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Past, Present and Future - Assessing Changes in aquatic Environments using Subfossil Diatoms

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Abstract

The deterioration of surface waters is one of the most important issues in the environmental management of the European Union. Thus, the EU Water Framework Directive 2000/60/EC (WFD) requires "good ecological and chemical status" of surface waters by 2015 allowing only a slight departure from ecological reference conditions characterized by the biological communities typical for the conditions of minimal anthropogenic impact. The WFD requires the determination of ecological reference conditions and the present ecological status of surface waters. To meet this legislative demand, sedimentary diatom assemblages were used in these studies with various methods 1) to assess natural and human activity induced environmental changes, 2) to characterize background conditions 3) to evaluate the present ecological status and 4) to predict the future of the water bodies in the light of palaeolimnological data. As the WFD refers to all surface waters, both coastal and inland sites were included.

Two long and two short sediment cores from the Archipelago Sea in the northern Baltic Sea were examined for their siliceous microfossils in order to assess (1) the Holocene palaeoenvironmental history and (2) the recent eutrophication of the area. The diatom record was divided into local diatom assemblage zones (LDAZ, long cores) and diatom assemblage zones (DAZ, short cores). Locally weighted weighted averaging regression and calibration (LWWA) was applied for the quantitative reconstruction of past TN concentrations (short cores). An age model for the long cores was constructed by using independent palaeomagnetic and AMS-^{14}C methods. The short cores were dated using radiometric (^{210}Pb, ^{226}Ra and ^{137}Cs) methods.

The long cores date back to the early history of the Archipelago Sea, which was freshwater – no salinity increase referable to the brackish phase of the Yoldia Sea is recognized. The nutrient status of the lacustrine phase was slightly higher in the Archipelago Sea than in the Baltic Proper. Initial brackish-water influence is observed at 8 150 ±80 cal. BP (LDAZ4), but fully brackish conditions were established at 7 700 ±80 cal. BP (LDAZ5). The diatom assemblages indicate increasing salinity, warming climate and possible eutrophic conditions during the lacustrine to brackish-water transition. The decreasing abundance of *Pseudosolenia calcar-avis* (Schultze) Sundström and the increasing abundance of the ice-cover indicator species *Pauliella taeniata* (Grunow) Round and Basson indicate decreasing salinity and climatic cooling after ca. 5 000 cal. BP.

Signs of eutrophication are visible in the most recent diatom assemblage zones of both short cores. Diatom-inferred total nitrogen (DI-TN) reconstructions partially fail to trace the actual measured total nitrogen concentrations especially from the late 1980s to the mid 1990s. This is most likely due to the dominating diatom species *Pauliella taeniata*, *Thalassiosira levanderi* Van Goor and *Fragilariopsis cylindrus* (Grunow) W. Krieger being more influenced by factors such as the length of the ice-season rather than nutrient concentrations. It is concluded that the diatom assemblages of the study sites are principally governed by climate fluctuations, with a slight influence of eutrophication visible in the most recent sediments. There are indications that global warming, with reduced

ice cover, could impact the spring blooming diatom species composition in the Archipelago Sea. In addition, increased sediment accumulation in the early 90s coincides with the short ice-seasons suggesting that warming climate with decreasing ice-cover may increase sedimentation in the study area.

The diverse diatom assemblages dominated by benthic species (54 %) in DAZ1 in the Käldö Fjärd core can be taken as background diatom assemblages for the Archipelago Sea. Since then turbidity has increased and the diatom assemblages have been dominated by planktonic diatoms from around the mid 1800s onwards. The reconstructed reference conditions for the total nitrogen concentrations fluctuate around 400 µg l^{-1}.

Altogether two short sediment cores and eight short cores for top-bottom analysis were retrieved from Lake Orijärvi and Lake Määrjärvi to assess the impact of the acid mine drainage (AMD) derived metals from the Orijärvi mine tailings on the diatom communities of the lakes. The Cu (Pb, Zn) mine of Orijärvi (1757 – 1956) was the first one in Finland where flotation techniques (1911 – 1955) were used to enrich ore and large quantities of tailings were produced. The AMD derived metal impact to the lakes was found to be among the heaviest thus far recorded in Finland. Concentrations of Cu, Pb and Zn in Lake Orijärvi sediments are two to three orders of magnitude higher than background values. The metal inputs have affected Lake Orijärvi and Lake Määrjärvi diatom communities at the community levels through shifts in dominant taxa (both lakes) and at the individual level through alteration in frustule morphology (Lake Orijärvi). At present, lake water still has elevated heavy metal levels, indicating that the impact from the tailings area continues to affect both lakes. Lake Orijärvi diatom assemblages are completely dominated by benthic species and are lacking planktonic diatoms. In Lake Määrjärvi the proportion of benthic and tychoplanktonic diatoms has increased and the planktonic taxa have decreased in abundance. *Achnanthidium minutissimum* Kützing and *Brachysira vitrea* (Grun.) R. Ross in Hartley were the most tolerant species to increased metal concentrations. Planktonic diatoms are more sensitive to metal contamination than benthic taxa, especially species in the genus *Cyclotella* (Kützing) Brébisson.

The ecological reference conditions assessed in this study for Lake Orijärvi and Lake Määrjärvi comprise diverse planktonic and benthic communitites typical of circumneutral oligotrophic lakes, where the planktonic diatoms belonging to genera *Cyclotella* , *Aulacoseira* Thwaites, *Tabellaria* Ehrenberg and *Asterionella* Hassall dominate in relative abundances up to ca. 70%. The benthic communities are more diverse than the planktonic consisting of diatoms belonging to the genera *Achnanthes* Bory, *Fragilaria* Lyngbye and *Navicula* St. Vincent.

This study clearly demonstrates that palaeolimnological methods, especially diatom analysis, provide a powerful tool for the EU Water Frame Work Directive for defining reference conditions, natural variability and current status of surface waters. The top/bottom approach is a very useful tool in larger-scale studies needed for management purposes. This “before and after” type of sediment sampling method can provide a very time and cost effective assessment of ecological reference conditions of surface waters.

Contents

List of original publications

This thesis is based on the four publications listed below, which are referred to by their Roman numerals (**I – IV**) in the text:

I Tuovinen, N., Virtasalo, J.J. and Kotilainen, A.T. 2008: Holocene diatom stratigraphy in the Archipelago Sea, northern Baltic Sea. Journal of Paleolimnology 40: 793-807.

II Tuovinen, N., Weckström, K. and Virtasalo, J.J. 2009: Assessment of recent eutrophication and climate influence in the Archipelago Sea based on the subfossil diatom record. Journal of Paleolimnology DOI: 10.1007/s10933-009-9390-z.

III Salonen, V-P., Tuovinen, N. and Valpola, S. 2006: History of mine drainage impact on Lake Orijärvi algal communities, SW Finland. Journal of Paleolimnology 35: 289-303.

IV Tuovinen, N., Weckström, K. and Salonen, V-P: Acid mine drainage impact on lake Orijärvi and Määrjärvi diatom communities, SW Finland. *Submitted to Boreal Environmental Research*

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Author's contribution to the articles

I The study was planned by J.J. Virtasalo, N. Tuovinen and A.T. Kotilainen. A.T. Kotilainen and J.J. Virtasalo provided the cores. N. Tuovinen carried out the diatom analysis. N. Tuovinen and J.J. Virtasalo wrote the article, which was commented on by A.T. Kotilainen and M. Räsänen.

II The study was planned by N. Tuovinen. The Seili core sampling was done by N. Tuovinen and J.J. Virtasalo. The Kjäldö Fjärd core was sampled by S. Vaalgamaa, K. Weckström and T. Suominen. Diatom analyses were carried out by N. Tuovinen (The Seili core) and K. Weckström (The Kjäldö Fjärd core). Total nitrogen (DI-TN) reconstructions were carried out by K. Weckström. J.J. Virtasalo provided the lithological description of the Seili core. The results were interpreted and the article written by N. Tuovinen and K. Weckström. The article was commented on by J.J. Virtasalo.

III The study was mainly planned by Prof. V-P. Salonen. Sampling and fieldwork were conducted by all authors. N. Tuovinen carried out the diatom analysis and S. Valpola the chrysophycean cyst analysis. The results were interpreted and the paper written by all authors.

IV The study was planned by V-P. Salonen and N. Tuovinen. Sampling was done by N. Tuovinen with assistance of H. Venho. N. Tuovinen carried out the diatom and data analysis. The results were interpreted and the paper written by N. Tuovinen. The article was commented on by K. Weckström and V-P. Salonen.

1. Introduction

1.1. The EU Water Framework Directive

Eutrophication, acidification and chemical pollution of surface waters have been pressing issues for decades and, consequently, also policy makers have become increasingly concerned about the deterioration of surface waters. As a result, the European Water Framework Directive 2000/60/EC (WFD) was executed in the year 2000. This directive requires “good ecological and chemical status” of surface waters in the EU by 2015, allowing only a slight departure from conditions, which would be expected under minimal anthropogenic impact (i.e. reference conditions; Anon. 2000). The directive regards the definition “good ecological status” as an innovative step for EU water legislation. To achieve a good ecological status, the factors harming water ecosystems and the methods for assessing the ecological status for a range of biological elements will have to be addressed by the member states. Recently, a lot of work has been done to meet this legislative demand and to assess the contemporary chemical and biological quality of freshwater, coastal and estuarine systems (e.g., Allan et al. 2006, Kelly et al. 2008, Borja et al. 2009, Cabecinha et al. 2009, Ptacnik et al. 2009). Many of these studies, however, emphasise how difficult it is to assess ecological reference conditions. Especially Kelly et al. (2008) point out that the verification of reference sites, i.e. sites with no anthropogenic influence, has been a very time-consuming task for all Member States of the EU, and has been critically dependent upon the availability of suitable data.

1.2. Palaeolimnology

Palaeolimnogical methods offer a powerful tool for defining conditions of minimal anthropogenic impact. Palaeolimnology uses a wide range of fossil and subfossil indicators preserved in aquatic sediments representing the past flora (diatoms, chrysophyte cysts, dinoflagellates, aquatic plant macrofossils, pollen, pigments) and fauna (chironomids, ostracods, cladocerans, fish scales) to reconstruct the pre-pollution aquatic ecosystems (Bennion & Battarbee 2007). Especially subfossil diatoms combined with numerical techniques (transfer functions) provide reliable quantitative reconstructions of past environmental conditions, e.g. nutrient status, salinity and pH (e.g. Birks 1998, Battarbee et al. 1999, Andersen et al. 2004, Miettinen 2005, Räsänen et al. 2006, Leira et al. 2006, Weckström 2006, Bennion & Battarbee 2007). By means of palaeolimnology we can have a good glimpse of the past, understand the pathways that have led to the present and get the information we need to predict the future.

1.3. Diatoms

Diatoms (Bacillariophyceae) are microscopic unicellular algae abundant in almost all aquatic habitats; they are key components of food webs in nearly all freshwater and saline environments (e.g. Dixit et al. 1992). Their cell walls are composed primarily of biogenic silica (SiO) and due to this feature they are generally well preserved in sediments. The taxonomy of diatoms is based on the unique, ornamented structure of their cell walls (frustules). Hence they can be identified to species level and beyond, which increases the amount of ecological information obtained. Many diatoms have specific optima and tolerance for a range of environmental variables and therefore shifts in e.g. salinity, pH, nutrient concentrations or temperature are likely to result in changes in species composition. Due to these characteristics diatoms have been widely used in palaeoenvironmental reconstructions (e.g. Dixit et al. 1992, Battarbee et al. 2001), but also in contemporary monitoring programmes to assess the present water quality of lakes, rivers and reservoirs (e.g. Dixit & Smol 1994, Kelly & Whitton 1995, Eloranta & Soininen 2002, Atazadeh et al. 2007).

1.4. The Baltic Sea and the Archipelago Sea

In the Baltic Sea, diatoms are one of the most important taxonomic groups of phytoplankton (Niemi 1973, 1975, Niemi & Åström 1987) and they have been used widely in Holocene palaeoenvironmental reconstructions around the Baltic Sea Basin (BSB) (e.g. Alhonen 1971, Eronen 1974, Abelmann 1985, Heino 1973, 1987, Hyvärinen 1984, Åker et al. 1988, Thulin et al. 1992, Witkowski 1994, Sohlenius et al. 1996, Westman & Sohlenius 1999, Lepland et al. 1999, Andrén et al. 2000a, 2000b, Heinsalu et al. 2000). The late-Pleistocene and Holocene development of the Baltic Sea Basin (BSB) consists of successive palaeoenvironmental phases known as the Baltic Ice Lake, the Yoldia Sea, the Ancylus Lake, the Littorina Sea and the present Baltic Sea (Sauramo 1958, Winterhalter et al. 1981, Björck 1995). In addition, a transitional phase between the Ancylus Lake and Littorina Sea phases is sometimes referred to as the Mastogloia Sea (Hyvärinen 1988) or Early Littorina Sea (Berglund et al. 2005) in the coastal zone, but as the Initial Littorina Sea (Andrén et al. 2000b, Heinsalu et al. 2000) in the offshore sediments. The palaeoenvironmental phases implicate salinity variations in the BSB, which were originally inferred from molluscs (De Geer 1890, 1913), and later interpreted from sedimentary diatom assemblages (Alhonen 1971, Eronen 1974, Hyvärinen 1984, Åker et al. 1988, Sohlenius et al. 1996, Andrén et al. 2000a, 2000b, Heinsalu et al. 2000). Yet, the Baltic Ice Lake, Yoldia Sea and Ancylus Lake phases are in practice often distinguished in the sediments by clay-varve correlation and changes in lithology (e.g. Wastegård et al. 1995, Sohlenius et al. 1996, Andrén et al. 1999) due to the scarcity of diatoms in these late-glacial and early post-glacial deposits. The onset of the Littorina Sea in coastal sediments is frequently defined based on the appearance of a brackish diatom flora with abundant *Campylodiscus clypeus* (Ehrenberg) (Eronen 1974, 1983), while in the offshore sediments, the beginning of the Littorina Sea is commonly deduced from the appearance of brackish-marine species and increased sedimentary carbon content (Heino 1973, 1987, Sohlenius et al. 1996, Westman

& Sohlenius 1999, Andrén et al. 2000a, 2000b, Heinsalu et al. 2000, Berglund et al. 2005, Borgendahl & Westman 2006)

Due to the complex interactions between the retreat of the Fennoscandian ice-sheet, glacio-isostatic rebound and glacio-eustatic sea-level change, the onsets of some individual palaeoenvironmental phases have been diachronous, and the characteristics of the phases and their corresponding diatom communities differ around the BSB. The conventional classification of the palaeoenvironmental phases is, therefore, based on an obscure mixture of biostratigraphical and lithostratigraphical textures, which has led to increasing criticism of the conventional classification as being ambiguous (Hyvärinen 1988, Gibbard 1992, Virtasalo et al. 2005b) and not conformal to international stratigraphic division practices described in the International Stratigraphic Guide (Salvador 1994). A stratigraphic division practice, independent of local differences in sedimentary microfossil taxa, could provide a more straightforward and unambiguous tool for the inter-regional correlation of sediments in the BSB such as the recently applied descriptive allostratigraphic division practice for sediments in the Archipelago Sea by Virtasalo et al. (2005b).

Subfossil diatoms have also been used to assess recent eutrophication in coastal waters around the Baltic Sea (Andrén 1999, Andrén et al. 1999, Clarke et al. 2003, Ellegaard et al. 2006, Weckström 2006). Eutrophication has become a significant environmental threat for many coastal marine areas (Jørgensen & Richardson 1996). This trend is also evident in the Baltic Sea with a densely populated, highly industrialized and intensively cultivated drainage area (Larsson et al. 1985, Sweitzer et al. 1996). The Archipelago Sea is listed as an agricultural “Hot Spot” by the Helsinki Commission (HELCOM) Joint Comprehensive Programme (HELCOM 2003). The Hot Spots are serious pollution areas and identifying and restoring them is an essential part of the Joint Comprehensive Programme. The Finnish Environment Institute (SYKE) coordinates the national coastal water-monitoring programme, which includes measurements of total phosphorus (TP) from the year 1974, total nitrogen (TN) from the year 1983 and the phytoplankton species composition and biomass from 1990. This time period of monitoring is, however, too short to reliably assess the onset and magnitude of recent eutrophication, suggesting the use of alternative means to infer the past such as palaeolimnological techniques.

