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# Elemental composition of a deep sediment core from Lake Stocksjön in the Forsmark area

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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### Abstract

A deep sediment core was taken from Lake Stocksjön, situated within the Forsmark site investigation area. The 55 cm long sediment core, representing the entire history of the lake (approx 430 years) was sliced in 5 cm portions and analysed for various chemical elements, using ICP-MS technique. In total, 54 different elements – classified as main elements, heavy metals and trace elements – were analysed.

In general terms, three different patterns of stratigraphy were derived from all the analysed elements. Calcium, manganese, lead and mercury occurred in highest concentrations in the upper sediments (< 30 cm depth). Phosphorus, zinc, cadmium, antimony, tin and strontium occurred in more even proportions throughout the sediment core. All the other elements were substantially reduced in the upper parts (< 30 cm) compared to the deeper parts of the sediment core.

Metals that are considered as airborne pollutants were found in low or moderate concentrations. This is in concert with other investigations of pollutants that have been performed in the Forsmark area.

The sediment of Lake Stocksjön is highly organic, and has been so during the entire history of the lake. Much of the organic material seems to be refractory and less susceptible for mineralisation and respiration during the prevailing environmental conditions. This corresponds well with the characteristic gelatinous cyanophycée gyttja found in the lower parts of the sediment core.

Although speculative, the pronounced changes in elemental composition of the sediment at 30 cm depth may correspond to the final isolation of the lake from the Baltic Sea, which occurred approximately 230 years ago. The deeper parts (below 30 cm depth) thus may represent the time period with regular intrusions of brackish water into the lake basin.

One important factor governing the environmental conditions and the resulting elemental composition of the sediment is the unusually thick "microbial mat", which is characteristic for the surface sediments of Lake Stocksjön and other oligotrophic hardwater lakes in the Forsmark area. Reducing conditions and low pH, which frequently are found close beneath the surface layers of many lake sediments, are in this case directed to the deeper layers. The primary producers of the microbial mat promotes precipitation of calcium carbonates and co-precipitation of phosphorus compounds, and prevents recycling of e.g. phosphorus to the lake water during large parts of the year.

The data gathered in this investigation will be further used in future evaluations of transport and turnover of various elements within the catchments of the Forsmark site investigation area, as well as in research regarding ontogenetic patterns of lake ecosystems.

### Sammanfattning

En 55 cm lång sedimentkärna från Stocksjön i Forsmarksområdet har analyserats med hjälp av ICP-MS-teknik. Sedimentkärnan representerar en tidsperiod på ca 430 år, med start från den postglaciala sandiga lera som avsattes medan bassängen ännu var en del av Östersjön. Totalt analyserades 54 olika grundämnen, som delades in i kategorierna huvudkomponenter, tungmetaller och spårelement.

Tre olika typer av stratigrafiska mönster kunde identifieras för koncentrationerna av de olika grundämnena. Kalcium, mangan, bly och kvicksilver hade högst koncentration i de översta 30 cm av sedimentet. Fosfor, zink, kadmium, antimon, tenn och strontium uppvisade mer jämna koncentrationer genom hela sedimentkärnan. Alla övriga grundämnen uppvisade istället kraftigt minskade koncentrationer i de översta 30 cm jämfört med djupare lager.

Metaller som anses vara luftburna föroreningar fanns endast i låga eller måttliga koncentrationer, vilket indikerar att Stocksjön och dess avrinningsområde inte varit utsatt för några större mängder av denna typ av föroreningar. Detta överensstämmer med resultat från tidigare undersökningar som gjorts i området.

Koncentrationen av organiskt material var mycket hög genom hela sedimentkärnan. Det tyder på att det organiska materialet är svårnedbrytbart under rådande miljöförhållanden. Ett exempel på detta är den karaktäristiska geléaktiga cyanophycée-gyttjan, som hittades i de djupare delarna av sedimenten.

Det är möjligt att den skarpa gräns i koncentrationsfördelningen hos de olika grundämnena som hittades vid 30 cm djup representerar den tidsperiod när sjöbassängen slutligt isolerades från havet. De underliggande sedimenten representerar i så fall den tidsperiod under vilken regelbundna salt/brackvattenintrång skett på grund av havsvattenståndets variationer under året.

Stocksjön har, i likhet med övriga kalkoligotrofa sjöar i Forsmarksområdet, en tjock "mikrobiell matta" som består av såväl autotrofa som heterotrofa mikroorganismer längs bottnen. Detta påverkar bl a syrgas-, pH- och redoxförhållandena i de övre sedimentlagren, och därmed också koncentrationer och utbyte av olika ämnen mellan sediment och vatten. Reducerande miljöförhållanden och lågt pH hittas vanligtvis ganska nära under sedimentytan i sjöar, men i Stocksjön hålls troligen en betydande del av de ytliga sedimenten syresatta och vid högt pH på grund av den fotosyntesaktivitet som pågår under stora delar av året. Därmed hämmas bl a återcirkulationen av fosfor till vattenmassan.

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### 1 Introduction

The chemical stratigraphy of a sediment core can give a picture of the historical development of the lake and its catchment. However, the interpretation of the results of such analyses can be very difficult, due to the complexity of the mechanisms that governs the distribution of different elements in lake sediment. Examples of these difficulties, identified and discussed by /Engstrom and Wright 1984/ are:

- i) Varied and not easily identified sources of the elements.
- ii) Variations in the deposition to the sediment.
- iii) Post-depositional redistribution of elements.

The sources of the organic component in lake sediment include both a share produced within the lake and a share produced within the catchment. The inorganic component consists of weathered mineral particles from the bedrock or the soil deposits of the catchment and inorganic ions dissolved in the inflowing water or from the precipitation.

Changed physical and chemical conditions may influence the depositional process in a lake. Shifts from oxic to anoxic environment and changed alkalinity due to alterations in the catchment are some of the factors that are important for the deposition of materials.

Multiple core studies have shown that the chemical composition of sediment varies also across a lake /Engstrom and Wright 1984/. Once deposited, waves, currents and slides may redistribute the sediment material. Bioturbation by burrowing organisms, post-depositional migration of elements and resuspension due to changed limnological conditions are other factors that influence the chemical stratigraphy of lake sediments.

