Technical Report

TR-06-37

Radionuclide transport in peat lands

A complete profile from Klarebäcksmossen (PSM006562) analysed by gamma spectrometry and ICP-AES

Fredrik Lidman, Umeå universitet

October 2009

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co

Box 250, SE-101 24 Stockholm
Phone +46 8 459 84 00

Radionuclide transport in peat lands

A complete profile from Klarebäcksmossen (PSM006562) analysed by gamma spectrometry and ICP-AES

Fredrik Lidman, Umeå universitet

October 2009

Abstract

In this study a complete core with ombrotrophic peat, minerotrophic peat, gyttja sediments and clay from Klarebäcksmossen has been analysed by gamma spectrometry, ICP-AES and additional chemical analyses. Hence, profiles of more than 70 elements, isotopes or chemical parameters are presented in this report. The overall objective has been to create a better understanding of how important elements behave during the development of a mire.

The composition of the core reflects the development of Klarebäcksmossen from sea bottom to lake bottom and further on to a fen and, now, a bog. Using isotopic disequilibrium, it is shown that Ra-226 is being leached from the gyttja and transported to the peat along with calcium, strontium and other elements. In average, between 0.02 and 1.4% of the radium is estimated to be lost annually. However, no signs of radium transport through the clay were observed. The isotopic ratios also show that uranium has been accumulated in the sediments, but mobilised from underlying the clay.

The concentrations in gyttja, minerotrophic and ombrotrophic peat respectively are compared in order to draw conclusions concerning the behaviour of various elements. For many elements there are signs of transport from the gyttja to the peat, e.g. lanthanides, yttrium and scandium. On the other hand, alkali metals and silicon appear to be leached from the peat.

Calcium and strontium are strongly enriched in the peat, and it is not improbable that radium could be enriched by the same mechanisms. Strong enrichment of bromine was also observed, which could mean that something similar would be possible for iodine.

The report also contains a literature review and discussions of the behaviour of the various elements in peat based on the measurements in Klarebäcksmossen and elsewhere. A comparison of the distribution coefficients used in earlier safety analyses shows that they have no strong connection to the degree of accumulation or mobilisation in the peat.

Good agreement between gamma spectrometry and ICP-AES was observed for uranium and thorium, but not for potassium, where ICP-AES gives substantially lower values.

Sammanfattning

I denna studie har en komplett kärna med ombrotrof torv, minerotrof torv, gyttjesediment och lera från Klarebäcksmossen (PSM006562) analyserats med gammaspektrometri, ICP-AES och ytterligare kemiska analyser. Således presenteras profiler för mer än 70 grundämnen, isotoper och kemiska parametrar i denna rapport. Det övergripande syftet har varit att skapa en bättre förståelse för hur viktiga ämnen beter sig under utvecklingen av en myr.

Kärnans sammansättning speglar Klarebäcksmossens utveckling från havsbotten till sjö och vidare till kärr och mosse. Med hjälp av isotopojämvikter visas att Ra-226 läcker från sedimenten och troligtvis ackumuleras i torven tillsammans med kalcium, strontium och andra ämnen. I medel beräknas mellan 0,02 och 1,4 % av radiumet årligen transporteras bort. Inga tecken på transport av radium genom leran kunde dock observeras. Isotopkvoterna visar också att uran har ackumulerats i sedimenten, men mobiliserats från leran.

Uppmätta koncentrationer i gyttja, minerotrof respektive ombrotrof torv jämförs för att dra slutsatser om de olika ämnenas beteende. För flera grundämnen finns spår som tyder på transport från gyttja och upp i torven. Speciellt anmärkningsvärt är att de flesta lantanider liksom yttrium, lantan och skandium är mer eller mindre kraftigt anrikade i torven jämfört med konservativa grundämnen som titan och zirkon. Alkalimetaller och kisel tycks å andra sidan ha läckt från torven.

Kalcium och strontium är också kraftigt anrikade i torven och det kan inte uteslutas att radium också kan anrikas på samma sätt. Likaså observerades kraftig anrikning av brom i torven, vilket kan tyda på att detsamma är möjligt även för jod.

Rapporten innehåller även en litteraturgenomgång och diskussioner kring de olika ämnenas beteende i torv med utgångspunkt från dessa och andra mätningar. En jämförelse av fördelningskoefficienterna för tidigare säkerhets analyser visar att de inte tycks ha något större samband med graden av ackumulation eller mobilisering i torven.

Mättekniskt konstaterades god överensstämmelse mellan gammaspektrometri och ICP-AES för uran och torium, men inte för kalium, där ICP-AES ger betydligt lägre mätvärden.

Contents

1 Background

1.1 Introduction

1.1.1 Critical Ecosystems and Radionuclides

Nuclear waste contains a wide variety of elements, each one with its specific biogeochemical properties that govern its behaviour in the environment. Thus, in case of a canister failure in a future deep repository of nuclear waste some radionuclides are more likely than others to escape and eventually reach the surface. Calculations of the radionuclide transport from a deep repository show than above all I-129 and Ra-226 tend to dominate in the scenarios where the highest doses are predicted, but all radionuclides must of course be considered.

If any radionuclides would reach the surface there are different ecosystems, which they could enter, some of which are more critical than others. Wetlands, peat lands and sediments, for instance, are environments where material continuously is being accumulated. Often there is a high content of organic material in these environments, which favours the accumulation of many metals. The final doses, however, will also depend on the exposure pathways. Since peat lands can be used both as a source of fuel and for agricultural purposes, they are considered to be one of the most critical ecosystems. For instance, in SR97 mires were identified as the ecosystem that potentially could cause the highest radiation doses to man /SKB 1999/.

Due to the land rise mires are a biotope that most likely will be common in both site investigation areas in the future. Often they are formed in local depressions where one could expect an outflow of deeper groundwater, which potentially could carry radionuclides from a deep repository, but it is also possible that a mire is contaminated by radionuclides that somehow have reached its catchment. Hence, wetlands have been identified as particularly important ecosystems to study /SKB 2004/.

Modelling is a commonly used method to study complex environmental processes, which in this case has been attempted by /Karlsson et al. 2001, Vikström and Gustavsson 2006, Kellner 2007/. However, whenever possible models should be compared to empirical data for calibration and validation. Some of the elements in the nuclear waste are such elements that do not naturally occur in the environment, e.g. technetium and some of the actinides. Hence, their long-term behaviour in various ecosystems is hard to study and one most to a large extent rely on models or comparisons with naturally occurring elements. However, most of the elements in nuclear waste are naturally occurring, either as radioactive isotopes, e.g. radium, uranium and thorium, or as stable isotopes, e.g. iodine, which occurs as I-127. The behaviour of such elements can be studied under natural conditions, since the transport processes to a large extent will be the same as if they had come from nuclear waste. Hence, studying the natural behaviour of these elements is a good way to strengthen the credibility of the safety assessment for deep repository of spent nuclear fuel.

1.1.2 Purpose

This study is a first attempt to map and interpret the radionuclide content and elemental composition of a peat profile in the Simpevarp area. The report is partly based on my M. Sc. Thesis Work "Isotopic Disequilibrium for Assessment of Radionuclide Transport in Peat" /Lidman 2005/, where gamma spectrometry was used to measure several key radionuclides in a complete peat profile with underlying sediments, gravel and clay from Klarebäcksmossen. With a fine spatial resolution – sometimes as little as a few centimetres – very detailed information on the distribution of the analysed radionuclides was achieved. Since then by additional elemental analyses by ICP-AES have been carried out. The new measurements have allowed verification of some of the radiometric measurements and will provide a better background for understanding the radionuclide profiles. Many of the stable elements that were analysed by ICP-AES also have long-lived radioactive isotopes that occur in nuclear waste, e.g. C-14, Cl-36, Ni-59, Nb-94 and Cs-135 /Chapman and McCombie 2003/. Thus, we now have a good picture of the chemical composition of this peat profile and especially the transition from sediments to peat.

The ambition of this report is not only to present the collected data, but also to try to put them in a scientific context and discuss why the profiles look the way they do. The interpretation is complicated, however, by the fact that only a limited amount of background data apart from the chemical and radiometric measurements are available for the system. Elements such as radium and uranium are given extra attention; this is not only because they are important in nuclear waste, but also because the decay chain dynamics can provide additional information about their mobility. Together with data from other sediment and wetland profiles, which were sampled within the same measuring programme /Nilsson 2005/, this report will hopefully contribute to a better understanding of what transport processes that are important and how different elements behave during the development of wetlands.

1.2 Theory

1.2.1 Radioactivity in the Environment

Environmented radioactivity can in principle be of three different types. The dominating group is the primordial radionuclides that have been present on Earth since its formation. Some of these radionuclides are characterized by very long half-lives which have allowed them to persist in significant levels throughout the history of the Earth, e.g. U-238, U-235 and Th-232. However, as these long-lived radionuclides decay other more short-lived radionuclides are produced in a series of decays. Many of these decay chain radionuclides are important in nuclear waste, e.g. Ra-226.

Radionuclides are also continuously produced in the upper parts of the atmosphere, e.g. C-14 and H-3 (commonly referred to as tritium). These are so-called cosmogenic radionuclides, whose presence in the environment also is natural. However, there are also radionuclides in the environment that do not belong there, but have been created and released by man, for instance by atmospheric testing of nuclear weapons or accidents in nuclear power plants. For instance, the caesium isotopes Cs-137 and Cs-134 that were released in the Chernobyl accident belong to the anthropogenic or artificial radionuclides.

