Lake condition changes of a boreal lake over the past ca. 6500 years based on varve geochemistry

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Abstract

The purpose of this study was to assess changes in the in-lake conditions of lake Kassjön, northern Sweden, in response to environmental and climate changes over the past ca. 6500 years. Sediment concentrations of different elements and biogenic silica (bSi) were measured with wavelength dispersive X-ray fluorescence spectrometry (XRF) and Fourier transform infrared spectroscopy (FTIR), respectively. The lake-water total organic carbon (LWTOC) content was inferred based on near-infrared spectroscopy (NIRS). The marine sediment was distinguished from the lacustrine sediment by higher dry bulk density, lithogenic element concentrations and Br content, and lower bSi concentrations. After lake formation, the dry bulk density, lithogenic element concentrations and metal contents decreased, while organic matter (OM), bSi and LWTOC increased. The main reasons for these changes are soil development and vegetation establishment. Spruce immigration around 3000 BP induced considerable changes to the sediment concentrations indicative of increased erosion versus weathering, and LWTOC declined. These changes are mainly related the different characteristics of spruce compared to birch. Human influences in the catchment were also clearly visible, but the rest of the sediment sequence demonstrated that natural changes can be of a similar magnitude. Overall, relatively small-scale, catchment specific processes seem to be more important for changes in the lake conditions than general climate change.

Key Words: varved lake sediment, total element concentrations, biogenic silica, lake-water organic carbon, Holocene
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1 Introduction

1.1 Background

The climate has always been changing, but due to the anthropogenic influences of the last few centuries the rate of these changes is greatly enhanced (IPCC 2013). Pre-disturbance conditions give an insight into natural variability, which can be useful for distinguishing between actual trends and environmental noise (Smol 2010). Therefore, long-term data on both climate and smaller-scale environmental processes like vegetation changes are crucial for good understanding of the current developments and possible predictions for the future.

Because there is a lack of directly measured long-term climate and environmental data, natural archives are a commonly used alternative for obtaining data from the past (e.g., Kaupilla and Salonen 1997, Smol 2010). Lake sediments are an example of natural archives that contain data on different climatic and environmental aspects (Kaupilla and Salonen 1997, Meyer-Jacob et al. 2014, Meyer-Jacob et al. 2015). Major and trace element variations over time can tell something about the change in conditions in the lake itself, but also in the catchment area and the atmosphere (Kaupilla and Salonen 1997, Peinerud 2000). Something else that can be very informative is biogenic silica (bSi), which is a proxy for in-lake productivity (Conley 1988, Peinerud 2000, Meyer-Jacob et al. 2014). Lastly, lake-water total organic carbon (LWTOC) content is a combination of organic carbon (OC) obtained from in-lake organic matter (OM) production and terrestrial input and plays an important role in the global carbon cycle (Meyer-Jacob et al. 2015).

Varved (or annually laminated) lake sediments have been studied since the early 20th century (e.g., Berry 1930). Research on this topic became more extensive during the last few decades and varves have been used as indicators of changes in the past climate and environment (e.g., Renberg 1981, Segerström 1990, Ojala et al. 2008, Augustsson et al. 2010, Haltia-Hovi et al. 2010, Meriläinen et al. 2010). Their value lies in the fact that each varve represents one year, meaning that past environmental dynamics can be studied with good chronological precision. In boreal lakes, the years can be distinguished based on the thin dark layers that are formed every winter. During winter, the surface of boreal lakes is frozen, as a result of which no new mineral material from the catchment is added to the sediment. Only OM from within the lake and fine-grade material that was already in suspension are deposited, forming a thin layer that covers the entire bottom of the lake (Renberg 1981).

Kassjön is a lake close to Umeå, northern Sweden (figure 1), which has already been the study object of several scientists (e.g., Segerström et al. 1984, Segerström 1990, Anderson et al. 1995, Petterson et al. 2010). It is a dimictic lake, meaning that it mixes twice a year. Because the turnover periods during spring and autumn are short and the lake bottom thus remains oxygen-free most of the year, the yearly varves are well preserved (Petterson et al. 2010). This process of varve formation started ca. 6500 years ago when the land around the lake rose above sea level (Segerström et al 1984, Segerström 1990).

Figure 1. Map of Sweden, indicating the location of Kassjön.
Segerström et al. (1984) were one of the first to conduct a research in the lake Kassjön. They performed a pollen analysis, which is now incorporated in the European Pollen Database (2017). Pollen data can be used for dating vegetation changes, both natural and human induced. The main focus of Segerström et al. (1984) was on the agricultural period. This time period was extended back to lake formation by Segerström (1990).

Anderson et al. (1995) measured the bSi concentration in Kassjön with an average resolution of 18 years. The data shown in their article covered the time period 800 AD to 1995 AD. The research of Petterson et al. (1999) was about a comparable time period, namely 476 AD to 1015 AD. They aimed to develop image analysis to estimate accumulation rates of different sediment components like minerogenic matter, OM and bSi and look at the relative importance of these components.

The latest research in Kassjön was about the minerogenic accumulation rate of the lake sediment over the period 4486 BC to 1900 AD (Petterson et al. 2010). Grey-scale variation of the varves was determined with image analysis and varve thickness was calculated based on varve counting. The combined data from grey-scale determination and varve counting resulted in a time series of the minerogenic accumulation rate on a 5-year basis.

