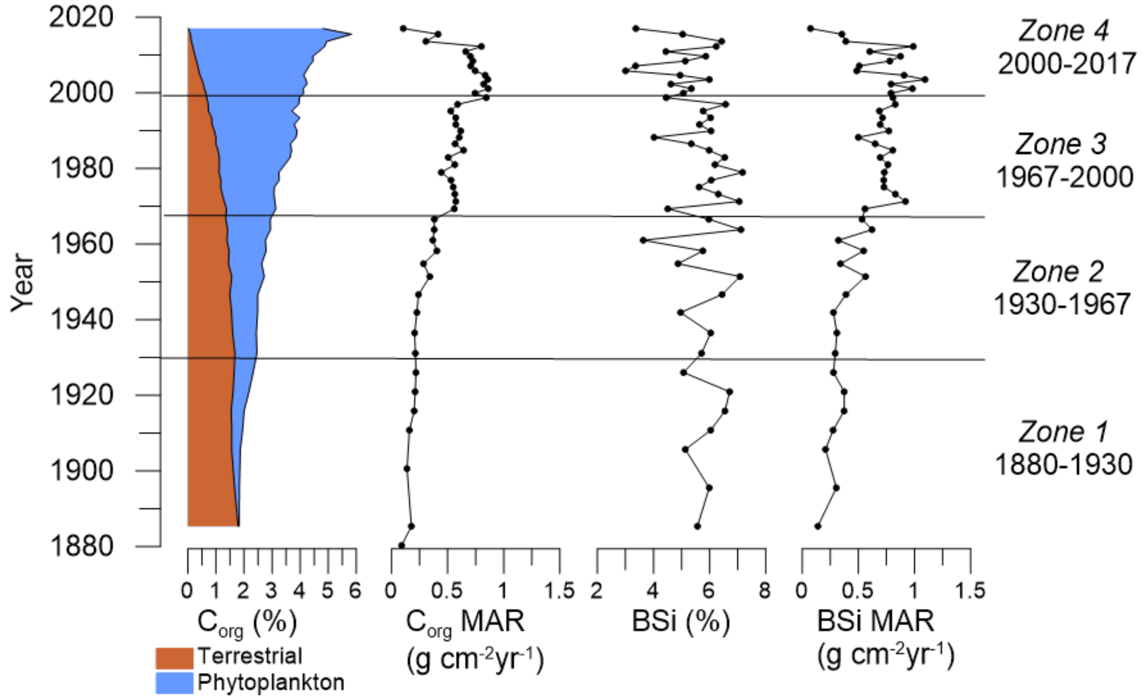

Fig. 16 Records of total organic carbon (C_{org} %) divided into terrestrial and phytoplanktonic (C_{terr} vs. C_{phy}), C_{org} MAR, C_{org} / N_{tot} ratio, biogenic silica (BSi %), and BSi MAR with results from the Gp2. The mass accumulation rate (MAR) for BSi and C_{org} is represented in cm-2 year-1). All records are plotted against age and divided into four zones based on the changes in the SR and organic matter in Fig. 2.

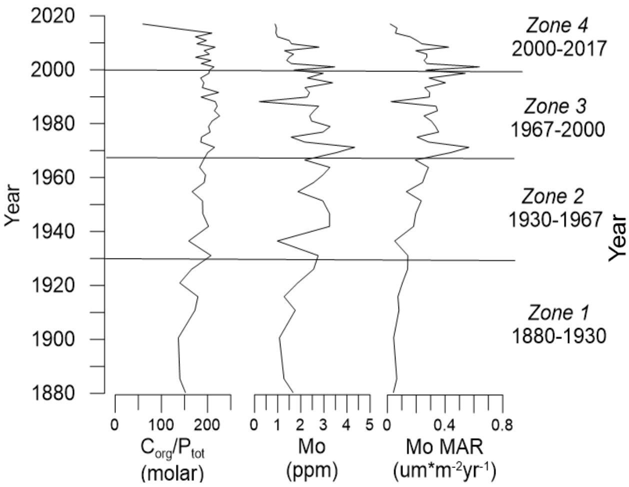

Fig. 17 Records of redox proxies for Gp2. C_{org}/P_{tot} ratio (<75=oxic, >200=hypoxic), Mo (ppm) and Mo MAR. All records are plotted against age and divided into four zones based on the changes in the SR and organic matter seen in Fig 9.