1.2.2 Secular Equilibrium

There are many examples of applications of stable and radioactive isotopes in environmental science. In this study special attention will be given to the uranium-thorium series radionuclides, not only because some key radionuclides in nuclear waste are found in this group, but also because they are particularly easy to study. This is because it can be shown that if the half-life of the parent is long in relation to the half-life of the daughter, the daughter will in time acquire essentially the same activity as the parent – provided that the system is closed. This state, when a parent and its daughter nuclide have the same activity, is called secular equilibrium. The degree of equilibrium is often quantified as an activity ratio, which at secular equilibrium should be unity.

A condition for the establishment of secular equilibrium is that there is a closed system, e.g. none of the radionuclides is being transported in or out of the system. Hence, the presence of secular equilibrium can be used as an indication that there has been no significant migration on the time-scale at which the equilibrium is established. Conversely, the absence of secular equilibrium can be used as a proof that migration has occurred, provided that the material is old enough to allow establishment of secular equilibrium. What periods of time that are needed is dependent on the half-life of the daughter and the initial conditions, but starting from zero, secular equilibrium will in practice be reached within five or six half-lives of the daughter. Only in cases when the initial concentration of the daughter is much higher than that of the parent will it take longer. The mathematical derivation of the Bateman equation describing secular equilibrium is shown in Appendix A, where the equation for secular equilibrium is derived.

In this manner, secular equilibrium – or the degree of disequilibrium – can be used to assess the mobility of the radionuclides in the naturally occurring decay chains. As compared to other radioactive or stable isotopes this is a major advantage, since it automatically provides a reference level to compare the measurements to. Hence, it is possible to talk about an excess or a deficit of a specific radionuclide and in some cases even estimate transport rates.

What processes that can be studied is limited by the half-life of the radionuclides of the naturally occurring decay chains, since the half-lives must correspond to the time-scale of the studied processes. For instance, radionuclides with a half-life of only a few minutes or less are uninteresting when studying weathering processes, as they commonly are much slower. Ra-226, on the other hand, has half-life of 1,600 years, which means that it can be expected to occur in secular equilibrium with its long-lived parent, Th-230, after approximately 6,000 years in a closed system. These time-scales better correspond to possible migration processes in soil and the development of wetlands. Accordingly, disequilibrium between Ra-226 and Th-230 in old soil samples provides clear evidence of migration of at least one of the two radionuclides.

In this study gamma spectrometry has been used to determine the content of several gamma-emitting nuclides in a profile from Klarebäcksmossen in the Oskarshamn site investigation area. The resolution of the measurements has been only a few centimetres, which has resulted in more or less complete activity profiles for several radionuclides.

1.2.3 The Naturally Occurring Decay Chains

Originally there were four naturally occurring decay chains with mass numbers 4n, 4n + 1, 4n + 2 and 4n + 3 respectively, where n is an integer. The factor 4 is explained by the fact that alpha decay always decreases the mass number by 4, while beta decay does not change the mass number at all. Hence, the mass numbers of the uranium-thorium series nuclides always reveal which decay chain they belong to.

The thorium chain (A = 4n) does not play an important role in the composition of spent nuclear waste, but it can still be of importance in radioecological studies of this kind, since it includes isotopes of interesting elements such as radium and thorium.

The radionuclides that can be of any interest in studies of the long-term migration of radionuclides are Th-232, Ra-228 and Th-228. Because of the relatively short half-lives of the two latter radionuclides, the thorium chain is best suitable for assessing rather rapid processes, i.e. on time-scales of years or possibly decades. The remaining radionuclides, however, are too short-lived to be capable of migrating any longer distances in soil.

The neptunium chain (A = 4n + 1) should not really be referred to as a naturally occurring decay chain anymore, since it has decayed to negligible amounts by now. Its most long-lived member, Np-237, has a half-life of 2.14 million years, which is short compared to the age of the Earth. These radionuclides are, however, abundant in spent nuclear fuel. Since the atmospheric testing of nuclear weapons in the late 1950s and early 1960s it is also possible find the Pu-241 daughter Am-241 in recent deposits in some environments, but they should then be regarded as artificial radionuclides.

$$ {}^{232}Th \overset{\alpha}{\underset{14.0\,Ga}{\Rightarrow}} {}^{228}Ra \overset{\beta^-}{\underset{5.76\,a}{\Rightarrow}} {}^{228}Ac \overset{\beta^-}{\underset{6.15\,h}{\Rightarrow}} {}^{228}Th \overset{\alpha}{\underset{1.913\,a}{\Rightarrow}} {}^{224}Ra \overset{\alpha}{\underset{3.36\,d}{\Rightarrow}} {}^{220}Rn \overset{\alpha}{\underset{5.56\,s}{\Rightarrow}} {}^{216}Po \overset{\alpha}{\underset{0.145\,d}{\Rightarrow}} {}^{212}Pb \overset{\beta^-}{\underset{10.64\,h}{\Rightarrow}} $$

$$ {}^{212}Bi \left\{ \begin{array}{l} 64.1\% \overset{\beta^-}{\underset{1.009\,h}{\Rightarrow}} {}^{212}Po \overset{\alpha}{\underset{0.298\,\mu s}{\Rightarrow}} \\ 35.9\% \overset{\alpha}{\underset{25m}{\Rightarrow}} {}^{208}Tl \overset{\beta^-}{\underset{3.053\,m}{\Rightarrow}} \end{array} \right\} {}^{208}Pb\ (stable) $$

Figure 1-1. *The thorium chain (A = 4n).*

The most interesting of the naturally occurring decay chains in a study like this is the so-called uranium chain (A = 4n + 2). This decay chain does not only include Ra-226 which has been identified as a particularly critical radionuclide, but also two long-lived uranium isotopes, U-238 and U-234, Th-230, the long-lived parent of Ra-226, and Pb-210.

However, the capability of a radionuclide to migrate does not only depend on the half-life, but also on the chemical properties. Therefore, it is also important to note the radon isotope Rn-222. Being a noble gas it is inert and can migrate considerable distances despite its comparatively short half-life of 3.8 days. Intrusion of Rn-222 into buildings is one of the most important sources of ionising radiation for an average Swede.

The actinium chain (A = 4n + 3) is interesting because it starts with U-235, which the uranium isotope that is used in the fission process in nuclear reactors. U-235 is enriched in nuclear fuel. In terms of environmental behaviour U-235 is similar to U-238. In applied radioactivity, the protactinium isotope Pa-231 with a half-life of 32,400 years is also of interest.

$$^{238}U \overset{\alpha}{\underset{4.47\,Ga}{\Rightarrow}} {}^{234}Th \overset{\beta^-}{\underset{24.10\,d}{\Rightarrow}} {}^{234}Pa \overset{\beta^-}{\underset{6.69\,h}{\Rightarrow}} {}^{234}U \overset{\alpha}{\underset{246\,ka}{\Rightarrow}} {}^{230}Th \overset{\alpha}{\underset{75.4\,ka}{\Rightarrow}} {}^{226}Ra \overset{\alpha}{\underset{1600\,a}{\Rightarrow}} {}^{222}Rn \overset{\alpha}{\underset{3.8235\,d}{\Rightarrow}} {}^{218}Po \overset{\alpha}{\underset{3.10\,m}{\Rightarrow}}$$

$$^{214}Pb \overset{\beta^-}{\underset{27\,m}{\Rightarrow}} {}^{214}Bi \left\{ \begin{array}{l} 99.98\,\% \overset{\beta^-}{\underset{19.9m}{\Rightarrow}} {}^{214}Po \overset{\alpha}{\underset{164\,\mu s}{\Rightarrow}} \\ 0.02\,\% \overset{\alpha}{\Rightarrow} {}^{210}Tl \overset{\beta^-}{\underset{1.30m}{\Rightarrow}} \end{array} \right\} {}^{210}Pb \overset{\beta^-}{\underset{22.3\,a}{\Rightarrow}} {}^{210}Bi \overset{\beta^-}{\underset{5.01\,d}{\Rightarrow}} {}^{210}Po \overset{\alpha}{\underset{138.4\,d}{\Rightarrow}} {}^{206}Pb\,(stable)$$

Figure 1-2. *The uranium chain (A = 4n + 2).*

$$^{235}U \overset{\alpha}{\underset{704\,Ma}{\Rightarrow}} {}^{231}Th \overset{\beta^-}{\underset{1.603\,d}{\Rightarrow}} {}^{231}Pa \overset{\alpha}{\underset{32.8\,ka}{\Rightarrow}} {}^{227}Ac \overset{\beta^-}{\underset{21.77\,a}{\Rightarrow}} {}^{227}Th \overset{\alpha}{\underset{18.72\,d}{\Rightarrow}} {}^{223}Ra \overset{\alpha}{\underset{11.43d}{\Rightarrow}} {}^{219}Rn \overset{\alpha}{\underset{3.96\,s}{\Rightarrow}}$$

$$^{215}Po \left\{ \begin{array}{l} \sim 100\,\% \overset{\alpha}{\underset{1.78ms}{\Rightarrow}} {}^{211}Pb \overset{\beta^-}{\underset{36.1\,m}{\Rightarrow}} \\ 0.0002\,\% \overset{\beta^-}{\Rightarrow} {}^{215}At \overset{\alpha}{\underset{0.10\,s}{\Rightarrow}} \end{array} \right\} {}^{211}Bi \left\{ \begin{array}{l} 99.7\,\% \overset{\alpha}{\underset{2.14\,m}{\Rightarrow}} {}^{207}Tl \overset{\beta^-}{\underset{4.77\,m}{\Rightarrow}} \\ 0.28\,\% \overset{\beta^-}{\underset{2.14\,m}{\Rightarrow}} {}^{211}Po \overset{\alpha}{\underset{0.516\,s}{\Rightarrow}} \end{array} \right\} {}^{207}Pb\,(stable)$$

Figure 1-3. *The actinium chain (A = 4n + 3).*

2 Material and Methods

2.1 Site Description

2.1.1 Klarebäcksmossen

Klarebäcksmossen is situated close to the nuclear power plant in Simpevarp, north of Oskarshamn. The area is shown in Figure 2-1. The red arrow in the upper left corner, between European highway 22 and Misterhult, represents Klarebäcksmossen (PSM006562). Klarebäcksmossen is situated rather high in the coastal landscape – 27 m above sea level – and, consequently, its catchment area is rather small. It has been estimated from SKB's hydrological models that the catchment is three to four times the size the bog itself. Based on its elevation it has been estimated that what was to become Klarebäcksmossen was isolated from the Baltic Sea 11,250 years ago /Nilsson 2004/.

