

The complementary power of pH and lake-water organic carbon reconstructions for discerning the influences on surface waters across decadal to millennial time scales

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Abstract. Lysevatten, a lake in southwest Sweden, has experienced both acidification and recent changes in the amount of lake-water organic carbon (TOC), both causing concern across Europe and North America. A range of paleolimnological tools – diatom-inferred pH, inferred lake-water TOC from visible-near-infrared spectroscopy (VNIRS), multi-element geochemistry and pollen analysis, combined with geochemical modeling were used to reconstruct the lake's chemistry and surroundings back to the most recent deglaciation 12 500 years ago. The results reveal that the recent anthropogenic impacts are similar in magnitude to the long-term variation driven by natural catchment changes and early agricultural land use occurring over centuries and millennia. The combined reconstruction of both lake-water TOC and lithogenic element delivery can explain the major changes in lake-water pH and modeled acid neutralizing capacity during the past 12 500 years. The results raise important questions regarding what precisely comprises “reference” conditions (i.e., free from human impacts) as defined in the European Water Framework Directive.

to factors including climate warming (Freeman et al., 2010) and/or recovery from acidification (Lepisto et al., 2008). However, these studies are based on only a few decades of monitoring data. Therefore, it is difficult to assess the variation in these variables prior to the start of large-scale atmospheric emissions of sulfur and nitrogen or assess the importance of longer-term processes, such as climate, soil development and land-use changes. Given the major and wide-ranging influence of TOC on aquatic ecosystems and drinking water quality, there is considerable interest in understanding the causes and effects of these changes. Surface water acidification was one of the factors hypothesized to affect TOC, but is also one of the factors significantly affected by TOC (Evans et al., 2007).

Research on surface-water acidification over the past decades has shown that the acidification of acid-sensitive, oligotrophic lakes is a complex issue that includes several important factors. These include long-term natural processes such as lake ageing (lake ontogeny), soil weathering, vegetation succession and climate (Warfinge et al., 1995; Engstrom et al., 2000; Boyle, 2007), as well as human-related factors such as small-scale agriculture (cultivation or forest grazing), forestry, and sulfur and nitrogen deposition (Renberg et al., 1993a, b; Erlandsson et al., 2008a). While sulfur deposition has been central to the problem of acidification during the 20th century, the biogeochemistry of acidification is also now understood to be more complex; in particular research over the past decades has emphasized the role that dissolved organic carbon (DOC) – and thus organic acidity – plays in acidification processes (Campbell et al., 1992; Wigington et al., 1991; Erlandsson et al., 2008b).

1 Introduction

The concentration of total organic carbon (TOC) in surface waters has increased over the past two decades across large parts of Europe and North America (Evans et al., 2005; Monteith et al., 2007). This has been suggested to be attributed



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Siliceous diatoms are well-preserved algae in sediment that can be used to infer lake-water pH (Battarbee et al., 2010). Renberg et al. (1993a, b) used the technique to show that increases in lake-water pH in many acid-sensitive southern Swedish lakes occurred already 1000–2000 years ago in conjunction with increasing land use that included both forest grazing and small-scale agriculture – the so-called cultural alkalization period. However, what remains uncertain is the role of lake-water TOC, catchment erosion and weathering for the long-term changes in pH (Boyle, 2007; Klaminder et al., 2011).

More recently, studies have shown that near-infrared spectroscopy (NIRS) can be used to infer past changes in lake-water TOC (Rosén, 2005) as well as how climate, tree-line changes, mire development or permafrost dynamics can affect the TOC development in areas with a low degree of human impacts (Rosén and Hammarlund, 2007; Kokfelt et al., 2009; Rosén et al., 2009; Rydberg et al., 2010). Recently Cunningham et al. (2010) used the same technique to show that the inferred TOC levels in four southern Swedish lakes have decreased substantially over the last few hundred years relative to the levels in ca 1980, before recent European and N. American increases in TOC began. Importantly, this decrease in TOC of these southern Swedish lakes started already before the 1920's, which is when sulfate deposition began to increase most strongly and before any TOC “suppression” by acidification effect would begin (Erlandsson et al., 2008a).

The results from both Renberg et al. (1993a, b) and Cunningham et al. (2010) indicate that early land use was likely important for lake-water TOC development too. The results raise important questions not only for the mechanisms responsible for these changes in lake-water TOC but also a range of ecosystem functions related to DOC including pH, because TOC has such a strong control on pH in weakly buffered boreal waters (Köhler et al., 1999). This leads to the question of what precisely comprises ‘reference’ conditions (i.e., free from human impacts) according to the current European guideline for managing surface waters, as defined in the European Water Framework Directive.

In this study we use approaches by Renberg et al. (1993a, b) and Cunningham et al. (2010) to independently reconstruct lake-water pH and TOC in order to better assess the role of Holocene catchment development and early agricultural activities on lake-water chemistry. We also use the strong relationship between TOC, pH and acid neutralizing capacity (ANC) to infer the output of weathering products from the soils as represented by lake-water ANC modeled from the reconstructed pH and TOC.

As a case study we use Lysevatten, a lake that is representative of many of the lakes in the acid-sensitive region of southwestern Sweden, which has been an important study region in acidification research both nationally and internationally. The pH development of Lysevatten, based on diatom-inferred pH, follows the schematic model outlined by Ren-

berg et al. (1993a, b) with (1) a gradual long-term natural acidification during the first few thousand years following deglaciation (ca. 12 500 years ago), when pH declined from circum-neutral values to about 5.3–5.5 – at which level the pH remained until about 1100 years ago; (2) a period of elevated pH values, 6.0–6.5, in conjunction with early small-scale agriculture; (3) acidification during the late 19th and early 20th centuries, presumably in response to both changing land-use practices and especially increasing sulfur deposition; and finally (4) temporary increases in pH due to liming during the mid-1970's and mid-1980's (Renberg and Hultberg, 1992).