1.2 Purpose
Even though there has been quite a bit of research on Kassjön’s sediment record already, the work done on geochemistry is very limited. Previous work was mostly about identifying environmental and climate changes through varves. Here, I assess changes in lake conditions in response to these environmental and climate changes. My main focus is on the relative contribution of erosion versus weathering in the catchment and on the biological productivity, both terrestrial and in the lake itself. I use the varves and available pollen record as an advantage to make the timings of different environmental and local catchment changes as accurate as possible. The time scale of my research ranges from pre-6500 BP (marine sediment) until present. The marine sediment is included for putting the magnitude of the changes within the lacustrine sediment in contrast to changes between different sedimentation systems.

2 Materials and methods

2.1 Fieldwork
In January 2017, a complete sediment sequence was collected from the deepest basin of the lake (63.92433 °N; 20.01026 °E), where the most continuous sedimentation would take place. Previous research from Kassjön has confirmed the formation of continuous varve series since lake formation until ditching operations took place in the beginning of the 20th century (Segerström et al. 1984). The sediment sequence consisted of 12 Russian peat cores collected in parallel holes through ice, about 2 m apart. The upper 3 cores were taken using a 1 m long corer (8 cm diameter), with each core overlapping by roughly 20 cm. For the sediments below, a 50-cm corer (5 cm diameter) was used with an overlap of approximately 10 cm. A parallel sediment sequence of the uppermost 2 m was collected, allowing comparison of results to test representativity. For the uppermost 30 cm of the sediment, an HTH gravity corer was used (Renberg and Hansson 2008), because this sediment is loose and therefore difficult to collect with a Russian corer. The gravity core was sliced in the field into 1-cm sections, while the cores from the Russian corer were transported as a whole.

2.2 Sample preparation
Prior to taking samples from the cores, the surfaces of all Russian cores were cleaned to remove disturbances and contamination caused by coring or packing in the field. Cleaning also makes the varves better visible. After cleaning, the cores were aligned based on varve characteristics. The total depth of the aligned sediment sequence was determined to be 556 cm. At
approximately 20 cm depth a clay layer occurs, which corresponds to the ditching operations from the early 20\textsuperscript{th} century (Segerström et al. 1984). Volumetric samples were taken every 2 cm from that point downwards using a syringe (1.2 cm inner diameter) pressed carefully into the sediment cores. The volume of the samples was generally 1.0 to 2.0 mL. For the sediment above the clay layer, the 1-cm slices of the gravity core were used for analysis. All samples (n = 299) were freeze-dried and with the dry weight and the exact volumes, the dry bulk density was calculated. The duplicate cores were subsampled every 8 cm (n = 22), to check how representative one sediment sequence is for the general trends in past environmental dynamics over the whole catchment. Representativity was based on the similitude of trends in element concentrations over depth between the main sequence and the duplicates.

2.3 Element concentrations

The total concentrations of both major (Na, Mg, Al, Si, S, K, Ca, Fe) and trace (P, Cl, Ti, V, Mn, Ni, Cu, Zn, Br, Rb, Sr, Y, Zr, Ba, Pb) elements were measured with wavelength dispersive X-ray fluorescence spectrometry (XRF) (n = 98). The XRF analyses were based on 50 mg dry sample, using a modification of the 200 mg calibration of Rydberg (2014). Additionally, replicates were run for checking the reliability of the results. This was done in two ways. Firstly, some samples were replicated by pouring the same sample from one cup into another, to determine the uncertainty of the XRF instrument and the analytical method. Secondly, another batch of samples was replicated by taking new subsamples out of the larger samples, to check how well the samples had been homogenized. The instrument used was a Bruker S8-Tiger WD-XRF analyzer, equipped with a Rh-anticathode X-ray tube, five analyzing crystals (XS-55: W/Si multilayer crystal; XS Ge-C: Curved germanium crystal; LIF200 and 220: Lithium fluoride crystals; PET: pentaerythrite crystal), different collimators and filters, a flow proportional counter for light elements (Na to V) and a scintillation counter for heavy elements (Cr to Pb).

2.4 Biogenic silica (bSi)

Fourier transform infrared spectroscopy (FTIR) with the calibration of Meyer-Jacob et al. (2014) was used to determine bSi concentrations. Meyer-Jacob et al. (2014) mixed 11 mg of sample with 500 mg of KBr, I used 5.5 mg of sample mixed with 250 mg of KBr (n = 79). A Bruker Vertex 70 was operated, equipped with a MCT (Mercury–Cadmium–Telluride) detector, a KBr beam splitter, and a HTS-XT accessory unit (multi-sampler).

2.5 Lake-water total organic carbon (LWTOC)

LWTOC was inferred based on visible and near-infrared spectroscopy (NIRS). A Foss XDS NIR rapid content analyzer was operated, equipped with a spinning cup module in diffuse reflectance mode in the wavelength range from 400 to 2500 nm at 0.5-nm intervals, yielding 4200 data points. After every tenth sample, alternatively two internal standards were run. When all samples were analyzed, 11 random replicates were run for quality control. To convert the measured values into actual LWTOC concentrations, an updated model of Meyer-Jacob et al. (2015) was used that includes calibration samples from Sweden, Finland and Canada.

2.6 Data analysis

2.6.1 Weathering ratios

As shown by Kauppila and Salonen (1997), sometimes element concentrations alone do not give all desired information. Therefore, ratios can be useful to obtain more information on changes in geochemistry from the same data set. The K/Al ratio is a measure of erosion versus chemical weathering. More weathering results in a lower K/Al ratio, because K is more favorable to be transported down in the soil (Kauppila and Salonen 1997). Another measure of erosion versus weathering is the Chemical Index of Alteration (CIA), which was calculated using equation 1 (Nesbitt and Young 1982).

\[
\text{CIA} = \frac{[\text{Al}_2\text{O}_3]/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})]} \cdot 100
\]
A higher CIA value indicates that the material is more weathered and the CIA should thus have an opposite pattern to the K/Al ratio. The CIA in this report is plotted with a reversed y-axis for easier comparison with the K/Al ratio.