Different lakes have different characteristics due to dissimilarities in the catchments and within the lakes. /Brunberg and Blomqvist 1999/ have described the ontogeny and characteristics of the most common lake type within the Forsmark area, the oligotrophic hardwater lake. As new land areas rise from the sea due to the shoreline displacement occurring in this area, shallow coastal bays are successively isolated from the sea. A successive change from brackish water to freshwater occurs and weathering of the calcium rich till begins. The carbonates from the till are transported to the lake, where they are precipitated as calcite in a light-exposed soft-bottom zone dominated by *Chara* meadows and an unusually thick microbial mat consisting of cyanobacteria and diatoms. Knowledge about the hydrology of the lakes, the accumulation of substances from the catchment, and biological and chemical processes within the sediments of these lakes are considered to be important for the understanding of the complex system that constitutes the oligotrophic hardwater lake /Brunberg and Blomqvist 1999/.

Some of the lakes within the Forsmark area are not completely isolated from the sea and are therefore still influenced by brackish water. Other lakes in the area have just begun their oligotrophic hardwater stage. The shoreline displacement and the following changes in lake ecosystem characteristics and environmental conditions occur rapidly – at least in geological perspective. Hence, many simultaneously varying parameters affect and complicate the interpretation of the elemental composition of the sediments. On the other hand, the resulting sediment composition may show distinct patterns caused by these rapid changes.

The aim of this study was to describe the chemical stratigraphy of a deep sediment core from Lake Stocksjön, one of the oligotrophic hardwater lakes in the Forsmark site investigation area. The information gathered has been evaluated from a limnological point of view, and the dataset is published unabridged, with the purpose to make it available for further evaluation and interpretation.

### 2 Execution

#### 2.1 Area description

Lake Stocksjön is situated in the Forsmark site investigation area (Figure 2-1), within the catchment Forsmark 2 /Brunberg et al. 2004/. Lake Eckarfjärden is situated upstream within the catchment. The outlet from Lake Stocksjön flows through Lake Bolundsfjärden and later enters the Baltic Sea in Asphällsfjärden.

Lake Stocksjön is a small shallow lake with maximum depth of 0.8 m, mean depth of 0.2 m and a very short theoretical water renewal time, only 8 days. The threshold of the lake is situated at a level of 2.75 m above RH 70 /Brydsten and Strömgren 2004/. The catchment is almost 1.5 km<sup>2</sup> and is dominated by a forest consisting of mostly birch trees with portions of younger coniferous trees. Lake Stocksjön is almost completely dominated by a litoral habitat with emergent and floating-leaved vegetation. Further details regarding the catchment, lake morphometry parameters and lake ecosystem parameters are described in /Brunberg et al. 2004/.



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Figure 2-1. Lake Stocksjön and its catchment.

### 2.2 Sampling and analysis of a sediment core from Lake Stocksjön

A 55 cm deep sediment core was taken with a Livingstone sampler from the deepest part of Lake Stocksjön (coordinates: N6697580, E1632220) in March 2002. This core represents the entire sediment layer deposited in the lake. The sediment was sliced in 5 cm thick sections down to 50 cm. The last part of the sediment core was divided in one 4 cm and one 1 cm thick section.

The sediment was analysed for 55 different elements by Analytica AB (Table 2-1, Appendix 1), using the technique of ICP-MS. As the samples were expected to have varying amounts of organic matter, two different methods were used for sample preparation. One set of subsamples were analysed with the analyse packages G0-N and G5-N (in total 46 elements), which are designed for samples with high mineral content. The samples were prepared by drying at 105°C, fusing with lithium metaborate and dissolving the samples in dilute nitric acid /Analytica 2005a/. Another set of subsamples were analysed according to the M4-N-program /Analytica 2005b/ intended for samples with high organic content, and thus more suitable for the upper parts of deep sediment cores. These samples were prepared by oxidation/digestion with nitric acid and hydrogen peroxide. As a result of the different extraction methods and analyse packages used, there was an overlap in results for some of the elements. We have chosen to use the concentrations of arsenic, mercury, cadmium, cobalt, cupper, nickel, lead, and zinc from the M4-N-program instead of the values from the G0-N-program, due to the volatility of these elements. Chromium, tin, and vanadin were also analysed twice, but since they are not volatile the concentrations from the G0-N-program were used. Aluminium, calcium, iron, potassium, magnesium, manganese, sodium, phosphorus, silicon, and titanium (Appendix 1) were reported in oxide form from Analytica AB and were therefore recalculated to the pure elements. The result of the recalculation is presented in Appendix 2.

Note that the reported % dry substance (%TS) in Appendix 1 does not represent the original wet sediment. The samples sent to Analytica AB were already dried, and the figures in the table were achieved when drying the samples again, after transportation and some time of storage. The original dry content in the sediment core ranged between 2.5 and 10.1% (Brunberg unpublished data).

All data from the elemental analyses of the sediment core reported here have been included in the SKB database SICADA, with under the object identification number PFM004509 (Lake Stocksjön).

Main elements	Heavy metals	Trace elements
Ca, Si, Al, Fe, K, Mg,	Cu, Zn, Pb, Ni, Cr,	Ba, Zr, Y, Li, Cs, U, La, Dy, Ho, Ce, B, Sr,
Na, Ti, Mn, P, S	As, Cd, Hg, Co,	Lu, Sb, Rb, Sm, Sc, Be, Nb, Mo, Nd, Th, Pr,
% ash	V, Sn	Er, Ta, Eu, Tb, W, Yb, Hf, Tm, Gd

Table 2-1. Analyses performed on the sediment core from lake Stocksjön.

### 3 Results

The sediment core from Lake Stocksjön (Figure 3-1) showed visual variations in sediment composition and was originally approximately 70 cm long. The upper 20 cm was the green "microbial mat" that is characteristic for the oligotrophic hardwater lakes in the Forsmark area. This layer is very loose (high water content) and is easily resuspended. Underneath the microbial mat followed a 20 cm layer of calcareous grey/green/brown sediment, also very loose and with high water content. The last five cm of this layer had a very light grey/brown colour indicating large amount of calcareous material. Further down the core had a 25 cm layer of cyanophycée-gyttja, with the characteristic gelatinous consistency and red colour. The lower part of this section was banded with darker layers. Finally, the core ended with 5 cm of transition between cyanophycée-gyttja and grey clay (marine, post-glacial clay). During transportation to the laboratory a substantial part of the upper loose sediments were compressed and when the core was sliced some water was also lost from the uppermost layers. Hence, the resulting sediment samples corresponded to a total core length of 55 cm. The 25–30 cm sample represents the light calcareous layer originally found at a depth of 35-40 cm. The two last samples, 50-54 cm and 54-55 cm, represent the transition between cyanophycée-gyttja and clay. The last centimetre (54–55 cm) was only grey clay, and was kept as a separate sample during the analyses.