Our aim here is to demonstrate the power of parallel paleolimnological reconstructions to assess the role that changes in lake-water TOC and lithogenic elements have for the acidity of the lake. To achieve this aim we employ a range of paleolimnological tools – diatom-inferred pH, NIRS-inferred TOC, multi-element geochemistry and pollen analysis – with geochemical models of the major pH buffering systems in surface waters. In doing so, we will also reveal the millennial dynamics of TOC in a region where recent decadal-scale increases in TOC have raised concern.

2 Materials and methods

2.1 Study areas

Lysevatten (58°04' N, 12°02' E) is a lake located in an upland area (113 m a.s.l.) together with Gårdsjön, an experimental lake immediately adjacent to Lysevatten (Andersson and Olsson, 1985). The study area is about 10 km from the present-day coast and was formed following the deglaciation of the region ca. 12 500 BP. The drainage area is 146 ha and lake area 39 ha. The maximum lake depth is 18.5 m and the mean depth 4.7 m. The retention time is ca. 2.5 yr. The yearly precipitation is about 1070 mm yr⁻¹.

2.2 Sample collection and analysis

We collected a complete sediment profile (185 cm) from the deepest basin of Lysevatten when the lake was covered by ice in February 2003. This sampling included a freeze corer for the unconsolidated uppermost sediment (Renberg and Hansson, 1993c) and two overlapping cores taken with a 1-m long Russian-type barrel peat corer (Renberg et al., 1993a). All samples were freeze dried before further analyses. Diatom analysis was performed on a sediment profile sampled in 1986 (Renberg et al., 1993a).

The age-depth model for the recent sediment is based on direct radiometric analyses of sediment using ²¹⁰Pb along with ¹³⁷Cs, and a constant rate of supply (CRS) model (Fig. 1; Appleby and Oldfield, 1978). Because we found no macrofossils for AMS dating, the inferred ages for older sediments are based on established changes in lead associated with pollution (Renberg et al., 2001). The indirect

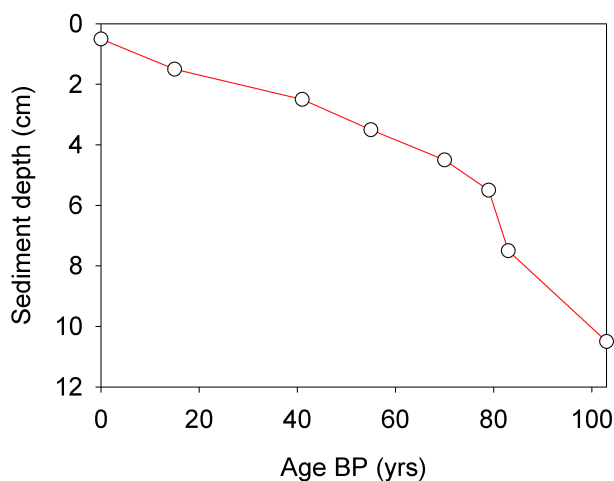


Fig. 1. Depth-age model for the sediment profile from Lake Lysevatten based on direct radiometric analyses of sediment using ^{210}Pb along with ^{137}Cs , and a constant rate of supply (CRS) model.

dates from the lead record were supported by AMS dates on bulk sediment and similar changes in lead concentration in the nearby lakes Härsvatten and Måkevatten (Bindler et al., 2001). The bottom of the core is assumed to be from the deglaciation in the area ca. 12 500 yr BP. The diatom-inferred lake-water pH was analyzed from a separate core taken in 1986 using a weighted averaging calibration model with a root mean squared error of prediction of 0.3 pH units (Renberg and Hellberg, 1982; Renberg and Hultberg, 1992). The correlation between the cores taken in 1986 and 2003 is based on the age-depth model from each core (Renberg and Hultberg, 1992).

The organic matter content of the sediments was established either by direct analysis of carbon and nitrogen (PerkinElmer CHNS analyzer) or inferred from loss-on-ignition (Heiri et al., 2001). Total concentrations of selected major and trace elements were determined using X-ray fluorescence (Boyle, 2000). The biogenic silica content (or non-detrital silica) is inferred based on Si:Ti ratios (Peinerud et al., 2001).

Near-infrared spectroscopy (NIRS) was used to infer changes in the total organic carbon (TOC) content of the water using a calibration model based on 140 Swedish lakes covering a TOC gradient from 0.7 to 24 mg L⁻¹. (Cunningham et al., 2010).

Pollen and microscopic charcoal particles were prepared and analyzed using standard methods as described by Barber (1981). At least 500 terrestrial pollen grains were counted per sample, and the pollen data are expressed as percentages of total terrestrial pollen. Pollen derived from cultivated crops are called anthropocores and native species with the ability to profit from human activities are called apophytes (Behre, 1981, 1988; Hicks, 1993, 1995; Räsänen, 2001).

We used principal component analysis (PCA) to reduce the numbers of dimensions given by the geochemistry and inferred lake-water TOC data (lake-water pH excluded in the PCA) and to assess when major changes occurred in the sediment record that might explain the variation in the lake-water pH. PCA was also used separately to assess major changes in the pollen and charcoal record, where fewer sample levels were analyzed. Finally, PCA was performed including all pollen types, elements and inferred water chemistry to assess major changes and correlations between all proxies throughout the Holocene. The loading values (sediment depth) and score values (environmental variables) were plotted together to assess correlations among all variables through time.