Nowadays Klarebäcksmossen is a wooded bog. The pines growing on it are not very tall, which at least partly is due to the poor nutrient status in the bog. Possibly, the age of the pines may also be a contributing factor. Parts of Klarebäcksmossen were drained in the late 19th or early 20th century, which may be related to this, but it is not entirely clear how the hydrology of Klarebäcksmossen was affected by the ditching.

Judging from the appearance of Klarebäcksmossen and the present vegetation, the bog appears to be homogeneous in its central parts. Apart from the pines there are some shrubs on the ground, predominantly *Rhododendron tomentosum* [eng. wild rosemary, sv. skvattram] and *Sphagnum* [eng. bog moss, sv. vitmossa]. The core from Klarebäcksmossen was initially chosen for radiometric analysis because of the *Sphagnum*, since it is suitable for Pb-210 dating thanks to its vertical growth pattern.

From GSD-Fastighetskartan © Lantmäteriet Gävle 2001, Consent M2001/5268

SKB, 2004-09-23, 09:41

Figure 2-1. *Map of the Oskarshamn area with the sample sites marked. The red arrow indicates the location of Klarebäcksmossen (PSM006562).*

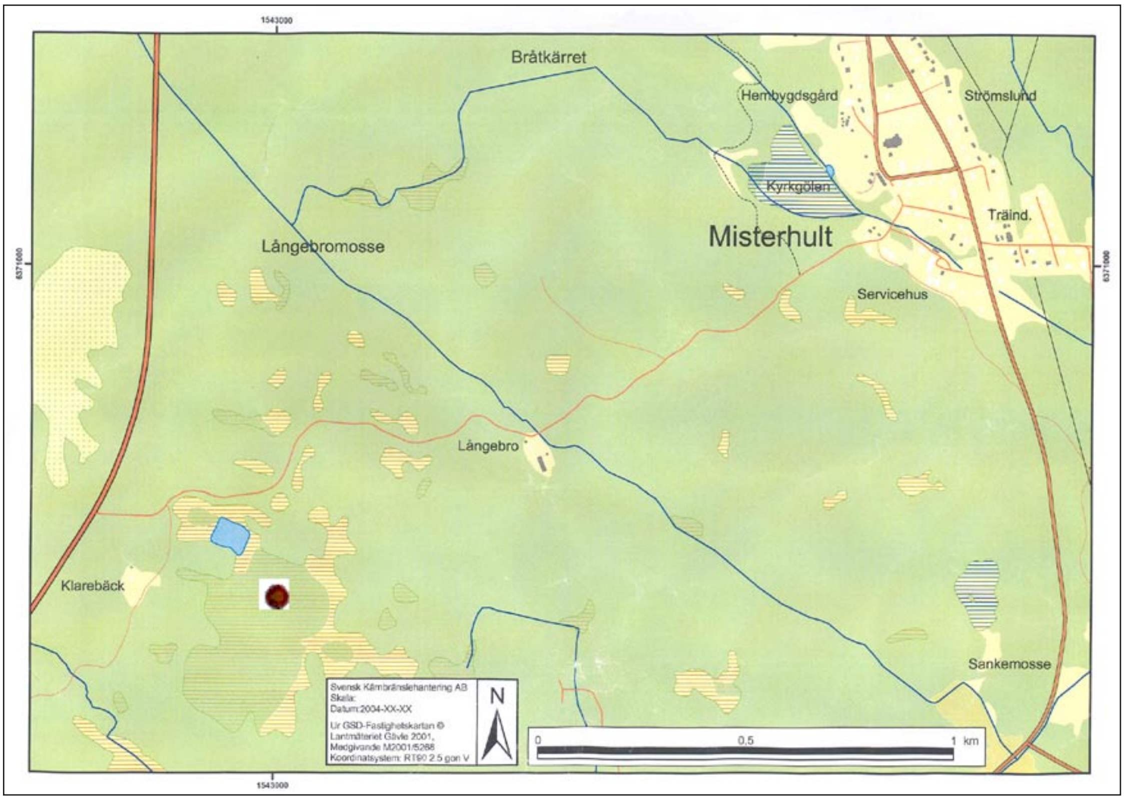


Figure 2-2. *Klarebäcksmossen and its vicinity. Klarebäcksmossen is the striped area in the lower left corner and the red marker indicates the approximate sampling site. Misterhult is seen in the upper right corner and European Highway 22 extends in the north-south direction to the left of Klarebäcksmossen.*

Klarebäcksmossen is mainly surrounded by forest soils with some exposed bedrocks. Although the major parts of the bog now are wooded, there are still some open areas, especially along the edges of the bog and in its lower parts. There is also an open water surface left in the upper parts of the bog. Unfortunately, not very much is known about the hydrology of Klarebäcksmossen but it appears to be drained by the stream in the lower left corner of Figure 2-2.

2.1.2 The Core

During August and September of 2004 cores from the sample sites shown in Figure 2-1 were collected by Geosigma AB using a Russian peat corer. Two cores were sampled for each site, of which one was analysed by Geosigma and the other one was kept in a cold-storage room at the Äspö Laboratory. The latter one was used in these analyses.

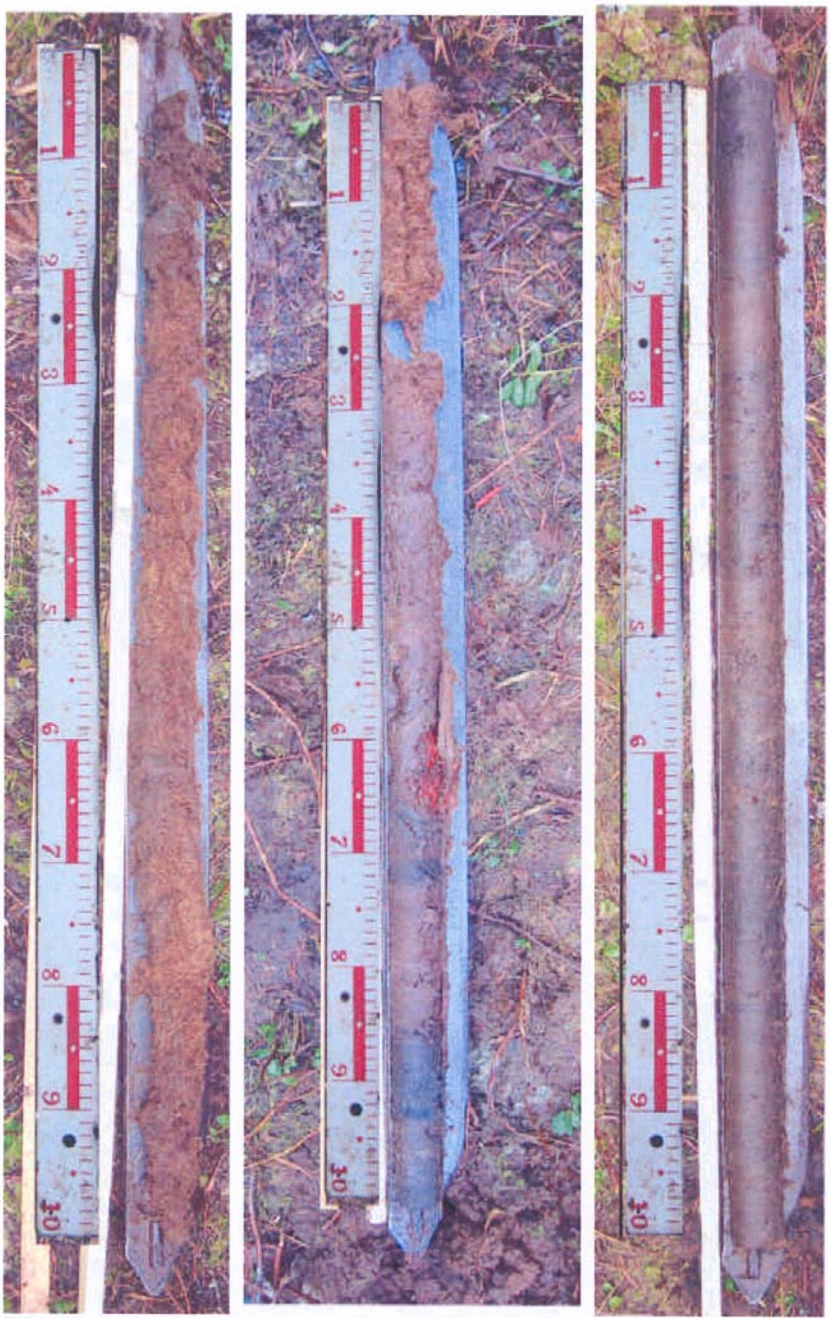
Interpretations of the soil layers in the different cores have been presented by /Nilsson 2004/. According to this soil layer interpretation, the core from Klarebäcksmossen has the following composition:

However, Table 2-1 is based on the core that was analysed by Geosigma, and therefore it is not strictly valid for the core that was investigated by gamma spectrometry and ICP-AES. This is also apparent if the soil layer interpretation is compared to Figure 2-3 and Figure 2-4, where the complete core that was analysed in this study is pictured. The photographs are taken from Gert Nilsson's report on wetlands and peat lands in the Simpevarp area (2004).