Figure 3-1. The sediment core from Lake Stocksjön. (The white area on left side at 35–36 cm is old tape on the plexiglass core.)

The results of the analysis of 55 elements show a distinct pattern in which some of them occur in the largest amounts in the upper part of the sediment core, down to 30 cm (corresponding to 40 cm in Figure 3-1), and occur in much lower concentrations below this border. Other elements show an inverse pattern, occurring in much smaller amounts in the upper 30 cm and have their highest concentration below this border. Some elements do not fit into any of these two main patterns. The border between 25 and 30 cm seems to be the key to the understanding of the chemical stratigraphy of the sediment core. Other trends can also be distinguished within these two "main" patterns.

In the following presentation of results, the analysed elements are divided into main elements, heavy metals and trace elements (cf Table 2-1).

#### 3.1 Main elements

The main elements include ten elements that are common main components in silicate bedrock. Sulphur is also included in this group due to its high concentration in the sediment. We also report the proportion of ash, i.e. the inorganic component of the sediment in this part of the report.

The ten main components of silicate bedrock as well as the ash content in the sediment were analysed in the G0-N-program (Appendix 1). Sulphur was analysed in the M4-N-program (Appendix 1).

Calcium (Ca) was the dominating element in the sediment core. The amount of calcium was very high in the upper 30 cm (Figure 3-2), with a marked peak between 25–30 cm, corresponding to the light coloured area at 35–40 cm in the unsliced core (Figure 3-1). Below this zone the concentration decreased markedly and in the last 16 cm it was almost constant and very low. Calcium was the only element among the main elements that had this type of stratigraphy.

Silicon (Si), aluminium (Al), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), and titanium (Ti) showed a completely opposite pattern (Figure 3-2). The smallest amounts of these elements were found in the first 30 cm. There was a marked increase between 30 and 35 cm and a gradual decrease from that level down to 40–45 cm, where the minimum concentrations in the interval of 30–54 cm were found. There was a gradual rise in concentration from the next level and downwards to the bottom of the sediment core. All these elements had very similar patterns of variation between 30 and 55 cm, although at different levels of concentrations.

Manganese (Mn), phosphorus (P), and sulphur (S) differed in chemical stratigraphy from the rest of the main elements.

The manganese concentration was highest in the first (upper) 15 cm of the sediment core, followed by lower values in the next interval down to 30 cm (Figure 3-2). After that, this element had the same pattern of variation as the major part of the main elements, i.e. decreasing concentration from 30 cm down to 45 cm, and then higher concentrations and increasing trend in the last three samples down to 55 cm.

The amount of phosphorus was highest in the first 5 cm; 546 mg/kg DW (Figure 3-2). Next layer, 5–10 cm, showed a marked reduction. In the next level the concentration increased again, followed by a gradual decrease down to 30 cm, where the lowest quantities of phosphorus in the sediment were analysed. Below 30 cm, the concentrations were again higher and increased slightly downwards to a level of approximately 436 mg/kg DW.

The concentrations of sulphur were relatively low in the 0–30 cm layers, with minimum values in the surface sediment (0–5, 5–10 cm) and maximum value at 15–20 cm (Figure 3-2). Below 30 cm depth, the concentrations increased substantially with a maximum level of 34,500 mg/kg DW at 40–45 cm. The bottom layer of the core, at the 50–55 cm level, seems to be almost completely depleted of sulphur.



**Figure 3-2.** Concentration of calcium (a), silicon (b), aluminium (c), iron (d), potassium (e), magnesium (f), sodium (g), titanium (h), manganese (i) phosphorus (j), sulphur (k), and the proportion of ash in a 55 cm deep sediment core from Lake Stocksjön. Note that the two lowest sediment samples from the core represent layers that are less than 5 cm thick.

The proportion of ash was high and increasing down to a maximum of 70% of DW at 30 cm depth. Below that level, this parameter followed the same pattern as the concentrations of silicon, aluminium, iron, potassium, magnesium, sodium, titanium, and manganese, i.e. decreasing from 30 cm down to 45 cm, and then higher concentrations and increasing trend in the last three samples down to 55 cm, where again the level was at approx 70% of DW. Concentrations of phosphorus did not seem to be related to the ash content, while the concentrations of sulphur showed an inverse pattern to ash content at levels below 30 cm depth.

### 3.2 Heavy metals

The 11 heavy metals described below are the most important ones considering pollution, according to the Swedish Environmental Protection Agency /Naturvårdsverket 2005/. Arsenic is included in this group even though it is not a heavy metal. Concentrations of chromium, tin and vanadin were taken from the G0-N analysis programme and the rest of the elements from the M4-N program.

The pronounced change in sediment composition at 30 cm depth was reflected also in the concentrations of most of the heavy metals (Figure 3-3). Some of the elements had substantially lower concentrations in the upper 30 cm layer (Cu, Ni, Cr, Co, V). Within this layer, most elements (also those with very low concentrations compared to deeper layers) showed similar variations with maximum concentration at 15–20 cm (Cu, Zn, Pb, Ni, As, Cd, Hg, Co, V). Zinc, lead, cadmium and mercury had high peaks or generally high levels in the upper 30 cm compared to the lower part of the core. Below 30 cm depth, most elements were present in higher or at least equal amounts as in the upper sediments, in many cases with increasing concentrations downwards. Arsenic and tin showed peaks at the level of 50–54 cm.

The surface sediment concentrations of eight of these heavy metals were classified according to the Swedish Environmental Protection Agency (Table 3-1). No comparison values exist for Co, V and Sn. A major part of the other elements (7 of totally 8) were classified to "class 1", very low content. Copper was the only exception and belonged to class 2, i.e. moderate content.



**Figure 3-3.** Concentration of copper (a), zinc (b), lead (c), nickel (d), chromium (e), arsenic (f), cadmium (g), mercury (h), cobalt (i), vanadin (j), and tin (k) in a 55 cm deep sediment core from Lake Stocksjön. Missing values are due to too small amount of sample and/or values below detection limit. Note that the two lowest sediment samples from the core represent layers that are less than 5 cm thick.