Electro-neutrality in water specifies a relationship between the dissolved constituents (Eq. 1). Dissociated organic anions (RCOO^-) are a major part of the ion-balance in weakly buffered, organic-rich boreal waters. Because such waters are common in Fenno-Scandia, a useful feature of electro-neutrality is that there is a strong relationship between surface-water pH, the buffering capacity represented by acid neutralizing capacity (Eq. 1), the partial pressure of CO_2 , and the TOC concentration in Swedish lakes (Erlandsson et al., 2008). The RCOO^- was estimated using a triprotic model (Hruška et al., 2003). Important variables in this model are the three pK_a -values, as well as the site density of organic acids. The model has demonstrated itself to be generally valid for lakes across Sweden with an error margin of 0.16 pH-units (Köhler et al., 2000).

$$\text{ANC} = ([\text{OH}^-] + [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{RCOO}^-] - [\text{H}^+] - n \cdot [\text{Al}^{n+}]) \quad (1)$$

The input parameters needed to solve the equation for ANC are H^+ , TOC (used to iteratively estimate RCOO^-), pCO_2 and inorganic aluminium (Al_{in}). The pre-industrial ANC is thus estimated by the inferred pH and TOC values, supported by assumptions about the inorganic aluminium and pCO_2 . Inorganic aluminium was considered to be negligible for the pre-industrial conditions. The pCO_2 was set to 4 times the atmospheric pressure as in Bishop et al. (2008) and is the mean value for Swedish lakes (Erlandsson et al., 2008c).

3 Results

Based on the visually observed large congruent changes in lake water pH, lake-water TOC and lithogenic elements during the past 12 500 yrs the sediment record from Lysevatten can be divided into five general periods (Fig. 2).

3.1 Early lake ontogeny: 185–120 cm sediment depth (ca. 12 500–7000 yrs BP).

The diatom-inferred pH declines gradually from about 6.5 to <6.0 during the oldest part of the record (185–120 cm; Fig. 2). The NIRS-inferred lake-water TOC concentrations

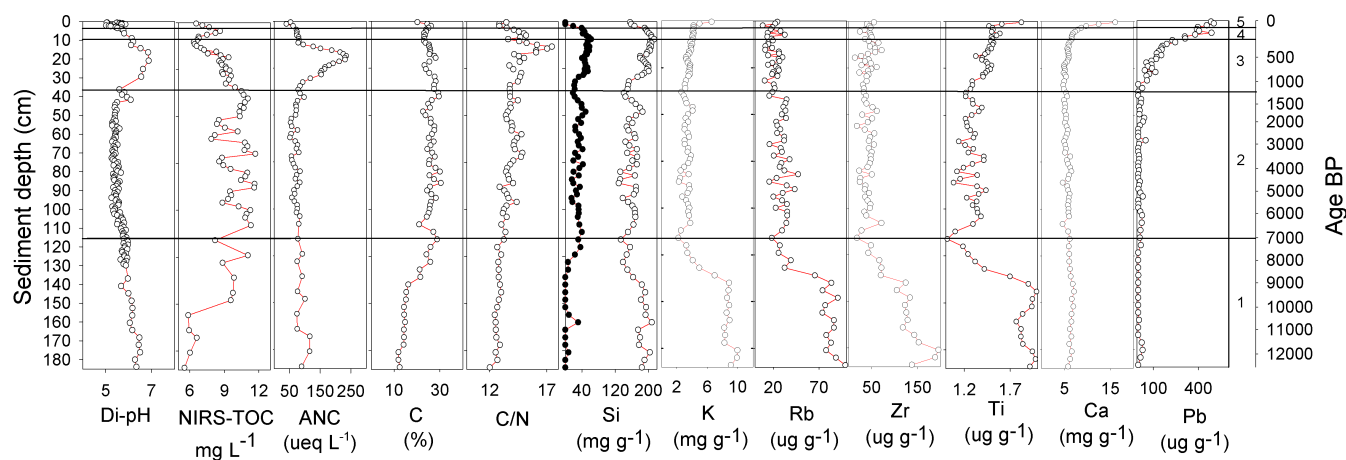


Fig. 2. Records of diatom-inferred lake water pH (Di-pH), lake-water total organic carbon inferred from near infrared spectroscopy (NIRS-TOC), modeled ANC and sediment content of organic carbon (C), ratio of organic carbon to nitrogen (C/N), total silica (Si) (open circles) along with biogenic silica (BSi) (filled circles), potassium (K), rubidium (Rb), zirconium (Zr), titanium (Ti), calcium (Ca) and lead (Pb) along the Holocene sediment core from Lake Lysevatten. Five different periods are indicated (1) early lake ontogeny with large changes in the proxy data, ca. 12500–7000 BP; (2) a stabilization phase, ca. 7000–1100 BP; (3) an early anthropogenic disturbance and catchment change phase, ca. 1100–200 BP; (4) recent acidification, ca. 200 BP–AD 1974 and (5) a liming phase.