2.6.2 Statistical relationships
Correlations (r- and p-values) between all elements were calculated with R-package ‘psych’ in R version 3.2.2 and later manually combined into a correlation matrix. All correlations with $p<0.01$ were considered significant. On top of the correlation matrix, a PCA was performed based on both the concentration data from the XRF and the dry bulk density. The idea of a PCA is to reduce the number of variables by dividing the initial variables over a defined number of principal components. Before running a PCA, z-scores have to be calculated in order to standardize the data. This was done using R-package ‘base’ in R version 3.2.2. The PCA was run with the package ‘psych’ in the same version of R. After running several versions of PCAs, two of them were chosen to represent my results. The first one including the marine sediments, the second one without that (see Results for exact depth). The before mentioned division was made because the main focus of this report is on the lacustrine environment. Cl was excluded from both PCAs, because it had no significant correlation with any of the principal components. Ba was also excluded, because even with all four components together, less than 60% (58%) of its variation was explained. Both from the correlation matrix and the PCAs, the upper 8 cm of the sediment was excluded because of the liming and fertilizing activities during the last century (Segerström et al. 1984, Petterson et al. 2010, Länsstyrelsen 2017).

3 Results

3.1 General patterns
From 444 cm downwards, both the varves start to diminish and distinct changes in the XRF data occur (figure 2). Below this depth, both the dry bulk density and the lithogenic element concentrations are high, indicating a minerogenic sediment. Also, the Br concentration is high with values around 25 ppm (figure 2B). High Br concentrations are typical for a marine environment (Emelyanov and Vaikutiene 2013). Therefore, 444 cm is assigned to the marine-lacustrine transition that took place ca. 6500 BP (Segerström et al. 1984, Segerström 1990). The next substantial change can be found at a depth of 200 cm, corresponding to ca. 3000 BP (figure 2, Segerström et al. 1984). The mineral matter input increases again, but Br shows a distinct drop at this time (figures 2A, B, C, D, J). P and bSi drop as well (figures 2H, K). Around this time, spruce started to immigrate into the area around Kassjön by replacing the birch trees (figure 3, Segerström 1990, Giesecke 2005). Around 70 cm depth, many element concentration patterns start changing again (figure 2). Br increases and the lithogenic elements decrease (figures 2B, C, D, J). Zn, P and bSi increase as well (figures 2G, H, K). This corresponds to the start of agriculture that occurred around 1160 AD in this area (figure 3, Segerström et al. 1984). Lastly, the clay layer at 20 cm depth represents the start of more intense human activities, with for example the ditching that caused the clay layer and fertilizing activities afterwards (Segerström et al. 1984, Petterson et al. 2010). Especially Zn and Ca stand out in this phase with Zn concentrations reaching 263 ppm at its highest point and Ca going up to 8% as compared to ≤1% in the entire sequence below (figure 2I).

Based on aforementioned events, the sediment sequence is divided into 5 main phases:
1. 556 – 444 cm (marine sediment)
2. 444 – 200 cm (lake formation to spruce immigration)
3. 200 – 70 cm (spruce immigration to agriculture)
4. 70 – 20 cm (early agriculture)
5. 20 – 0 cm (modern period)
Figure 2. Summary of biogeochemical data with on the left panel the dry bulk density, Br, Al, K, K/Al and CIA, and on the right panel Zn, P, Ca, total Si, detrital Si and bSi. Note that the y-axis of the CIA is reversed for easier comparison with the K/Al ratio. The arrow indicates how the K/Al ratio and CIA relate to the degree of weathering.
3.2 Statistical relationships
3.2.1 Correlation matrix
The cross-correlations between Na, Mg, Al, Si, K, Ti, Rb, Sr, Y, Zr and Ba are both strong and significant, representing the lithogenic elements (table 1). However, the correlations with Si are weaker than for the other elements because of the contribution of bSi. Strong and significant cross-correlations are also found between Fe, S, Cu, Zn, Br and Pb. These elements are grouped as partly organically bound. Not all elements of the aforementioned two groups are presented separately, but based on the PCA, a few elements are used as representative for the whole group in further results.
3.2.2 PCA
For both the PCA including the whole sediment sequence (except for the upper 8 cm which is affected by liming) (PCA_all) and the PCA without the marine sediments (PCA_lake) four principal components are identified. Together these explain 88% of the variance in PCA_all and 91% in PCA_lake. In PCA_all, more than half (53%) of the variance is explained by the first component (PC1_all). The elements with strong positive weights on this component are K, Mg, Na, Al, Ti, Rb, Ca, Sr, Zr, Si, and Y; also the dry bulk density is strongly positively correlated with this component (figure 4A). P has a strong negative weight on PC1_all. Especially because of the strong positive weights of above mentioned elements and the dry bulk density, PC1_all is assigned to the lithogenic elements. Except for Sr, Si and Y, the same elements have a significant positive relationship with PC1_lake as with PC1_all (figure 4B). That Si does not have a significant relationship with PC1_lake is because total Si is divided into detrital Si and bSi in the lake sediment (figures 2J, K). On top of the elements that are positively correlated with PC1_lake, the dry bulk density has a high positive weight as well. Br and P have the strongest negative weights on PC1_lake. Considering this element distribution, PC1_lake represents the lithogenic material (i.e., mineral versus organically bound elements) and these elements can thus be grouped for the whole sediment sequence. The elements used as examples for the minerogenic material are Al and K. Because of the generally similar pattern of Ca compared to Al, K and detrital Si until the modern period, Ca is not discussed separately in these phases. Only in the last phase there is a distinct difference in patterns (figure 2I) and here Ca is thus discussed on its own. Figures 2C, D, J show that the detrital Si (total Si – bSi) follows the same pattern as Al and K and is therefore not discussed in further detail.
PC2\textsubscript{all} gives especially strong positive values for Zn, Cu, Fe, and Pb and V (figure 4A). None of the elements show a strong negative correlation with PC2\textsubscript{all}. On PC2\textsubscript{lake}, the before mentioned elements have strong positive weights as well (figure 4B). In addition to that, S has a 83% explanation of its variation by PC2\textsubscript{lake} and Br 67%. A negative correlation of 54% is found with the dry bulk density. Based on both PC2\textsubscript{all} and PC2\textsubscript{lake}, the organically bound elements form one group. However, S and Br follow a different pattern over time than the metals. Therefore, the group of organically bound elements is split into two with Br representing the OM input to the lake and Zn representing the metals. PC3 and PC4 did not contribute to grouping more elements for further results and are therefore not described in further detail.