1.5. Heavy metal pollution of lakes

In addition to eutrophication, the chemical deterioration of surface waters is a major problem today. For example, metal inputs from mining activities, especially acid mine drainage (AMD), is one of the biggest environmental problems decreasing the quality of lakes and other surface waters (Austin & Deniseger 1985, Cattaneo et al. 2004, Cattaneo et al. 2008, Sarmiento et al. 2009). Mining involves the removal, processing and disposal of vast volumes of rock and wastes and, therefore, the main direct release of metals is from tailings, polishing ponds and emissions later in the exploitation of the ore (Allan 1997). AMD generated by oxidation of iron-rich sulphide waste rocks and tailings is an extensive problem in

Finland, where during the past centuries nearly two hundred sulphide ores have been actively mined (Puustinen 2003). The heavy metals released to aquatic environments have severe effects on primary producers. Toxicity of heavy metals to algae results primarily from their binding to sulphydryl groups in proteins or disruption of protein structure or displacement of an essential element (De Filippis & Pallaghy 1994). Metal pollutants also disturb the oxidative balance in algae, which leads to unbalanced cellular redox status (Pinto et al. 2003). Algae also accumulate heavy metals and can pass them through the food chain up to top consumers.

1.6. Aims of the present study

The general objectives of this PhD thesis are 1) to use subfossil diatom assemblages to assess natural and human activity induced environmental changes 2) to characterize pre-disturbance background conditions of two different types of water bodies 3) to evaluate the present ecological status and 4) to predict the future of water bodies in the light of obtained palaeolimnological data. The research papers included in this thesis had the following objectives:

I To provide the first comprehensive Holocene palaeoenvironmental reconstruction based on diatom analysis for the Archipelago Sea in the northern Baltic Sea. The second aim was to compare the stratigraphical zonation based on diatoms with the descriptive allostratigraphic classification recently presented for the area by Virtasalo et al. (2005b) in order to study how the unconformal boundaries of the allostratigraphic units relate to observed palaeoecological changes.

II To assess post-industrial trends in eutrophication and the influence of climate on algal communities in the Archipelago Sea area, and further to provide ecological pre-disturbance reference conditions for the area.

III To specify the toxic metal impacts on diatom and chrysophycean assemblages by applying palaeolimnological techniques. The aim was to compare these two proxies in a radiometrically dated sediment core taken from the lake that has received the strongest acid mine drainage (AMD) derived metal load observed in Finland.

IV To assess the spatial patterns and the extent of the AMD derived metal impact on the diatom communities of the lakes Orijärvi and Määrjärvi using the “top/bottom” palaeolimnological approach, and to provide ecological reference conditions for these lakes.

This summary provides an overview of the research papers. For a more thorough description of materials and methods, data interpretation and discussion, the reader is referred to the original articles **I–IV.**

2. Study areas

2.1. The Archipelago Sea, papers I and II

The Archipelago Sea is located at the junction of the Gulf of Bothnia, the Gulf of Finland and the Baltic Proper (Fig. 1). It is an extensive archipelago of nearly 8000 km^2 with a mosaic of more than 22 000 islands (Granö et al. 1999). The average water depth is only 23 m, but some deeps reach over 100 m. The waters are annually covered by ice for 3–4.5 months, the ice-bound period usually ending in April (Seinä 1994). The surface salinity ranges from 4 to 7 ‰ from the inner archipelago towards the open sea. There is no permanent halocline in the Archipelago Sea (Virtasalo et al. 2005a), even though that is the dominant feature of the Baltic Sea proper. The shallowness and the abundance of islands prevent substantial water exchange between the archipelago and the open sea areas (Mälkki et al. 1979). Strong, although not permanent horizontal and vertical gradients of salinity, temperature, oxygen and exposure are characteristics of the Archipelago Sea, and result in numerous biotopes and complicated ecological networks (Hänninen et al. 2000; Virtasalo et al. 2005a).

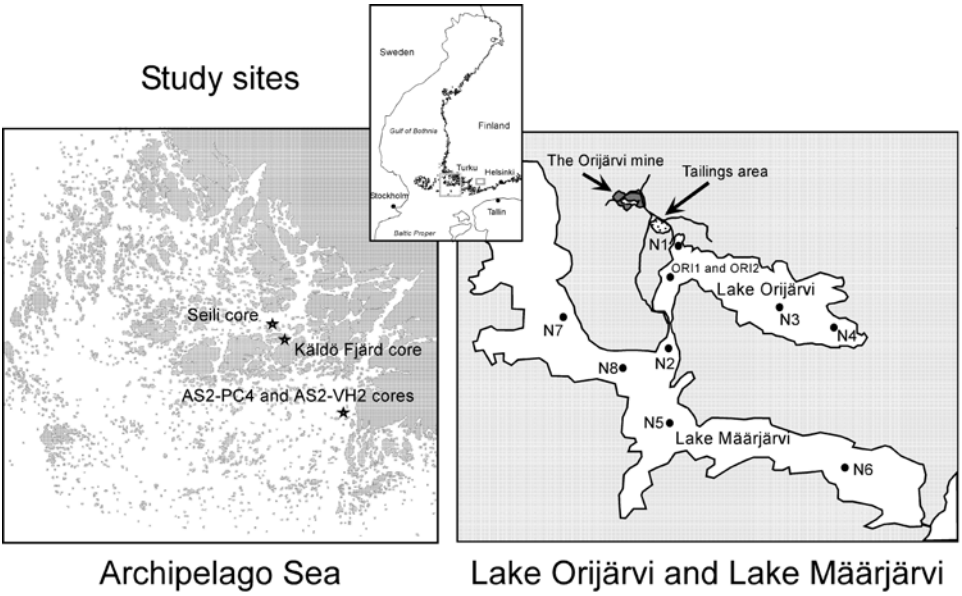


Fig. 1 Map of the study area and sampling sites.

The deglaciation of the Archipelago Sea began when the Fennoscandian ice-sheet retreated from the Second Salpausselkä ice-marginal accumulation in the southeastern part of the area at 11 590 ±110 calendar years before present (calibrated BP) (Saarnisto & Saarinen 2001). Most of the underlying crystalline bedrock was covered with till and glaciofluvial deposits. This substratum is overlain by glaciolacustrine varved silts and clays (Dragsfjärd Alloformation) (Virtasalo et al. 2005b). They, in turn, are overlain by the post-glacial lacustrine

Korppoo Alloformation comprising two units: the Trollskär Formation that consists of reworked varvite clasts in a clay–silt matrix, and the Sandön Formation, which is composed of weakly layered to strongly bioturbated, sulphide-bearing clays. Superimposed are organic-rich, brackish-water muds characterized by alternating strongly bioturbated to thinly laminated lithofacies (Nauvo Alloformation). Deposition of the brackish-water muds of Nauvo Alloformation began when the glacio-eustatic ocean-level rise resulted in the transgression of the Atlantic into the BSB through the sounds in the Kattegat, leading to the onset of brackish-water conditions and estuarine circulation in the basin. The onset of brackish-water deposition in the study area was at ca. 7 600 cal. BP (Eronen et al. 2001, Virtasalo et al. 2006). Since then, the relative sea level in the area has fallen progressively due to the glacio-isostatic land uplift, and the salinity has decreased as a result of the narrowing of the connection between the BSB and the Atlantic.

In the present Archipelago Sea area, increasing phosphorus (P) and nitrogen (N) concentrations were evident in the 1970s and the 1980s (Pitkänen et al. 1987) and eutrophication proceeded in the 1990s (Bonsdorff et al. 1997). Total P concentrations in the middle Archipelago have increased steadily during the last decades, while total N concentrations have decreased since the peak of late the 1980s – early 1990s (monitoring data). On the whole, the increased nutrient load from agricultural activities, municipal wastewaters, fish farming, and from atmospheric deposition has led to increased summer phytoplankton biomass, changes in phytoplankton species composition, decreased water transparency, increased oxygen consumption of decaying organic matter, and changes in zoobenthos and fish communities (Bonsdorff et al. 1997, Virtasalo et al. 2005a).

2.2. Lake Orijärvi and Lake Määrjärvi, papers III and IV

Lake Orijärvi and Lake Määrjärvi (60°14' N 23°35' E) are located in Southwest Finland, about 70 kilometers west from Helsinki (Fig. 1). They are two headwater lakes of the river system of Fiskars river. Water quality monitoring has been carried out in both lakes since the 1960's (Vogt 1998), and highly elevated concentrations of copper (Cu), lead (Pb), cadmium (Cd) and especially zinc (Zn) have been measured in both lakes. The elevated metal concentrations are derived from the oxidation of iron-rich sulphide tailings of the Orijärvi copper mine. Mining in the area started in 1758 and since then, during 200 years of mining, altogether 1 200 000 tons of sulphide ore and gangue were extruded and enriched for copper, zinc and lead concentrates. During the first 150 years only copper was produced. The enrichment plant with a flotation line was established in 1911 in order to produce zinc from the former gangue minerals. After a short break, the copper production started anew in the 1930s, and during the years 1945 – 1956 the ore was intensively exploited for copper, zinc and lead concentrates. Total production of the mine was 8 200 tons of copper, 14 600 tons of zinc and 4 100 tons of lead (Turunen 1957).

The enrichment plant and the tailings area, which contains ca. 400 000 tons of mine waste rich in metal sulphides, were directly adjacent to Lake Orijärvi. After the closure of the mine, open pits, waste rock piles and tailings were left uncovered in the open air, which has led to substantial weathering of the tailings surface. The unweathered tailings contain, on average, 1.0 % copper, 6 % zinc and more than 1% lead (Ewurum 2000), whereas the weathered 20 – 40 cm thick surface layer of the tailings contains 0.2 % copper, 0.6 % zinc and 0.7 % lead. It can be estimated that weathering of tailings has affected on average the topmost 50 cm of the tailings, which equals to about 100 000 tons of mine waste. The released total metal load to the lake can thus be estimated to equal 800 tons of copper, 5 400 tons of zinc and 300 tons of lead. The leachate water in the brook connecting the tailings area and the lake was typical AMD water (SO_4^{-2} 217 mg l^{-1}, Pb 40 µg l^{-1}, Cu 640 µg l^{-1}, Zn 14 300 µg l^{-1}) (Räisänen et al. 2005). The tailings area has recently undergone some remediation and the direct drainage to the lake has been dammed.

3. Materials and Methods

3.1 Sampling

3.1.1The Archipelago Sea

Sediment cores AS2-VH2 (**I**) (60°03.31N, 22°17.49E in WGS84) and AS2-PC4 (**I**) (60°02.60N, 22°17.71E in WGS84) were retrieved onboard R/V Aranda (Finnish Environment Institute) (Fig. 1). The coring locations were selected on the basis of results from acoustic sub-bottom profiling. Core AS2-VH2 (length 438 cm) was retrieved with a vibro-hammer corer, while AS2-PC4 (length 597 cm) was retrieved with a piston corer. The water depths for AS2-VH2 and AS2-PC4 were 34 m and 32 m, respectively. The sampling of the Seili core (length 55 cm, **II**) was carried out onboard R/V Aurelia (The Archipelago Research Institute). The sampling site, which is a basin deeper than its surroundings, was located at the Seili intensive monitoring station (60°15.34 N and 21°57.20 E) (Fig. 1). Water depth at the sampling site was 50.6 m. The Käldö Fjärd core (**II**) was collected in a sheltered bay located at 60°13.02 N and 21°59.69 E. The core (length 87 cm) was retrieved at the deepest part of the bay (12.3 m) with a mini-Mackereth corer (Mackereth 1969).

3.1.2 Lake Orijärvi and Lake Määrjärvi

The sampling of the ORI-1 and ORI-2 (**III**) was done from the 11 meter deep depression about 800 meters from the outer edge of the tailings (Fig. 1). A crust-freeze core (ORI-1) was collected to describe the sediment structures and to collect material for diatom and chrysophyte cyst analyses. Subsamples for elemental analyses and datings (ORI-2) and the “top/bottom” cores N1-N8 (**IV**) (Fig. 1) were obtained using the Limnos gravity corer (Kansanen et al. 1991).

3.2. LOI and chemical analysis

Organic matter content of the subsamples (**I**, **II**, **III** and **IV**) was quantified as the weight loss on ignition (LOI) at 550 °C for 2.5 h (Bengtsson & Enell 1986).

The top 15cm of the core ORI-2 (**III**) was analysed for Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sr, Ti, and Zn at the laboratory of the Geological Survey of Finland by ICP-AES to reconstruct the history of metal load from the past mining activities. A detailed methodology can be found in paper **III**.

3.3. Dating of the sediment cores

Dating is one of the most important issues in palaeolimnological research. It provides a distinct frame within the results can be interpreted and compared. For the long sediment cores from the Archipelago Sea (**I**) the sediment chronology was obtained by a combination of palaeomagnetic and AMS ^{14}C methods as described for AS2-VH2 in Virtasalo et al. (2006), and for AS2-PC4 in Virtasalo et al. (2007). The shorter cores (Seili and Käldö Fjräd, **II**) were analysed for ^{210}Pb, ^{226}Ra and ^{137}Cs by direct gamma assay in the Liverpool University Environmental Radioactivity Laboratory using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors. Sediment chronologies were calculated using the constant rate of supply (CRS) dating model for ^{210}Pb together with chrono-stratigraphic dates determined from the ^{137}Cs record. The Ori-1 core (**III**) analysis for ^{210}Pb and ^{137}Cs was carried out at the Accelerator Laboratory of the Department of Physics, University of Jyväskylä. A chronology was obtained using the CIC model (constant initial concentration), which was in good agreement with ^{137}Cs and soot particle concentrations (Salonen & Tuovinen 2001).

3.4. Microfossils

3.4.1 Diatom analysis

The microfossil samples were prepared for analysis according to the method described in Battarbee (1986) and Renberg (1990). Identifications were carried out with light microscopes using phase-contrast illumination at 1000x magnification. A minimum of 300 diatom valves, excluding *Skeletonema costatum* (Greville) Cleve and *Chaetoceros* spp., were counted at each level. Diatom taxonomy is based on Krammer & Lange-Bertalot (1986–1991), Cleve-Euler (1951-1955), Mölder & Tynni (1967–1973), Snoeijs et al. (1993-1998), Witkowski (1994), Witkowski et al. (2000), Håkansson (2002) & Hausman & Lotter (2001). The use of taxa aggregates (**II**) followed taxonomic conventions of the MOLTEN project (http//:craticula.ncl.ac.uk/MOLTEN/jsp). *Chaetoceros* spp. resting spores, chrysophyte cysts and ebridians were also enumerated but, as their indicator value is partially unknown, no comprehensive conclusions are based on their occurrence (**I** and **II**). The assignment of diatom species to ecological and pH groups was done according to Krammer & Lange-Bertalot (1986-1991), Lowe (1974), van Dam et al. (1994) and Stevenson et al. (1991), and with respect to their salinity tolerance into marine, brackish-water and freshwater taxa according to Snoeijs et al. (1993–1998), Krammer & Lange-Bertalot (1986–1991) and Mölder & Tynni (1967–1973).

3.4.2. Data analysis

The diversity index Shannon H' (**III** and **IV**) was calculated using the PAST statistical software (Hammer et al. 2001) and species richness (**II**) using rarefaction analysis implemented with the program RAREPOLL (Birks & Line 1992). The compositional changes in the diatom assemblages over time were detected with detrended correspondence analysis (DCA, **III** and **IV**) and with detrended canonical correspondence analysis (DCCA, **II**) using the CANOCO for Windows, version 4.0. DCA is a unimodal indirect ordination method that is well suited for analysing relative percentage data (ter Braak & Šmilauer 1998). DCCA is the constrained (canonical) form of detrended correspondence analysis (DCA) (Hill & Gauch 1980). The Software package Zone v. 1.2 (Juggins 1991) was used for stratigraphically constrained cluster analysis (**I** and **II**) and the number of statistically significant zones was calculated using the broken-stick model described in Bennett (1996). The diatom record was divided into local diatom assemblage zones (LDAZ, article **I**) and diatom assemblage zones (DAZ, article **II**) based on the results of cluster and correspondence analysis combined with diatom salinity and habitat grouping.