are lower below 140 cm, $<6 \text{ mg L}^{-1}$, but thereafter increase to about 9 mg L^{-1} . The sediment carbon and nitrogen contents approximately double, and the period shows decreasing concentrations of major and trace elements associated with lithogenic material (i.e. mineral matter), such as potassium, rubidium, titanium and zirconium (cf. Engstrom and Wright, 1984; Koinig et al., 2003). Other elements that are in part related to a lithogenic source, such as iron and silica, also decline. Base cations that have an important nutrient role and may be taken up in forest vegetation (Watmough and Dillon 2003), such as potassium and rubidium, decline in relation to more conservative lithogenic elements that participate in fewer biogeochemical processes (Kauppi and Salonen, 1997), such as titanium, i.e., K/Ti and Rb/Ti ratios both decline upwards through the lowermost sediment section. An alternative reason for a decline in the K/Ti ratio can also be changes in the runoff and lake margin storage of sediment. The inferred contribution of biogenic silica, estimated using titanium as the normalizing element (using rubidium or zirconium to calculate non-detrital silica produce the same trends), is close to zero from 185 to 140 cm depth, indicating that most of the silica in the sediment is of geogenic source. Above 140 cm the biogenic silica content increases to about 25–50 % of the total silica content.

The first principal component (PC 1) shows that the early lake ontogeny phase displays the largest changes during the entire Holocene in the sediment geochemical data and the inferred lake-water TOC (Figs. 4–6). The changes captured in PC1 are clearly related to the relative inputs of organic and mineral matter to the sediment, which change most significantly during the early phase of landscape development following deglaciation. Low scores represent greater propor-

tions of carbon, nitrogen, bromine in the sediment (an organically bound element; Rasmussen et al., 1998) and lake-water TOC, while high scores represent greater proportions of all of the lithogenic elements.

A diatom-inferred pH value of about 6.5, ca. 12 000 yr BP, when the NIRS-inferred TOC value was 6 mg L^{-1} ; yields a modeled ANC value of $116 \mu\text{eq L}^{-1}$. Between 9000–7000 yrs BP the TOC values increased to above 9 mg L^{-1} . Assuming a constant ANC value of $116 \mu\text{eq L}^{-1}$, the lake-water pH would be around 6.2, which is higher than the diatom-inferred pH of 5.9 at this time. Because the lithogenic contribution to the sediment declined over this period, it is expected that the TOC increase was not the only cause of the pH decline. And indeed, the ANC from the inferred TOC (8.2 mg L^{-1}) and pH (5.9) values at 7000 BP is $78 \mu\text{eq L}^{-1}$.

The pollen data suggest a forest type dominated by deciduous trees as indicated by relatively high percentage values for *Betula* spp., *Alnus* spp., *Quercus* spp. *Ulmus* spp. and *Tilia cordata* (Fig. 3). There is no indication of *Picea* and the pollen data suggest only a minor contribution from *Pinus*. Furthermore, low relative concentrations of charcoal indicate a low frequency of fires.

3.2 Stabilization phase: 120–35 cm depth (ca. 7000–1100 yrs BP).

The sediment sequence from 120 to 35 cm depth is characterized by generally stable lake chemistry. During this period the diatom-inferred pH indicates a continued, but very gradual decline from ~ 5.8 early in the period to values of about 5.3–5.5 (Fig. 2). NIRS-inferred TOC concentrations vary within the interval of $9\text{--}12 \text{ mg L}^{-1}$, but without any specific

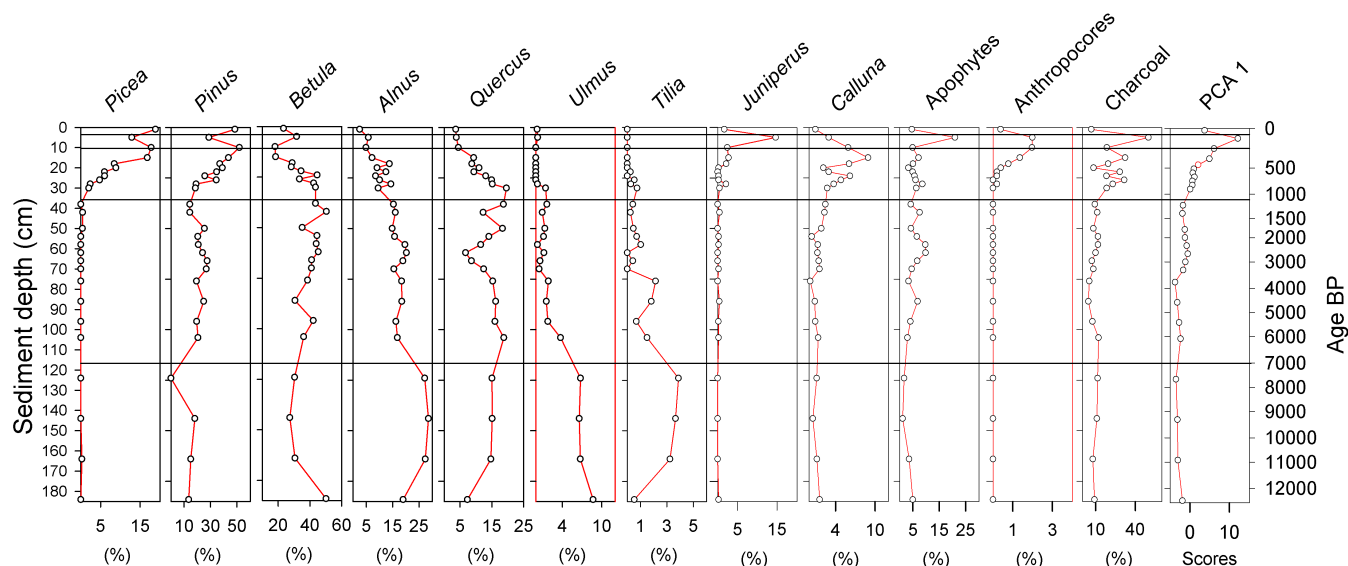


Fig. 3. Percentage diagram of pollen and charcoal from Lysevatten. Frequencies of both pollen and charcoal are expressed as percentages of the total pollen sum at each level. Anthropocores are pollen from cultivated crops and apophytes are pollen types associated with human impact (39, 40, 41). The principal component (PC) 1 summarizes major changes in frequency of all pollen types and charcoal identified in the Lysevatten sediment.