### 3.3 Phase 1 (marine sediment: 556 – 444 cm)

The marine sediment is distinguished from the rest of the sediment record by higher dry bulk density and lithogenic element concentrations, a higher Br content and lower bSi concentrations (figures 2A, B, C, D, K). From the bottom of the sequence up to 482 cm depth, the dry bulk density fluctuates around 0.9 g/cm\textsuperscript{3} (figure 2A). Between 480 cm and 456 cm, it varies around 0.7 g/cm\textsuperscript{3}, after which a drop down to ~0.5 g/cm\textsuperscript{3} can be observed during the transition from marine to lacustrine environment. Br starts with relatively high concentrations of around 25 ppm at the bottom of the sequence, with a peak up to 45 ppm at 484 cm depth (figure 2B). The patterns of Al and K are identical to each other, with a decline right before the marine-lacustrine transition (Al drops from 6% to 5% and K from 2.5% to 1.9%) (figures 2C, D). That Al and K show the same pattern can be seen in the K/Al ratio as well (figure 2E), indicating no change in the quality of the mineral matter. The K/Al ratio has some fluctuations around 0.4, but there is no clear trend. The CIA mainly fluctuates around 97.1, without any specific trend (figure 2F).

Zn shows an increase in concentration towards the lake sediment (from 105 ppm to 160 ppm) (figure 2G). The variation in Zn concentrations is small up to 500 cm depth, after which the increase both in total concentration and in variation between two consecutive points starts. The concentration increase right before lake formation is the steepest in this section. In the marine sediment, P has a concentration fluctuating around 650 ppm, with two small peaks (figure 2H). At the transition from marine to lacustrine sediments, a peak of 6000 ppm occurs. The bSi concentration is rather constant slightly above 0% up to 460 cm depth (figure 2K). After that it jumps to almost 4% during the transition from marine to lacustrine environment.
3.4 Phase 2 (lake formation to spruce immigration: 444 – 200 cm)
After the decline in dry bulk density during the transition phase, it rises up to 0.8 g/cm$^3$ at 444 cm depth (figure 2A). From there, the dry bulk density decreases to 0.3 g/cm$^3$ at the end of phase 2, with a rate that decreases when moving up in the sequence. The Br concentration right after lake formation is about half of what it was before (~12 ppm) (figure 2B). From that point up to when the spruce come in, the concentration increases gradually to 20 ppm. For both Al and K, the lacustrine values right after lake formation are similar to the marine values (figures 2C, D). Between 444 cm and 200 cm depth, the Al and K concentrations decrease (Al from 6% to 5%, K from 2.5% to 1.7%). The fact that the K/Al ratio also decreases between 444 cm and 200 cm, means that K decreases more than Al (figure 2E). All lithogenic elements thus follow the same trend, but some elements decrease more than others. Opposite to the K/Al ratio, the CIA increases from 97.4 at the marine-lacustrine transition to 98.1 at 200 cm depth (figure 2F).

Zn decreases between lake formation and spruce arrival almost down to its values in the early marine sediment (~130 ppm) (figure 2G). The P concentration goes back to similar values as in the marine sediment immediately after lake formation (figure 2H). From that point upwards, the P concentration rises to 2300 ppm at 200 cm depth. Between lake formation and spruce arrival, bSi shows a general increase from almost nothing (0.2%) to ~7% at 200 cm depth (figure 2K).

3.5 Phase 3 (spruce immigration to agriculture: 200 – 70 cm)
In this phase, the long-term decline in dry bulk density is interrupted with as much as a two-fold increase to about 0.6 g/cm$^3$ (figure 2A). There are two drops in the stage of high dry bulk density, but it is only in the upper 15 cm of phase 3 that the density stays low (~0.3 g/cm$^3$). The Br concentration shows a steep drop when the spruce come in, after which it fluctuates around 8 ppm (figure 2B). Two peaks up to ~16 ppm can be found at 164 cm and 108-92 cm depth. Al and K show an opposite pattern, with a sharp increase when the spruce come in and two drops at the same depths as the peaks in Br concentration (figures 2C, D). By following the same pattern as the Al and K concentrations, the K/Al ratio shows again that the relative change in K is larger than that in Al (figure 2E). That the degree of weathering is changing can be seen in the CIA as well, which has a pattern opposite to the K/Al ratio (figure 2F). The CIA drops to 97.5 when the spruce come in and has two peaks at the locations of the drops in K/Al ratio.