For instance, it is obvious that the gravel layer in Figure 2-4 is not found between 462 and 470 cm as given in Table 2-1, but rather between 450 and 458 cm. Moreover, the transition between gyttja and peat seems to be deeper in this core than in the core that was analysed by Geosigma. Judging from Figure 2-4, it should be closer to 400 cm than 370 cm.

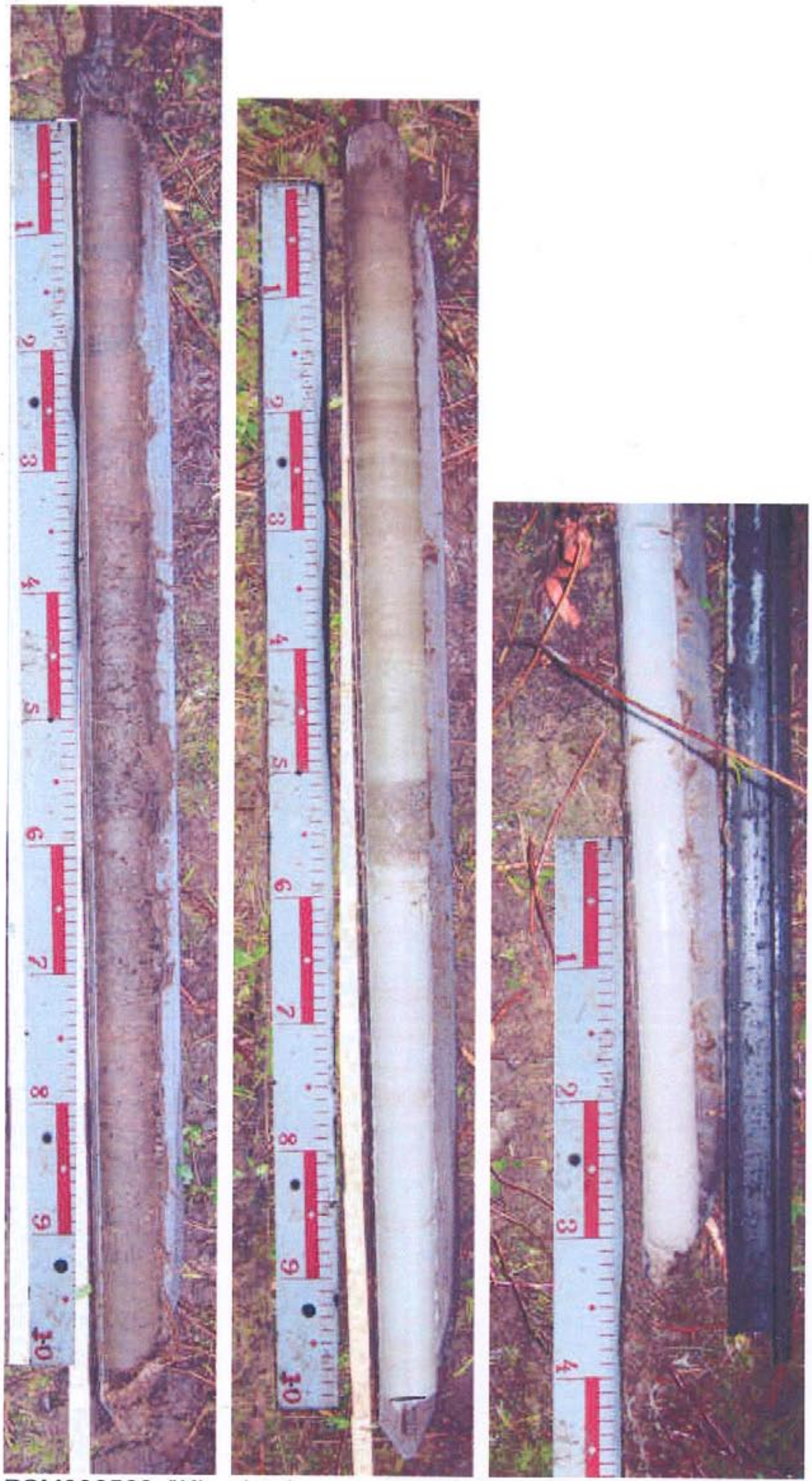
Table 2-1. Interpretation of soil layers in Klarebäcksmossen.

Depth [cm]	Type	Abbrev.	Comments	Swedish Name
0–130	Peat	S	*Sphagnum*, H3-4	Vitmosstorv
130–160	Peat	ERS	*Sphagnum/Eriophorum*, H3-4	Vitmosstorv, tuvdun
160–170	Peat	LC	*Lignidi/Carex*, H4-5	Lövkärrtorv
170–310	Peat	SC1	*Sphagnum/Carex*, H4-5	Starrtorv
310–370	Peat	SC2	*Sphagnum/Carex*, H3-4	Starrtorv
370–437	Gyttja	GY1	Brownish gyttja	Gyttja
437–462	Gyttja	GY2	Olive green gyttja	Gyttja
462–470	Gravel	G	Particle diameter < 3 cm, wave washed	Grus
470–524	Clay	LE	Greyish clay, probably till underneath the clay	Lera



PSM006562- "*Klarebäcksossen*", peat/clay column 0 - 300 cm.
Increasing depth down - and rightwards.

Figure 2-3. *The upper 3 m of the analysed core. Photographer: Gert Nilsson.*



PSM006562- "*Klarebäcksossen*", peat/clay column 300 - 530 cm.
Increasing depth down - and rightwards.

Figure 2-4. *The lower parts of the analysed core. Photographer: Gert Nilsson.*

The wave-washed gravel layer represents a hiatus in the record. Accordingly, the gyttja can be considerably younger than the clay. Without C-14 dating of this material it is hard to tell what periods of time the hiatus may represent, but it may be thousands of years.

Figure 2-5 shows the water content throughout the core. It is noteworthy that the change in colour around 400 cm in Figure 2-4 coincides with at change in the water content. Figure 2-6 shows that there also is change in the dry density at this depth. All together, this strongly suggests that the transition from gyttja to peat in this core occurs below 400 cm.

Figure 2-5 and Figure 2-6 also show that there is some change in the composition of the material around 160–170 cm, which seems to coincide with the change form pure *Sphagnum* peat to *Sphagnum/Carex* peat. According to /Franzén 1985/ *Carex* species are common in fens, in other words minerotrophic mires that are supplied with nutrients from the groundwater. On the other hand, *Carex* species are rarely found on bogs, which are defined as ombrotrophic mires. Since they only are supported by nutrients from rainwater, they tend to be very nutrient poor and dominated mostly by *Sphagnum* species. Accordingly, these changes are probably associated with a transition from minerotrophic to ombrotrophic conditions. This transition of a peat land from a fen to a bog is a common step in the natural development of peat lands, as they are characterised by a continuous accumulation of peat. Eventually the peat will become so thick that it will lose contact with the ground water. The peat land will no longer be a discharge area, but a recharge area.

The ash content of the profile is shown in Figure 2-7. Not unexpectedly, the ash content in the peat is very low, locally less than 1%, but with somewhat higher values in the minerotrophic peat. The ash content increases drastically in the gyttja below 400 cm and reaches its highest levels in the clay, where hardly any organic material is present in the deepest sample analysed.

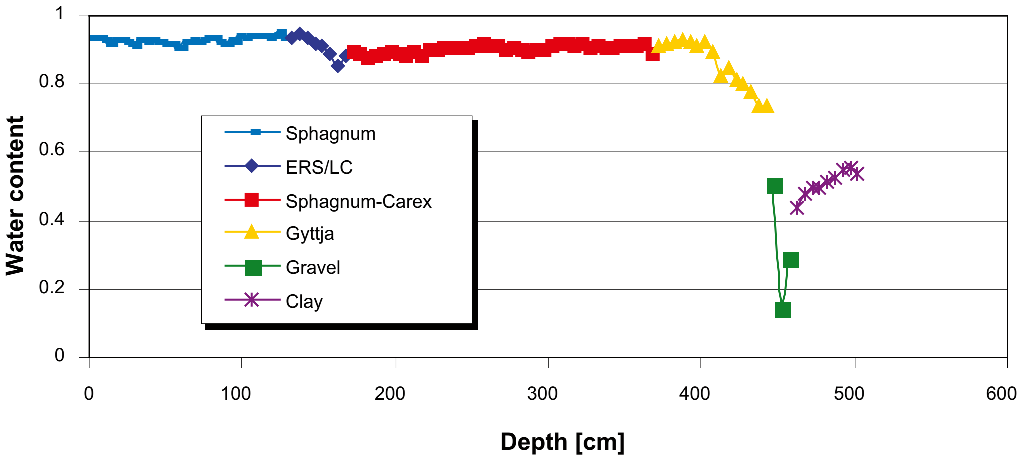


Figure 2-5. *Water content by weight for the different layers in the analysed profile.*