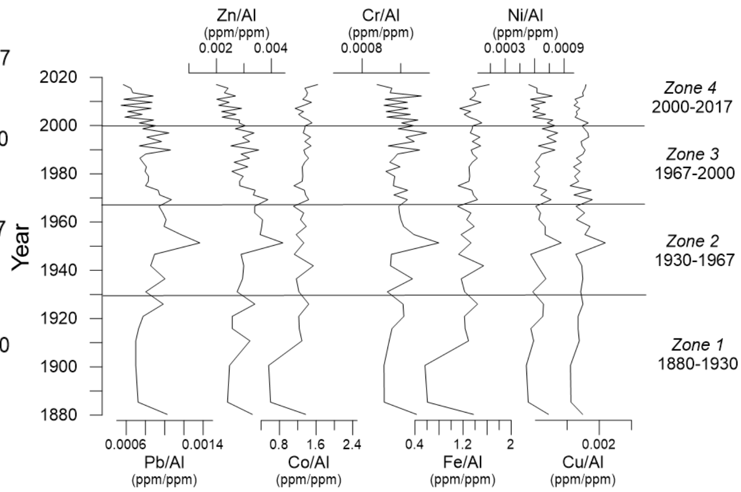

Fig. 18 Records of various metals normalized to Al and potentially linked with anthropogenic activities, measured in ppm/ppm from Site Gp2. All records are plotted against age and divided into four zones based on the changes in the SR and organic matter seen in Fig. 9.

resolve seasonal signals of different blooms. Still, the high range of values in the measurements of Gp1 implies that some blooms are captured. BSi MAR is showing the content of BSi in relationship to the sedimentation rate, and the variations in the values could be an imprint of spring blooms.

C_{org} and BSi MAR have opposite trends in Gp1 and Gp2, with an increase at Gp2 and a decrease at Gp1 from the beginning to the end of zone 2, which implies more deposit of organic matter in the outer part of the inlet. The blooms must have occurred further out in the inlet with better conditions for the primary producers to grow and this reflects the increase at Gp2.

6.2.3 Hypoxia

In the archipelago hypoxia expanded in the 1960's and further increased during the 1970's and 1980's (Persson & Jonsson 2000). In coastal zones of the Baltic Sea hypoxic conditions are known already from the 1950's according to Conley et al. (2011). At Gp2 a high ratio of C_{org}/P_{tot} are indicating hypoxic conditions (Jilbert & Slomp 2013), is already seen in 1930 followed by a decrease until 1941. Between 1941 and 1970 the ratio is 175, which is indicative of lower oxygen levels in the bottom waters (Jilbert & Slomp 2013). Mo and Mo MAR are also increasing within this zone (Fig. 17) and back up the interpretation of oxygen depletion during this time (Jilbert & Slomp 2013)

6.2.4 Pollutants

Elevated trace metal contents are shown for 1950 in the sedimentary record at Gp2, which are reflecting the intensification of anthropogenic inputs. According to Gezelius et al. (2011), the population moved from the archipelago to the cities and open fields became spruce plantations. Therefore, the increase in metals is most likely related to the industrialization in general, causing an increased input of water- and airborne pollutants from regional settings.

Zn/Al and Cu/Al are stable throughout the zone. Sources of those elements include road dust and boat colors, which both were increasing during these years as shown by a study at Gåsfjärden by Ning et al. (2018)

6.3 Zone 3 1967-2000

6.3.1 Water energy

The bathymetry of the inlet can contribute to the low sedimentation rate at Gp1 and a higher rate in the deeper part (Gp2). The shallower area is more affected by physical processes, such as wind strength and direction and wave activity. Resuspension of finer particles occurs in the water column of the shallower areas and is followed by deposition in the deeper areas (McCave 1995).

Jonsson & Persson (1996) investigated Gropviken and calculated a mean sedimentation rate of 16 mm (2-37 mm) per year. Records of my study in Gropviken show that Gp1 (19 m water depth) had a lower sedimentation rate than Gp2 (30 m water depth). The mean sedimentation rate was 5.1 mm at Gp2 and 4.3 mm per year at Gp1, which is substantially lower than the measurements by Jonsson & Persson (1996).

Persson & Jonsson (2000) argue that the difference in the depositional rates in S:t Anna archipelago are due to changes is wind pattern. Their records show an increase of sedimentation rate during 1977-1983 and 1992-1993 and a decrease of sedimentation rate in 1983-1990 due to gale frequencies (wind >14 m s^{-1}) measured at the weather station Gotska Sandön, 100 km east of S:t Anna archipelago. In my study in Gropviken there was no comparable change in the sedimentation rate values during this time span (see Fig. 13: Gp1 1977-1983: 1.64 mm, 1983-1990: 1.53 mm, 1992-1993 1.51 mm; Fig. 14: Gp2 1977-1983 5.02 mm, 1983-1990: 5.02 mm, 1992-1993: 5.6 mm). Accordingly, no indication is given that variations in the wind pattern changed the depositional rate in Gropviken during these years.

Further, at the Gp2 station sedimentation rate measurements show the opposite trend, with an increase during 1983-1990, which could be related to increased precipitation and therefore higher river runoff bringing more particles from soil erosion into the inlet. This interpretation matches the measured increase of mean precipitation between 1980-1990 in Sweden by SMHI (2017b). Another reason for the changes in sedimentation rate throughout zone 3 could be change in the river input from Börrumsån. According to Länsstyrelsen (2018) there has been some dredging in the stream. Since no years were stated, this cannot be confirmed further.

6.3.2 Organic matter & primary productivity

Analyses of the sediment cores indicate a change in species composition of primary producers in the beginning of zone 3 (based on BSi and Cphy content and MAR). A decrease of BSi and increase of C_{phy} at the inner station, Gp1, as well as BSi MAR decreasing relatively more than C_{org} MAR, strengthen the interpretation of a rapid change in the phytoplankton composition.