The Zn concentration starts with an increase compared to phase 2, up to 140 ppm at 124 cm depth (figure 2G). Above that, the Zn concentration declines and it ends around 110 ppm at the start of agriculture. In the P concentration, the arrival of spruce is clearly visible (figure 2H). The concentration drops to 1000 ppm, less than half of what it was before the spruce came in. After this steep decline, there is an increasing trend in P concentration during phase 3, making it end around 1600 ppm right before the start of agriculture. The bSi concentration shows a distinct drop to ~0.8% at the moment of spruce arrival (figure 2K). Two peaks can be seen in the bSi content with the first peak being smaller than the second (3.2% at 164 cm and 6.4% at 92 cm depth).

3.6 Phase 4 (early agriculture: 70 – 20 cm)
During phase 4, the dry bulk density fluctuates between 0.1 g/cm$^3$ and 0.3 g/cm$^3$, but there is no specific trend (figure 2A). Br starts with an increase up to 35 ppm at 52 cm depth (figure 2B). After this, there is a decrease to 18 ppm, and then again an increase up to 33 ppm. Al and K show an opposite pattern, indicating fluctuations in the relative proportions of mineral matter (Al, K) and OM (i.e., Br). The lithogenic elements decrease during the first period of agriculture (Al down to 4% and K to 1.2%, both at 52 cm depth), then increase where Br decreases, and decrease again at the same depth as the second increase in Br (figures 2C, D). In the K/Al ratio it can be noted that especially the first decrease is more distinct for K than for Al, with a K/Al ratio going down to 0.3 at 52 cm depth (figure 2E). The second decrease can be
seen in the ratio as well, but less clear. In the CIA both changes in sediment quality are visible as peaks, the first one to 98.7 (52 cm) and the second one to 98.5 (28 cm) (figure 2F).

Zn shows an increase to 122 ppm at 52 cm depth (figure 2G). Above that, there are many fluctuations, but the overall pattern seems to be an increase up to about 155 ppm right before the clay layer. Just like many other elements in this phase, P shows two peaks (figure 2H). One of 3400 ppm at 52 cm depth and one of 2400 ppm at 27 cm depth. The two peaks or drops that are visible in almost all graphs during phase 4, are thus around the same depths for all elements and ratios. The bSi concentration shows and overall increasing trend from 0.8% to 12% during phase 4, but with large variations (figure 2K).

3.7 Phase 5 (modern period: 20 – 0 cm)
Immediately after ditching (Segerström et al. 1984), the dry bulk density, as well as the Al and K concentrations, show a peak corresponding to the clay layer at 20 cm depth (figures 2A, C, D). They all decrease after that to their lowest values at the sediment surface. However, there is a difference between the peak of the dry bulk density and the peaks of Al and K: Al and K have their actual highest values in this peak, while the dry bulk density comes to only half of the density the sediment had in the marine phase (0.4 g/cm³). The Al concentration at the highest point of the peak is 6.8%, K is 2.6% there. The drop of Br in the clay layer goes to concentrations similar to those before the start of agriculture (~4 ppm) (figure 2B). The Br concentration then increases towards ca. 45 ppm in the upper few cm of the sequence, but before reaching this high value, another drop in concentration is visible at 5 cm depth. Just like in all other phases, the change in K is larger than the change in Al, and the K/Al ratio thus shows a peak in the clay layer and a decline to its lowest values at the sediment surface (figure 2E). The CIA drops to 97.3 in the clay layer and increases afterwards (figure 2F). The CIA is not shown in the upper 8 cm due to the effects of liming on the Ca concentration (figure 2I, Länsstyrelsen 2017).

Zn increases steeply immediately after the ditching activities and then continues with a decrease to 160 ppm at 5 cm depth (figure 2G). Above that, the Zn concentration increases again to ~210 ppm in the upper few cm of the sediment sequence. P goes back to pre-agricultural values in the clay layer (~1000 ppm) and then increases towards 2800 ppm in the upper few cm, interrupted by a small disturbance around 5 cm depth (figure 2H). The bSi concentration drops to 1.8% in the clay layer and is highly variable after that with variations between 2.8% and 8.7% (figure 2K).

3.8 Lake-water total organic carbon (LWTOC)
When considering the whole sequence, the variation in LWTOC concentration between two successive points becomes larger while moving up in the profile. In the upper 30 cm, the variation seems to decrease again, but this is because the distance between the points there is 1 cm instead of 2 cm. Although the model does not cover marine samples, the suggested LWTOC concentration in the marine sediment would be ~3 mg/L (figure 5). For comparison, modern TOC values in the Gulf of Bothnia range from 3.5 to 4.3 mg/L (Algesten et al. 2006). Between 444 cm and 258 cm depth the concentration rises to 10 mg/L. Above that, the concentration varies around the same value until spruce come in at 200 cm depth. At the moment of spruce arrival, the LWTOC concentration shows a dip. The concentration does not reach the low values that it had at the time of lake formation though. The lowest concentration in the dip is 4.6 mg/L, around 145 cm depth. During the rest of phase 3, the LWTOC concentration starts increasing again, eventually reaching the 10 mg/L that it was before spruce arrival. This increase in concentration continues in phase 4 to a value of 14.3 mg/L at 50 cm depth. Afterwards, it drops back to 5.0 mg/L in the clay layer (20 cm depth). Above the clay layer, the LWTOC concentration starts rising once more to a concentration of about 13 mg/L at the top of the sediment.
4 Discussion