Table 3-1. Concentration of heavy metals in the 0–5 cm level of a sediment core from Lake Stocksjön compared to classification of heavy metal concentration in surface sediment (0–1 cm) according to Swedish Environmental Protection Agency /Naturvårdsverket 2005/. Heavy metal concentration: 1 = very low content, 2 = low content, 3 = moderate content, 4 = high content, and 5 = very high content.

CI co ac Pr	assific ncent cordir otecti	cation of h ration in s ng to /Swe on Agenc	neavy met surface se edish Envi y 2005/	al diment (0–1cm) ronmental	Heavy metal concentrati 0–5 cm level of a sedime lake Stocksjön	on from the nt core from
1:	Copp	er mg/kg-	<sup>1</sup> DW	< = 15		
2:	15	<	"	< = 25	Copper mg/kg⁻¹ DW	= 19.4
3:	25	<	"	< = 100		
4:	100	<	"	< = 500		
5:	500	< Coppe	r mg/kg <sup>_1</sup> [	W		
1.	Zinc r	na/ka-1 D	N	< = 150	Zinc ma/ka-1 DW	= 53 3
2.	150	<	"	< = 300		00.0
<u>3</u> .	300	<	"	< = 1 000		
۷. 4	1 000	<	"	< = 5 000		
5:	5.000	< Zinc m	na/ka⁻¹ DW	, I		
4.				1 - 50		- 40 4
1:	Lead	mg/kg⁻¹ L	"	< = 50	Lead mg/kg <sup>-1</sup> Dvv	= 12.1
2:	50	<	"	< = 150		
3:	150	<	"	< = 400		
4:	400	<		< = 2,000		
5:	5,000	< Zinc m	д/кд⁻+ Dvv			
1:	Cadm	nium mg/k	g⁻¹ DW	< = 0.8	Cadmium mg/kg <sup>-1</sup> DW	= 0.2
2:	0.8	<	"	< = 2		
3:	2	<	"	< = 7		
4:	7	<	"	< = 35		
5:	35	< Cadmi	um mg/kg⁻	<sup>-1</sup> DW		
1:	Chror	nium mg/l	kg⁻¹ DW	< = 10	Chromium mg/kg <sup>-1</sup> DW	= 1.7
2:	10	<	"	< = 20		
3:	20	<	"	< = 100		
4:	100	<	"	< = 500		
5:	500	< Chrom	ium mg/kg	l⁻¹ DW		
1:	Nicke	l ma/ka <sup>-1</sup>	DW	< = 5	Nickel ma/ka <sup>-1</sup> DW	= 4.4
2:	5	< 3 5	"	< = 15	5 5 5	
3:	15	<	"	< = 50		
<u>4</u> .	50	<	"	< = 250		
5:	250	< Nickel	ma/ka <sup>_1</sup> D'	W		
4.	A	io ma///a=		< - F	Areania malka-1 DNA	- 1 0
1. n.	Arsen	lic mg/kg	" DVV	< = 5	Arsenic mg/kg * Dw	= 1.0
2. 2.	5 40		"	< = 10		
3: 4.	10	<	"	< = 30		
4:	30	<		< = 150		
э.	150	< Arsenio	; mg/kg=' i	200		
1:	Mercu	ury mg/kg <sup>-</sup>	<sup>-1</sup> DW	< = 0.15	Mercury mg/kg <sup>-1</sup> DW	= 0.07
2:	0.15	<	"	< = 0.3		
3:	0.3	<	"	< = 1		
4:	1	<	"	< = 5		
5:	5	< Mercur	y mg/kg <sup>-1</sup>	DW		

### 3.3 Trace elements

Due to the high number of trace elements analysed, only a selection of them are shown in Figure 3-4 and Figure 3-5. However, they represent the general patterns found in the sediment core of Lake Stocksjön. The other trace elements that were analysed are included in Appendix 1 and 3.

The concentrations of caesium, lithium, boron, and antimony were taken from the results of the M4-N program (Appendix 1) and the values for barium, zirconium, yttrium, uranium and strontium from the G0-N-program (Appendix 1). Other elements shown in Figure 3-4 and Figure 3-5 were taken from the G5-N analyse program (Appendix 1).



**Figure 3-4.** Concentration of barium (a), zirconium (b), yttrium (c), lithium (d),caesium (e) uranium (f) lanthanum (g) dysprosium (h), and holmium (i) in a 55 cm deep sediment core from Lake Stocksjön. Note that the two lowest sediment samples from the core represent layers that are less than 5 cm thick.



150

c)

Sr 🗆

*Figure 3-5.* Concentration of cerium (Ce), boron (B), strontium (Sr), lutetium (Lu), and antimony (Sb) in a 55 cm deep sediment core from Lake Stocksjön. Note that the two lowest sediment samples from the core represent layers that are less than 5 cm thick.

Again, there were in most cases clear shifts in concentration levels between the layers above and below 30 cm. Examples of the most common stratigraphy are gathered in Figure 3-4, while examples of other patterns are given in Figure 3-5. In general terms, a large majority of the trace elements were found in much higher concentrations below the 30 cm level (Figure 3-4). The only exceptions from this were antimony, which had higher concentrations above the 30 cm layer (Figure 3-5 e), and strontium, which had small variations between the layers above and below a maximum value at 25–30 cm (Figure 3-5 c).

Among the elements that showed the general pattern, the concentrations within the upper 30 cm often showed a maximum value at 15–25 cm (e.g. Zr, Y, Li, Cs, U, La, Dy, and Ho in Figure 3-4; Ce, Lu, and Sb in Figure 3-5). Holmium (Ho, Figure 3-4 i) and boron (B, Figure 3-5 b) had relatively high values in the uppermost surface sediment. Cerium (Ce, Figure 3-5 a) had a pronounced peak at 20–25 cm depth.

In the deeper sediment below 30 cm, some elements (Ba, Zr, Y, Li, Cs in Figure 3-4, Sr in Figure 3-5) decreased to a minimum level at 40–45 cm depth and then increased again downwards in the core. Other elements (U, Dy, Ho in Figure 3-4; Ce in Figure 3-5) instead had their maximum concentrations at the 40–45 cm level and then decreased towards the bottom layer of clay.