Diatom-inferred total nitrogen (DI-TN) reconstructions (**II**) were calculated for the cores using a transfer function, which builds upon a previously generated model by Weckström et al. (2004). The calibration data set for the present model includes altogether 103 sites along the Finnish coastline from the Gulf of Bothnia, the Archipelago Sea and the Gulf of Finland. Locally weighted weighted averaging regression and calibration (LWWA) was applied for the quantitative reconstruction of past TN concentrations. Leave-one-out cross-validation was used to give a more realistic estimation of the model performance. Data were screened for outliers and as a result eight sites were removed from the model due to their large residuals (3 standard deviation units) along the TN gradient. The resulting LWWA model is robust with an apparent R^2 of 0.8, an R^2_{jack} of 0.69 and a RMSEP of 0.11 $\mu g\ l^{-1}$(log_{10} units). The model building and reconstruction was executed using the program C2 1.5 (Juggins 2007) and is described in detail in paper **II**. The percentage of taxa that were rare in the calibration data set was calculated in all fossil samples, as the optima estimations for such taxa are potentially unreliable. A rare taxon was defined having a Hill's N2 (Hill 1973) of 5 or less in the calibration data set (Engels et al. 2008). Squared residual distance of the modern samples to the TN axis in a canonical correspondence analysis (CCA) was used as a criterion of lack of fit to TN. Fossil samples can be passively positioned on the TN axis through transition formulae. A fossil sample with a residual distance equal to or larger than the residual distance of the extreme 10 % of the calibration data set was considered to have a poor fit to TN (Birks et al. 1990). CCA was performed with CANOCO for Windows, version 4.0.

4. Results and discussion

4.1. The Archipelago sea

4.1.1. Core lithology and sediment chronology of cores AS2-PC4 and AS2-VH2

The lithology, formal stratigraphy, physical properties and the chronology based on combined palaeomagnetic and AMS ^{14}C methods for AS2-VH2 and AS2-PC4 have been presented in Virtasalo et al. (2005b, 2006, 2007, in press) and they are only very briefly summarised below.

The basal part of AS2-PC4 consists of varved glaciolacustrine rhythmites (Dragsfjärd Alloformation, **I**) deposited between 11 350 and 11 100 cal. BP. An erosional truncation separates the glacial rhythmites from the overlying unit composed of rhythmite clasts floating in a clay–silt matrix deposited during 11 100 – 10 300 cal. BP (Trollskär Formation). The mixed unit is interpreted to be a debris-flow deposit partly composed of material reworked from the underlying rhythmites. This unit is overlain by a gradational lithofacies succession comprising of weakly to indistinctly layered clay facies, monosulphide-banded clay facies, monosulphide-mottled clay facies and bluish-grey clay facies. The last two facies are rich in pyrite concretions. These are the post-glacial lacustrine clays of Sandön Formation accumulated during 10 300 – 7 600 cal. BP. LOI values increase at the unit base, remain relatively constant upwards, and increase again in the bluish-grey facies. The upper parts of the monosulphide mottled facies and the bluish-grey facies are also included in AS2-VH2. An erosional unconformity bounds the formation at the top. Superimposed are the organic-rich muds characterized by alternating strongly bioturbated, weakly laminated, and thinly laminated lithofacies. These brackish-water muds (Nauvo Alloformation) have been deposited since 7 600 cal. BP. LOI values are high and increase upwards. Pyrite concretions are abundant as well, but they are smaller than those in the underlying deposits.

4.1.2. Core lithology and sediment chronology of the Seili and the Käldö Fjärd cores

The lithology, physical properties and the chronology have been described in detail in article **II** and are briefly summarised below.

The Seili core is dark-coloured, organic-rich mud characteristic of the brackish-water muds of the Baltic Sea (Nauvo Alloformation in Virtasalo et al. 2005b, **II**). The sediment structure is more or less laminated in the topmost 35 cm, indicating predominantly low-oxygen conditions on the seafloor. The laminae thickness is thinner than the calculated annual sediment accumulation rate suggesting that the lamination is non-annual, but records shorter-term fluctuations in the lateral energy transport. The core has a thin, loosely consolidated, oxidized surface layer.

The basal part of the Käldö Fjärd core is grey. Above the depth of 28 cm the core is dark coloured and organic rich. The core top is black with patches of white sulphur bacteria indicative of oxygen deficiency. The top 6 cm of the core are laminated with the laminae thickness approximating the sedimentation rate of 1 cm yr^{-1} suggesting that the laminae are annual.

The results of the total ^{210}Pb activity and the artificial fallout of ^{137}Cs from the 1986 Chernobyl accident date the base of the Seili core at 55 cm to 1962. In the Käldö Fjärd core, the CRS ^{210}Pb dating model together with the ^{137}Cs stratigraphy place 1986 at a depth of 12.5 cm. For sediment sequences older than the ^{210}Pb record at Käldö Fjärd, a constant rate of mass sedimentation was assumed and ages were extrapolated to the base of the sediment core using an age-depth model (3rd order polynomial function; $r = 0.98$).

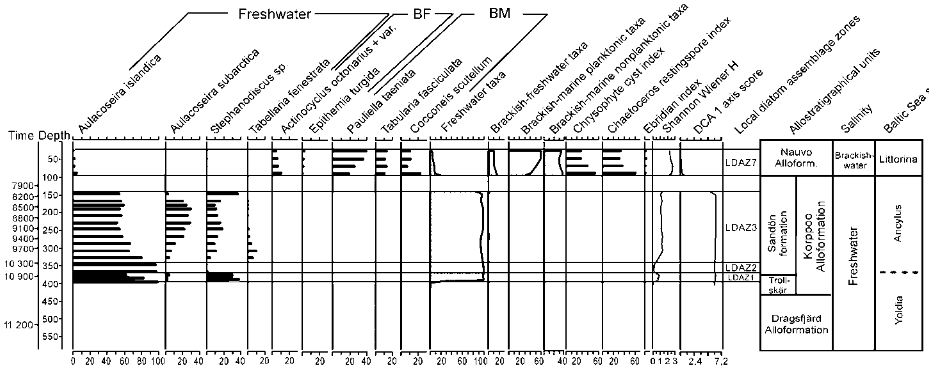
Both cores show relatively uniform sedimentation rates up to ca. 1970 in Käldö Fjärd and to the mid 1980s in Seili. Since then sedimentation rates have generally been higher, with brief episodes of rapid accumulation around 1980 in Käldö Fjärd and in the early 1990s in Seili, and again during the last few years. The mean sedimentation rate in Käldö Fjärd since 1998 is more than three times the pre-1970 value. The ^{210}Pb inventory of the Seili core corresponds to a mean annual flux of ca. 500 Bq m^{-2} y^{-1}. Since this is about five times the estimated atmospheric flux, it would appear that the Seili coring site is subject to significant sediment focussing.

4.1.3 Diatom analysis; cores AS2-PC4 and AS2-VH2

4.1.3.1. Freshwater deposits (before 8 150 cal. BP)

The earliest late-glacial deposits of the Archipelago Sea are barren of diatoms. This seems to be characteristic of sediments in pro-glacial lakes (Risberg et al. 1999, Kabailinié 2000, Lapointe 2000, Andrén et al. 2000b, Heinsalu et al. 2000). According to Heinsalu et al. (2000), the very high sedimentation rates near the receding ice margin may dilute diatom concentrations in sediments. Also, the diatom productivity was probably low in turbid, cold water near the receding ice margin (Andrén et al. 2000b, Heinsalu et al. 2000). The first diatoms appear in the Trollskär Formation at the depth of 400 cm around ca. 10 550 cal. BP (Fig. 2). The diatom composition of LDAZ1–3 indicates that in the late-glacial and early post-glacial the Archipelago Sea was a freshwater environment and no salinity increase referable to the Yoldia Sea phase is recognized (**I**). LDAZ 1 (age of top boundary 10 230 cal. BP) and LDAZ 2 (10 230 – 10 030 cal. BP) are dominated by the planktonic freshwater taxa *Aulacoseira islandica* (O. Müller) Simonsen (Fig. 2).

AS2-PC4



AS2-VH2

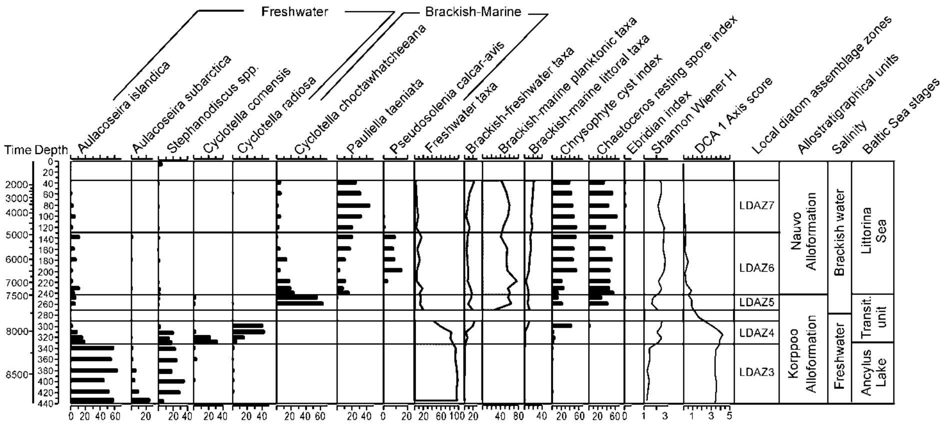


Fig 2. Local diatom assemblage zones and other siliceous microfossils in the cores AS2-PC4 and AS2-VH2. Only the most important diatom taxa are presented. Intervals, where diatoms were too few to be counted with confidence, are toned. Also, the allostratigraphical units (Virtasalo et al. 2005b, in press) and the Baltic Sea palaeoenvironmental phases (Sauramo 1958, Winterhalter et al. 1981, Björck 1995) are presented. From Tuovinen et al. (2008); used with permission. © Springer 2008.

LDAZ 3 (10 030 – 8 100 cal. BP) contains the maximum occurrence of *Aulacoseira subarctica* (37 %), while the relative abundance of *A. islandica* decreases compared to the underlying unit (Fig. 2). *Cyclotella comensis* Grunow, *Cyclotella radiosa, Cyclotella atomus* Hustedt, *Cyclotella schumannii* (Grunow) Håkansson and *Cyclotella tripartita* are also present in small amounts. LDAZ3 is similar to the Ancylus Lake diatom assemblages from the Bornholm Basin (Andrén et al. 2000a), Gotland Basin (Andrén et al. 2000b, Sohlenius et al., 1996) and Gulf of Finland (Åker et al. 1988, Heinsalu et al. 2000) indicating higher nutrient concentrations than the assemblages in the preceding zones. The higher diatom diversity of LDAZ3 and the presence of eutrophic *Cyclotella* species, like *Cyclotella atomus*, may be due to the higher temperature and nutrient content of surface water. The LDAZ3 top boundary roughly coincides with the lower boundary of the bluish-grey facies of the Sandön Allomember in AS2-PC4 (Fig. 3, **I**).

4.1.3.2. Freshwater to brackish-water transition (8 150 – 7 600 cal. BP)

The Holocene lacustrine to brackish-water (Ancylus–Mastogloia–Littorina) transition of the BSB is recorded in core AS2-VH2 as a two-phase transition (LDAZ4 and LDAZ5) during 8 150 – 7 600 cal. BP. (Fig. 2, **I**). This two-phase transition in AS2-VH2 appears distinct from the offshore sediments of the BSB, where the Ancylus–Mastogloia limit is stratigraphically often poorly defined or even impossible to distinguish (Winterhalter et al. 1981). The Ancylus–Mastogloia transition is recorded in most cases by the increasing abundances of non-planktonic freshwater and brackish-freshwater species, the first occurrence of the planktonic *Chaetoceros* spp., and by the decreasing abundances of planktonic *Aulacoseira islandica* and *Stephanodiscus* spp. (Åker et al. 1988, Andrén et al. 2000a, 2000b, Heinsalu et al. 2000, Borgendahl & Westman 2006). In AS2-VH2, the transition is reflected as a shift in dominant planktonic species, from *A. islandica* to *Cyclotella comensis* and *Cyclotella radiosa* (LDAZ4 8 150 – 7 900 cal. BP), and later to *Cyclotella choctawhatcheeana* Prasad (LDAZ5 7 700 – 7 600 cal. BP). An interval poor in diatoms at 295–260 cm (7 900 – 7 700 cal. BP) separates LDAZ4 from the overlying LDAZ5. Krammer & Lange-Bertalot (1986 – 1991) note that *C. radiosa* is commonly found in eutrophic lakes. However, many diatom taxa indicating eutrophication in freshwater may occur in brackish water as well (Lange-Bertalot 1979, Hoffmann 1994). These species have a wide conductivity tolerance, and they are generally poor indicators of eutrophy in brackish waters, where the conductivity is very high regardless of trophy levels due to the high ion concentrations (Snoeijs 1999). Therefore, the increase of *C. radiosa* in LDAZ 4 may record increasing surface water salinity instead of increasing nutrient availability. The appearance of the *Chaetoceros* ssp. resting spores in the uppermost part of LDAZ4 (7 950 cal. BP) indicates weakly brackish conditions (Fig. 2, **I**). In the present Baltic Sea, *C. radiosa* is found in salinities ranging from 0 ‰ to 8 ‰ in the Lithuanian and Latvian coastal waters (Snoeijs & Potapova 1994). A slight salinity increase is also implied by the appearance of an impoverished assemblage of identifiable bioturbation structures (trace fossils) in these sediments at ca.7 800 cal. BP (Virtasalo et al. 2006).

An interval with a very low abundance of diatoms overlies LDAZ4 (Fig. 2). A similar interval seems to be characteristic for the Ancylus – Littorina transition in the Baltic Proper (Åker et al. 1988, Sohlenius et al. 1996, Andrén et al. 2000a, Andrén et al. 2000b, Heinsalu et al. 2000). According to Andrén et al. (2000b), the high number of littoral taxa in this diatom-poor section indicates deposition of diatoms transported from the coastal zone, and very low pelagic diatom production in the basin. Yet, LOI increases in the diatom-poor interval in AS2-VH2 (**I**) indicating higher biological productivity than in the underlying units. This also coincides with an increase in cyanobacterial blooms in the BSB (Bianchi et al. 2000), which likely contributes to the increase in organic carbon content in the sediment.