4.1 Landscape development (556 – 200 cm): pre-6500 BP – 3000 BP

The dry bulk density in the marine sediment is 0.9 g/cm$^3$, which is nearly equal to values for the dry bulk density of soils in this region (~1.4 g/cm$^3$), indicating a very minerogenic sediment. The lithogenic elements have high concentrations in the marine sediment as well. This is due to the constant mineral matter supply by wave action. However, Br has the most distinct difference between the marine and lacustrine environments, with marine concentrations being twice as high than those in the lacustrine sediment. The reason for the high Br concentrations in the marine sediment is that Br is one of the components of sea salt (Emelyanov and Vaikutiene 2013). Immediately after lake formation, the Br concentration drops to half of the marine values, because sea salt does not have an effect anymore (Emelyanov and Vaikutiene 2013). The small peak in CIA at the end of the marine phase suggests that some weathered material from the land started to come into the water. The increase in dry bulk density and high Al and K concentrations directly after the marine-lacustrine transformation are because the mineral matter input right after the isolation of Kassjön from the Bothnian Bay was high. This is due to down cutting of runoff water into the soils, caused by the high uplift rate at that time (Petterson et al. 2010, Poutanen and Steffen 2014). The dry bulk density and mineral matter indicators decrease after that with about 25% until spruce arrival. On top of that, the K/Al ratio decreases and the CIA increases, inferring that more weathering starts to take place. This is confirmed by a diminishing of the uplift rate over time (Poutanen and Steffen 2014), causing the erosion to slow down. Due to the slower erosion more weathering can take place, because the upper soil is not constantly removed anymore at such a high rate. Weathering in its turn causes the soil to be more stable, so this is a positive feedback. However, the diminishing of the uplift rate is only relevant for slowing down erosion in the first stage of lake formation. Afterwards, the higher weathering rates are caused by the establishing of vegetation and development of soils (Petterson et al. 2010). Vegetation establishment is also the reason for the general increase in Br during this period of landscape development. Haltia-Hovi et al. (2010) also found a decrease in mineral matter input and an increase in OM input to the lake sediment of a lake in Finland during initial basin development, which they relate to vegetation establishment as well. The peaks in Al and K, and the drop in Br at 316 cm depth are most likely due to small-scale processes like temporary sediment storage within the inflow channels (Petterson et al. 2010). During a colder year, the snow cover is thicker causing more intense spring melting and thus a higher input of mineral matter to the lake sediment (Ojala et al. 2008, Petterson et al. 2010).
In the upper part of the marine sediment, the metal concentrations increase because the weathering of the surrounding land that rises above sea level releases metals from the soil, which can then be transported to the sediment (Starr et al. 2003, Antoniadis and Golia 2015). The concentration increase was not as distinct for all the metals due to differences in mobility (Sauvé et al. 2003, Starr et al. 2003). After lake formation, the metal concentrations show a decline as a result of further weathering of the soils, causing the metals to percolate into deeper soil layers, making it harder to transport them to the lake (Starr et al. 2003, Antoniadis and Golia 2015).

The peak in P around the transition from marine to lacustrine environment is supported by the visibility of vivianite in the sediment. This suggests large changes in sediment geochemistry at this time.

Detrital Si and total Si concentrations are basically the same in the marine sediment, given that the measured bSi concentration is around 0%. From the marine-lacustrine transition onward the bSi concentration increases up to ~7% at spruce arrival. This general increase is again due to the landscape development and thus weathering that takes place after isolation from the sea (Petterson et al. 2010). Weathering results in better access to dissolved nutrients, which has been shown to be one of the limiting factors of diatom growth (Lotter and Bigler 2000, Mata et al. 2010).

LWTOC is dependent on both in-lake production and terrestrial input (Meyer-Jacob et al. 2015). The aforementioned catchment stabilization through the development of soils and establishment of vegetation thus increases the LWTOC content as well, both because of a higher terrestrial OM input and because of the increase in diatom growth due to higher nutrient availability (Lotter and Bigler 2000, Mata et al. 2010, Meyer-Jacob et al. 2015). An increase in LWTOC directly after deglaciation was found by Rosén (2005) as well for two of the three boreal lakes he investigated, indicating that this is a common trend for lakes in an early stage of landscape development.

4.2 Spruce immigration (200 – 70 cm): 3000 BP – 1160 AD

Around 3000 BP, both the dry bulk density and the lithogenic elements increase to what their values were at the time of lake formation over a period of only ~200 years. Opposite to that, Br decreases over these 200 years to its value at lake formation. Augustsson et al. (2010) did not find such a sudden change in the mineral matter versus OM distribution over that same time period in their lake sediment from Finland, indicating that this change is related to catchment-specific processes rather than general climate change. During this short time period, spruce immigrated to Kassjön from the northeast by replacing the birch trees (figure 3, Segerström 1990, Giesecke 2005). The large woody debris from spruce is less than from birch (Dahlström et al. 2005). On top of that, spruce has no understory, so there is no contribution of litter from there either (Hansson et al. 2011). K and Al are both more abundant in the upper 30 cm of the soil with spruce than with birch (Hansson et al. 2011). If elemental concentrations in the upper soil are higher, the concentrations in the eroded material will be higher as well, because erosion mainly takes place at the soil surface. Even though this higher abundance of K and Al in the topsoil is not significant in the research of Hansson et al. (2011), my data suggest that it does have a measurable effect. The increases in mineral matter and dry bulk density imply relatively more erosion. This is confirmed by the rise in K/Al ratio and the decrease in CIA, which indicate a lesser degree of weathering. The lack of understory under the spruce trees is a major explanation for this (Hansson et al. 2011). Without an understory the soil is more open and thus more easily erodible.