### 4 Discussion

Sediments are the historical records of lakes, reflecting the ontogeny of the catchment ecosystems. The changes that are recorded along a depth profile may be natural as well as of anthropogenic origin. However, due to the complexity of the mechanisms that govern the distribution of different elements in sediments, the interpretation requires a broad knowledge in e.g. physical, chemical, geological, hydrological and biological processes that may affect the final composition of the deposited material. The long time perspective needed when interpreting deep sediment cores also adds the various diagenetic processes that have to be considered. Paleo-limnologists generally use data from many different analyses to track the historical development of lake ecosystems. For example, diatom analysis can be used to reconstruct former pH and salinity levels in lakes. Pollen analysis can give some information about the vegetation development in the surrounding areas of lakes.

The present investigation includes the chemical stratigraphy of many different elements. Some of them, e.g. the common main compartments in lake sediments and some of the heavy metals, are well known and investigated. Others, like many of the trace elements, are less known and information regarding their variation and role in lake ecosystems are lacking. However, the data gathered here may give new information that can be combined with other sediment investigations in the Forsmark area in order to get a better picture of the lake ecosystem characteristics.

Lake Stocksjön is a very small and shallow lake with the typical oligotrophic hardwater characteristics that are common among the lakes in the Forsmark area /Brunberg and Blomqvist 1999/. Sediment cores are usually taken in the deepest part of a lake, where the sediment is least influenced by waves, currents, and other disturbing factors. Since Lake Stocksjön is so shallow (maximum depth 0.8 m and average depth only 0.2 m /Brunberg et al. 2004/), the sediment is most certainly not undisturbed. Hence, spatial variation in the chemical stratigraphy might be expected /Engstrom and Wright 1984/. On the other hand, the small lake area (0.04 km<sup>2</sup>) and the wind shield provided by surrounding vegetation (currently 75% of catchment covered by forest and 85% of lake area by emergent vegetation) may prevent too much of heterogenity /Brunberg et al. 2004/.

Lake Stocksjön is situated 2.70 m above current sea level (threshold measured in RH-70 by /Brydsten and Strömgren 2005/), which implies an age as lake ecosystem of 430 years /Brydsten and Strömgren 2004, Påsse 1997/). This corresponds well to the depth of the sediment that was sampled. Modelling of sedimentation rates, based on data from 8 lake basins in the area, revealed an average sedimentation rate of 1.3 mm/year /Brydsten 2006/. When using this value, the age of the deepest part of the sediment core was calculated to approximately 420 years. There are two other lakes in the Forsmark area with similar age as Lake Stocksjön; Lake Labboträsk (elevation 2.65 m.a.s.l.) and Lake Kungsträsket (elevation 2.31 m.a.s.l.).

The most pronounced shift in elemental composition of the analysed sediment core was found at the depth of 30 cm below the surface sediment, which corresponds to approximately 230 years BP (calculated from 1.3 mm sedimentation/year according to /Brydsten 2006/). Although speculative, it might be assumed that this was the time when the lake was finally and completely isolated from major intrusions of brackish water from the Baltic Sea. The time for isolation calculated from the elevation of the threshold represents the time when the lake was separated from the yearly average level of the Baltic Sea. Although still dominated by brackish water, the lake basin was then protected from the substantial wave erosion of the coast. Signs of this erosion has been shown in Lake Stocksjön as well as in other lakes in the area, as lack of marine sediment layers /Hedenström 2004/. Accordingly, the deepest part of the investigated core (54–55 cm) was sandy clay. Identification of species composition in the diatom flora from different sediment depths (i.e. shift between marine and freshwater species') would confirm whether these speculations are true or not. Nevertheless, substantial changes in environmental conditions must have occurred at the time period corresponding to 30 cm sediment depth, in order to cause such differences in sediment composition.

In general terms, three different patterns of stratigraphy were derived from all the analysed elements. Calcium, manganese, lead and mercury were elements that occurred in highest concentrations in the upper sediments (>30 cm). Phosphorus, zinc, cadmium, antimony, tin and strontium occurred in more even proportions throughout the sediment core. All the other elements were substantially reduced above the 30 cm level of the sediment core.

Results from other lakes in the Forsmark area that have been sampled and partly analysed for the same parameters (e.g. P, Ca, Fe and organic content of deep sediment cores from Lake Eckarfjärden and Lake Hällefjärd) indicate that the stratigraphic pattern found in Lake Stocksjön is a general pattern of the oligotrophic hardwater lakes in the area. The transition zone where pronounced changes in concentrations occur varies slightly in sediment depth, maybe due to varying ages of the freshwater ecosystems, but the pattern remains similar between the lakes (Brunberg, unpublished data).

The most calcareous part of the sediment in Lake Stocksjön (211,550 mg Ca/kg DW) was deposited at 25–30 cm depth, i.e. probably just after the final isolation from the sea. The sediment at 30–40 cm depth shows elevated calcium concentration compared to the deeper layers, and may represent the time period of transition between freshwater and brackish conditions, during which occasional intrusions of saline water occurred (e.g. at low pressure weather conditions). Compared to Swedish lake sediments in general, the upper 40 cm of the core from Lake Stocksjön is very calcareous. This reflects the high concentrations of Ca in the till and soils predominating in the Forsmark area. Earlier investigations in the same lake /Hedenström 2004/ found maximum concentrations of CaCO<sub>3</sub> (57–63% = 228,000–252,000 mg Ca/kg DW) in sediments situated 0.87–0.97 m below the water surface, which corresponds roughly to the layers with maximum calcium concentration in this investigation.

The phosphorus concentrations at different levels of the sediment core shows a profile that is characteristic for the oligotrophic hardwater lakes in this area, but rare compared to other lakes in general. The most common profile for sediment phosphorus concentrations is increased levels towards the sediment surface, where mobile forms of phosphorus recirculate between sediment and lake water on a seasonal basis, governed by e.g. temperature and redox conditions. In Lake Stocksjön, as well as in other oligotrophic hardwater lakes in the Forsmark area, surface sediments hold a remarkably low concentration of phosphorus compared to many other Swedish lakes. On the other hand, the commonly found decrease in concentration downwards in the sediment has not been detected in Lake Stocksjön or other oligotrophic hardwater lakes. This might be interpreted as the phosphorus is trapped in the sediment and stays at the level where it was originally deposited without too much of vertical transport.