trend (Fig. 2). The concentrations of carbon and almost all major trace elements in the sediment remain essentially constant in the sediment (e.g., potassium and titanium) or decline quite gradually (e.g., calcium and iron) (Fig. 2). This stability also includes elemental ratios, which together suggest fairly stable catchment conditions. PC 1, which summarizes the organic and lithogenic elements and inferred-lake water TOC, also shows stable values (Figs. 4, 6).

The inferred lake-water pH varies from 5.3 to 5.9. Assuming that the median inferred-pH value of 5.5 is connected to the inferred TOC median of 10.5 mg L^{-1} , the modeled ANC would be $75 \mu\text{eq L}^{-1}$.

The forest around the lake was probably still dominated by deciduous trees as indicated by high percentage values from *Betula* spp., *Alnus* spp., *Quercus* spp. and *Tilia cordata* pollen, but with less contribution from *Ulmus* spp. compared to the period before (Fig. 3). The first indication of changes in the pollen of species more competitive following human disturbance (apophytes) is an increase at 90 cm depth (ca. 4000 yrs BP), however the anthropocores – cultivated plants – remains low.

3.3 Early anthropogenic disturbance and catchment change: 35–10 cm sediment depth (ca. 1100–200 yrs BP).

The sediment sequence from 35 to 10 cm depth is characterized by major changes in several proxies, and the diatom-inferred lake-water pH increases from approximately 5.6 to 6.8 (Figs. 2, 4). The inferred lake-water TOC de-

clines from 10 to 6.5 mg L^{-1} , but without any corresponding changes in sediment carbon content that occurred in the early Holocene. In conjunction with the increase in diatom-inferred lake-water pH, the non-detrital Si (biogenic Si) also increases, which indicates increased autochthonous production. Among the elements in the sediment related to mineral matter, potassium, iron, rubidium and strontium increase again, which is an indication of increased catchment export. The PCA, which summarizes the organic and lithogenic elements in the sediment and inferred-lake water TOC, shows the second largest change during the entire Holocene (PC2, PC3; Figs. 4–6). Of further interest, however, is the changes within the mineral fraction that occur once the main effect of the major changes captured in PC1 are removed (Figs. 5, 6). While titanium remains generally stable even after the dominant changes are removed, the residual changes in potassium and rubidium – mostly captured within PC2 – is consistent with a depletion in these elements relative to the total mineral contribution in the sediment during this phase of the sediment record. Lake-water TOC also shows a decline once the main influence of PC1 is removed.

Assuming the constant ANC of $75 \mu\text{eq L}^{-1}$ from the previous period, the inferred decrease in TOC from 10 to 6.5 mg L^{-1} would raise pH to 6.1, which was the pH ca. 250 yr BP. However, to achieve a pH of 6.8 with a TOC of around 9 mg L^{-1} , as was the case ca. 500 yr BP, the ANC would need to be $230 \mu\text{eq L}^{-1}$. From the reconstructed pH and TOC of this period the organic acid dissociation model indicates lake-water ANC between $120\text{--}230 \mu\text{eq L}^{-1}$ from 900 to 300 yr BP.

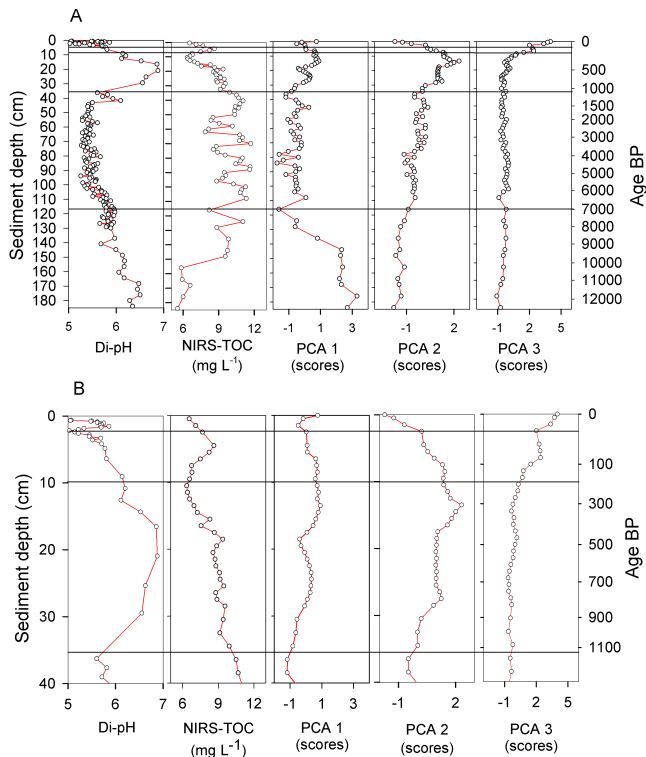


Fig. 4. Diatom inferred pH, NIRS inferred TOC and scores from a principal component analysis (PCA) summarizing the inferred lake-water TOC and geochemistry data into three significant components along (A) the entire Holocene (B) up-scaling of the past 1200 years. The PC 1-3 captured 46, 21 and 20 % of the total variance, respectively.