The base of LDAZ5 is taken to indicate the onset of fully brackish-water conditions in the area at 7 700 cal. BP (Fig. 2). The abundance of *C. choctawhatcheeana* in LDAZ5 indicates substantially higher salinity and trophic state of the basin than in underlying zones. This species has been associated with anthropogenic disturbances and increasing eutrophication in the present Baltic Sea (Andrén et al. 2000b, Weckström 2006). However, it is worth noticing that the most abundant planktonic diatom species in LDAZ4 (*C. comensis*, *C. radiosa*) and in LDAZ5 (*C. choctawhatcheeana*) are referred to as warm water species in the literature (Stoermer 1977, HELCOM 2004). They are components of the summer plankton, and therefore unlikely to be major contributors in the spring bloom. According to Heiskanen & Kononen (1994), during the ice-free winters, or when the ice-cover breaks up early in March, the spring phytoplankton bloom at the entrance of Gulf of Finland is generally dominated by dinoflagellates. When the ice-cover lasts until April, diatoms dominate the vernal bloom together with the dinoflagellate *Peridiniella catenata* (Kononen & Niemi 1984). Furthermore, Heiskanen (1998) suggests that in the present northern Baltic Sea, increasing eutrophication together with a warming climate may result in decreased diatom production in the pelagic spring bloom. Recently, the spring diatom biomass in the Baltic Sea has dropped dramatically from 1988 to 1989 and has stayed at this low level, whereas dinoflagellate biomasses have shown a steady increase from 1989 onwards (Wasmund & Uhlig 2003). This may partly be caused by recent silica limitation in the Baltic Sea due to eutrophication (Papush & Danielsson 2006), but could also be a result of the generally warm winters, reduced ice cover and earlier thermal stratification of the water column in spring. The problem with percentage abundances is that a real increase in one species' abundance is reflected in an apparent decrease in other species' abundances. Therefore, the relative increase of summer plankton taxa in LDAZ4 and LDAZ5 can be a result of a true decrease of the spring-blooming species or it might be the result of eutrophication that triggered an increase in the (eutrophic) summer species, which overpower the abundances of other diatoms. Therefore, it is difficult to draw conclusions whether the increase in summer plankton in LDAZ4 and LDAZ5 (and the concomitant decrease in spring-blooming diatoms) is a result of warming climate, eutrophication or both. The LDAZ5/LDAZ6 boundary coincides with the Korppoo Alloformation / Nauvo Alloformation boundary in AS2-VH2 (Fig. 3).

4.1.3.3 Brackish-water deposits (after 7 600 cal. BP)

The appearance of the marine planktonic species *Pseudosolenia calcar-avis*, *Thalassionema nitzschioides* (Grunow) Grunow ex Hustedt, and *Thalassiosira oestrupii* (Ostenfeld) Hasle in LDAZ6 (7 600 – 4 950 cal. BP) indicate higher salinity than in the underlying zones (Fig. 2). The diatom flora is similar to that in the Gotland basin during the most saline sub-phase of the Littorina Sea (Sohlenius et al. 1996, Andrén et al. 2000b). An increased trace-fossil diversity also reflects increased salinity at this level (Virtasalo et al. 2006). The presence of *Pauliella taeniata* indicates ice-formation during the winters. The decreasing abundances of *Pseudosolenia calcar-avis* with the simultaneous increase of *Pauliella taeniata* in LDAZ7 (4 950 – 1 830 cal. BP) indicate a colder climate and lower salinity after 5 000 cal. BP. This is in accordance with Emeis et al. (2003), who concluded that surface and deep-water salinities were highest in the Gotland Deep during the Holocene maximum warming at 7 800 – 5 100 cal. BP, but decreased during 5 100 – 3 100 cal. BP.

The intervals with very low diatom abundances in the brackish-water muds typically coincide with strongly bioturbated lithofacies, or with thin layers of plant debris or coarser clastic material indicative of reworking of the older sediments. In addition, the diatom valves are strongly fractured within these intervals. Comparable co-occurrence of low diatom abundance and sediment bioturbation has been reported for the Gotland Basin (Andrén et al. 2000b, Sohlenius et al. 2001). The presence of weakly silicified diatom valves along with the fractured diatom frustules suggests mechanical breakage of the valves rather than dissolution.

4.1.4. Stratigraphic considerations

This study shows that the Yoldia Sea and Ancylus Lake deposits are difficult to tell apart in the Archipelago Sea based on sedimentary diatoms. In addition, the two-phase transition recorded by the sedimentary diatoms during the lacustrine (Ancylus Lake) to brackish-water (Littorina Sea) transition in the area is different from those described earlier for both the coastal and offshore areas of the Baltic Sea Basin. It appears that the conventional practice of sediment classification based on the palaeoenvironmental phases of the Baltic Sea Basin provides a poor means for correlating the late- and post-glacial sediments of the Archipelago Sea to sediments from other areas of the basin.

The LDAZ3/LDAZ4 boundary roughly coincides with the lower boundary of the bluish-grey facies of the Sandön Allomember in AS2-PC4 (Fig. 3, **I**). The base of LDAZ6 coincides with the Korppoo Formation / Nauvo Formation boundary in AS2-VH2. However, most of the LDAZ boundaries do not correlate with a visual change in the sediments, and vice versa. Therefore, in order to understand and compare spatial differences in the palaeoecological and palaeoenvironmental development of BSB, biostratigraphic units have to be treated independently from the visual sediment characteristics.

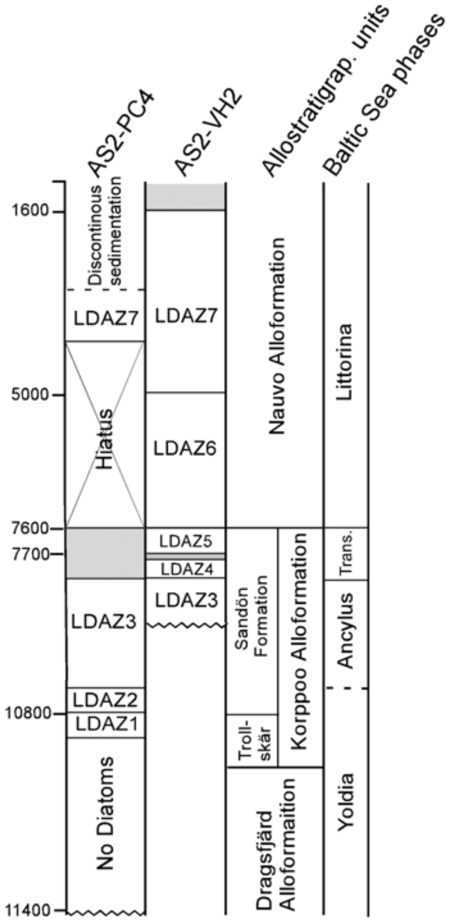


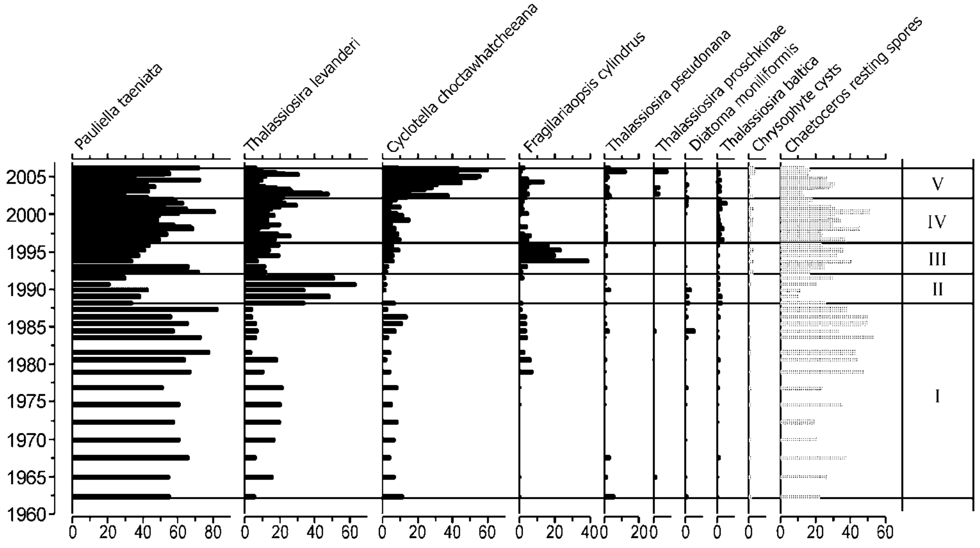
Fig. 3. Correlation between LDAZs and allostratigraphic units by Virtasalo et al. (2005b). Also, the Baltic Sea palaeo-environmental phases (Sauramo 1958, Winterhalter et al. 1981, Björck 1995) are presented. Zigzag lines indicate core bottoms. Intervals, where diatoms were too few to be counted with confidence, are toned. Modified from Tuovinen et al. (2008), used with permission. © Springer 2008.

4.1.5. Diatom analysis; Seili and Käldö Fjärd cores

Overall, the diatom assemblages were dominated by the species *Pauliella taeniata* (mean abundance approximately in the Seili core 50 % and in the Käldö Fjärd core 60 %) (Fig. 4). The diatom assemblages of the cores were divided into 5 (Seili core) and into 3 (Käldö Fjärd core) statistically significant diatom assemblage zones (DAZ).

The oldest zone in Käldo Fjärd core (DAZ 1) (pre ca. 1825) includes only one sample (Fig. 4). This sample shows a marked component of benthic species (54 %) in addition to the dominance of *P. taeniata*. In DAZ 2 (ca. 1825 – 1996) the abundance of benthic taxa decreases clearly and the zone is dominated by planktonics (mean approximately 80 %). In DAZ 3 (1996 –present), *Cyclotella choctawhatcheeana* and *Thalassiosira proschkinae* Makarova increase substantially, with a reciprocal decrease in *P. taeniata*. *Fragilariopsis cylindrus* (Grunow) Krieger peaks to its highest abundance in the topmost sample. *Chaetoceros* spp. resting spores are abundant throughout the core, but reach their highest percentage abundances during the 1960s – 1970s.

Seili core



Käldö Fjärd core

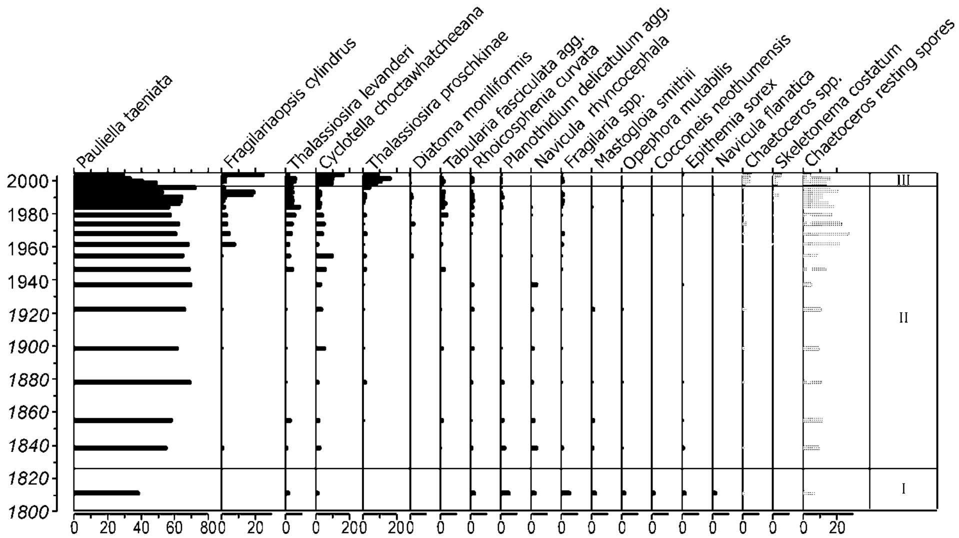


Fig. 4. Diatom assemblage zones and other siliceous microfossils in the Seili core and the Käldö Fjärd core. Only the most important diatom taxa are shown. From Tuovinen et al. (2009); used with permission. © Springer 2009.

The brackish planktonic species *P. taeniata* dominates the DAZ1 (1962 – 1988) in the Seili core (Fig. 4). *F. cylindrus* increases in abundance in the upper part of the zone, where also *Chaetoceros* spp. resting spores have their maximum occurrence. DAZ 2 (1988 – 1992) is characterised by the highest relative abundance of the brackish planktonic *Thalassiosira levanderi*. DAZ 3 (1992 – 1996) starts with a peak of *P. taeniata* but is generally characterised by the high abundances of *F. cylindrus*. In DAZ 4 (1996 – 2002), the dominant species are *P. taeniata* and *T. levanderi*. The topmost zone, DAZ 5 (2002 – 2006), is characterised by an increase in *C. choctawhatcheeana*, *Thalassiosira pseudonana* Hasle and *T. proschkinae* and a decrease in the abundance of *Chaetoceros* spp. resting spores.

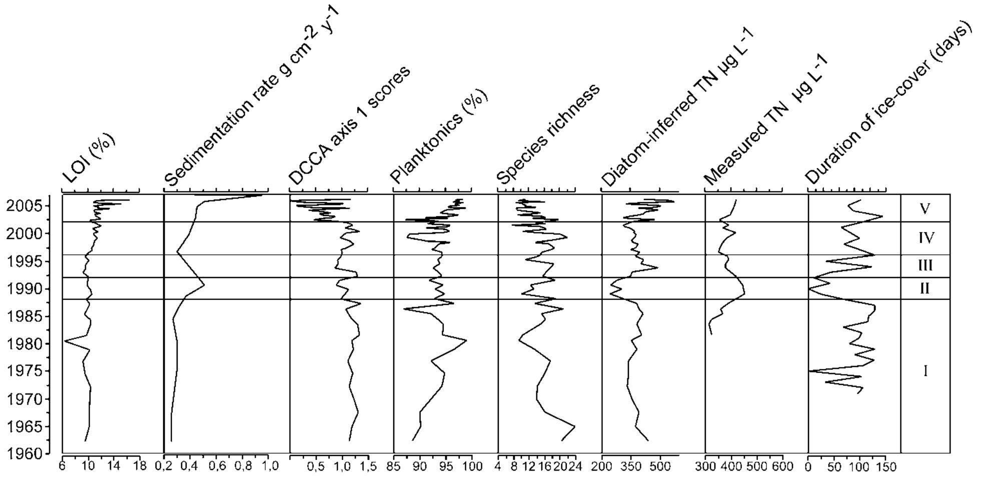
The lowermost sample in DAZ 1 in the Käldö Fjärd core dating to the early 1800s has a reconstructed TN value of about 380 µg l^{-1} (Fig. 5). In DAZ 2, TN concentrations varied relatively little around about 400 µg l^{-1} with higher values in 1991 (about 450 µg). In DAZ 3, concentrations show a steady increase to just above 500 µg l^{-1} at the core top. In DAZ 1 in the Seili core, reconstructed TN values vary between about 300 and 440 µg l^{-1}, with the highest values at the core bottom and again close to the upper part of the zone (Fig. 5). There is a marked drop in TN concentrations in DAZ 2 to about 240 µg l^{-1}. TN increases again in DAZ 3 and peaks to a value of about 490 µg l^{-1} in 1994 decreasing thereafter. DAZ 4 shows relatively little variation around about 360 µg l^{-1} TN. In the topmost DAZ 5, the concentrations show a generally increasing trend with the highest inferred value of about 570 µg l^{-1} in the Seili core in 2006. The fossil diatom taxa in the cores are well-represented in the modern calibration data set, as all core samples have less than 5 % of rare taxa (N2 <5). However, except for the topmost zone of the cores, the majority of the samples have a poor fit to TN.

4.1.5.1. Indications of eutrophication

Eutrophication has been observed to increase the abundance of small planktonic diatoms both in marine and freshwaters due to increased turbidity (Cooper & Brush 1991, Bennion et al. 2004, Weckström 2006). In the Seili and Käldö Fjärd cores, *Cyclotella choctawhatcheeana*, *Thalassiosira proschkinae* and *Thalassiosira pseudonana* become more abundant (the last taxon only at Seili) towards the core tops starting in the late 1990s at Käldö Fjärd and in the early 2000s at Seili (Fig. 4). These taxa are common in eutrophied coastal embayments in the Baltic Sea (Clarke et al. 2003, Weckström 2006, Ellegaard et al. 2006). Increased sedimentation rates in the late 1990s – early 2000s in both cores coincide with these changes (Fig. 5, **II**).

The diatom-inferred TN reconstructions, which are based on yearly means of measured TN data in the calibration data set, generally show little variation except for an increase in TN values at the core tops concomitant with the increase in small planktonic taxa, and a marked decrease in the Seili core in the late 1980s – early 1990s. The increase at the core tops likely reflects very recent eutrophication at both sites, whereas the decrease at Seili is more likely to be a reconstruction error caused by taxa in the inference model responding to other environmental variables than TN. This will be discussed in more detail in the following chapters. The background (pre-1900) TN concentrations at Käldö Fjärd fluctuate around 400 µg l^{-1} with concentrations staying at this level until the late 1990s. It is likely that the background concentrations at Seili are similar. However, the core only reaches back to the 1960s.