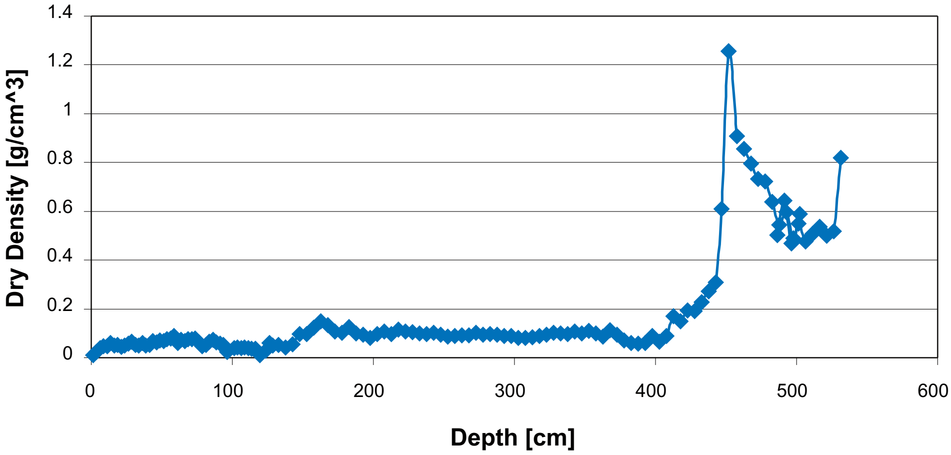


Figure 2-6. *Dry density of the profile.*

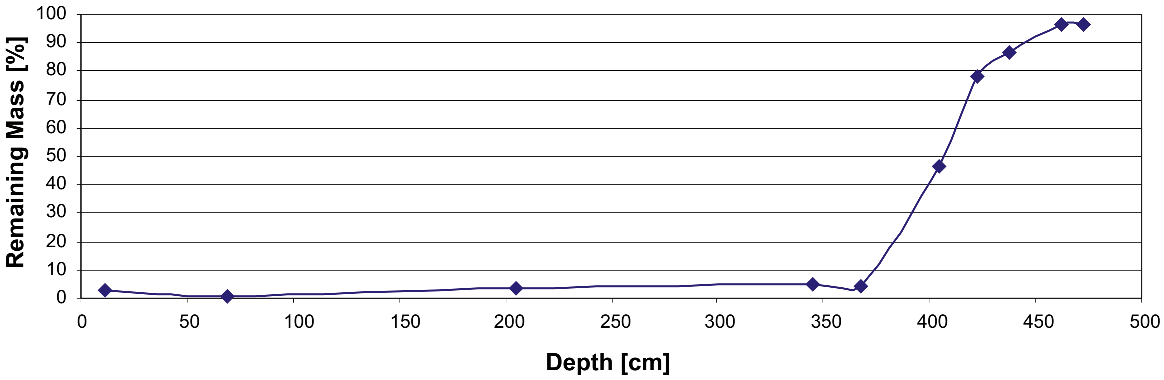


Figure 2-7. *The remaining mass after ashing at 550°C expressed as percentage of the initial mass (dry weight).*

A major difficulty in the analysis of the data from Klarebäcksmossen is that little is known about the local hydrology, which is a key factor in the assessment of transport processes. Everything indicates that central Klarebäcksmossen nowadays is a true bog, i.e. it is solely supplied with nutrients from rainwater. Thus, there must be a downward component in the groundwater flow near the surface. However, below the ombrotrophic peat there is minerotrophic peat, which shows that the Klarebäcksmossen was supplied by more nutritious water than rainwater during an earlier stage of its evolution.

The chemical conditions in the pore water also remain unknown to a large extent, since no chemical analyses of the bog water were made. In the ombrotrophic peat (60–90 cm) a pH value of 4.1 was measured /Nilsson 2004/. This seems to be a typical value for ombrotrophic peat /Sjörs and Gunnarssson 2002, Shotyk 1988/. Further down in the minerotrophic peat (320–370 cm) the pH value was 5.4 /Nilsson 2004/, which is not extraordinary, but rather uncommon according to /Sjörs and Gunnarsson 2002/. Their measurements were concentrated to the northern and central parts of Sweden, but if the results are applicable for Klarebäcksmossen, this would indicate that the nutrient status is in the range from intermediate to extremely poor. Generally, pH values higher than 5.4 are expected in fens according to /Sjörs and Gunnarsson 2002/.

2.2 Gamma Spectrometry

2.2.1 General

Gamma radiation is emitted when atomic nuclei de-excite, which sometimes may occur subsequent to alpha or beta decay of radioactive nuclides. The gamma particles, which are photons, can be detected by their interaction with matter and their energies determined. Two common types of gamma detectors are scintillation detectors and semiconductor detectors. In these measurements the latter type was used.

Semiconductor detectors have a positively and a negatively doped region with a so-called depletion region in between. When a photon interacts with the depletion region, charge carriers – electrons and electron holes – will be freed and start to drift in the electric field inside the diode. It is then possible to amplify these minimal induced currents and convert it into a measurable electric pulse that is proportional to the energy of the original photon. Semiconductors are mainly constructed from silicon or germanium, where electron-electron hole pairs easily are created. In the case of germanium for instance, the required energy to create such an electron-electron hole pair is less than 3 keV. Hence, it is possible to measure gamma energies from a few keV to several thousands of keV. However, it is seldom interesting to measure energies above the 1,500 keV in environmental gamma spectrometry. By connecting the detector to a computer, it is possible to keep track of the detected photons and sort them according to their energies. In this manner a gamma spectrum will be acquired.

If there is a radioactive source close to the detector that emits gamma radiation, peaks will build up in certain parts of the spectrum over time. Since all gamma-emitting nuclides have unique gamma energies, it is possible to associate these peaks with special radionuclides. If the intensity of the peak is sufficiently high in comparison with the background radiation, it is possible to accurately determine the number of counts per time unit for a certain peak. By correcting for factors such as emission probability of the gamma line, background radiation, detector efficiency and – in some cases – self-absorption and interference from radionuclides with similar gamma energies, it is possible to determine the activity of the radionuclide, whose decay causes the peak in the gamma spectrum.

Since the energy resolution of gamma detectors generally is good and the gamma peaks often are well separated, it possible to simultaneously determine the activity of several radionuclides. This does not only make the measurements more effective, but it also makes all chemical preparation of the samples superfluous. The only requirements are generally that the samples are homogeneous and that they are radioactive enough. Hence, in some cases the preparations may involve grinding to improve the homogeneity or ashing to increase the density of the samples.

However, in order to control the efficiency of the measurements it is necessary that the samples are encapsulated in certain containers with a fixed geometry. The detector must then be calibrated for this geometry. Otherwise advanced calculations are required to determine the efficiency of the geometry. One advantage of gamma spectrometry is that it generally is a non-destructive technique. Hence, once the samples have been analysed, the material can be used for other purposes.

2.2.2 The Gamma Analyses

The gamma measurements presented in this report were made at the Ångström Laboratory in Uppsala. Four different detector systems were used in the measurements: two well detectors for smaller samples, one planar and one sandwich detector for bigger samples. All detectors were HPGe (High Purity Germanium) detectors and one of the well detectors had two NaI(Tl) detectors as an anti-coincidence shield.

The software Genie 2000 was used for evaluating the spectra. In all analyses updated radionuclide data from /Laboratoire National de Henri Becquerel 2004/ was used. The used library contained all gamma-emitting radionuclides from the naturally occurring decay chains plus many other radionuclides that could be suspected to occur in environmental samples.

U-238 was measured using the 63 keV peak of Th-234. However, no correction has been made for self-absorption, which could lead to an underestimation of the U-238 activity in samples with a high mineral content. However, it is possible to check the effect of self-absorption based on the ICP-AES analyses of uranium. Another problem with this peak is that it is overlapped by a small gamma line (63.81 keV) of Th-232. This could be a problem in samples with a low U/Th ratio. Ra-226 was measured using the radon daughter Pb-214, above all its peak at 351.9 keV. In order to assure that Pb-214 would be in secular equilibrium with Ra-226 the samples were left for at least three weeks after preparation before they were measured. Pb-210 was analysed using its 46.5 keV peak. Again, no correction has been made for self-absorption. Quantification of Th-230 was attempted using its 67.67 keV peak, although the branching ratio for this gamma peak is low (0.376%). For more reliable and precise measurements alpha spectrometry or mass spectrometry is recommended. The same goes for U-234, which has a small peak at 53.20 keV with a branching ratio of (0.123%). This peak is also overlapped by a peak from Pb-214 at 53.23 keV with a branching ratio of 1.07%. Since the Pb-214 activity is possible to determine using other peaks, it is theoretically possible to correct for the interference if the sample has a high uranium content and a low radium content. However, alpha spectrometry or mass spectrometry would be a much better choice. For these reasons the Th-230 and U-234 should be considered as uncertain until proper analyses have been made. Because of the great importance for the interpretation of the radionuclide distribution in the core, they have nevertheless been included in this report.

In the thorium series, Ra-228 can be quantified using its daughter Ac-228. Ac-228 has several gamma lines, but the best one to use is probably the 338.32 keV line. In stronger samples it is possible to use more than one peak to improve the accuracy of the measurements. In a similar manner, Th-228 can be measured using some of its daughters such as Pb-212 or Tl-208. In this case the 238.63 keV of Pb-212 was used.