The change in in the phytoplankton composition can be for various reasons, an increase of new species or growing population of some less silicified phytoplankton that reflect an increase of C_{phy} and decrease in BSi.. At the outer station the change is not extreme, but a larger increase is seen in C_{phy} than BSi content, which also point to a change in the primary productivity. Tolerance for nutrients and trace elements varies between the phytoplankton species (National Reseach Council 2000). Therefore, the biodiversity changes with the environmental conditions, as some species can adapt and increase in abundance, whiles other decrease or go extinct when the conditions become unfavourable (Ning et al. 2018).

The use of artificial fertilizers increased during the 1950's in the Batlic Sea region (HELCOM 2009; Gustafsson et al. 2012), which favors some phytoplankton. Nitrogen-fixers like cyanobacteria could have increased during this time period while the diatoms decreased.

The availability of silica is decreased by eutrophication, when the nutrient enrichment of nitrogen and phosphorus (N/Si and P/Si ratios) increases in coastal waters. The growth of diatoms will cease when silicon availability decreases in the water column and other phytoplankton can successfully grow instead. One reason for decreases of dissolved silica in an inlet may be, for example, that silica is trapped upstream by new ecosystems in the freshwater as of result erosion of industrial fertilizer (nitrogen and phosphate enrichment). This can lead to limited growth of diatoms in the inlet or a shift in the species composition from heavy silicified to less silicified diatoms (Rabalais et al. 1996).

Another contributing factor is less transparency of the water caused by increased weathering and particle inputs from the streams. This could influence the diatoms that live deeper in the water column negatively, as sunlight cannot reach to greater water depths.

6.3.3 Hypoxia

The C_{org}/P_{tot} ratio increases to the maximum of 226 between 1970 and 1982. After 1982 to the end of zone 3 it is stable. The redox parameters Mo and Mo MAR also show an increase from zone 2 to zone 3. This indicates lower oxygen levels in the bottom waters of zone 3. According to Carstensen et al. (2014), hypoxia has expanded in the Bornholm Basin and Gotland Basin (in the Baltic Sea) from 5.000 km^2 in 1906 to >60.000 km^2 in 2012 as a result of enhanced anthropogenic nutrient input and increasing precipitation and runoff in the 1980's.

Further, increased temperatures, as well as the growth of nitrogen-fixing cyanobacteria, during the last two decades maintain hypoxic conditions in the Baltic Sea (Carstensen et al. 2014). Persson & Jonsson (2000) found that the lamination of sediments in S:t Anna archipelago started in the 1960's and reached its maximum during 1980's, which is another indication for low oxygen conditions. There could be many reasons for why the oxygen levels decreased in the outer part of Gropviken, such as increased input of nutrients that have increased the organic matter in the inlet.

A study of Persson & Jonsson (2000) implies that the trend may be connected to the hypoxia development offshore in the Baltic proper. Therefore, it is reasonable to suggest that the causes for hypoxia in Gropviken might have been the same as cited for the Baltic Sea.

6.3.4 Pollutants

The decline of Pb in zone 3 could reflect the lead-free petrol that was introduced during the 1970's (Ning et al. 2018). The other element ratios are stable.

6.4 Zone 4 2000-2017

6.4.1 Water energy

Overall, the sedimentation rate is at its maximum for both stations. In the shallower part of the inlet, i.e Gp1, the sedimentation rate distinctly increases between zone 3 and zone 4 (Fig 13). This could be an indication for changes in the riverine input from the streams (Passdalsån & Börrumsbäcken). In Gp2, the deeper area of the inlet, the sedimentation rate does not show the same trend and is on a generally higher level (mean sedimentation rate 7.6 mm per year) than in Gp1 (mean sedimentation rate 6.8 mm per year). The grain size distribution is similar to zone 3, with a slight increase of grain particles >4 µm in Gp2. This could be an effect of more particles from soil erosion being introduced by riverine input, as studies of Börrumsån indicated this being the reason for the waters apparent low transparency (Länsstyrelsen 2018).

6.4.2 Organic matter & primary productivity

In Zone 4 the highest values for most parameters (C_{org}, C_{org} MAR, BSi, BSi MAR and SR) of all the zones and in both locations are recorded. BSi and C_{org} MAR are rapidly increasing at Gp1 in the beginning of zone 4 and thereafter stable. The outer part of Gropviken underwent also a massive increase of $C_{phy,}$ with the same overall content as Gp1, which indicates the same trend in primary productivity throughout the inlet. The switch in C_{phy} and BSi could indicate a change in the nutrient input from land. Even if the nitrogen and phosphorus input into the Baltic Sea has decreased between 1994 and 2010 by 16 % and 14 % (HELCOM 2014), respectively, there is no evidence of decreased primary productivity as a result in the inlet. Instead, the content of BSi and C_{phy} increased rapidly during zone 4. The decreased nutrient input may have changed the phytoplankton composition from less silica-rich species to more silica-rich species, as zone 3 indicated as well.

From 2013 a decrease occurs in both BSi MAR and Corg MAR. Together with the low DIN and phosphate values measured by SMHI in 2017 (Fig. 2), it could indicate of a better ecological status in Gropviken.