Seili core



Käldö Fjärd core

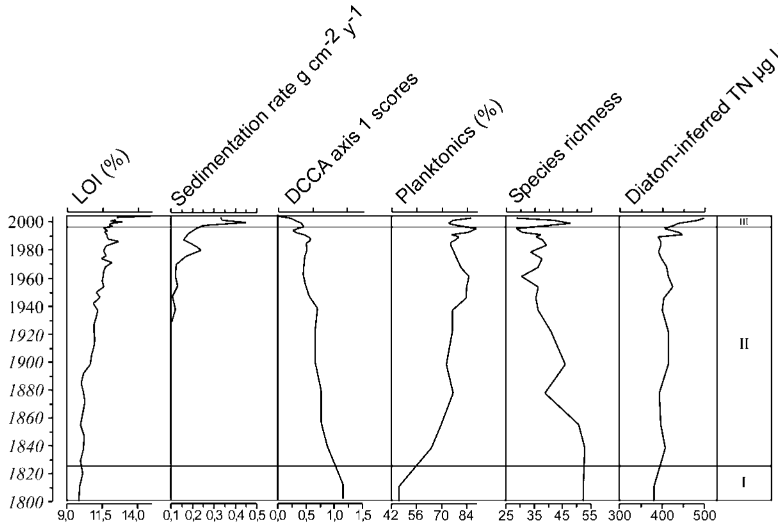


Fig. 5. Summary diagram of the Seili core and the Käldö Fjärd core showing LOI, sedimentation rate, DCCA1 axis scores, abundance of planktonic taxa, diatom species richness, diatom-inferred TN, measured TN (only in the summary diagram of the Seili core, provided by the Finnish Environment institute) and duration of ice-cover (only in the summary diagram of the Seili core, provided by the Ice Service of the Finnish Institute of Marine Research). All dates prior 1928 are extrapolated and written in italics. From Tuovinen et al. (2009); used with permission. © Springer 2009.

Apart from the increase in small planktonic taxa and the moderate increase in reconstructed TN concentrations at the core tops, no clear signs of eutrophication can be seen in the diatom assemblages. However, it seems that turbidity has increased in the Archipelago Sea, as the diverse diatom assemblages were dominated by benthic species in DAZ1 in the Käldö Fjärd core, but also in LDAZ7 in the cores AS2-PC4 and AS2-VH2 benthic species abundance is greater than in all the zones of the Seili core and DAZ3 in the Käldö Fjärd core. Hence it can be concluded that the sedimentary diatom assemblages have been dominated by planktonic taxa since around the mid 1800s. Although signs of eutrophication have been evident in the Archipelago Sea since the 1970s (Pitkänen et al. 1987), our study sites show only relatively recent and moderate nutrient enrichment. Both sites are located in the middle archipelago zone with less nutrient loads from municipalities and agriculture compared to waters close to the mainland (Hänninen et al. 2000).

4.1.5.2. Climatic signals

In the Seili core, TN reconstructions partially fail to trace the actual measured TN concentrations (Fig 5). Especially from the late 1980s to the mid 1990s, the dominating diatom species are most likely more influenced by other factors, like the length of the ice season, than nutrient concentrations. The clear increase in the abundance of *Thalassiosira levanderi* in DAZ 2 causes a marked decrease in the reconstructed TN concentrations due to the relatively low TN optimum this taxon has in the "local" LWWA calibration data sets used for these samples. This decrease is concomitant with the short ice seasons in the late 1980s and early 1990s (Fig. 5). It is possible that *T. levanderi* has an advantage when ice cover is weak or absent, since *Pauliella taeniata* is dependent on the formation of an ice cover (Müller-Haeckel 1985). The above example stresses the importance of comparing the quantitative reconstructions with the actual changes in the individual species abundances and their ecological implications in order to correctly interpret reconstructions. The short ice seasons are not visible in the Käldö Fjärd diatom record. Käldö Fjärd is shallower and more sheltered than Seili and may therefore have been at least partly frozen during the mild winters in the late 1980s to the mid 1990s. Also the short-lived peaks of *T. levanderi* in 2003 and 2005 cannot be explained by the short ice seasons. The peak in the sedimentation rates at Seili in the early 1990s is concomitant with the short ice seasons, most likely due to increased primary production and erosion.

It seems that the diatom assemblages in the coastal areas of the Archipelago Sea, which are located further away from the mainland with relatively low anthropogenic impact, are principally governed by climate fluctuations with a moderate influence of eutrophication visible in the most recent sediments. Olli et al. (2008) report very similar results from the Bothnian Sea. The situation is different in shallow and sheltered coastal embayments along the mainland, where the nutrients override the effects of climate and cause marked changes in diatom assemblages such as pronounced increases in small planktonic *Cyclotella* and *Thalassiosira* taxa and a clear decrease in species richness (Weckström 2006, Weckström et al. 2007).

4.2. Lake Orijärvi and Lake Määrjärvi

4.2.1. Core lithology and sediment chronology

The analyzed ORI-1 core consists of four lithofacies units (**III**). The lowermost part from 60 to 8 cm depth is olive green to greenish grey fine detritus gyttja. Above it, there is a distinct light grey layer between 8 and 6 cm of the sediment core. This portion is sticky and very fine grained. From 6 to 2 cm the sediment is homogenous olive green fine detritus gyttja with occasional black mottling. The topmost 2 cm is brownish loose sediment.

Measured ^{210}Po activity reaches background at the15 cm level and the measured ^{137}Cs activity at about 7 cm depth (**III**). Sediment below 15 cm represents layers older than the 1880's and the uppermost 15 cm of sediment has an average sedimentation rate of 1.4 mm/year. The Cesium-curve indicates that the depth level 7 cm represents the late 1940s, and that the Chernobyl-peak from 1986 is at about 3 cm below the sediment surface.

4.2.2. History of the metal load

Mining started in the Orijärvi area in the 1750s. However, the early mining did not have a major impact on Lake Orijärvi based on the results of diatom analysis (Fig. 6) and on the fact that most of the metals display a concentration curve peaking in the middle of the analysed uppermost 15 cm sequence in ORI-2 core (**III**). Modern effective mining techniques started in Orijärvi in the 1910s. From this point onwards, the metal load to the lake has been high and the maximum values for zinc, lead, copper and sulphur are more than two orders of magnitude higher than the average background levels for unpolluted lake sediments in Finland (Lahermo et al. 1996). Deposition of copper, lead and zinc (and cadmium) is closely connected with the last extensive mining phase in the 1940s and 1950s. Concentrations of these metals released by the oxidation process are exceptionally high, maximum values for zinc being 3.4 %, for copper 0.39 % and for lead 0.29 % at the depth of 8 to 5 cm below the sediment surface. The estimated copper load has altogether been ca. 800 tons, which is comparable to the load which impacted Lake Orta in Italy (Ruggiu et al. 1998). The metal load to Lake Orta was as much as 60 - 70 t/year from the late 1920s to late 1950s, leading to a water concentration of 100 μg l^{-1} copper in the late 1950s. This led to a collapse of the aquatic ecosystem including severe changes in diatom assemblages. In addition, Lake Orijärvi was impacted by zinc, lead and cadmium. Altogether this has severely affected the lake ecosystem.

4.2.3 Impact on diatoms

In the past, the diatom assemblages of Lake Orijärvi and Lake Määrjärvi have been slightly different from each other, however, both lakes had diverse planktonic and benthic communitites typical of circumneutral oligotrophic lakes. (Table 1, **III** and **IV**). Altogether 219 species belonging to 27 genera were found. The planktonic diatoms dominated in relative abundances (combined altogether from ca. 40 % up to ca. 70 %), but the benthic communities were more diverse. Out of the 219 species 188 were benthic and only 27 planktonic. The most abundant planktonic species in both lakes belonged to the genera *Cyclotella, Aulacoseira, Tabellaria* and *Asterionella* (Table 1). The most abundant species in the genus *Cyclotella* were *C. radiosa* (Grunow) Lemmermann, *C. rossii* Håkansson, *C. pseudostelligera* Hustedt, *C. tripartita* Håkansson and species belonging to the *C. bodanica* -group. Within the genus *Aulacoseira* the dominant species was the planktonic *Aulacoseira subarctica* (O. Müller) Haworth. Also the tychoplanktonic *Tabellaria flocculosa* (Roth) Kützing and the planktonic *Asterionella formosa* Hassal were fairly abundant. The dominant benthic genera were *Achnanthes, Fragilaria* and *Navicula*.

The main changes in the diatom flora have been concomitant with the changes in metal concentrations in the sediment (**III**). The relative abundances of *Cyclotella radiosa* and *C. pseudostelligera* started to decrease at the depth of 17.5 cm but the first marked changes in diatom assemblages occurred between the depths 10 cm and 5 cm in the ORI-1 core (Fig. 6). The relative abundances of *Tabellaria flocculosa* and *Asterionella formosa* first increased reaching their maxima at the depths 7 cm and 9 cm, respectively, and drastically decreased close to zero at the depth 6 cm. The species in the *Fragilaria capucina* -group and *Brachysira vitrea* ((Grun.) R. Ross in Hartley) increased in relative abundances markedly at the depth of 7 cm. Above that level the planktonic diatoms belonging to the genera *Aulacoseira* and *Cyclotella* became rare until at the depth 56 cm they disappeared completely. In the top 5 cm of the core ORI-1 the relative abundance of *Achnanthidium minutissimum* (Kützing) increased markedly and the abundances of *Brachysira vitrea* and the species in the *Fragilaria capucina* -group decreased.

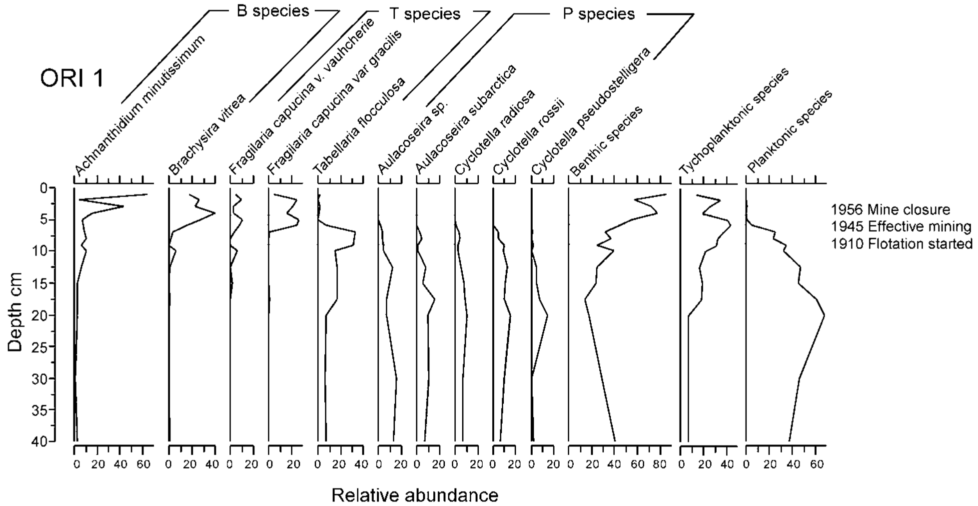


Fig. 6. Summary diagram of the ORI-1 core showing the most important diatom taxa, and the proportions of the benthic, tychoplanktonic and planktonic diatoms (Modified from Salonen et al. 2006).

Table 1. The most abundant diatom species in Lake Orijärvi and Lake Määrjärvi sediments.

Lake Orijärvi background assemblages	**Lake Orijärvi present assemblages**
Tabellaria flocculosa	*Achnanthidium minutissimum*
Aulacoseira sp.	*Brachysira vitrea*
Aulacoseira subarctica	*Fragilaria capucina* var *vaucherie*
Cyclotella rossii	*Fragilaria capucina* var *gracilis*
Cyclotella radiosa	*Achnanthes helvetica*
Brachysira vitrea	*Caloneis tenuis*
Cyclotella pseudostelligera	*Achnanthes pusilla*
Fragilaria brevistriata	*Fragilaria capucina* var *rumpens*
Achnanthidium minutissimum	*Fragilaria construens* var *ventner*
Navicula aboensis	*Navicula* spp.
Cyclotella bodanica var *lemanica*	*Tabellaria flocculosa*
Achnanthes pusilla	*Achnanthes daonensis*
Navicula vitiosa	*Achnanthes* sp.
Achnanthes helvetica	*Neidium hercynicum*
Cyclotella tripartita	*Achnanthes acares*
Lake Määrjärvi background assemblages	**Lake Määrjärvi present assemblages**
Aulacoseira sp.	*Aulacoseira subarctica*
Aulacoseira subarctica	*Brachysira vitrea*
Cyclotella radiosa	*Achnanthidium minutissimum*
Tabellaria flocculosa	*Aulacoseira* sp.
Cyclotella rossii	*Fragilaria capucina* var *gracilis*
Cyclotella pseudostelligera	*Cyclotella rossii*
Asterionella formosa	*Tabellaria flocculosa*
Achnanthidium minutissimum	*Fragilaria nanana*
Navicula aboensis	*Fragilaria capucina* var *vaucherie*
Cyclotella iris	*Achnanthes helvetica*
Cyclotella bodanica var *lemanica*	*Cyclotella radiosa*
Cyclotella tripartita	*Fragilaria capucina* var *rumpens*
Stephanodiscus sp.	*Nitzschia* sp.
Navicula vitiosa	*Stephanodiscus* sp.
Fragilaria exigua	*Fragilaria brevistriata*

The spatially spread top/bottom samples N1, N3 and N4 of Lake Orijärvi show similar marked changes, i.e. a shift to a complete dominance of benthic species and very low biodiversity, despite the greater distance from the tailing area compared to core ORI-1 (Fig. 7, **IV**). In the top samples of N1, N3 and N4 no planktonic species were present, and they were dominated by the benthic species *Achnanthidium minutissimum* and *Brachysira vitrea* (Table 1). In the top sample N1 ca. 10 % of the *Achnanthidium minutissimum* valves were deformed (**IV**).

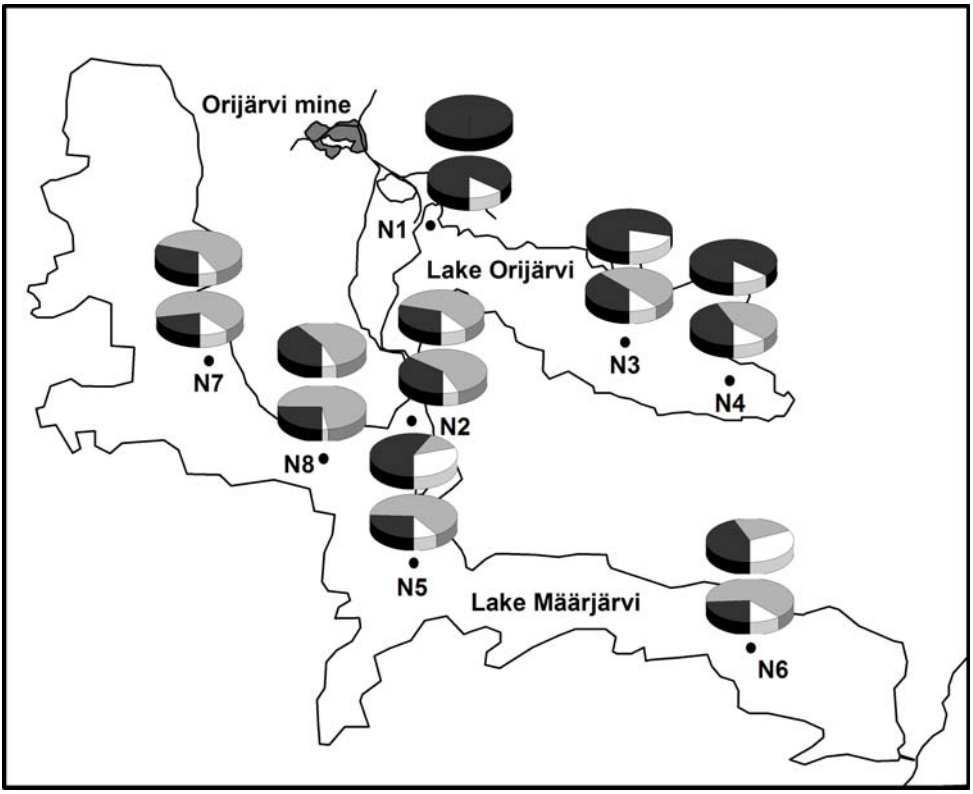


Fig. 7. Proportions of the benthic (dark grey), planktonic (light grey) and tychoplanktonic (white) diatoms in the top and bottom samples of Lake Orijärvi and Lake Määrjärvi.