The increase in metal concentrations during the first approximately 1300 years (76 cm) after spruce arrival is due to the lower soil pH in the surrounding of spruce compared to birch trees.
Metals are more mobile with a lower pH and can thus be transported to the lake more easily after dissolving in the runoff water (Pérez-Esteban et al. 2014). But not only will they dissolve more easily in the runoff water, the metals will leach faster down to deeper soil layers as well. After a while, leaching starts to counterbalance the effect of easy transport with runoff, flattening out the rise in metal concentrations in the lake. Eventually the initial increase turns into a decrease of, in this case, even more than 20%.

The decline in P concentration at spruce arrival to less than 50% of its value before has two main causes. Firstly, it is simply diluted by mineral matter. Both from the correlation matrix and PC1 it is clear that P is negatively correlated with the lithogenic elements (table 1, figure 4). Secondly, spruce take up more P than birch and it is thus stored in the canopy instead of in the soil. Several studies indicate that spruce contain less P in mg/kg dry weight than birch (Reimann et al. 2001, Reimann et al. 2007). However, spruce are larger than birch and the total amount of P/ha in the litterfall of spruce is higher than in that of birch trees, indicating that the total amount that the spruce take up from the soil is higher as well (Hansson et al. 2011). This only has an effect during the first ~200 years though. The slow increase afterwards is because of soil acidification. It takes some time for the soil around spruce to become more acidic than it was around birch, but when it happens it will make the nutrients less available for the trees and they can thus be eroded down to the lake (Thelin et al. 2002, Hannson et al. 2011).

The decline in LWTOC of about 50% that I find after spruce arrival is opposite to the trend that Rosén (2005) found for one of the three boreal lakes in his research. However, I have additional geochemical data to support my result. LWTOC is a combination of allochthonous input of C to the lake and production in the lake itself, so with both Br and bSi decreasing at the moment of spruce arrival, it would be only logical if the LWTOC decreases as well (Meyer-Jacob et al. 2015). At 145 cm depth, corresponding to about 2000 BP (based on the data of Segerström et al. 1984), the LWTOC starts increasing again. The dry bulk density shows an opposite pattern, suggesting a decrease in mineral matter input. These observations are confirmed by drops in Al, K and Al/K ratio, and peaks in CIA and bSi. The peak for Br is not as distinct as for bSi, indicating that higher in-lake production is most likely the cause for the increased LWTOC.

Based on Segerström et al. (1984), the drops and peaks that occur around 164 and 92 cm depth in the figures for Br, Al, K and bSi are linked to 2400 BP and 1200 BP respectively. These drops/peaks are related to changes on a smaller time-scale (decades). Mineral matter input is reduced during warmer periods, because the thinner snow cover causes less intense spring melting (Petterson et al. 2010). The bSi, and partly Br, concentrations are enlarged during warm events due to less growth limitation by temperature (Sorvari et al. 2002, Mata et al. 2010). Therefore, these two anomalies are most likely related to short warm periods. There are also peaks visible at these moments in LWTOC, but they are less clear because LWTOC has more data points and the peaks are thus surrounded by other data points that make the graph smoother.
4.3 Agriculture (70 – 20 cm): 1160 AD – 1900 AD

At the start of agriculture, the Br concentration doubles in about 200 years, while the lithogenic elements and the dry bulk density decrease. The main cause of the doubling of OM is the increase in diatom production due to the, probably very small, increase of nutrient input (Anderson et al. 1995). Because both crop cultivation and animal husbandry became important and the land used for animals can be covered with grass or small plants during the entire growing season, erosion did not directly increase drastically (Segerström 1990). There was also a general decreasing trend in precipitation, meaning less snow cover during winter and thus less intense spring floods (Seppä and Birks 2002, Petterson et al. 2010). The increase in mineral matter and decrease in OM in the later years of agriculture are because more and more land is opening up, causing more erosion to take place. This is confirmed by the increase in K/Al ratio and decrease in CIA. The reversion of trends shortly before the clay layer is because around 1850 AD, crop cultivation started to decrease very rapidly (figure 3). On top of that, the high bSi concentrations dilute the lithogenic elements. The decrease in lithogenic elements is slightly delayed compared to the increase in OM, because it takes some time for plants to regrow to such an extent that they can stabilize the soil.

The increasing Zn concentration is related to the crop harvesting that occurred from 1160 AD onwards (figure 3, Segerström et al. 1984). Soil pH decreases when crop residues are not placed back on the land (Butterly et al. 2013). Because metals are more mobile with a lower pH, runoff water can transport them more easily to the lake (Pérez-Esteban et al. 2014). The decrease in crop cultivation from ca. 1850 AD onwards (figure 3) does not cause the soil pH to immediately increase again.

The increasing OM input is the main cause of the rise in P, agreeing with PC1 of the PCA. Even though animal densities were probably not very high during the early stages of agriculture, animal manure had some effect as well. Manure is positively correlated with total P concentrations in runoff, so the manure from animal husbandry somewhat increases the P concentration in the lake sediment as well (Kleinman and Sharpley 2003).