The actinium chain radionuclides are harder to measure because they occur in much lower activities. The 185.7 keV of U-235 has a high branching ratio, but it is unfortunately overlapped by a Ra-226 peak. Since Ra-226 can be quantified in other ways it is possible to correct for the disturbance and indirectly determine the U-235 activity. If the activities were high enough the 143.76 keV peak was also used. Measuring Pa-231 is even more complicated and in this case a combination of Th-227, Ra-223 and Rn-219 peaks was used to try to get an estimation of the Pa-231 activities. Th-227 has a gamma line at 235.96 keV with emission probability 12.6%, which unfortunately is close to the intensive 238.63 keV gamma line of Pb-212. With good energy resolution, however, it should be possible to make reliable measurements. Ra-223 has a gamma line at 269.46 keV with fairly high emission probability (13.7%), but unfortunately there is an apparent risk of interference from Ac-228 (270.24 keV) and – unfortunately – also the best gamma line of Rn-219 at 271.23 keV. For this reason, the Pa-231 data is also very uncertain, but since so little is known about the behaviour of protactinium in peat is known the data is still included in this report.

2.2.3 Pb-210 Dating of Peat

Since large amounts of Rn-222 are able to escape from the ground, there will be a significant production of Rn-222 daughters in the atmosphere. The most long-lived among these daughters is Pb-210 with a half-life of 22.3 years. Since lead is a particle reactive element, the Pb-210 that is produced in the atmosphere will bind to aerosols, which sooner or later will be deposited on the ground. In this manner, there is a continuous atmospheric flux of Pb-210 to the ground. If Pb-210 is deposited in some environment where there is an ordered build-up of some kind of material, such as sediments or peat. Provided that the lead remains immobile in the layer were it was deposited this can provide a geochronology. As the peat grows and new peat layers are added, the atmospherically deposited Pb-210 will decay and eventually reach undetectable levels. However, by measuring the Pb-210 activities at different depths and relating them to one another, it is possible to calculate how fast the peat is growing, since the half-life of Pb-210 is known.

There are different ways to perform these calculations and they are all based on different assumptions. The most straightforward model for Pb-210 dating is, however, the so-called CIC model, where CIC stands for Constant Initial Concentration. As the name suggests, the basic assumption of the CIC model is that the concentration of Pb-210 in the upper layer always is constant. If this is true, it can be shown that the time t that has passed since deposition, in other word the age of the peat layer, must be

$$t = \frac{1}{\lambda}\ln(\frac{A_0}{A}), \qquad \text{Equation 2-1}$$

where λ is the decay constant of Pb-210, A the specific activity at some depth at A_0 the initial specific activity. The initial specific activity must be extrapolated from a series of measurements.

There are of course more advanced and maybe more proper models for Pb-210 dating, but it this case the simplicity of the CIC model and the rather low requirements that it puts on the measurements seem to make it a good choice, in this case.

A comparative study by /El-Daoushy et al. 1982/ showed good agreement between Pb-210 dating and the moss increment method. Some questions regarding the reliability of the Pb-210 dating method for peat were later raised by /Shotyk 1988/, who proposed that downward migration of lead in peat can lead to an underestimation of the age and, accordingly, to an overestimation of the growth rate. There is now growing evidence that lead can be mobilised from peat, probably by binding to DOC, which raises many question marks concerning Pb-210 dating of peat. The results are therefore published with these reservations.

2.3 ICP-AES

ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) was used to determine the elemental composition of ten samples from the profile. The measurements were made by Analytica AB in 2005. Prior to Analytica's measurements most samples had been analysed by gamma spectrometry in order to allow comparisons. This should not constitute a problem, since gamma spectrometry is a non-destructive method that does not alter the samples in any significant way.

When measuring arsenic, caesium, cobalt, copper, mercury, nickel, lead, sulphur and zinc the samples were dried at 50°C and dissolved in concentrated nitric acid (14 M) and concentrated hydrogen peroxide (30%) in a closed container in a microwave oven. The contents are adjusted to dry weight at 105°C. The other elements were ashed at 550°C and then fused using lithium metaborate. Finally they were dissolved in diluted nitric acid. For the fused elements the measurements should represent the total content.

The parameter PO^{4-} in the tables represents the amount of bioavailable phosphate. The fraction is extracted using a so-called CAL-solution, which is a buffered extract (pH 4.1) of calcium acetate, calcium lactate and acetic acid. The extraction is based on techniques described by Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten.

2.4 Sample Preparation

The cores were fetched from the cold-storage room at the Äspö Laboratory in October 2004 and sliced into 2.5–5 cm thick samples. They were put in plastic containers, in which they were transported to Uppsala. Unfortunately, the samples could be kept frozen during the transport. At Uppsala University the samples were freeze-dried at the Department of Ecology and Evolution. The samples were weighed before and after the freeze-drying to determine the water content.

The samples were then encapsulated in the special containers that were used in the gamma analyses. Some of the peat and clay samples were integrated in order to increase the sample masses. In a few cases peat samples were ashed at a temperature of 550°C in order to increase the density of the material. This was necessary, since the activity of the peat in many cases was so low.

All samples, for which Ra-226 was measured, were stored for a minimum of three weeks before measurement in order to assure that Pb-214 was in secular equilibrium with Ra-226.

When the gamma analyses were finished ten samples were chosen for further analysis by ICP-AES and sent in plastic containers to Analytica AB in Luleå. In order to achieve sufficient sample masses, two or more samples were integrated in some cases.

3 Results and Analysis

3.1 Radiometric Data

3.1.1 The Uranium Chain

The most important radionuclides from the uranium chain are shown in Figure 3-1. Generally, the activities in the peat were very low, when compared to the gyttja and the clay. For most radionuclides the highest activities are encountered in the clay (below 450 cm), but the uranium isotopes constitute an important exception to this pattern. Instead the highest uranium activities are encountered in the gyttja (approximately 400–450 cm).

There are clearly elevated Pb-210 activities near the surface due to atmospheric deposition. More intriguing, however, is the Pb-210/Ra-226 disequilibrium in the gyttja because of the comparatively short half-life of Pb-210. In the clay, the Pb-210 and Ra-226 activities agree very well however. Ra-226 also appears to be in secular equilibrium with its parent, Th-230, in the clay, which suggests that there is little transport in this region. In the gyttja, on the other hand, there is an excess of Th-230 relative to Ra-226, which is an indication of Ra-226 leakage, and/or Th-230 accumulation.

Compared to the U-234 and U-238 activities there are, however, low Th-230 activities in the gyttja. The situation where U-234 > U-238 > Th-230 is not uncommon and indicates accumulation of uranium from some kind of solution. In the clay, on the other hand, there is a depletion of uranium, which implies that uranium has been mobilised from this material during some stage of its history. Alternatively, thorium has been enriched in the clay, but that seems less likely. Later it will be discussed in more detail what implications all these disequilibria have for the interpretation of the transport of the radionuclides.

It is clear from Figure 3-1 that the profiles for Th-230 and U-234 are not complete. As was discussed earlier, those two radionuclides are very hard to measure accurately by gamma spectrometry in environmental samples. U-234 could be detected in some samples in the gyttja thanks to the low Ra-226 content and the high uranium content. This implied that there was a significant contribution from U-234 to the 53.2 keV peak, which in normal samples is dominated by Pb-214. Likewise, long

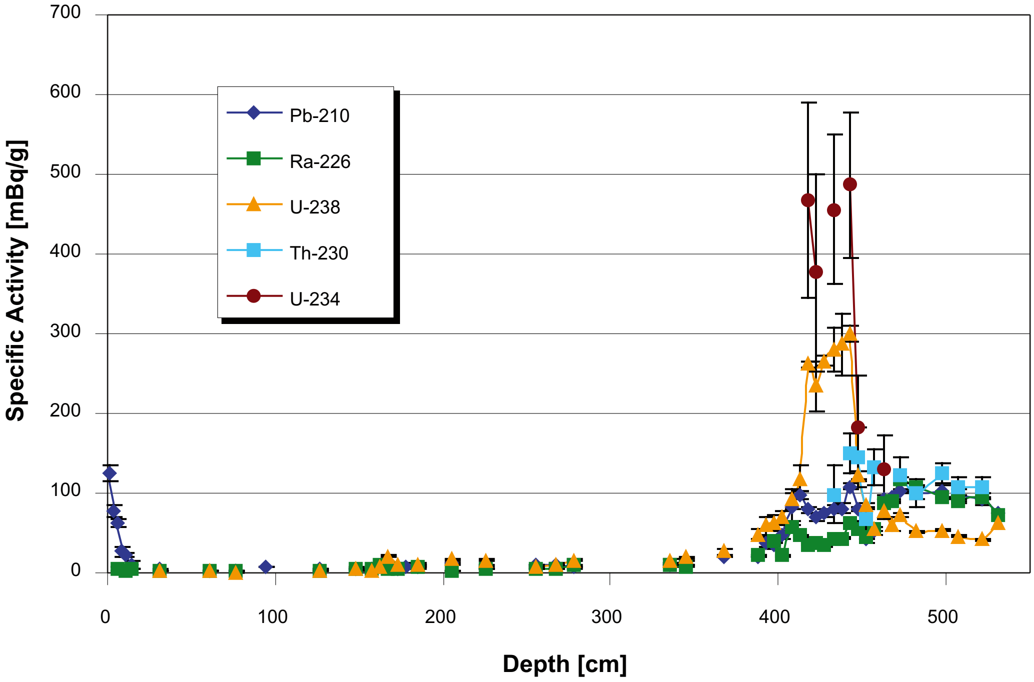


Figure 3-1. Specific activities for the uranium chain nuclides. The gyttja is found approximately between 400 and 450 cm.

measuring times and large sample masses allowed determination of Th-230 in some samples, above all in the clay. However, it must be emphasized that the uncertainties of the U-234 and Th-230 activities are very high, which also is clear from the error bars. However, the results do seem sensible, and the agreement between Th-230, Ra-226 and Pb-210 in the clay suggests that Th-230 activities are fairly reliable, they have large uncertainties. Therefore, it will be assumed in the analyses of these measurements, that the U-234 and Th-230 profile presented here reflect the actual activities of these radionuclides in the core. It is, however, advisable to complete these analyses with more reliable and accurate data of Th-230 and U-234, since the uncertainty and questionable reliability of the measurements of lower the credibility of the conclusions drawn.