When summarizing all pollen-types found in the sediment record and the charcoal data in PC1 the data suggest the largest change in the catchment vegetation during the entire Holocene (Fig. 3). Especially charcoal and pollen from cultivated crops (anthropocores) and pollen from native species with the ability to profit from human activities (apophytes) increase in relative abundance. During the same time pollen from other plants indicating a more open forest, such as *Calluna* and *Juniperus*, increase, while the deciduous forest is gradually changing into a coniferous forest with high relative abundance of *Picea* and *Pinus* pollen.

3.4 Acidification phase: 10–2 cm sediment depth (ca. 200–20 yrs BP).

The changes in the sediment properties from 10 to 2 cm depth are mainly captured by PC3 and are characterized by major changes in sediment components associated with pollution, such as sulfur, lead and zinc (Figs. 2, 4 and 5). This corresponds well with the decreasing trend in diatom-inferred lake-water pH from approximately 6 to 5 (Fig. 2). At about 7 cm there is a sudden increase in TOC from 6 to above 8 mg L⁻¹, which corresponds to the time of inten-

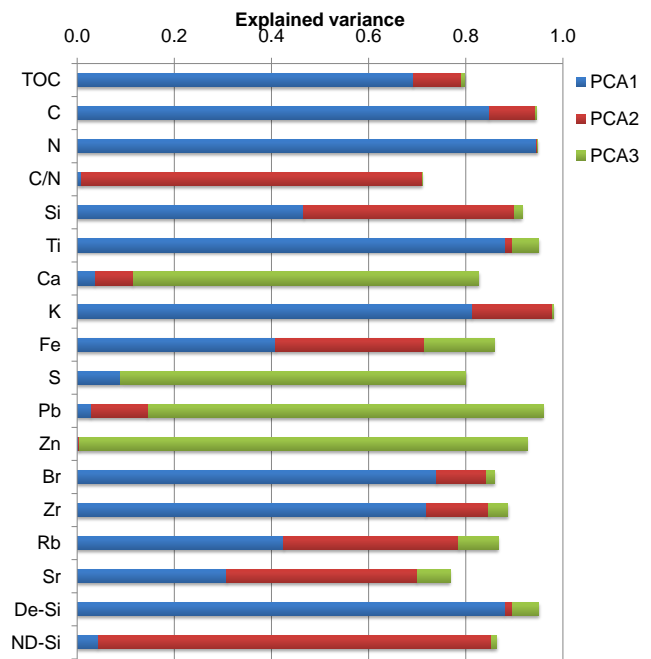


Fig. 5. Explained variance for PCA 1-3 including the geochemistry data and inferred lake-water TOC.

sive clear cutting known to have occurred in the catchment in the beginning of the 20th century (Olsson, 1985). After this rapid increase in TOC, the inferred values are again lower (~ 6 mg L⁻¹).

During the 18th and 19th centuries the lake-water pH declined from a peak value of 6.8 to about 6 while the inferred lake-water TOC increased from about 6.4 to 8.5 mg L⁻¹. For that TOC change to account for this pH change, the ANC would be about 70 $\mu\text{eq L}^{-1}$.

During the time of extensive clear-cutting there is an expected and sudden drop in the *Picea* and *Pinus* pollen, while *Juniperus*, apophytes, anthropocores and charcoal show their highest values during the entire Holocene (Fig. 3).

3.5 Liming phase: 2–0 cm sediment depth (ca. 20–0 yrs BP).

The most recent sediment (2–0 cm, ca. 20–0 yrs BP) is characterized by increasing lake-water pH from ca. 5 to a maximum value of 5.9 (Fig. 2). This corresponds to the time when the lake was limed in 1974 and 1986 and accordingly the calcium concentration in the sediment also shows a sharp increase. The resolution in the inferred lake-water TOC, the geochemical and pollen data is too low in the topmost section for any interpretation of trends (2 values). The top surface sediment shows pollen percentage values that are similar as prior to the clear-cutting that occurred around AD 1900.

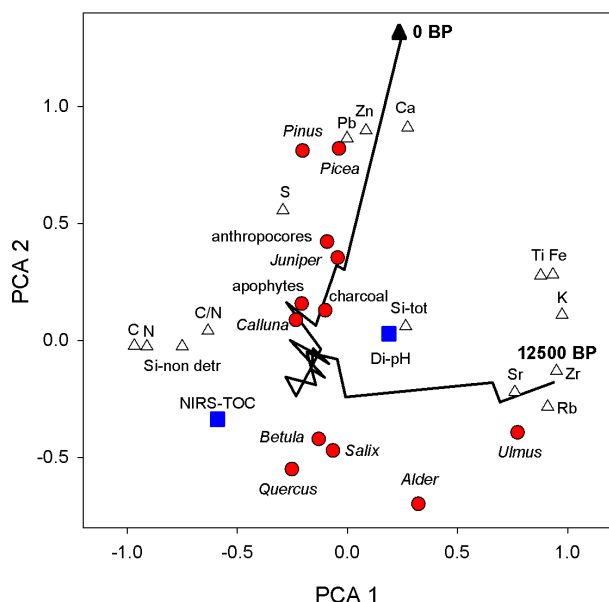


Fig. 6. Principal component analysis of all major pollen types, elements and inferred water chemistry. The loading values (sediment depth) and score values (environmental variables) are plotted together to assess correlations among all variables through time.