The sediment of Lake Stocksjön has very high content of organic material. This is shown by the % ash (Figure 3-2), which represents the non-organic proportion of the sediment samples (including carbonates). The minimum value (i.e. maximum of organic content) was found at 40–45 cm depth, where only 33.5% of the dry content remained as ash after burning at 550°C. Hence, the sediment has been highly organic during the entire history of the lake, and much of the organic material seems to be refractory and less susceptible for mineralisation and respiration at the prevailing environmental conditions. This also corresponds well with the characteristic cyanophycée gyttja which was found in the lower parts of the sediment core (Figure 3-1).

Hence, two different characteristics of this sediment core can be identified: dramatic changes in sediment composition at the shift from a bay of the Baltic Sea to an isolated lake basin and, a pronounced stability of some compounds that often are expected to decline with depth in lake sediments. The most important factor governing both these characteristics is most probably the development of a "microbial mat" in the uppermost 10–20 cm of the sediment. This layer does not represent "true" sediment, if defined as settled organic and inorganic material originating from allochtonous sources or produced in other parts of the lake. The upper "sediment" is instead a green, thick layer of various photosynthesising microphytobenthic organisms (e.g. cyanobacteria, diatoms) that produce new organic material in large quantities /Andersson and Brunberg 2006a/. Reducing conditions and low pH, which frequently are found close beneath the surface layers of many lake sediments, are in this case directed to the deeper layers. The high pH caused by primary production of the microbial mat promotes precipitation of calcium carbonates and co-precipitation of phosphorus compounds, and prevents recycling of e.g. phosphorus to the lake water during large parts of the year /Davison et al. 1985/. Only occasionally, e.g. during extended periods of ice and snow cover, may anoxic and low redox conditions affect the release of nutrients to the lake water /Andersson et al. 2003/. Although there seems to be a certain release of organic compounds from the microbial mat /Andersson and Brunberg 2006b/, substantial amounts of the organic material produced at the site are permanently buried in the sediment. The thick layer of cyanophycée gyttja below 30 cm depth in the core from Lake Stocksjön indicates that cyanophytes have been an important constituent of the lake ecosystem for extended periods, maybe even before the lake basin was completely isolated. However, the very thick microbial mat present today does not seem to be common in the shallow bays that currently are in the transition process to lake ecosystems (Brunberg, unpublished observations). Further details regarding the important stage of conversion from brackish water to freshwater ecosystem thus need to be unravelled.

Except from phosphorus and sulphur, there is a good correspondence between the proportions of ash, i.e. the inorganic component in the sediment and most of the main elements in the levels below the 30 cm level. This probably reflects the chemistry of the catchment area, i.e. the primal source of these elements is the surrounding soils and bedrock. The elements that have a negative correlation to the inorganic compartment of the sediment are probably bound to and transported with organic material. These two patterns – either positive or negative correspondence to the ash content – are also found for the heavy metals and the trace metals.

Classification of eight heavy metals according to the Swedish Environmental Protection Agency (Table 3-1) showed very low or moderate content of these metals in the sediment. A comparison of data from the present study with selected sediment data from other parts of Sweden, (performed by /Tröjbom and Söderbäck 2006/) confirms this picture. This implies that Lake Stocksjön has not been exposed to any substantial atmospheric deposition of these pollutants. The results are in accordance with investigations in the upstream Lake Eckarfjärden, where low amounts of anthropogenic ash particles (originating from combustion of oil) in the sediments also indicate a low level of airborne pollutants /Brunberg and Korsman, in prep/. Earlier investigations of organic compounds in sediments from several lakes in the area also indicate low levels of pollution /Borgiel 2003/.

The elemental composition of lake sediments reflects the composition within the entire catchment, and is governed by the various environmental conditions operating at different levels and in different parts of the catchment ecosystems. Further comparisons of the present data with the elemental composition of the surrounding soils and bedrock may answer questions regarding transport and accumulation of various substances at different sites within the catchment of Lake Stocksjön. Attempts have already been made in this direction by /Tröjbom and Söderbäck 2006/, who compared the data on sediment composition from Lake Stocksjön with other parts of the regolith in the Forsmark area. The data gathered will be used also in future evaluations of transport and turnover of various elements within the catchments of the Forsmark site investigation area, as well as in research regarding ontogenetic patterns of lake ecosystems.

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Concentrations of (	eleme	nts in	a 55 cl	m deep	o sediı	ment c	ore fro	om Lal	ke Stor	sksjön	_		
Note that the % TS reported in the table were achieved w 2.5 and 10.1% (Brunberg un	l here doo vhen dryi npublishe	es not repling the sal	resent the nples ag	e original ain, after	wet sedii transport	ment. The ation and	e samples some tin	sent to A ne of stor	vnalytica , age. The e	AB were original o	already c lry conter	lried. The it ranged	figures between
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10: Svensk Karnbranslenantering Program: G0-N	g AB Ket:	uirik kautsi	ky luirik.ka	utsky@skb Order was	.sej renistred 3	2003-12-05							
Ordernumber: L0312062				Order was	analysed 2	2003-12-23							
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Element Sample	TS %	Aska %	SiO2 % TS	AI2O3 % TS	CaO % TS	Fe2O3 % TS	K20 % TS	MgO % TS	MnO % TS	Na2O % TS	P205 % TS	ТіО2 % TS	Summa % TS
STOCK 1 0-5 cm 020312	95.9	45.3	13.2	0.359	16.6	0.331	0.165	0.19	0.0527	0.133	0.125	0.0234	31.2
STOCK 2 5–10 cm 020312	94.6	46	13.5	0.397	15.9	0.336	0.142	0.183	0.0554	0.0957	0.0808	0.0346	30.7
STOCK 3 10–15 cm 020312	95	53.3	15.2	0.599	18.7	0.512	0.15	0.208	0.0515	0.122	0.0945	0.0321	35.7
STOCK 4 15-20 cm 020312	95	55.5	18.2	0.752	18.1	0.698	0.157	0.191	0.0275	0.15	0.0844	0.0329	38.4
STOCK 5 20–25 cm 020312	92.6	57.5	18.2	0.488	20.6	0.588	0.122	0.173	0.0226	0.114	0.0675	0.0203	40.4
STOCK 6 25–30 cm 020312	96.5	69.5	14.3	0.53	29.6	0.674	0.185	0.247	0.0344	0.129	0.0468	0.0235	45.8
STOCK 7 30–35 cm 020312	95.1	56.5	29.5	4.61	8.11	2.65	1.2	0.822	0.0357	0.654	0.0855	0.221	47.9
STOCK 8 35-40 cm 020312	94.8	48.8	23	3.25	8.92	2.18	0.827	0.614	0.0293	0.528	0.0807	0.158	39.6
STOCK 9 40–45 cm 020312	93.8	33.5	15.6	2.8	3.16	2.21	0.718	0.57	0.0273	0.491	0.0838	0.139	25.8
STOCK 10 45–50 cm 020312	94.7	48.8	27.7	5.59	3.02	3.21	1.39	1.01	0.0401	0.868	0.0938	0.279	43.2
STOCK 11a 50–54 cm 020312	95.5	53.3	31.5	6.15	3.04	3.46	1.52	1.09	0.0408	0.911	0.0944	0.302	48.1
STOCK 11b 54–55 cm 020312	97.3	72.9	46.5	8.43	2.93	3.73	2.29	1.28	0.0444	1.18	0.1	0.368	6.9