3.1.2 The Actinium Chain

The analysed actinium chain nuclides are presented in Figure 3-2 below. Clearly, the U-235 profile shows a close resemblance to the U-238 profile in Figure 3-1. The U-235 activities in the peat are very low, while there is dramatic increase in the gyttja. In the gravel layer, the specific activity drops sharply and does not increase considerably in the clay samples. The similarities to the U-238 profile are expected and will be discussed further in Section 3.6.1.

Pa-231 does not appear to be in secular equilibrium with U-235 in the gyttja layers, while the discrepancy is much smaller in the clay. As for U-234 and Th-230, there are limitations in the measurements due a combination of low activities and low emission probabilities. However, the U-235/Pa-231 disequilibrium in the gyttja is consistent with the observations from the uranium chain and strengthens the conclusion that uranium has been accumulated in the sediments. Furthermore, the fairly good agreement between U-235 and Pa-231 in the clay adds more credibility to the measured Pa-231 activities.

3.1.3 The Thorium Chain

There are two interesting radionuclides in the thorium chain that can be measured by gamma spectrometry, Ra-228 and Th-228. In addition the Th-232 activities have been calculated from the ICP-AES measurements and included in Figure 3-3 below. Evidently, all three radionuclides agree very well throughout the core, which is not surprising considering the comparatively short half-lives of Ra-228 and Th-228: 5.75 and 1.91 years respectively. As it seems, both Ra-228 and Th-228 are in secular equilibrium with Th-232. The apparent deviations just below 400 cm appear to be a result of the interpolation for the Th-232 profile.

As for the radionuclide profiles presented above, there are low levels of thorium chain nuclides in the peat, while the levels increase sharply below 400 cm, where there is a transition from peat to gyttja. However, the maximum specific activities are not found in the gyttja, as for uranium, but in the clay. One can assume that this is connected the low mobility of thorium.

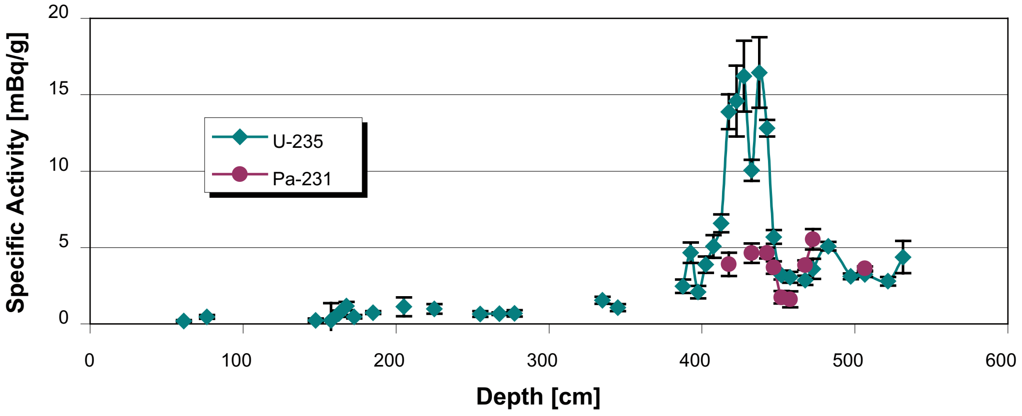


Figure 3-2. *Actinium chain nuclides.*

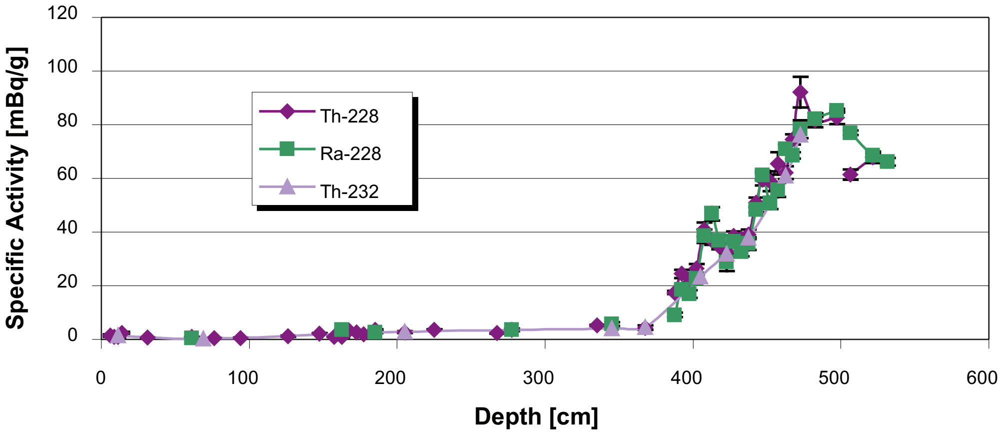


Figure 3-3. *Thorium chain nuclides. Th-228 and Ra-228 are measured by gamma spectrometry, while Th-232 has been calculated from the ICP-AES measurements.*

3.2 Miscellaneous Radiometric Data

3.2.1 Caesium-137

Because of its relatively short half-life, 30.17 years, Cs-137 itself is not a problem in nuclear waste. There is, however, a much more long-lived caesium isotope in nuclear waste, Cs-135, which is more important in this context. Furthermore, being an artificial radionuclide Cs-137 interesting for other reasons, for instance because it can give some hints concerning the hydrology of Klarebäcksmossen. Before the late 1950s no Cs-137 was present in nature and, therefore, wherever Cs-137 is found, it must have been transported there in less than 50 years.

The specific activity for Cs-137 is shown in Figure 3-4, and the highest specific activities are obviously found in the uppermost layers of the peat. This could indicate that there is an extensive biological uptake of Cs-137 or, possibly, that it is strongly bound to the peat. However, strong binding to organic matter does not agree well with what is known about caesium biogeochemistry. Had there been no post-depositional redistribution of Cs-137 in the peat, one would expect two distinct peaks: the first one representing the atmospheric testing of nuclear weapons in the late 1950s and early 1960s and the second one representing the Chernobyl accident in the spring of 1986. However, a corresponding pattern is not observed for natural caesium, Cs-133. Instead the concentrations of Cs-133 in the peat seem to be quite constant with only a minor increase in the uppermost sample. Yet another possibility is that Cs-137 was deposited in some particulate form. This would explain the differences between Cs-137 and Cs-133.

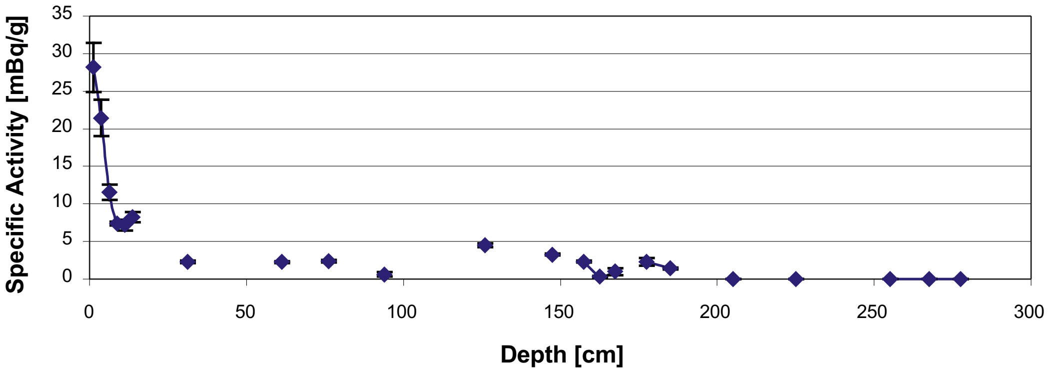


Figure 3-4. *Cs-137 activity profile. No Cs-137 could be detected below 200 cm.*

Despite the fact that much Cs-137 appears to be caught in the uppermost peat layers, parts of the Cs-137 have been transported surprisingly deep. Apparently the front must have moved downwards at an average speed of at least 4 cm/yr. Unfortunately, no hydrological measurements are yet available for Klarebäcksmossen, but measurements from the Simpevarp area have shown that the average discharge is 180 mm/yr /Larsson-McCann et al. 2002/. Therefore, it does not seem unlikely that ground water advection is responsible for transporting Cs-137 to these depths. Thus, the Cs-137 profile indicates that the groundwater flow has a downward component in this part of Klarebäcksmossen. It is not possible to judge whether there also is a horizontal component form these analyses, but the bigger the horizontal component is, the longer the Cs-137 must have been transported through the peat. Hence, the depth represents a minimum distance.

/Landström and Sundblad 1986/ also found Cs-137 deep in a peat (150–180 cm) and suggested that this could be the result of an upward migration through the fracture zones in the bedrock below. No Cs-137 could be detected in samples below 200 cm in Klarebäcksmossen, however, so it seems clear that it hardly has come from below, but that there has been a transport from the surface. There is extensive literature showing that caesium indeed is highly mobile, especially in peat, and affected by both biological uptake and advection /Turetsky 2004/.

Traces of Am-241 were noticed in the uppermost layers of the peat, but the activities were too low to allow reliable quantification. As it seems americium has not been transported in any higher degree. Since all major peaks in the gamma spectra are believed to have been identified with reasonable accuracy, it can be concluded that no other gamma-emitting artificial nuclides than Cs-137 and Am-241 are present in detectable levels.