6.4.3 Hypoxia

Parameters for redox (Mo/Al, Mo, C_{org}/P_{tot}) are slightly decreasing in zone 4, which indicates less oxygen depletion in the bottom waters compared to zone 3, possibly due to a decrease in input of nutrients. Improvements of the bottom water conditions have been studied in the Stockholm archipelago by Caballero-Alfonso et al. (2015) and records have shown that, due to reductions of nutrient input, the oxygen content has increased in the bottom waters. Studies of Carstensen et al. (2006) have shown the same for the Danish Straits.

The oxygen content of the bottom water overlying the sampling stations Gp1 and Gp2 is 4-5.3 ml/l (Fig. 6 & 7), correspond to oxic conditions at the sediment-water interface at the time of sampling. This matches the interpretation of the proxies with regards to the oxygenation status and could mean that a water exchange recently occurred.

6.4.4 Pollutants

A slight decline in trace elements, except for Cu, is occurring in zone 4. Studies from Ning et al. (2018) and Jonsson et al. (2003) are all showing an increase of trace elements during this time. The digestion of elements was not preformed correctly (see results section) and therefore the slight decrease should be interpreted with caution even if the trend should be the same.

6.5 General environmental changes in Gropviken

Although Gropviken always had a natural oxygenation cycle with fluctuating oxygen levels at the seafloor due seasonal bottom water exchanges (Jonsson et al. 2003), the occurrences of low-oxygen conditions have intensified during the last 50 years. Gropviken has typically 100 days in between the water exchanges due to the thermocline stratification (Jonsson et al. 2003). A water exchange occurs when the thermocline breaks down, as suggested for other coastal areas in a study by Conley et al. (2011), when the surface water has similar temperatures as the bottom waters. The water exchange is also limited by the shallow sills.

The records indicate an increase of low-oxygen conditions that could only be explained by an increased eutrophication. The top layer of the water column is formed by the riverine input of freshwater from Börrumsån and Passdalsån in the inner part of Gropviken. The stagnant conditions in the bottom water of the deepest location lead to increased oxygen depletion before the water exchange, which occurs during spring and autumn. My results demonstrate a rapid increase of primary productivity at Gp2 and hypoxic conditions in the bottom waters as a result. Gropvikens seafloor is easily oxygen depleted due to high nutrient loading that increases the primary productivity.

During the last 140 years Gropviken experienced changes in the environment due to anthropogenic impacts. In the beginning of the century Gropviken was a trade route for shipping iron ores from a mine close by. Theses impacts cannot be tracked in the elemental analysis or in the organic matter composition. Ning et al. (2018) have tracked changes in the ecosystem and environment in Gåsfjärden since the 1800's, due to an operating copper mine close to the inlet and intensified land use. A change in the ecosystem, in Gåsfjärden, seen in both diatom composition and geochemical proxies, was caused by the increase in trace metals. While the elemental record of Gropviken during this time period does not indicate a switch in the primary productivity, but the increase of C_{phy} and decrease of BSi around 1965 do show a rapid change in the primary producers composition. An increase of nitrogen and phosphorus in the surface water can be the reason why the change occurred in the phytoplankton composition and can be related to intensified land use and use of industrial fertilizers later on.

In general, the sedimentation rate is highest in the deeper part of Gropviken, Gp2. The inner site, Gp1, is exposed to more wave action, resuspension and when the thermocline weakens the water mixes easily. Whereas in the deeper station it seems that the thermocline and the salinity difference are making the environment more stable and therefore finer particles can be deposited. The sedimentation rate increases in the outer station Gp2 from the 1950's until present. Agriculture and open farmlands were expanding around Gropviken during this time. The farmlands were located in clay-filled valleys that stretched through the landscape (Fejes et al. 2002) and the streams running through these landscapes brought soil and nutrients from soil erosion into the inlet. This resulted in the increasing sedimentation rate. When the riverine input increased the transparency of the water in Gropviken decreased, and this can also be a contributing factor to why diatoms abundance was decreasing during this time and other phytoplankton increased.

At the same time of the rapid change in the primary productivity occurred in 1965, an indication was given for low-oxygen conditions at the Gp2 station. C_{org}/P_{tot} content is increasing already from 1930 onwards and varies around values of ~ 150-230 at the Gp2 site. Therefore, the C_{org}/P_{tot} ratio suggests severely low dissolved oxygen periods in all zones.