Appendix 1

25

Ba mg/kg TS	Be mg/kg TS	Co mg/kg TS	Cr mg/kg TS	Cu mg/kg TS	Ga mg/kg TS	Hf mg/kg TS	Mo mg/kg TS	Nb mg/kg TS	Ni mg/kg TS	Rb mg/kg TS	Sc mg/kg TS
103	<0.3	<3	<5	5.22	<1	<0.1	<2	<0.2	<5	<2	<0.5
106	<0.3	<3	<5	3.71	<1	0.214	<2	<0.2	<5	<2	<0.5
91.4	<0.3	<3	6.81	5.55	<1	<0.1	3.94	0.524	<7	<2	0.932
68.4	<0.3	<3	6.69	3.15	<1	0.78	7.34	1.46	<6	<2	1.37
59.3	<0.3	<3	<6	3.9	<1	0.601	8.02	0.875	<6	<2	1.03
71	<0.4	<4	<8	8.66	<1	0.246	<2	0.46	<8	<2	<0.8
214	0.749	<3	30.6	5.36	<1	2.88	24.9	10.7	15.8	93.9	5.11
157	0.664	<3	20.1	7.21	<1	3.2	23.8	6.7	16.6	68.5	3.61
134	0.58	2.68	19.2	4.49	<1	3.63	76.4	13.4	3.87	104	3.31
245	1.07	4.01	35.5	6.81	<1	4.82	41.6	13.6	7.33	124	5.96
261	1.28	4.15	39.5	8.15	<1	4.35	27	14.2	19.8	124	6.6
378	1.62	5.94	49.1	6.13	<1	4.44	20.2	11.1	19.2	132	8.07

Sn mg/kg TS	Sr mg/kg TS	Ta mg/kg TS	Th mg/kg TS	U mg/kg TS	V mg/kg TS	W mg/kg TS	Y mg/kg TS	Zn mg/kg TS	Zr mg/kg TS	LabID
<1	51	<0.06	1.22	2.94	2.95	0.642	4.34	48.1	6.61	117670-00
<1	48.2	0.0639	1.6	3.22	2.65	1.09	4.67	44.1	7.98	117671-00
2.62	60.3	0.0981	1.83	16	6.23	1.38	7.4	77.9	11	117672-00
2.01	62.2	0.262	2.6	31.8	7.8	1.39	12.4	104	15.2	117673-00
2.65	70.1	<0.06	2.42	36.1	7.49	1.55	11.8	67.5	11.8	117674-00
1.31	105	<0.06	0.866	15.9	4.65	<0.4	7.86	37	11.5	117675-00
2.68	73.9	0.884	8.72	32.7	32.8	2.12	16.5	84	59.2	117676-00
2.7	68.7	0.649	8.01	40.2	23.5	2.65	14.5	74.7	54.3	117677-00
3.05	49.4	1.97	12.9	93.1	22.1	4.62	14.4	78.1	41.9	117678-00
3.03	69.8	1.24	12.9	42.1	39.6	7.85	21.6	124	78.5	117679-00
5.24	73.8	1.04	13	30.1	42.2	3.6	22.5	152	88	117680-00
2.9	86.8	0.866	11.6	24.1	51.2	2.64	23.8	91.9	120	117681-00

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Program: G5-N

Ordernumber: L0312063

Report created: 2004-01-23 by Eva

Element Sample	La mg/kg TS	Ce mg/kg TS	Pr mg/kg TS	Nd mg/kg TS	Sm mg/kg TS	Eu mg/kg TS	Gd mg/kg TS
STOCK 1 0–5 cm/020312	7.97	13.4	<1	6.96	<0.3	<0.05	<0.3
STOCK 2 5-10 cm 020312	9.14	14.7	5.23	8.66	<0.4	0.275	<0.4
STOCK 3 10–15 cm 020312	13.2	20.1	6.78	16.1	3.13	<0.05	<0.4
STOCK 4 15–20 cm 020312	22.3	31.3	8.73	24.4	3.21	0.499	1.1
STOCK 5 20–25 cm 020312	18.7	151	9.01	20.1	4.08	0.284	1.4
STOCK 6 25–30 cm 020312	10.5	18.2	6.01	12.6	1.4	0.112	<0.4
STOCK 7 30-35 cm 020312	34.4	68	13.3	30.6	6.89	0.83	2
STOCK 8 35-40 cm 020312	37.3	69.2	10.7	34	5.74	0.855	2.92
STOCK 9 40-45 cm 020312	57.1	108	18.8	53.8	8.41	1.38	6.04
STOCK 10 45-50 cm 020312	54.7	104	18.3	55.2	8.21	1.02	5.07
STOCK 11a 50–54 cm 020312	56.1	108	16.6	51	9.18	1.14	6.39
STOCK 11b 54–55 cm 020312	43.3	82.7	14.8	39.1	5.6	0.856	1.77