The Lake Määrjärvi diatom communities show less drastic changes than the ones in Lake Orijärvi. However, the AMD from the tailings has still had a clear impact on the diatom communities, especially on the populations N5 and N6 (Fig. 7). The proportion of both planktonic diatoms and species diversity in the top samples have decreased indicating moderate contamination. In the top samples of N5 and N6 the dominating species were *Fragilaria capucina* var *gracilis* (Östrup) Hustedt, *Brachysira vitrea* and *Achnanthidium minutissimum* (Table 1).

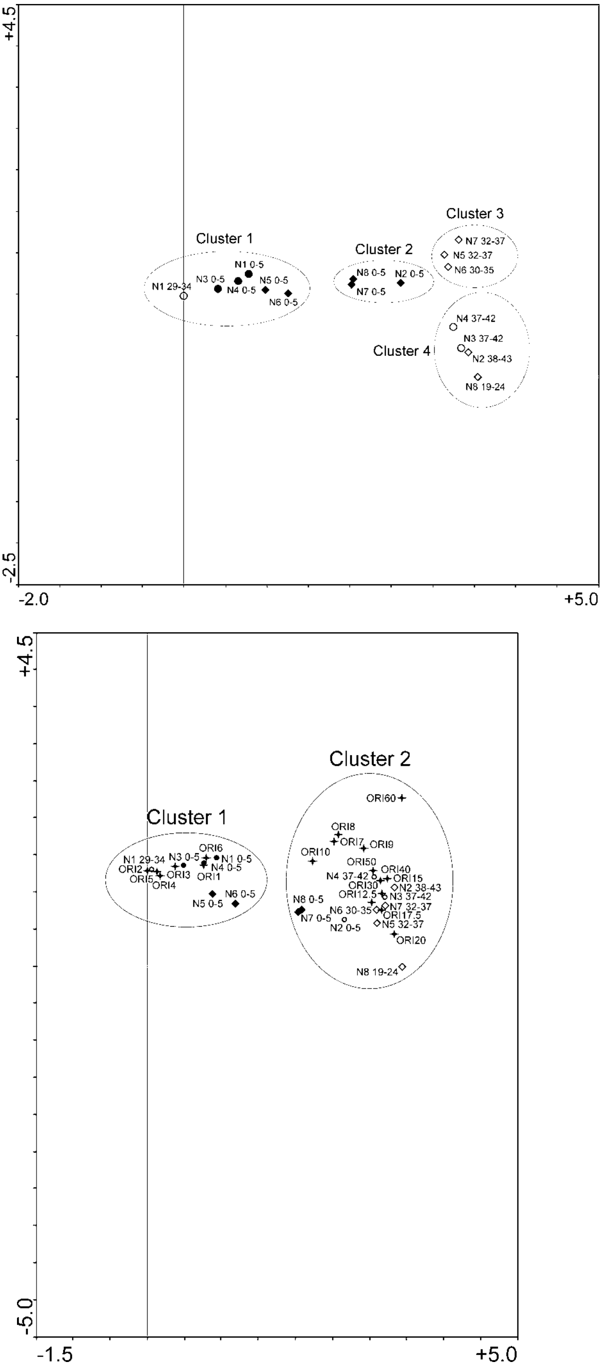
The core N7 is not so strongly affected by the current carrying the contaminated water from Lake Orijärvi, and therefore it is surprising that there are also marked changes in the planktonic communities of this core (Fig. 7). In the top sample of N7 the most abundant species were *Aulacoseira subarctica*, *Aulacoseira* sp., *Achnanthidium minutissimum, Fragilaria nanana* Lange-Bertalot and *Brachysira* *vitrea.* The proportion of planktonic taxa in the top sample N7 was only slightly smaller than in the bottom sample while the diversity was clearly lower.

Cores N2 and N8 are somewhat problematic, because they show only little or no changes in diatom assemblages. In the top samples of N2 and N8, the dominating species were the planktonic *Cyclotella rossii, Aulacoseira* sp., *A. subarctica*, and *Achnanthidium minutissimum.* Core N2 has been derived from a slope where the accumulation of sediment due to the bottom topography and bottom currents may not have been continuous. Hence, it may be that the top sample does not represent contemporary sedimentation. The diatom valves in the bottom sample of core N8 were eroded, and therefore the difference between the top and bottom samples might be biased.

The results of the DCA analysis for the top/bottom samples and for the combined dataset of the top/bottom samples and ORI-1 core show very similar results (Fig. 8, **IV**). The samples coinciding with the pre-impact period (ORI-1 core samples below the depth of 7 cm and all bottom samples excluding N1) and the samples showing only a slight impact (top N2, top N7 and top N8) are plotted in one cluster at the right end of axis 1. The samples corresponding to the most severe impacts (the top samples of Lake Orijärvi, ORI-1 core samples above 6 cm and the bottom N1 sample) are clustered at the left end of the first axis. Between these two groups are the top samples of N5 and N6 showing moderate metal impact.

These changes in the diatom flora are clearly the result of the tailings-derived metal impact (cf. Takamura et al. 1989). Similar changes in the diatom communities may occur due to acidification (Battarbee et al. 1999), but there are no signs of decreasing pH according to monitoring data in either of the lakes (**IV**). Due to this characteristic these two lakes provide a unique opportunity to study the effect of metals on diatom communities, since increased metal concentrations are usually accompanied by other perturbations like acidification or cultural eutrophication (Davies et al. 2004, Reavie et al. 2005).

According to this study, planktonic diatoms are more sensitive to metal contamination than benthic taxa, especially the species in the genus *Cyclotella* (*C. radiosa* and *C. pseudostelligera* more sensitive than *C. rossii*). Therefore a decrease in their relative abundance can be seen as an indication of minor metal contamination. As has been noted in many previous studies, particularly *Achnanthidium minutissimum* and *Brachysira vitrea* appear to be very tolerant to extreme metal contamination (Takamura 1990, Ruggiu et al. 1998, Cattaneo et al. 2004, Cattaneo et al. 2008). Cattaneo et al. (2008) reported almost identical changes in plankton communities under severe metal contamination in a Canadian lake. Also the *Fragilaria capucina* -group seems to be tolerant to quite high metal concentrations.



Top/bottom samples

Combined dataset of the top/bottom samples and ORI-1 core

Fig. 8. DCA (detrended correspondence analysis) results showing principal patterns of variation in the diatom assemblages for the top/bottom samples and for the combined dataset of the top/bottom samples and ORI-1 core. Top samples of Lake Orijärvi are marked as filled circles and top samples of Lake Määrjärvi as filled diamonds. Bottom samples of Lake Orijärvi are open circles and bottom samples of Lake Määrjärvi open diamonds. ORI-1 subsamples are shown as crosses (numbers refer to depth of the sample in the Ori-1 core).

The response of individual taxa to metal pollution may reflect different metal handling strategies (Rijstenbil et al. 1994), and the higher stress tolerance of benthic taxa as a whole could be due to a better ability of benthic organisms to adapt to living in a highly variable environment (Cattaneo et al 2007). Ivorra et al. (2000) concluded that the growth form of the *Achnanthidium minutissimum* together with its inherent metal tolerance might explain why this species proliferated after Zn and Cd exposure in their study of the protective role of biofilms for micro-organisms against harmful effects of Zn and Cd. Biofilms are consortia of autotrophic and heterotrophic organisms imbedded in a matrix of polymers and particles, and according to Ivorra et a. (2000) they diminish the effects of metal exposure. This depends on the development stage of the biofilms, because an increased density of the biofilm can lead to increased recycling of nutrients within the biofilms (Riber & Wetzel 1987) hence reducing the dependence of external conditions outside the biofilms.

5. Conclusions

5.1. The Past

5.1.1 The Archipelago Sea

After the last deglaciation, the Archipelago Sea was a freshwater environment. Weak brackish-water influence was observed by 7 950 ±80 cal. BP, but fully brackish-water conditions were not established until 7 700 ±80 cal. BP. The diatoms record fully brackish-water conditions 100 years earlier than was previously inferred using other sediment proxies in the area. The diatom assemblages indicate increasing salinity, warming climate and increased nutrient conditions during this lacustrine to brackish-water transition. The decreasing abundance of *Pseudosolenia calcar-avis*, and the increasing abundance of the ice-cover indicator species *Pauliella taeniata* reflect climate cooling and reduced salinity after 5 000 cal. BP, i.e. after the Holocene temperature maximum.

The European Water Framework Directive regards pre-1850 as realistic background or reference conditions for surface waters. At Käldö Fjärd the reconstructed background concentrations for TN fluctuate around 400 µg l^{-1} staying at this level until the late 1990s. The background concentrations at Seili are assumed to be similar. However, the inference data only reaches back to the 1960s. The diverse diatom assemblages dominated by benthic species (54 %) in DAZ1 in the Käldö Fjärd core can be taken as background diatom assemblages for the Archipelago Sea. Since then, the turbidity has increased and the diatom assemblages have been dominated by planktonic diatoms since around the mid 1800s. It is somewhat surprising that no clear signs of eutrophication were found until very recently. However, both sites are located in the Middle Archipelago Zone with less nutrient loads from municipalities and agriculture compared to waters close to the mainland. TN reconstructions partially fail to trace the measured TN concentrations suggesting that changes in the diatom assemblages at the study sites are generally governed by other factors such as climate fluctuations rather than nutrient concentrations.

5.1.2. Lake Orijärvi and Lake Määrjärvi

In the past, both lakes had diverse diatom assemblages. The ecological reference conditions assessed in this study for Lake Orijärvi and Lake Määrjärvi comprise diverse planktonic and benthic communitites typical of circumneutral oligotrophic lakes, where the planktonic diatoms belonging to the genera *Cyclotella, Aulacoseira, Tabellaria* and *Asterionella* dominate in relative abundances up to ca. 70 %. The benthic communities are more diverse than the planktonic, consisting of diatoms belonging e.g. to the genera *Achnanthes, Fragilaria* and *Navicula*. The mining activity has impacted Lake Orijärvi and Lake Määrjärvi with a severe load of copper, lead, zinc and cadmium but without marked changes in pH. The AMD derived metal impact on the lakes is the strongest thus far recorded in Finland and it has affected the Lake Orijärvi and Lake Määrjärvi diatom communities in two ways; at the community level through a shift in dominant taxa and life forms and at the individual level through alteration in frustule morphology. Lake Orijärvi is extremely affected by the metal impact, whereas there are less drastic changes in the diatom communities in Lake Määrjärvi.

5.2. The present

5.2.1. Archipelago Sea

Recent eutrophication is visible in the topmost diatom assemblage zones of the Seili and Käldö Fjärd cores. TN reconstructions partially fail to trace the actual measured TN concentrations especially from the late 1980s to the mid 1990s. This is most likely due to the dominating diatom species *Pauliella taeniata*, *Thalassiosira levanderi* and *Fragilariopsis cylindrus* being more influenced by factors such as the length of the ice-season rather than the nutrient concentrations. It is concluded that at the study sites the diatom assemblages are nowadays principally governed by ice cover fluctuations, with a slight influence of eutrophication visible in the most recent times.

5.2.2. Lake Orijärvi and Lake Määrjärvi

At present, both lakes still have elevated heavy metal levels, indicating that the impact from the tailings area continues to affect the lakes. Lake Orijärvi diatom assemblages are completely dominated by benthic species and are lacking planktonic diatoms. In Lake Määrjärvi, the proportions of benthic and tychoplanktonic diatoms has increased while the proportion of planktonic diatoms has decreased. The zinc, copper and cadmium concentrations in Lake Orijärvi are three to four times higher and the lead concentration ca. 1,4 times higher than in Lake Määrjärvi.

5.3. The future

5.3.1. Archipelago Sea

The coupling found between ice cover duration and diatom species composition implies that global warming, with reduced ice cover, would have a clear impact on the spring-blooming diatom species composition in the Archipelago Sea area. This is also seen in the LDAZ5 diatom assemblages, which are deposited during the Holocene thermal optimum. The changes within the diatom (and other algal) communities as well as changes between groups of primary producers are likely to have an effect throughout the existing food webs. In addition, increased sediment accumulation in the early 1990s also coincides with the short ice cover seasons, suggesting that warming climate and decreasing ice cover may also enhance organic sedimentation from primary production and increase the storm reworking of seafloor in shallow areas.

5.3.2. Lake Orijärvi and Lake Määrjärvi

In the future, if the metal concentrations of the Lake Orijärvi water decrease to the same level as they are now in Lake Määrjärvi, it is likely that planktonic diatoms will reappear in Lake Orijärvi. However, since planktonic diatoms have also decreased in Lake Määrjärvi, the metal concentrations should be reduced to background levels depicted by Lahermo et al. 1996 for a full recovery of the diatom communities to take place.

5.4. Concluding remarks

The results presented here convincingly demonstrate that palaeolimnological methods, especially diatom analysis, provide a powerful tool for the EU Water Framework Directive for defining reference conditions, long-term trends and also the current status of surface waters. The core-top-and-bottom approach is a very useful means for larger-scale studies. This “before and after” type of sediment sampling method is very time and cost effective for the assessment of ecological reference conditions of surface waters. Therefore, palaeolimnological methods, such as diatom analysis, should not only be incorporated into the WFD as a tool for defining reference conditions, but also for water quality classification and monitoring of surface waters.

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"In your life you may choose desolation
And the shadows you build with your hands
If you turn to the light, that is burning in the night
Then your Journeyman's day has begun"
© Iron Maiden, Dance of Death album 2003

References

Abelmann, A. 1985. Palökologische und ökostratigraphische Untersuchungen von Diatomeenassoziationen an holozänen Sedimenten der zentralen Ostsee, *Berichte-Reports, Geologisch-Palaeontologisches Institut der Universität Kiel* 9, 1–200.

Åker, K., Eriksson, B., Grönlund, T., Kankainen, T. 1988. Sediment stratigraphy in the northern Gulf of Finland. In: Winterhalter B. (ed.) The Baltic Sea. *Geological Survey of Finland Special Paper* 6, 101–117.

Alhonen, P. 1971. The stages of the Baltic Sea as indicated by the diatom stratigraphy. *Acta Botanica Fennica* 92, 1–18.

Allan, I.J., Vrana, B., Greenwood, R., Mills, G.A.; Roig, B., Gonzalez, C. 2006. A “toolbox” for biological and chemical monitoring requirements of the European Union’s Water Framework Directive, *Talanta* 69 (2), 302–322.

Allan, R. 1997. Introduction: mining and metals in the environment. *Journal of Geochemical Exploitation* 58, 95–100.

Andersen J.H., Conley D.J., Hedal, S. 2004. Palaeoecology, refrence conditions and classification of ecological status: the EU Water Framework Directive in practise. *Marine Pollution Bulletin* 49, 97–127.

Andrén, E. 1999. Changes in the composition of the diatom flora during the last century indicate increased eutrophication of the Oder estuary, southwestern Baltic Sea. *Estuarine, Coastal and Shelf Science* 48, 665–676.

Andrén E., Shimmield G., Brand T. 1999. Environmental changes of the last three centuries indicated by siliceous microfossil records from the Southwestern Baltic Sea. *The Holocene* 9, 25–38.

Andrén, E., Andrén, T., Sohlenius, G. 2000a. The Holocene history of the south-western Baltic Sea as reflected in a sediment core from the Bornholm Basin. *Boreas* 29, 233–250.