During the switch in BSi and C_{org}, the highest values of C_{org}/P_{tot} are also recorded, which is indicating that this period was hypoxic in particular. Mo and Mo MAR are also increasing during this period and strengthen the interpretation. The split core, recovered close to Gp2, has a distinct lamination in the uppermost 19 cm, which reflects this event as well (Fig. 3). Lamination is typically a characteristic of oxygen-depleted settings, because laminated sediments reflect seasonal changes in deposition and are preserved in low-energy settings under hypoxic to anoxic conditions (Jokinen et al. 2015). The increased lamination at Gp2 reflects the bottom water oxygen deficiency due to anthropogenic eutrophication during the last decades. Laminated sequences have been well studied in the deep basins of the Baltic and are reflecting hypoxic and anoxic bottom conditions due to restricted vertical mixing due to a strong halocline and enhanced primary productivity (Jokinen et al. 2015). Flux of organic matter due to enlarged productivity in the surface water is characterizing the hypoxic events in the Baltic Sea (Gustafsson et al. 2012). This has been tracked using redox proxies such as Mo/Al and C_{org}/P_{tot} in a study by Jilbert & Stomp (2013) in the Fårö Basin in the Baltic Sea. During hypoxic events, ammonium and phosphorus are released from the sediments and mixed up in the surface water and contribute to further fertilization (Jilbert & Stomp 2013). A minor decrease in C_{org}/P_{tot} and Mo is measured from 2000 until present which implies higher oxygen conditions in the bottom water. High dissolved oxygen levels are also measured at both stations during the sampling in June 2017 (Fig. 6 & 7).

At the same time a decrease is seen in the redox proxies, a change in BSi and C_{org} content is recorded. The phytoplankton composition is incresing in year 2000, where an increase of BSi and C_{org} is recorded. This indicates that the phytoplankton composition is the same throughout the inlet. Even if the nutrient input reduced during 1994-2012 (HELCOM 2014), a decrease in phytoplankton cannot be tracked, but the change in the composition between BSi and Cphy can be one of the feedbacks. Nevertheless, the nutrient input is still high in the area. SMHI has done a water exchange model called HYPE *(Hydrological Predictions for the Environment)* of the study area that simulated nutrient pathways from terrestrial to aquatic settings, among others, and estimated the total load of nutrients between 2005 to 2016. According to SMHI's coastal zone analysis, the total input of nitrogen (N) is +9.59 tons per year between 2005 and 2016. The input from land is +26.6 tons per year (49.8 % from forestry, 40.2 % from agriculture, sewers 1.5 %, lake 2.5 %). The net exchange with other water bodies is -19.7 tons per year. The atmospheric deposition of N is 2.61 tons per year. The total phosphorus (P) input is +0.372 tons per year. The input from land is +1.86 tons per year (31.4 % from forestry, 62.8 % from agriculture, sewers 1.8 %) and the net exchange to other water bodies is -1.5 tons per year. The atmospheric deposition of P is 0.0026 tons per year. The annual water runoff from land is 0.608 m^3/s and the net exchange with other water bodies is the same (HYPE 2017).

As a result of nutrient enrichment, the phytoplankton structure is changing and it is difficult to determine whether the change in primary productivity is indirect or direct. It can be a result of different changes in the nutrient input, but also a result of increased nutrient levels with increasing growth of productivity, which leads to increasing dissolved organic carbon that changes the community structure of phytoplankton (National Research Council 2000). Due to the nutrient over-enrichment there is a change in the ecological structure and planktonic composition, which can be tracked with the record of BSi and C_{phy}. Most likely there is a change in the benthic communities as well (National Research Counsil 2000).

A significant decrease is seen in multiple proxies in recent years, from 2013 to 2017, at both locations of Gropviken. The primary productivity is decreasing, and the oxygen conditions in the bottom waters are recovering. Measurements taken from SMHI (Fig. 2) are showing low DIN and phosphate values during 2017. Connections between lower bioavailable nutrient levels in the water and lower primary productivity indicates a recovery of the ecological status of Gropviken. This could be the first sign of recovery after a century of increasing eutrophication. A study by Karlsson et al 2010 shows that the Stockholm archipelago is also recovering from hypoxia. The study showed improved oxygen conditions in the sediment-water interface due to a successive removal of historical deposits prior to the installation of modern sewage treatment in the 1970s.

Murrey et al. (2019) predict that if nutrient reductions are implemented most of the Baltic Sea will meet the requirements for good status / good environmental status. The time required to achieve good status varies between different parts of the Baltic Sea, from decades in some areas to centuries in others. In the Baltic Proper good environmental status could be achieved around 2200. Murrey et al. (2019) claims that the improvement is greater in the beginning of a load reduction and therefore improvements could be seen in the Baltic Proper and the Bothnian Sea already at 2060 to 2070. The coastal inlet is connected to the Baltic Sea, and an estimate of the input from the open sea is not fully understood. We can see a recovery of the inlet of Gropviken but if the area is a well-connected system with the open waters, the area will not achieve good status until the rest of the Baltic Proper achieves the same status.

More studies of the diatom assemblage composition are needed to get insight about how the biodiversity has changed within the inlet. Additional measurements of the elements at Gp1 would be necessary to evaluate whether hypoxia also have occurred in shallower areas in the inlet as well.

7 Conclusions

This thesis presents a high-resolution environmental reconstruction from a narrow inlet of St. Annas archipelago in the Baltic Sea, covering the time span of 1880 to 2017. A multiproxy approach was applied to four high-resolution sediment cores. The study's goal was to investigate the historical development of two locations in the inlet of Gropviken. The key conclusions are that the organic matter was dominated by aquatic origins in the coastal inlet. The terrestrial matter input to the inlet was stable whereas the aquatic material increased during the century.