Order was registred 2003-12-05 Order was analysed 2003-12-23

Report signed by Solweigh Brandlöf

Tb mg/kg TS	Dy mg/kg TS	Ho mg/kg TS	Er mg/kg TS	Tm mg/kg TS	Yb mg/kg TS	Lu mg/kg TS	LabID
0.362	1.19	0.832	<0.1	0.315	<0.2	0.146	117682-00
<0.1	1.93	0.281	<0.1	<0.1	<0.2	0.116	117683-00
<0.1	2.19	0.604	2.69	0.132	0.639	0.134	117684-00
<0.1	3.95	0.968	2.46	0.358	1.67	0.308	117685-00
<0.1	3.04	0.757	2.68	0.188	1.72	0.43	117686-00
<0.1	2.27	0.375	1.67	<0.1	0.433	0.128	117687-00
0.321	5.97	1.27	3.97	0.586	1.52	0.563	117688-00
0.34	4.35	1.25	3.26	0.485	2.6	0.516	117689-00
0.949	9.76	1.93	5.62	0.709	4.6	0.637	117690-00
0.767	7.61	1.54	4.21	1.01	5.15	0.624	117691-00
0.826	7.2	1.54	4.44	0.374	3.33	0.644	117692-00
0.576	6.13	1.16	2.1	0.684	3.36	0.55	117693-00

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Program: M4-N

Ordernumber: L0312061

Report created: 2004-01-23 by Eva

Element Sample	TS %	As mg/kg TS	B mg/kg TS	Cd mg/kg TS	Co mg/kg TS	Cr mg/kg TS	Cs mg/kg TS	Cu mg/kg TS
STOCK 1 0-5 cm 020312	95.89	1.04	36.3	0.241	0.448	1.66	0.105	19.4
STOCK 2 5-10 cm/020312	94.55	1.51	38.8	0.254	0.51	1.86	0.139	5.79
STOCK 3 10-15 cm 020312	94.99	2.14	26.6	0.54	0.725	2.58	0.167	20.5
STOCK 4 15-20 cm 020312	94.97	4.42	21.8	0.774	0.965	3.81	0.214	29.1
STOCK 5 20-25 cm 020312	95.61	3.66	20.3	0.43	0.881	2.72	0.118	25.3
STOCK 6 25-30 cm 020312	96.54	1.87	15.6	0.154	0.591	2.6	0.153	14.6
STOCK 7 30-35 cm 020312	95.07	4.2	48.3	0.522	4.2	20.6	1.96	39.8
STOCK 8 35-40 cm 020312	94.79	2.86	50.2	0.496	3.01	12.6	1.11	37.7
STOCK 9 40-45 cm 020312	93.76	4.47	89.5	0.594	4.11	15.7	1.36	58.8
STOCK 10 45-50 cm 020312	94.69	4.45	68.3	0.592	4.58	23.8	2.19	43
STOCK 11a 50-54 cm 020312	95.49	8.69	57.2	0.653	5.58	25	2.15	43.9
STOCK 11b 54–55 cm 020312	97.35	4.53	37.2	0.76	7.25	34	3.39	44

Order was registred 2003-12-05 Order was analysed 2004-01-05 Report signed by Fredrik Ödman

Hg mg/kg TS	Li mg/kg TS	Mn mg/kg TS	Ni mg/kg TS	Pb mg/kg TS	S mg/kg TS	Sb mg/kg TS	V mg/kg TS	Zn mg/kg TS	LabID
0.0687	0.651	391	4.37	12.1	8,620	0.0888	1.56	53.3	117658-00
<0,1	0.891	431	5.66	13.1	8,600	0.098	1.81	56	117659-00
0.0824	1.01	396	9.34	29.6	11,300	0.177	3.49	88.8	117660-00
0.0926	1.33	221	12.5	37.3	14,900	0.26	5.16	111	117661-00
0.0645	0.774	130	8.78	23.4	14,200	0.164	6.06	66	117662-00
0.0284	0.977	215	7.17	11.1	11,000	0.0784	3.34	34.4	117663-00
0.0442	11.2	224	24.9	16.7	23,700	0.0506	20.7	75.1	117664-00
0.0485	6.93	177	22.6	15.6	25,300	0.11	11.4	66	117665-00
0.0555	7.18	197	29.1	24	34,500	0.113	16.9	83.8	117666-00
0.0377	13.2	243	33.7	15.7	28,600	0.0426	24.9	78.6	117667-00
0.0479	14.4	234	36.1	13.6	478	0.0717	21.4	89.2	117668-00
0.0576	20	261	34.6	12.7	474	<0.02	35.1	85.3	117669-00

Sediment depth [cm]	Si mg*kg⁻¹ DW	Al mg*kg⁻¹ DW	Ca mg*kg⁻¹ DW	Fe mg*kg⁻¹ DW	K mg*kg⁻¹ DW
0–5	61,665.6	1,900.0	118,638.7	2,315.1	1,369.7
5–10	63,067.1	2,101.1	113,635.9	2,350.1	1,178.8
10–15	71,008.9	3,170.2	133,647.2	3,581.1	1,245.2
15–20	85,023.8	3,980.0	129,359.1	4,882.0	1,303.3
20–25	85,023.8	2,582.7	147,226.3	4,112.6	1,012.8
25–30	66,804.5	2,805.0	211,548.5	4,714.1	1,535.8
30–35	137,813.4	24,398.5	57,961.4	18,534.8	9,961.8
35–40	107,447.7	17,200.7	63,750.4	15,247.5	6,865.3
40–45	72,877.6	14,819.0	22,584.2	15,457.3	5,960.5
45–50	129,404.4	29,585.1	21,583.7	22,451.6	11,539.1
50–54	147,156.7	32,548.9	21,726.6	24,200.1	12,618.2
54–55	217,231.3	44,615.9	20,940.4	26,088.6	19,010.4

## Recalculated concentrations of main elements in a 55 cm deep sediment core from Lake Stocksjön

Mg mg*kg⁻¹ DW	Mn mg*kg⁻¹ DW	Na mg*kg⁻¹ DW	P mg*kg⁻¹ DW	Ti mg*kg⁻¹ DW
1,153.5	408.1	986.7	545.5	140.2
1,111.0	429.0	710.0	352.6	207.4
1,262.8	398.8	905.1	412.4	192.4
1,159.6	213.0	1,112.8	368.3	197.2
1,050.3	175.0	845.7	294.6	121.7
1,499.5	266.4	957.0	204.2	140.8
4,990.4	276.5	4,851.7	373.1	1,324.5
3,727.6	226.9	3,917.0	352.2	947.0
3,460.5	211.4	3,642.5	365.7	833.1
6,131.7	310.5	6,439.3	409.4	1,672.2
6,617.4	316.0	6,758.3	412.0	1,810.0
7,770.9	343.8	8,753.9	436.4	2,205.6

### Figures from the concentrations of elements in a 55 cm deep sediment core from Lake Stocksjön