4 Discussion

While previous studies have established the link between large-scale changes in landscape characteristics (i.e., post-glacial lake ageing, later land use), what has remained uncertain from a long-term environmental change perspective is to what degree changes in pH were due to changes in lake-water TOC, soil-forming processes, changes in catchment vegetation, catchment erosion and fires (Renberg and Hultberg, 1992; Renberg et al., 1993a, b).

This study advances beyond the previous work by resolving the major driving forces behind Holocene changes in lake-water pH. Here we include sediment geochemistry and lake-water TOC. This combination allows for a more comprehensive interpretation that includes estimated changes in the ANC of lake water, which is a measure of the combined output of both weathering products and components of atmospheric deposition, including pollutants (Ca, Mg, Na, K, SO₄, NO₃, Cl).

To get a first insight into the role of lake-water TOC on the pH development relative to changes in the balance of inorganic acids and bases from the catchment (the charge balance ANC), we have used an organic acid dissociation model (Köhler et al., 2000) to calculate the acid neutralizing capacity (ANC) for Lysevatten during the past ca. 12 500 years.

4.1 The role of lake water TOC, lithogenic elements and vegetation for lake-water pH

The post-glacial period starts with an inferred pH value of about 6.5, ca. 12 000 yrs BP, with an inferred TOC value of 6 mg L⁻¹; this yields a modeled ANC value of 116 µeq L⁻¹. During the time of soil development and vegetation expansion the lake water TOC values increase to above 9 mg L⁻¹ between 9000–7000 yrs BP. Assuming a constant ANC value of 116 µeq L⁻¹, the lake-water pH would be around 6.3. The diatom-inferred pH at this time is 5.9, which indicates that the increase in lake-water TOC can only explain part of the decline in pH. However, during the same time-frame we also measure the largest decrease in element concentrations related to mineral matter and a doubling of the sediment carbon concentration. These two changes indicate a decline in catchment erosion and weathering, along with the increase of allochthonous and/or autochthonous input of organic carbon to the lake. The large changes are probably an effect of the establishment of vegetation, the development of soils and soil organic matter in the catchment and loss of base cations in the system, all of which can decrease lake-water pH (Engstrom et al., 2000; Boyle, 2007; Boyle, 2008).

From ca. 7000–1100 years BP the inferred lake-water pH varies from 5.3 to 5.8 and the lake-water TOC ranges from 9–12. During the same period of time there are almost constant concentrations of lithogenic elements and organic carbon in the sediment, which suggests stable catchment conditions with only minor changes in allochthonous input of weathering and erosion products. Assuming that the median inferred pH value of 5.6 is connected to the inferred lake water TOC median of 9 mg L⁻¹, the modeled ANC would be 68 µeq L⁻¹. If the ANC remains at this level, then during periods with the highest lake-water TOC values of 11.5, the model suggests a pH of 5.2. This means that the variations in lake-water TOC could explain a major part of the pH variation over these 6000 thousand years without any change in the ANC of lake water. Possible explanations for the changes in the inferred lake-water TOC over this time frame can possibly be variation in, e.g., vegetation and precipitation, which can influence the allochthonous input of organic carbon (Köhler et al., 2008).

Around 1100 yrs BP pollen types associated with human impacts, here grouped as anthropocores and apophytes, as well as an increased concentration of charcoal are visible in the sediment record. At the same time as these changes occur lake-water pH increases from 5.6 to 6.5. These observed changes conform to the so-called cultural alkalization period (Renberg et al., 1993a, b). The reasons for the substantial increase in lake-water pH over hundreds of years has been suggested to be due to human related activities and can include man-made fires, forest grazing by cattle and agriculture (Renberg et al., 1993a, b). The combined effects of small-scale cutting, forest grazing and burning of forest for agricultural use resulted in a relatively more open forest

with a lower canopy and lower biomass production per unit area; this landscape disturbance can possibly have increased the release of base cations (calcium, potassium, rubidium) and nutrients (carbon, nitrogen, phosphorus) from soils and biomass (Renberg et al., 1993a, b). Such changes in landscape characteristics would also have resulted in a reduced transport of organic carbon from the catchment to the lake.

The decrease in inferred lake-water TOC from 11 to 8.5 would only raise pH to 5.9 if the ANC remained at $75 \mu\text{eq L}^{-1}$. A substantial increase in ANC to over $150 \mu\text{eq L}^{-1}$ is needed as well to explain the increase in pH to 6.5. For the period 900 to 250 BP the modeled ANC was between two and three times as high as the ANC just prior to the start of the cultural alkalization period. From the geochemical record in the sediment we can infer that changes in base cation availability and in-lake productivity were involved in the increase in pH. The calculated biogenic Si increased during this phase, which agrees with observations of greater diatom abundance while counting the original slides. Higher biogenic silica values indicates higher lake bioproductivity, which may be due to a higher benthic diatom production as a response to clearer water and improved light conditions (Karlsson et al., 2009). Increased primary production may therefore also be part of the reason why lake-water pH increases. The PCA also indicates an increased depletion of base cations, e.g., potassium, relative to the total mineral fraction in the sediment; this depletion in the sediment requires an uptake and enrichment of potassium elsewhere, such as in catchment vegetation or through in-lake productivity. Along with the changes in sediment and lake-water biogeochemistry there were also changes from deciduous to coniferous forest and an increase in pollen from anthropocores, apophytes and charcoal that are indicative of early land use. Early settlements used forest burning to improve grazing (Norberg et al., 2010). We therefore suggest that all these changes taken together can explain the remaining part of the increase in lake-water pH – in addition to that related to TOC – in this case study from Lysevatten.