Another aim was to evaluate and compare the development of the sediments and sedimentation rates within the inlet. The sedimentation increased in the outer part of the coastal inlet. The location closer to land was fluctuating more due to resuspension and riverine input. The key conclusions from the study are that more particles accumulated after the 1950s, when the agriculture increased in the area.

The last purpose of the study was to estimate potential variability in anthrophonic input of nutrients and pollutants. Signs of an ongoing eutrophication in Gropviken are visible due to a gradual increase of primary productivity and a decrease in dissolved oxygen concentrations at the deeper location of the inlet. Changes in the primary productivity are also seen in 1965 and a rapid increase of C_{phy} that could be correlated with increasing carbon and nutrient input from the streams. This may have affected the biological values of the area. Indications of a rapid increase in metal pollutants during the 1950's are given as well.

The study shows that the sites are suitable as a reference for regional and local coastal surveys within the Baltic Sea.

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8 References

Appleby, P.G., 2001: Chronostratigraphic techniques in recent sediments. *In* W.M. Last & J.P. Smol (eds.): Tracking Environmental Change Using Lake Sediments. Volume 1: Basin Analysis, Coring, and Chronological Techniques, 171–203 *Developments in paleoenvironmental re search 1*.

Bernes, C., 2005: Förändringar under ytan: Sveriges havsmiljö granskad på djupet. *Monitor 19,* 1-192.

Boesch, D.F., 2002: Challenges and opportunities for science in reducing nutrient over-enrichment of coastal ecosystems. *Estuaries 25*, 886-900.

Brodie, C.R., Casford, J.S.L., Lloyd, J,M., Leng, M.J., Heaton, T.H.E., Kendrick, C.P. & Yongqiang, Z., 2011: Evidence for bias in C/N, δ13C and δ15N values of bulk organic matter, and on environmental interpretation, from a lake sedi mentary sequence by pre-analysis acid treat ment methods, *Quaternary Science Reviews 30*, 3076-3087.

Blåkusten, n.d.a: *Björnvik hamn*. Downloaded 2019-03-16, from http://blakusten.se/artiklar/gruvor/björnvik-hamn/

Blåkusten, n.d.b: *Frugelots brygga*. Downloaded 2019-03-16, from http://blakusten.se/artiklar/bryggor/frugelots-brygga/

Caballero-Alfonso, AM,, Carstensen, J. & Conley, D., 2015: Biogeochemical and environmental driv ers of coastal hypoxia. *Journal of Marine Sys tems 141*, 190-199.

Carstensen, J., Andersen, H.J., Gustafsson, B.G. & Conley, D.J., 2014: Deoxygenation of the Bal tic Sea during the last century. *Proceedings of the National Academy of Science of the United States of America 111*, 5628-5633.

Conley, D. J., Carstensen, J., Aigars, J., Are, P., Bonsdorff, E., Eremina, T., Haahti, B.-M., Humborg, C., Jonsson, P., Kotta, J., Lännegren, C., Larsson, U., Maximov, A., Medina, M. R., Lysiak-Pastuszak, E., Remekaite-Nikiene, N., Walve, J., Wilhelms, S., and Zillén, L., 2011: Hypoxia increasing in the coastal zone of the Baltic Sea, *Environmental Science & Technolo gy 45*, 6777–6783.

Conley, D.J., Björck, S., Bonsdorff, E., Carstensen, J., Destouni, G., Gustafsson, B. G., Hietanen, S., Kortetaas, M., Kuosa, J., Meier, H. E. M., Mül ler-Karulis, B., Nordberg, K., Norkko, A., Nurnberg, G., Pitkänen, H., Rabalais, N.N., Rosenberg, R., Savchuck, O. P., Slomp, C. P., Voss, M., Wulff, F., and Zillén L., 2009: Hy poxia related processes in the Baltic Sea, *Envi ronmental Science & Technology 43*, 3412–3420.

Conley, D. J., Humborg, C., Rahm, L., Savchuk, O.P., and Wulff, F., 2002: Hypoxia in the Baltic Sea and basin-scale changes in phosphorus biogeo chemistry, *Environmental Science & Technolo gy 36*, 5315–5320.

Clymans W., Barão L., Vander Putten N., Wastegård S., Gísladóttir G., Björck S., Moine B., Struyf, E. & Conley D.J., 2015: The contribution of tephra constituents during biogenic determinat ion: implications for soil and paleoecological studies. *Biogeosciences 12*, 3789-3804.

DeMaster, D.J., 1981: The supply and accumulation of silica in the marine environment. *Geochimica et Cosmochimica Atca 45*, 1715-1731.

Díaz, R.J. & Rosenberg, R., 2008: Spreading dead zones and consequences for marine ecosystems. *Science 321*, 926–929.

Duante, C.M., Conley, D.J., Carstensen, J. & Sánchez-Camacho, M., 2008: Return to Neverland: Shifting Baselines Affect Eutrophication Resto ration Targets. *Estuaries and Coasts 32,* 29-36.

EEA, 2018*: European waters Assessment of status and pressures 2018*. Report 2018/07. 90 pp.