Andrén, E., Andrén, T., Kunzendorf, H. 2000b. Holocene history of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland basin. *The Holocene* 10, 687–702.

Anonymous (2000) Directive 200/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal Letter* 327/1.

Atazadeh, I., Sharifi, M., Kelly, M.G. 2007. Evaluation of the trophic diatom index for assessing water quality in River Gharasou, western Iran. *Hydrobiologia* 589, 165–173.

Austin, A., Deniseger, J. 1985. Periphyton community changes along a heavy metals gradient in a long narrow lake. *Environmental and Experimental Botany* 25, 41-52.

Battarbee, R.W. 1986. Diatom analysis. In: Berglund B. E. (ed.) Handbook of Holocene palaeoecology and palaeohydrology. John Wiley and Sons, Chichester, pp 527-570.

Battarbee, R.W., Charles, D.F, Dixit, S.S., Renberg, I. 1999. Diatoms as indicators of surface water acidity. In: Stoermer, E.F. and Smol, J.P. (eds), The diatoms: applications for the environmental and earth sciences. Cambridge University Press, Cambridge, New York, Melbourne, pp 35 - 127.

Battarbee R.W., Jones V.J., Flower R.J., Cameron N.G., Bennion H., Carvalho L. & Juggins S. 2001. Diatoms. In: Last W.M., Birks H.J.B. and Smol J.P. (eds.) Tracking Environmental Change Using Lake Sediments, Vol 3: Terrestrial, Algal, and Siliceous Indicators. Kluwer, Dordrecht, pp. 155–202.

Bengtsson, L., Enell, M. 1986. Chemical analysis. In: Berglund B.E. (ed.) Handbook of Holocene Palaeoecology and Palaeohydrology. John Wiley and Sons, Cichester, pp 423-451.

Bennett, K.D. 1996. Determination of the number of zones in a biostratigraphical sequence. *New Phytologist* 132, 155-170.

Bennion, H., Fluin, J., Simpson, G.L. 2004. Assessing eutrophication and reference conditions for Scottish freshwater lochs using subfossil diatoms, *Journal of Applied Ecology* 41, 124–138.

Bennion, H., Battarbee, R.W. 2007. The European Union Water Framework Directive: opportunities for palaeolimnology. *Journal of Paleolimnology* 38, 285–295.

Berglund, B.E., Sandgren, P., Barnekow, L., Hannon, G., Jiang, H., Skog, G., Yu S.-Y. 2005. Early Holocene history of the Baltic Sea, as reflected in coastal sediments in Blekinge, southeastern Sweden. *Quaternary International* 130, 111–139.

Bianchi, T.S., Engelhaupt, E., Westman, P., Andrén, T., Rolff, C., Elmgren, R. 2000. Cyanobacterial blooms in the Baltic Sea: natural or human induced? *Limnology and Oceanography Bulletin* 45, 716–726.

Birks, H.J.B. 1998. Numerical tools in paleolimnology – progress, potentialities, and problems. *Journal of Paleolimnology* 20, 307–332.

Birks, H.J.B., Line, J.M., Juggins, S., Stevenson, A.C., ter Braak, C.J.F. 1990. Diatoms and pH reconstructions. *Philosophical Transactions of the Royal Society of London* B 327, 263–278.

Birks, H.J.B., Line, J.M. 1992. The use of rarefaction analysis for estimating palynological richness from Quaternary pollen-analytical data. *Holocene* 2, 1–10.

Björck, S. 1995. A review of the history of the Baltic Sea, 13.0–8.0 ka BP. *Quaternary International* 27, 19–40.

Bonsdorff, E., Blomqvist, E.M., Mattila, J., Norkko, A. 1997. Coastal Eutrophication: Causes, consequences and perspectives in the Archipelago Areas of the Northern Baltic Sea. *Estuarine Coastal and Shelf Science* 44, 63-72.

Borgendahl, J., Westman, P. 2007. Cyanobacteria as a trigger for increased primary productivity during sapropel formation in the Baltic Sea – a study of the Ancylus/Litorina transition. *Journal of Paleolimnology* 38, 1-12.

Borja, A., Bald, J., Franco, J., Larreta, J., Muxika, I., Revilla, M., Rodríguez, J.G., Solaun, O., Uriarte, A. & Valencia, V. 2009. Using multiple ecosystem components in assessing ecological status in Spanish (Basque Country) Atlantic marine waters. *Marine Pollution Bulletin* 59, 54–64.

Cabecinha, E., Cortes, R., Cabral, J.A., Ferreira, T., Lourenço, M. and Pardal, M.A. 2009. Multi-scale approach using phytoplankton as a first step towards the definition of reservoirs ecological status. *Ecological Indicators* 9, 329–345.

Cattaneo, A., Couillard, Y., Wunsam, S., Courcelle, M. 2004. Diatom taxonomic and morphological changes as indicators of metal pollution and recovery in Lac Dufault (Quebec, Canada). *Journal of Paleolimnology* 32, 149–162.

Cattaneo, A., Couillard, Y., Wunsam, S. 2008. Sedimentary diatoms along a temporal and spatial gradient of metal contamination. *Journal of Paleolimnology* 40, 115–127.

Clarke, A., Juggins, S., Conley, D. 2003. A 150-year reconstruction of the history of coastal eutrophication in Roskilde Fjord, Denmark. *Marine Pollution Bulletin* 46, 1615-1626.

Cleve-Euler, A. 1951-1955. Die Diatomeen von Schweden und Finnland. Kungliga Svenska vetenskapsakademiens handlingar Serie 4, 2/1: 1-163

(1951); 3/3: 1-153 (1952); 4/1: 1-158 (1953); 4/5: 1-225 (1953); 5/4: 1-232 (1955). Stockholm. Reprinted in: *Bibliotheca Phycologica Band* 5. Lehre, 1968.

Cooper, S.R., Brush, G.S. 1991. Long-term history of Chesapeake Bay anoxia. *Science* 254, 992–996.

Davies, S.J., Metcalfe, S.E., MacKenzie, A.B., Newton, A.J., Endfield, G.H., Farmer, J.G. 2004. Environmental changes in the Zirahuéen Basin, Michoacán, Mexico, during the last 1000 years. *Journal of Paleoliminology* 31, 77–98.

De Geer, G. 1890. Om Skandinaviens nivåförändringar under qvartärtiden. *Geologiska Föreningens i Stockholm Förhandlingar* 12, 61–110.

De Geer, G. 1913. Finiglaciala Yoldia relikter. *Geologiska Föreningens i Stockholm Förhandlingar* 35, 307–309.

De Filippis, L.F., Pallaghy, C.K. 1994. Heavy metals: sources and biological effects. In: Rai, L.C., Gaur, J.P., Soeder, C.J. (eds) Advances in Limnology Series: Algae and Water Pollution, E. Schweizerbartsche Verlagsbuchhandlung, Stuttgart, 1994, p. 31-77.

Dixit, S.S., Smol, J.P., Kingston, J.C.& Charles, D.F. 1992. Diatoms: Powerful indicators of environmental change. *Environmental Science and Technology* 26, 22–33.

Dixit S.S., Smol J.P. 1994. Diatoms as indicators in the Environmental Monitoring and Assessment Program-Surface Waters (EMAP-SW). *Environmental Monitoring and Assessment* 31, 275–306.

Ellegaard, M., Clarke, AL., Reuss, N., Drew, S., Weckström, K., Juggins, S., Andersson, N.J., Conley, D.J. 2006. Multi-proxy evidence of the long-term changes in ecosystem structure in a Danish marine estuary, linked to increased nutrient loading. *Estuarine Coastal and Shelf Science* 68, 567–578.

Eloranta P., Soininen J. 2002. Ecological status of some Finnish rivers evaluated using benthic diatom communities. *Journal of Applied Phycology* 14, 1–7.

Engels, S., Bohncke, J.P., Bos, J.A.A., Brooks, S.J., Heiri, O., Helmens, K.F. 2008. Chironomid-based palaeotemperature estimates for northeast Finland during oxygen isotope stage 3. *Journal of Paleolimnology* 40, 49–61.

Emeis, K.C., Struck, U., Blanz, T., Kohly, A., Voss, M. 2003. Salinity changes in the central Baltic Sea (NW Europe) over the last 10 000 years. *The Holocene* 13, 411–421.

Eronen, M. 1974. The history of the Litorina Sea and associated Holocene events (Supplement: Pollen and Diatom Diagrams). *Societas Scientiarum Fennica Commentationes Physico-Mathematicae* 44, 79–195.

Eronen, M. 1983. Late Weichselian and Holocene shore displacement in Finland. In: Shorelines and Isostacy. *Institution of British Geographers, Special Publication* 16, 183–207.

Eronen, M., Glückert, G., Hatakka, L., van de Plassche, O., van der Plicht, J., Rantala, P. 2001. Rates of Holocene isostatic uplift and relative sea–level lowering of the Baltic in the SW Finland based on studies of isolation contacts. *Boreas* 30, 17–30.

Ewurum, M.O. 2000. Environmental impacts of mining - A case study of Orijärvi mine. MSc -thesis, University of Turku.

Gibbard, P.L. 1992. Formal stratigraphy in the Pleistocene of Finland. *Bulletin of the Geological Society of Finland* 64, 125–134.

Granö, O., Roto, M., Laurila, L. 1999. Environment and land use in the shore zone of the coast of Finland. *Publicationes Instituti Geographici Universitatis Turkuensis* 160, 1-76.

Håkansson, H. 2002. A compilation and evaluation of species in the genera Stephanodiscus, Cyclostephanos and Cyclotella with a new genus in the family Stephanodiscaceae. *Diatom Research* 17, 1–139.

Hammer, O., Harper, D.A.T., Ryan, P.D. 2001. PAST: Palaeontological statistic software package for education and data analysis. *Palaeontologia Electronica* 4: article 4, 9p. http://palaeo-electronica.org/2001_1/past/issue1_1.htm

Hänninen, J., Vuorinen, I., Helminen, H., Kirkkala, T., Lehtilä, K. 2000. Trends and gradients in nutrient concentrations and loading in the Archipelago Sea, northern Baltic, in 1970–1997. *Estuarine Coastal and Shelf Science* 50, 153-171.

Hausmann, S., Lotter, A.F. 2001. Morphological variation within the diatom taxon Cyclotella comensis and its importance for quantitative temperature reconstructions. *Freshwater Biology* 46, 1323–1333.

Heiskanen, A.S. 1998. Factors governing sedimentation and pelagic nutrient cycles in the northern Baltic Sea. *Monographs of Boreal Environment Research* 8, 1–80.

Heiskanen, A.S., Kononen, K. 1994. Sedimentation of vernal and late summer phytoplankton communities in the coastal of Finland. *Archiv für Hydrobiologie* 131, 175–198.

Heino, A. 1973. Bottom deposits and sedimentation in northern Airisto in Southwestern Finland. *Bulletin of the Geological Society of Finland* 45, 131–142.

Heino, A. 1987. The percentual distribution and frequency of occurrence of diatoms in bottom sediments in the Airisto and Paimionlahti regions in southwest Finland. *Bulletin of the Geological Society of Finland* 59 (2), 155–170.

Heinsalu, A., Kohonen, T., Winterhalter, B. 2000. Early postglacial environmental changes in the western Gulf of Finland based on diatom and lithostratigraphy of sediment core B-51. *Baltica* 13, 51–60.

HELCOM 2003. The Baltic Sea Joint Comprehensive Environmental Action Programme (JCP) - Ten Years of Implementation. *Baltic Sea Environmental Proceedings* 88, 76pp

HELCOM (2004). Checklist of Baltic Sea Phytoplankton Species. *Baltic Sea Environmental Proceedings* 95, 208pp

Hill, M.O. 1973. Diversity and evenness: a unifying notation and its consequences. *Ecology* 54, 427–432.

Hill, M.O., Gauch, H.G. 1980. Detrended correspondence analysis: an improved ordination technique. *Vegetatio* 42, 47–58.

Hoffmann, G. 1994. Aufwuchs-Diatomeen in Seen und ihre Eignung als Indikatoren der Trophie. *Bibliotheca Diatomologica* 30, 1–241.

Hyvärinen, H. 1984. The Mastogloia stage in the Baltic Sea history: diatom evidence from southern Finland. *Bulletin of the Geological Society of Finland* 56, 99–115.

Hyvärinen, H. 1988. Definition of the Baltic stages. In: Donner J and Raukas A (eds) Problems of the Baltic Sea history. *Annales Academiae Scientiarum Fennicae A III* 148, 7–11.

Ivorra, N., Bremer, S., Guasch, H., Kraak, M.H.S., Admiraal, W. 2000. Differences in the sensitivity of benthic microalgae to Zn and Cd regarding biofilm development and exposure history. *Environmental Toxicology and Chemistry* 19, 1332–1339.

Jørgensen, B.B., Richardson, K. (eds) 1996. Eutrophication in coastal marine ecosystems. *Coastal and Estuarine studies* 52, American Geophysical Union, Washington DC, 272 pp.

Juggins, S. 1991. ZONE v 1.2 – unpublished computer programme. Department of Geography, University of Newcastle, UK.

Juggins, S. 2007. C2 version 1.5.0: a program for plotting and visualising stratigraphic data. University of Newcastle, U.K.

Kabailienè, M. 1995. The Baltic Ice Lake and Yoldia sea stages, based on data from diatom analysis in the central, south-eastern and eastern Baltic. *Quaternary International* 27, 69–72.

Kansanen, P.H., Jaakkola, T., Seppälä, J., Hökkä, M., Kulmala, S., Suutarinen, R., 1991. Chernobyl fallout nuclides used as tracers of sedimentation and sediment mixing in four Finnish lakes. International Symposium of the Use of Isotope Techniques in Water Resources Development IAEA-SM-319/10, 1–8.

Kelly, M.G., Whitton, B.A. 1995. The Trophic Diatom Index: a new index for monitoring eutrophication in rivers. *Journal of Applied Phycology* 7, 433–444.

Kelly, M.G., Bennett, Coste, C. M., Delgado, C., Delmas, F., Denys, L., Ector, L., Fauville, C., Ferreol, M., Golub, M., Jarlman, A., Kahlert, M., Lucey, J., Níchatáin, B., Pardo, I. Pfister, P., Picinska-Faltynowicz, J., Schranz, C., Chaumburg, J., Roseberry, J., van Dam, H. & Vilbaste, S. 2008. A comparison of national approaches to setting ecological status boundaries in phytobenthos assessment for the European Water Framework Directive: results of an intercalibration exercise. *Hydrobiologia* 621, 169–182

Kononen, K., Niemi, Å. 1984. Long-term variation of the phytoplankton composition at the entrance to the Gulf of Finland. *Ophelia, Supplement* 3, 101–110.

Krammer K., Lange-Bertalot H. 1986. Bacillariophyceae 1 Teil: Naviculaceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds) Süsswasserflora von Mitteleuropa, Band 2, Gustav Fischer Verlag, Stuttgart, 876 pp.

Krammer K., Lange-Bertalot H. 1988. Bacillariophyceae 2. Teil: Bacillariaceae, Epithemiaceae, Surirellaceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds) Süsswasserflora von Mitteleuropa, Band 2, Gustav Fischer Verlag, Stuttgart, 596 pp.

Krammer K., Lange-Bertalot H. 1991a. Bacillariophyceae 3. Teil: Centrales, Fragilariaceae, Eunotiaceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds), Süsswasserflora von Mitteleuropa, Band 2, Gustav Fischer Verlag, Stuttgart, 576 pp.

Krammer K., Lange-Bertalot H. 1991b. Bacillariophyceae 4. Teil: Achnanthaceae, Kritische Ergänzungen zu Navicula (Lineolatae) und Gomphonema. In: Ettl H, Gärtner G, Gerloff J, Heynig H, Mollenhauer D (eds) Süsswasserflora von Mitteleuropa, Band 2, Gustav Fischer Verlag, Stuttgart, 437 pp.

Lahermo, P., Väänänen, P., Tarvainen, T., Salminen, R. 1996. Suomen geokemian atlas osa 3: Ympäristögeokemia - purovedet ja -sedimentit. Geologian tutkimuskeskus. 150 pp.