During the past 300 yrs the lake-water pH has declined from a peak value of 6.5 to about 5.8, which is prior to when the most pronounced increase in atmospheric pollution of sulfur started after AD 1945. During the same time the inferred lake-water TOC increased from about 6.2 ca. AD 1800 to 8.5 mg L^{-1} ca. AD 1930. Assuming a constant ANC of $200 \mu\text{eq L}^{-1}$, this increase in TOC would change pH less than 0.2 pH units. An ANC decline to $73 \mu\text{eq L}^{-1}$ is needed to get a pH of 5.8 in 1930 with a TOC of 8.5 mg L^{-1} . We propose that these recent (AD 1800–1930) changes in lake-water pH, ANC and lake-water TOC are initially due to a reduction of catchment use by humans and grazing and later further driven also by intense forestry around AD 1900 and atmospheric pollution such as sulfur.

4.2 Recent changes in land use

The major changes in the catchment during the past two centuries are supported by literature data, land surveys and oral stories summarized for the area surrounding Lysevatten by Olsson (1985). In 1845 and 1888 the forest contained a mixture of deciduous and coniferous trees, although 25 percent of the village of Lunden that lies at Lysevatten's outlet was open outfields. Extensive outfield grazing occurred until 1950 in the area and in the larger Ucklum parish, of which the villages of Lilla Kamperöd and Lunden, which adjoin Lysevatten, were a part. Outfield grazing was extensive but not intensive in the areas near the lake, and prior to AD 1850 there were only about 10 sheep per km^2 , but this figure diminished to 5 sheep per km^2 around 1900 and only 1 per km^2 by 1950. Prior to AD 1900 the local population mainly used the forest for their own continuous needs rather than short-term economic profit, so only selective cutting was used. Intensive forest cutting did not occur until the early 1900's, when oral sources mentioned that a company bought the farm and the sawmill at Lilla Kamperöd, 1 km from Lysevatten. Some 40 people were employed and a locomotive and steam-powered engine guaranteed continuous work regardless of season, whereas previously the sawmill was only used during high stream-water discharge. A few years later the forest had been exploited and the company was gone. Oral sources stated that much of the forest was clear felled during these few years, 1900–1910. In the sediment levels from this same time, there is a sudden change in the vegetation inferred from pollen, where apophytes, anthropocores, *Juniperus* and charcoal increase to Holocene maximum values. The inferred lake-water TOC also shows a sudden increase of almost 2 mg L^{-1} to 8.5 mg L^{-1} at the time of intensive clear cutting in the catchment.

Since AD 1920 until ca. 1985 sulfur deposition increased, which is probably the main reason for the further decline in lake-water pH that has occurred over the past 100 years. But during the same time there were also large changes in the catchment. During the years 1910–1968 only a handful of people worked at the sawmill, and because much of the forest was already clear-cut most of the mill's timber came from outside the catchment. Following the clear cut around AD 1900 the forest has reestablished and in 1933 the forest next to Lysevatten was dominated by spruce (77 percent) with no trees older than 80 years and a dominating age class of 61–80 years (77 %). In 1959, the age structure had changed and 67 % of the trees were in the age class 81–100 yrs. From 1933 to 1968 a small increase of spruce occurred at the expense of pine and deciduous trees.

The lake was limed in 1974 with 60 tonnes of CaCO_3 and again in 1986 with 100 tonnes of ground limestone, which can be seen in the inferred lake-water pH as an increase from 5.0 to 5.8 and that the Ca concentration in the sediment increase substantially. After the liming, the lake gradually acidified again to pH values around 5 (Renberg and Hultberg,

1992). The inferred lake-water TOC value has too low resolution in recent time for any interpretations of trends.

4.3 Implications for managing surface waters

Previous studies have discussed the natural and anthropogenic variation in lake-water pH in the context of managing surface waters (Guhren et al., 2007; Renberg et al., 2009; Norberg et al., 2010). The data from Lysevatten together with previously published data on inferred lake-water TOC raise similar questions about the variability of reference conditions for lake-water TOC (Rosén, 2005; Cunningham et al., 2010). Our results indicate that the current increase in lake water DOC/TOC that has been observed across Europe and North America over the past decades (Monteith et al., 2007; Evans et al., 2007) is rather small when compared to the long-term variation in Lysevatten. The variation in lake-water pH is likely to be associated with changes in both lake-water TOC and the geochemical weathering/erosion that influence ANC. We argue that these changes can be due to both natural and human related activities, such as soil development processes in the early Holocene, major vegetation changes and early land use. These results raise important questions regarding what precisely comprises “reference” conditions (i.e., free from human impacts). According to current European guidelines, encapsulated in the European Water Framework Directive, the emphasis in managing surface waters is the establishment and maintenance of good physical, chemical and ecological status. “Good status” is defined as one that is free from or minimally impacted by humans. While this may be an ideal goal, we should critically address the definition of “reference conditions”, as well as whether it is desirable or feasible to have one “snapshot” from the dynamic history of lake chemistry as the goal for water management. If we are defining our goals from some other time period in a lake’s history it can become very expensive and probably not even possible to achieve given the differences between modern land-use practices, including agriculture and forestry. As discussed in Norberg et al. (2010) three targets should be considered while discussing water managing and target goals:

1. Natural conditions prior to human impact. In the case of Lysevatten this would be the time prior to 1100 yrs BP.
2. The historical human impact of early settlements. In case of Lysevatten this would be the time frame between 1100–150 yrs BP.
3. The impact of the modern society. In the case of Lysevatten this would be during the past 150 years which includes major changes in agriculture, forestry and airborne pollution.

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