Edlund, J., 2011: Naturvärdesinventering av 257 vat tendrag i Östergötland. Report / Länsstyrelsen Östergötland, 2011:12, 1-121.

Farmer, J. G., 1991: The perturbation of historical pol lution records in aquatic sediments. *Environ mental Geochemistry and Health 13*, 76-83.

FEHY., 2013: Fehmarnbelt Fixed Link. Marine Water-Baseline. Hydrography, Water Quality and Plankton of the Baltic Sea. *Report / FEHY, E1TR0057:1*, 1-164.

Fejes, J., Lindgren, C. & Zakrisson, J., 2002: Samman ställning av 40-års recipientkontroll, 1961-2000: för Motala ströms vattenvårdsförbund. IVL Svenska miljöinstitutet, Stockholm. 192 pp.

Gezelius, L., Larson, P-E., Larsson, M., Schaerling, K. & Åslund, M., 2011: Acta S:t Anna - Samver kansplan för BSPA-området S.t Anna-Missjö. Report / *Länsstyrelsen Östergötland, 2011:7, 1-158*

Gustafsson, B. G., Schenk, F., Blenckner, T., Eilola, K., Meier, H. E. M., Müller-Karulis, B., Neu mann, T., Ruoho-Airola, T., Savchuk, O. P., and Zorita, E., 2012: Reconstructing the deve lopment of Baltic Sea eutrophication 1850–2006, *Ambio 41*, 534–548.

Hangstum, P.J., Reinhardt,E.G., Boyce, J.I. and Clark, C., 2006: Changing sedimentation patterns due to historical land-use change in Frenchman's Bay, pickering, Canada: evidence from high resolution textural analysis, J Paleolimnol 37, 603-618.

HELCOM, 2009:Eutrophication in the Baltic Sea – An integrated thematic assessment of the effects of nutrient enrichment and eutrophication in the Baltic Sea region. *Baltic Sea Environment Pro ceedings*

HYPE, 2017: *World-Wide Hydrological Predictions* Downloaded: 2019-01-15 from: http:// hypeweb.smhi.se/

Jilbert, T., Asmala, E., Schröder C., Tijhonen, R., Mykkykangas, J.-P., Virtasalo, J.J., Kotilainen, A., Peltola, P., Ekholm, P. & Hietanten S., 2018: Impacts of flocculation on the distribu tion and diagenesis of iron in boreal estuarine sediments. *Biogeoscience 15,* 1243-1271.

Jilbert, T. & Slomp, C. P., 2013: Rapid high-amplitude variability in Baltic Sea hypoxia during the Holocene, *Geology 41*, 1183– 1186.

Jokinen, S.A., Saarinen, T., Virtasalo, J.J., Jilbert, T., Kaiser, J., Dellwig, O., Arz, H.W., Hänninen, J., Arppe, L. & Collander, M., 2018: A 1500-year multiproxy record of costal hypoxia from the northern Baltic Sea indicates unprecedented deoxygenation over the 20th century. *Biogeosci ences 5* 3975-4001.

Jokinen, S. A., Virtasalo, J.J., Kotilainen, A.T. & Saa rinen, T., 2015: Varve microfabric record of seasonal sedimentation and bottom flow-modulated mud deposition in the coastal north ern Baltic Sea. *Marine Geology 366*, 79–96.

Jonsson, P. & Persson, J., (1996): Bottenförhållanden som eutrofieringsindikator i S:t Anna skärgård. Report / Länsstyrelsen Östergötland, 1996:8, 1-63.

Jonsson, P., Persson. J. & Holmberg, P., 2003: Skär gårdens bottnar: en sammanställning av sedi mentundersökningar gjorda 1992-1999 i skär gårdsområden längst svenska ostkusten. Re port / Naturvårdsverket, 5212, 1-112.

Karlsson, O. M., Jonsson, P.O., Lindgren, D., Malmaeus, J. M. & Stehn, A., 2010: Indications of recovery from hypoxia in the inner Stock holm archipelago. *Ambio 39*, 486-495.

López G.I., 2017: Grain Size Analysis. *In A.S Gilbert* *(ed.):* Encyclopedia of Geoarchaeology, 341-348. *Encyclopedia of Earth Sciences Series.*

Länsstyrelsen, 2018: Beskrivning av värdetrakter för vattendrag i Östergötland. *In* Country Admi nistrative Board: *Handlingsplan för grön infra struktur i Östergötland*. 46 pp.

Meyers, P.A. & Ischiwatari, R., 1993: Lacustrine or ganic geochemistry – an overview of indicators of organic matter sources and diagenesis in lake sediment. *Organic Geochemistry 20*, 867-900

McCave, I. N., Hall., I. R. & Bianchi, G. G., 2006: Laser vs. settling velocity differences in silt grainsize measurements: estimation of paleo current vigour. *Sedimentology 53*, 919-928.

Mccave, I.N., Manighetti, B. & Robinson, S.G. 1995: Sortable silt and fine sediment size/composition slicing: parameters for paleocurrent speed and palaeocenography. Paleoceanography 10, 593-610.