Lange-Bertalot, H. 1979. Toleranzgrenzen und Populationdynamik benthischer Diatomeen bei unterschiedlich starker Abwasserbelastung. *Archiv für Hydrobiologie* - Supplement 56, 184–219.

Lapointe, M. 2000. Late quaternary paleohydrology of the Gulf of St. Lawrence (Quebec, Canada) based on diatom analysis. *Palaeogeogrphy, Palaeoclimatology, Palaeoecology* 156, 261–276.

Larsson, U., Elmgren, R., Wulff, F. 1985. Eutrophication and the Baltic Sea – Causes and consequences. *Ambio* 14, 9–14.

Leira, M., Jordan, P., Taylor, D., Dalton, C., Bennion, H., Rose, N., Irvine, K., 2006. Assessing the ecological status of candidate reference lakes in Ireland using palaeolimnology. *Journal of Applied Ecology* 43, 816–827.

Lepland, A., Heinsalu, A., Stevens, R.L., 1999. The pre-Littorina diatom stratigraphy and sediment sulphidization record from the west-central Baltic Sea: implications of the water column salinity variations. *GFF* 121, 57–68.

Lowe, R.L. 1974. Environmental requirements and pollution toleranve of freshwater diatoms. Environmental Monitoring Series. U.S. Environmental Protection Agency. Ohio.

Mackereth, F.J.H. 1969. A short core sampler for subaqueous deposits. *Limnology and Oceanography* 14, 145–151.

Mälkki, P., Koljonen, J., Valpasvuo, V., Julin, R., Jumppanen, K., Juusti, T. 1979. Saaristomeren virtaustutkimus. Virtaustutkimuksen neuvottelukunta, Turku, 265 pp. in Finnish

Miettinen, J. 2005. Sedimentary diatoms in inferring trophic status and limnological changes in boreal lakes. University of Joensuu, PhD Dissertations in Biology 36, 1-109.

Müller-Haeckel, A. 1985. Shade-adapted algae beneath ice and Snow in the Northern Bothnian Sea. *Internationale Revue der gesamten Hydrobiologie* 70, 325–334.

Mölder K., Tynni R. 1967. Über Finnlands rezente und subfossile Diatomeen I. *Comptes Rendus de la Société Géologique de Finlande* XXXIX, 199–217.

Mölder K., Tynni R. 1968. Über Finnlands rezente und subfossile Diatomeen II. *Bulletin of the Geological Society of Finland* 40, 151–70.

Mölder K., Tynni R.1969. Über Finnlands rezente und subfossile Diatomeen III. *Bulletin of the Geological Society of Finland* 41, 235–51.

Mölder K., Tynni R. 1970. Über Finnlands rezente und subfossile Diatomeen IV. *Bulletin of the Geological Society of Finland* 42, 129–44.

Mölder K., Tynni R. 1971. Über Finnlands rezente und subfossile Diatomeen V. *Bulletin of the Geological Society of Finland* 43, 203–20.

Mölder K., Tynni R. 1972. Über Finnlands rezente und subfossile Diatomeen VI. *Bulletin of the Geological Society of Finland* 44, 141–49.

Mölder K., Tynni R. 1973. Über Finnlands rezente und subfossile Diatomeen VII. *Bulletin of the Geological Society of Finland* 45, 159–79.

Niemi, Å. 1973. Ecology of the phytoplankton in the Tvärminne area SW coast of Finland. I. Dynamics of hydrography, nutrients, chlorophyll-a and phytoplankton. *Acta Botanica Fennica* 100, 1–68.

Niemi, Å. 1975. Ecology of the phytoplankton in the Tvärminne area SW coast of Finland. II. Primary production and environmental conditions in the Archipelago zone and sea zone. *Acta Botanica Fennica* 105,1–73.

Niemi, Å., Åström, A.-M. 1987. Ecology of the phytoplankton in the Tvärminne area SW coast of Finland. IV. Environmental conditions, chlorophyll-a and phytoplankton in winter and spring 1984 at Tvärminne Storfjärd. *Acta Botanica Fennica* 24, 333–352.

Olli, K., Clarke, A., Danielsson, Å., Aigars, J., Conley, D.J., Tamminen, T. 2008. Diatom stratigraphy and long-term dissolved silica concentrations in the Baltic Sea. *Journal of Marine Systems* 73, 284–299.

Papush, L., Danielsson, Å. 2006. Silicon in the marine environment: Dissolved silica trends in the Baltic Sea. *Estuarine, Coastal and Shelf Science* 67, 53–66.

Pinto, E., Sigaud-Kutner, T.C.S., Leitao, M.A.S., Okamoto, O.K., Morse, D., Colepicolo, P. 2003. Heavy metal-induced oxidative stress in algae. *Journal of Phycology* 39, 1008–1018.

Pitkänen, H., Kangas, P., Miettinen, V., Ekholm, P. 1987. The state of Finnish coastal waters in 1979–1983. *Vesi-ja Ympäristöhallituksen Julkaisuja* 8: 1-167. In Finnish

Ptacnik, R., Solimini; A.G., Brettum, P. 2009. Performance of a new phytoplankton composition metric along a eutrophication gradient in Nordic lakes. *Hydrobiologia* 633, 75–82.

Puustinen, K. 2003. Suomen kaivosteollisuus ja mineraalisten raaka-aineiden tuotanto vuosina 1530-2001, historiallinen katsaus erityisesti tuotantolukujen valossa. Geological Survey of Finland, unpublished report M 10.1/2003/3.578p. Internet pages at http://www.gtk.fi/aineistot/kaivosteollisuus (in Finnish)

Räisänen, M.-L., Heikkinen, P., Aatos, S., Pulkkinen, K., Korkka-Niemi, K. Salonen, V-P. 2005. Finland - Mine water quality in some abandoned and active metal sulphide mines. *Mine Water and the Environment* 24, 5-7.

Räsänen, J., Kauppila, T., Salonen, V-P. 2006. Sediment-based investigation of naturally or historically eutrophic lakes—implications for lake management. *Journal of Environmental Management* 79, 253–265.

Reavie, E.D., Robbins, J.A., Stoermer, E.F., Douglas, M.S.V., Emmert, G.E., Morehead, N.R., Murdoch, A. 2005. Paleolimnology of a fluvial lake downstream of Lake Superior and the industrialized region of Sault Saint Marie. *Canadian Journal of Fisheries and Aquatic Science* 62, 2586–2608.

Renberg, I. 1990. A procedure for preparing large set of diatom slides from sediment cores. *Journal of Paleolimnology* 4, 87-90.

Rijstenbil, J.W., Derksen, J.W.M., Gerringa, L.J.A., Poortvliet, T.C.W., Sandee, A., Van den Berg, M., Van Drie, J., Wijnholds, J.A. 1994. Oxidative stress induced by copper: defense and damage in the marine planktonic diatom *Ditylum brightwellii* (Grunow) West, grown in continuous cultures with high and low zinc levels. Marine Biology 119, 583–590.

Riber, H.H., Wetzel, R.G. 1987. Boundary-layer and internal diffusion effects on phosphorus fluxes in lake periphyton. *Limnology and Oceanography* 32, 1181–1194.

Risberg, J., Sandgren, P., Tellet, J.T. 1999. Siliceous microfossils and mineral magnetic characteristics in a sediment core from Lake Manitoba, Canada: a remnant of glacial Lake Agassiz. *Canadian Journal of Earth Sciences* 36, 1299–1314.

Ruggiu, D., Luglié, A., Cattaneo, A., Panzani, P. 1998. Paleoecological evidence for diatom response to metal pollution in Lake Orta (N. Italy). *Journal of Paleolimnology* 20, 333–345.

Saarnisto, M., Saarinen, T. 2001. Deglaciation chronology of the Scandinavian Ice Sheet from the Lake Onega Basin to the Salpausselkä End Moraines. *Global and Planetary Change* 31, 387–405.

Salonen, V-P and Tuovinen, N. 2001. Orijärvi: a lake impacted by acid mine drainage. In: Lehtonen T., Salminen J-P. and Pihlaja K. (eds,), The Fifth Finnish Conference of Environmental Sciences, Turku May 18.-19. 2001. Proceedings, 64. Finnish Society for Environmental Sciences, University of Turku, 336 pp.

Salvador, A. 1994. International Stratigraphic Guide, 2nd edition. International Union of Geological Sciences, Trondheim, and the Geological Society of America, Boulder, Colorado, pp 214

Sarmiento, A.M., Nieto, J.M., Olías, M., Cánovas, C.R. 2009. Hydrochemical charasteristics and seasonal influence on the pollution by acid mine drainage in the Odiel river basin (SW Spain). *Applied Geochemistry* 24, 697–714.

Sauramo, M. 1958. Die Geschichte der Ostsee. *Annales Academie Scientiarum Fennica A III* 5, 1–522.

Seinä, A. 1994. Extent of ice cover 1961–1990 and restrictions to navigation 1981–1990 along the Finnish coast. *Finnish Marine Research* 262, 3-34.

Snoeijs, P. 1993. Intercalibration and distribution of diatom species in the Baltic SeaVolume 1. Opulus Press Uppsala, 129 pp

Snoeijs, P., Vilbaste, S. 1994. Intercalibration and distribution of diatom species in the Baltic Sea Volume 2. Opulus Press Uppsala, 125 pp

Snoeijs, P., Potapova, M. 1995. Intercalibration and distribution of diatom species in the Baltic Sea Volume 3. Opulus Press Uppsala, 125 pp

Snoeijs, P., Kasperoviciene, J. 1996. Intercalibration and distribution of diatom species in the Baltic Sea Volume 4. Opulus Press Uppsala, 125 pp

Snoeijs, P., Balashova, J. 1998. Intercalibration and distribution of diatom species in the Baltic Sea Volume 5 (including check-list). Opulus Press Uppsala, 141 pp

Snoeijs, P. 1999. Diatoms and environmental change in brackish waters. In Stoemer E.F. (ed.) Diatoms: Applications for the Environmental and Earth Scineces, West Nyack, NY, USA: Cambridge University Press 1999, pp 298–333

Sohlenius, G., Sternbeck, J., Andrén, E., Westman, P. 1996. Holocene history of the Baltic Sea as recorded in a sediment core from the Gotland Deep. *Marine Geology* 134, 183–201.

Sohlenius, G., Emeis, K-C., Andrén, E., Andrén, T., Kohly, A. 2001. Development of anoxia during the Holocene fresh-brackish water transition in the Baltic Sea. *Marine Geology* 177, 221–242.

Stevenson, A.C., Juggins, S., Birks, H.J.B., Andersson, D.S., Andersson, N.J., Battarbee, R.W., Berge, F., Davis, R.B., Flower, R.J., Haworth, E.Y., Jones, V.J., Kingston, J.C., Kreiser, A.M., Line, J.M., Munro, M.A.R. Renberg I. 1991. The surface waters acidification project paleolimnology programme: Modern diatom/lake-water chemistry data-set. ISBN 1 871275 05 9. ENSIS Publishing. Lontoo.

Stoermer, E.F. 1977. Post-glacial diatom succession in Douglas Lake, Michigan. *Journal of Phycology* 13, 73–80.

Sweitzer, J., Langaas, S., Folke, C. 1996. Land cover and population density in the Baltic Sea drainage basin: a GIS database. *Ambio* 25, 191–198.

Takamura, N., Kasai, F. & Watanabe, M. M. 1989. Effects of Cu, Cd and Zn on photosynthesis of freshwater benthic algae. *Journal of Applied Phycology* 1, 39–52.

ter Braak CJF, Šmilauer P (1998) CANOCO Reference Manual and User's Guide to Canoco for Windows: Software for Canonical Community Ordination (version 4). Microcomputer Power, Ithaca, 352 pp

Thulin, B., Possnert, G., Vuorela, I. 1992. Stratigraphy and age of two postglacial sediment cores from the Baltic Sea. *Geologiska Föreningens i Stockholm Förhandlingar* 114/ 2, 165–179.

Turunen, E. 1957. Orijärven kaivos 1757 – 1957. *Vuoriteollisuus* 1957/2, 13–24.

van Dam, H., Mertens, A., Sinkeldam, J. 1994. A coded checklist and ecological indicator values of freshwater diatoms from the Netherlands. *Netherlands Journal of Aquatic Ecology* 28, 117–133.

Virtasalo, J.J., Kohonen, T., Vuorinen, I., Huttula, T. 2005a. Sea bottom anoxia in the Archipelago Sea, northern Baltic Sea -- implications for phosphorus remineralization at the sediment surface. *Marine Geology* 224, 103–122.

Virtasalo, J.J., Kotilainen, A.T., Räsänen, M.E. 2005b. Holocene stratigraphy of the Archipelago Sea, northern Baltic Sea: the definitions and descriptions of the Dragsfjärd, Korppoo and Nauvo Alloformations. *Baltica* 18, 83–97.

Virtasalo, J.J., Kotilainen, A.T., Gingras, M.K. 2006. Trace fossils as indicators of environmental change in Holocene sediments of the Archipelago Sea, northern Baltic Sea. *Palaeogeography, Palaeoclimatology, Palaeoecology* 240, 453–467.

Virtasalo, J.J., Kotilainen, A.T., Räsänen, M.E., Ojala, A.E.K. 2007. Late-glacial and post-glacial deposition in a large, low relief, epicontinental basin: the northern Baltic Sea. *Sedimentology* 54, 1323–1344.

Virtasalo, J.J., Kotilainen A.T. & Räsänen, M.E., in press: Definitions of Trollskär Formation and Sandön Formation in the Archipelago Sea, northern Baltic Sea. *Bulletin of the Geological Society of Finland*.

Vogt, H. 1998. Kiskon Määr- ja Orijärven veden laadun ja tilan tutkimus vuonna 1996-1997. Ekologitoimisto Ympäristötutkimus, H. Vogt. Raportti 20.11. 1998, 27 pp. In Finnish.

Wasmund, N., Uhlig, S. 2003. Phytoplankton trends in the Baltic Sea. *ICES Journal of Marine Science* 60, 177–186.

Wastegård, S., Andrén, T., Sohlenius, G., Sandgren, P. 1995. Different phases of the Yoldia Sea in the north-western Baltic Proper. *Quaternary International* 27, 121–129.

Weckström, K. 2006. Assessing recent eutrophication in coastal waters of the Gulf of Finland (Baltic Sea) using subfossil diatoms. *Journal of Paleolimnology* 35, 571–592.

Weckström, K., Juggins, S., Korhola, A. 2004. Quantifying background nutrient concentrations in coastal waters: A case study from an urban embayment of the Baltic Sea. *Ambio* 33, 324–327.

Weckström, K., Juggins, S. 2006. Coastal Diatom-environment relationship from the Gulf of Finland, Baltic Sea. *Journal of Phycology* 42, 21–35.

Weckström, K., Korhola, A., Weckström, J. 2007. Impacts of eutrophication on diatom life forms and species richness in coastal waters of the Baltic Sea. *Ambio* 36, 155–160.

Westman, P., Sohlenius, G. 1999. Diatom stratigraphy in five offshore sediment cores from the northwestern Baltic proper implying large scale circulation changes during the last 8500 years. *Journal of Paleolimnology* 22, 53–69.

Winterhalter, B., Flodén, T., Ignatius, H., Axberg, S., Niemistö, L. 1981. Geology of the Baltic Sea. In: Voipio A (ed) The Baltic Sea, Elsevier, Amsterdam, pp 1–121.

Witkowski, A. 1994. Recent and fossil diatom flora of the Gulf of Gdańsk, Southern Baltic Sea. Origin, composition and changes of diatom assemblages during the Holocene. *Bibliotheca Diatomologica* 28, J. Cramer, Berlin, 313 pp.

Witkowski, A., Lange-Bertalot, H., Metzeltin, D. 2000. Diatom flora of marine coasts I. In Lange-Bertalot H. (ed.) Iconographica Diatomologica, Annotated Diatom Micrographs 7. A.R.G. Gantner verlag K.G., Ruggell, 925 pp.