The doubling of the P concentration at the start of agriculture coincides with a bSi increase of more than five times. Total P concentrations are not a good indicator for bioavailable P, but because of the proven positive effect of P on diatom production (Schindler 1978), the strong correlation between total P and bSi suggests that bioavailable P increased at this time as well. A diatom increase in Kassjön due to agriculture was found by Anderson et al. (1995) as well, who suggested that even though the initial nutrient input was probably small, it had dramatic effects on the diatom population. The drop in bSi from 8% to 3% at ca. 1650 AD corresponds to the increase in erosion and thus mineral matter input into the lake, which cause a diminishing of the diatom growth due to light limitation (Lotter and Bigler 2000, Mata et al. 2010). When the mineral matter input decreases again, the diatoms bloom, shown with a bSi concentration of 12.4%. This is due to a combination of cultural eutrophication (Segerström et al. 1984, Mata et al. 2010) and less light limitation (Lotter and Bigler 2000, Sorvari et al. 2002, Mata et al. 2010).

The LWTOC increase that started around 2000 BP continues during the first more or less 300 years after agricultural settlement (Segerström et al. 1984, Segerström 1990). The decline from then until ca. 1850 AD is because a major expansion of field area took place around Kassjön (Segerström 1990). Trees had to be cut down to accomplish this and clear-felling of forests is a known reason of decreasing LWTOC (Cunningham et al. 2011). Also, crops are harvested regularly, removing OM from the land. This coincides with the decline in Br concentration. The peak shortly before ditching is not as distinct as the increase in Br, but the decrease in crop cultivation and thus forest regrowth, can be seen in the LWTOC as well.
4.4 Intensive human land use (20 – 0 cm): 1900 AD – present

First of all, the clay layer that was observed visually before starting with any analysis is clearly marked with a relatively high dry bulk density (0.4 g/cm³) and high concentrations of the lithogenic elements (Al: 6.8%, K: 2.6%). Due to these extreme concentrations of the lithogenic elements, the concentrations of the other elements are automatically low. Only Zn does not drop markedly in the clay layer, because metals are part of mineral structures as well (Fadiran et al. 2014). The fast erosion due to ditching is supported by the peak in K/Al ratio and the drop in CIA (Segerström et al. 1984). The low concentration of bSi is because the huge inflow of mineral matter blocks a considerable part of the light in the lake and thus reduces the photosynthesis (Mata et al. 2010).

The increase in OM deposition after ditching is due to cultural eutrophication (Segerström et al. 1984). Even though the cultivated area became smaller from ~1950 AD onwards, the use of fertilizers intensified (Segerström et al. 1984). The rise in P concentration supports this. Also the in-lake production increased, shown as an increase in bSi concentration. The inflow of mineral matter decreased shortly after the ditching operations, because this was only a short-time event and the catchment is thus likely to stabilize in some form afterwards. The further decrease in lithogenic elements later on is due to reforestation (Segerström et al. 1984). The metals increase very steeply after ditching with for example Zn reaching a value of 265 ppm. This sharp increase is because metals are partly organically bound and thus transported to the lake in larger amounts with the increased OM input (see correlation matrix and PCA).

It is obvious from the Ca graph that the Ca concentrations of the last few years are completely out of proportion with values reaching up to 8% compared to ≤1% in the rest of the sequence. These extreme Ca concentrations due to the recent liming activities cause the concentrations of the other elements and the bSi to be unreliable in the upper 8 cm of the sediment (Länsstyrelsen 2017). Therefore, these concentrations are not discussed any further.

LWTOC concentrations are low in the clay layer, because of the intense drainage that is generated by ditching (Segerström et al. 1984, Cunningham et al. 2011). After that, the LWTOC increases with almost 10 mg/L in about 100 years. Human presence has decreased during the last few decades, giving the forest the opportunity to regrow (Segerström et al. 1984). The cultivated areas that remained have been treated differently than before, with more intense fertilization (Segerström et al. 1984). A combination of these two factors leads to a continued increase in LWTOC until at least 1984 (Segerström et al. 1984, Meyer-Jacob et al. 2015). The recent increase in LWTOC is due to liming (Länsstyrelsen 2017). Diatoms are very sensitive to pH, and liming thus has a considerable effect on the in-lake productivity (Arzet et al. 1986, Sorvari et al. 2002).

4.5 Recommendations

With the bSi measurements of this research, only the total portion of bSi compared to the other compounds in the sediment could be obtained. This says something about total diatom production, but not about species distribution. Sometimes the diatom community structure can change, while the total diatom production remains constant (Anderson et al. 1995). Diatoms are more sensitive to catchment disturbances than the pollen accumulations that I used for determining major vegetation changes (Anderson et al. 1995). Therefore, I suggest an extension of the diatom record of Anderson et al. (1995) over the whole sediment sequence for a better understanding and a more precise timing of smaller-scale catchment processes.

4.6 Conclusion

The transition from marine to lacustrine sediment indicates that for the lithogenic elements, metals and bSi, the changes within the lacustrine sediment have a higher magnitude than the changes between marine and lacustrine sediments. Br and P stand out with very substantial concentration changes during the marine-lacustrine transition ca. 6500 BP. The main driver of the concentration changes between lake formation and spruce arrival is simply the fact that
the land is not covered by sea anymore. As a result of vegetation establishment and soil development, the erosion decreases, allowing higher in-lake productivity because of less light limitation. The replacement of birch by spruce ca. 3000 BP had drastic effects on element concentrations, as well as on the bSi and LWTOC contents. After the spruce were established, temperature fluctuations on a relatively small time-scale started to have some influence on the mineral matter versus OM distribution in the lake sediment, but still the effects of the vegetation change were most evident. It can thus be concluded that relatively small-scale, catchment specific processes are more important to the lake conditions than general climate changes. Furthermore, anthropogenic influences cause substantial changes in the catchment and in-lake conditions. However, the extreme Br concentrations in the marine sediment and the peak in P at marine-lacustrine transition, as well as the abrupt concentration changes at spruce arrival, indicate that large variations can occur without human influence as well.
References