Nartorpsbygden., n.d.: *Gruvområdet.* Downloaded 2019-03-16, from: http://nartorp.se/?page_id=36

Murray C. J., Müller-Karulis B., Carstensen J., Conley D. J., Gustafsson B. G., Andersen J. H., 2019: Past, Present and Future Eutrophication Status of the Baltic Sea. *Frontiers in Marine Science 6*.

National Research Council., 2000: *Clean Coastal Wa ters: Understanding and Reducing the Effects of Nutrient Pollution*. National Academy Press, Washington, DC. 446 pp.

Ning, W, Ghosh, A., Jilbert, T.,Clomp, C.P., Monsoor, K., Nyberg., Conley., D.J., Filipsson., H. L. 2016: Evolving Coastal Character of a Baltic Sea inlet during the Holocene Shoreline Re gression; Impact on Coastal Zone Hypoxia. *Journal of Paleolimnology 55*, 319-338.

Ning, W., Nielsen, A. B., Norbäck-Ivarsson, L., Jil bert, T., Åkesson, C. M., Slomp, C. P., Andrén, E., Broström, A., and Filipsson, H. L.2016: Anthropogenic and climatic impacts on a coastal environment in the Baltic Sea over the last 1000 years, *Anthropocene 21*,66– 79.

Persson, J. & Jonsson, P., 2000: Historical develop ment of laminated sediments – an approach to detect soft sediment ecosystem changes in the Baltic Sea. *Marine Pollution Bulletin 40*, 122-134.

Rabalais, N.N., Cai, W.J., Carstensen, J., Conley, D.J., Fry, B., Hu, X., Quiñones-Rivera, Z., Rosen berg, R., Slomp, C.P., Turner, R.E., Voss, M., Wissel., B. & Zhang, J., 2014: Eutrophication-driven deoxygenation in the coastal ocean. *Oceanography 27*, 172–183.

Rabalais, N.N., Turner, R.E., Sen Gupta, B.K., Boesch, D.F., Chapman, P. & Murrell, M.C., 2007: Hypoxia in the northern Gulf of Mexico: Does the science support the Plan to Reduce, Mitigate, and Control Hypoxia. *Estuaries and Coasts 30*, 753–772.

Rabalais, N.N., Turner R.E., Justic, D., Dortch, Q., Wiseman, W.J. & Sen Gupta B.K., 1996: Nutri ent changes in the Mississippi River and system responses on the adjacent continental shelf. *Estauries 19*, 389-407.

Ragueneau, O., Conley, D., Leynaert, A., Longphuirt, S.N., Slomp, C.P., 2006: Role of diatom in sili con cycling and coastal marine food webs. *In*: V. Ittekkot, D.Unger, C. Humborg, & N. Tac An, (Eds.): The silicon cycle – human perturba tions and impact on aquatic systems, 163-195.*Scope Series66*.

SGU., 2017: *Gruvor och miljöpåverkan.* Downloaded 2019-02-22, from: http://www.sgu.se/mineralnaring/gruvor-ochmiljopaverkan/

SGU., n.d.a: *Soil map, Gropviken* Downloaded 2019-02-10, from: http://apps.sgu.se/kartgenerator/leverans/jord25_100_Nz5fOqis74.pdf

SGU., n.d.b: *Beach map, Gropviken*. Downloaded 2019-03-06, from: http://apps.sgu.se/ kart generator/leverans/strand_6000_xdMu5mX1yd.pdf

SGU., n.d.c: *Bedrock map, Gropviken.* Downloaded 2019-01-30, from: http://apps.sgu.se/kartgenerator/leverans/rock_local_LYQe5USXhs.pdf

SMHI., 2017a: *Klimatindikator – nederbörd.* Downlo aded 2019-03-17, from: https://www.smhi.se/klimat/klimatet-da-och-nu/klimatindikatorer/klimatindikator-nederbord-1.2887

SMHI, 2017b: *Normal uppmätt årsnederbörd, medel värde 1961-1990*. Downloaded 2019-01-15 From: https://www.smhi.se/klimatdata/meteorologi/nederbord/normal-uppmatt-arsnederbord-medelvarde-1961-1990-1.4160

Stickland, J.D.H. & Parsons, T.R., 1968: A practical handbook of seawater analysis. *Bulletin of Fisheries Research Board of Canada 176,* 1-311.

Szymczycha, B., Zaborska, A., Bełdowski, J., Kuliński, K., Beszczyńska-Möller, A., Kędra, M. & Pempkowiak, J., 2019: The Baltic Sea In C.Sheppard (Ed.): *World Seas: an Environmental Evaluation (Second Edition),* 85-111. Academic Press.

VISS 2019: *Gropviken* Downloaded: 2019-01-05 From: https://viss.lansstyrelsen.se/Waters.aspx?waterMSCD=WA46378339

Vlasov, N., Brusendorff, A.C., Durkin, M., Korpinen, S., Laamanen, M., Stankiewicz, M., 2010: *HELCOM Atlas of the Baltic Sea*. Baltic Marine Environment Protection Commission, Helsinki.189 pp.

Zillén, L., Conley, D., Andrén, T., Andrén, E. & 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,* 77-92.

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