3.2.2 Growth Rate by Pb-210 Dating

As was described earlier, the accumulation of Pb-210 that can be seen in the upper layers of the peat is due to atmospheric deposition. Because of the small sample masses and the low activities in the peat samples, it was hard to make very accurate measurements of unsupported Pb-210, especially in the somewhat deeper samples where the amount of unsupported Pb-210 was very low. Since the accuracy of the unsupported Pb-210 in the deeper samples is very important in the CRS model, this model is not very suitable for dating in this case. Therefore, the CIC model was used instead. The result of this dating is shown in Figure 3-5. It should be noted that the linear regression in Figure 3-5 does not take the uncertainties of the measurements into account. Consequently, it is not as reliable as the figures presented in the paragraph below, which are based on weighted averages. In both cases it is assumed that the growth rate has been constant.

If the growth rates during the past 110 years (which is the age of the oldest peat that has been dated) are used to estimate an average growth rate for the peat, this would give a growth rate of 1.45 ± 0.06 mm/yr. This corresponds to an accumulation rate of 51.0 ± 0.8 g/m^2/yr (dry weight). If this figure can be assumed to be representative for the accumulation rate of the peat, it can be estimated by extrapolation that the transition from minerotrophic to ombrotrophic conditions took place approximately 1,300 years ago. There are, however, no guarantees that the peat growth has not varied and so one should be careful about the result of such extrapolations. A more reliable approach in this case would be to use C-14 dating.

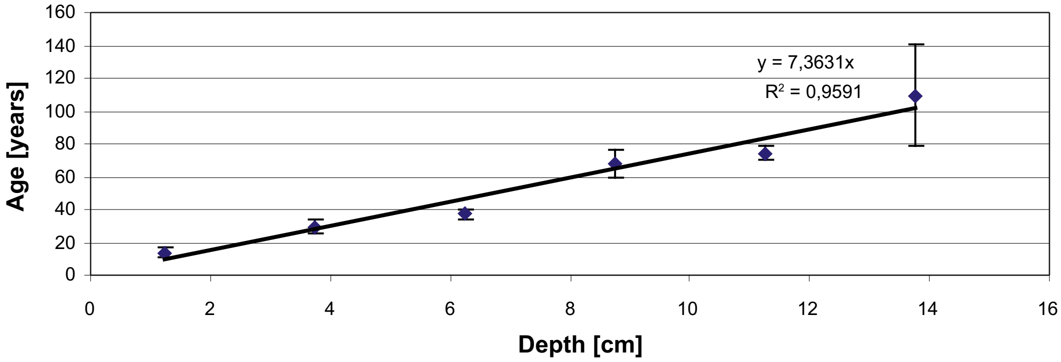


Figure 3-5. *Peat age as a function of depth as determined by the CIC method.*

The growth rate seems to agree well with what could be expected. Archaeological and dendrochronological dating of younger ombrogeneous peat in southern Sweden has shown vertical growth rates in the range 0.4–8 mm/yr. The mean values have been in between 1.5 and 2 mm/yr, which would mean that Klarebäcksmossen has quite normal growth rate /Franzén 1985/. These figures have also been verified by Pb-210 dating of *Sphagnum* peat in central Småland /Franzén 1985/. Since the Pb-210 profile does not show any signs of disturbance and the growth rate agrees well with other bogs in the same part of Sweden, it can be concluded that the dating most likely has succeeded.

3.3 Radium

3.3.1 Isotopic Ratios Involving Ra-226

From Figure 3-1 it was clear that Ra-226 is not in secular equilibrium with neither its parent Th-230 nor its daughter Rn-222 in the gyttja. This is also shown in Figure 3-6, where the Ra-226/Pb-210 and Ra-226/U-238 isotopic ratios are plotted.

The Ra-226/Pb-210 ratio varies throughout the peat, which probably should be attributed to migration of Rn-222. The low ratios at the surface are explained by atmospheric deposition of Pb-210. In the clay the Ra-226/Pb-210 ratios are close to unity, which indicates that none of the involved radionuclides are being transport here. This was also supported by the Th-230 profile, which showed similar activities in the clay. Since the half-life of Ra-226 is 1,600 years, this is a strong indication that there has been no extensive migration of radium in the clay during the past millennia.

More intriguing are the disequilibria in the gyttja. Both the Ra-226/Pb-210 and the Ra-226/Th-230 ratios indicate that there has been extensive migration in the gyttja. The half-life of Pb-210 is 22.3 years, which means in a closed system it would be in secular equilibrium with Ra-226 after 100–150 years, unless there initially was extremely much Pb-210 in relation to Ra-226. In material as old as the gyttja, which undoubtedly is at least 1,000 years old, it is, however, unrealistic that the disequilibrium would reflect the initial conditions of the deposited material. Because of the comparatively short half-life of Pb-210, the Ra-226/Pb-210 ratios provide evidence of recent and probably on-going migration of some radionuclide in the uranium chain. The two most likely candidates are Ra-226 and Rn-222.

Since the Ra-226 disequilibria are central for the conclusions drawn in this report, the reliability of the measurements has been tested carefully. The routines for analyzing Ra-226 are well established, and analyses with different detector systems have given similar results. No significant amounts of radium are expected to have been lost in connection with the sampling, because the fraction

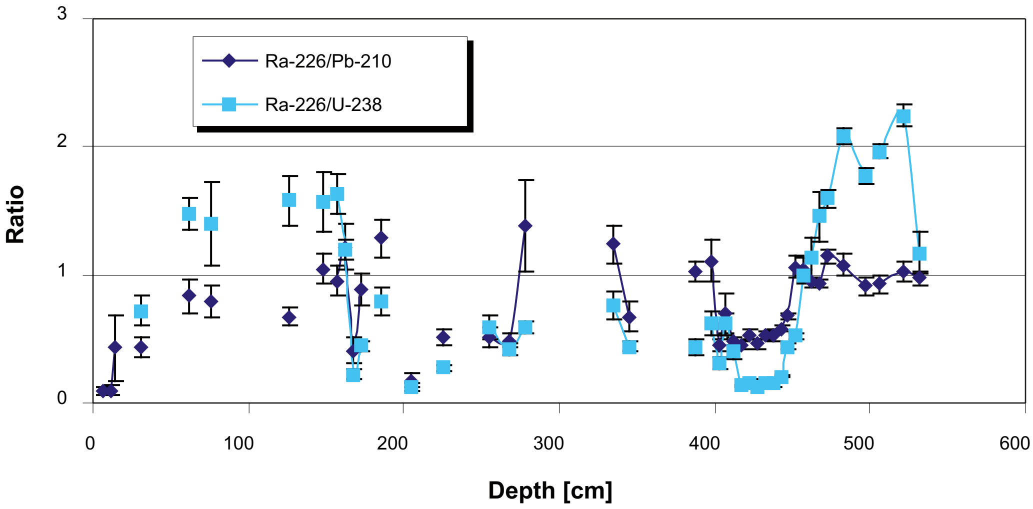


Figure 3-6. Key isotopic ratios for the uranium chain.

of radium in the pore water probably is very low, a percent or two at the very most according to K_d values presented by the /IAEA 1994/. Moreover, no significant amounts of water were lost in connection with the sampling, which definitely eliminates this possibility (Nilsson, private communication). Likewise, it seems impossible that the Ra-226/Pb-210 ratio was significantly altered during the storage at the Äspö Laboratory. Even if Rn-222 was allowed to escape, thereby stopping the production of Pb-210 in the core, the half-life of Pb-210 is too long to allow any significant change in the Pb-210 activity during the few months that passed between sampling and analysis.

Unfortunately, it was not possible to transport the samples in the frozen state between the Äspö Laboratory and Uppsala University. However, measurements have been performed on the plastic containers, in which the samples were transported and stored, and no detectable amounts of any radionuclide were found. Thus, the presented Ra-226 activities most likely represent the true conditions in the gyttja very well.

There are two possible hypotheses that could explain the isotopic disequilibria in the gyttja: either there is a very rapid leakage of Ra-226 that causes both the low Ra-226/Pb-210 and the low Ra-226/Th-230 ratios or either there is a more moderate leakage of Ra-226 and a substantial migration of Rn-222. Since it is possible to imagine a mixture of these processes, the two hypotheses do not exclude each other.

3.3.2 Leakage of Radium from the Gyttja

Provided that the measured Th-230 activities indeed are correct, there is clear evidence of radionuclide transport in the gyttja. As radium generally is more mobile than thorium, it should be safe to say that the disequilibrium is caused by migration of radium, i.e. radium is being leached from the gyttja.

With a half-life of 1,600 years Ra-226 could be expected to reach secular equilibrium with Th-230 in 6,000–8,000 years, provided that no Ra-226 was present at t = 0. If Ra-226 is present at t = 0, secular equilibrium will be reached even faster. The age of the gyttja is unfortunately not known, but it is undoubtedly old enough to reject the hypothesis that there has been no leakage of Ra-226.

In Figure 3-7 the exponential growth of the Ra-226/Th-230 ratio with time has been plotted. The initial Ra-226 activity in the figure is set to zero, but in reality the gyttja sediments should contain at least some amounts of Ra-226 when they were formed. However, if it is assumed that no Ra-226 was present in the gyttja during its formation, e.g. that the activities found there today are the result of *in situ* production, and that no Ra-226 has been lost, it is possible to use the Ra-226/Th-230 ratio to calculate the age maximum age of the gyttja sediments. For instance, the age of sample GY1-13 (430–435 cm) should be 1,290 ± 650 years according to this model. Similar calculations for the deeper samples, GY2-1 (440–445 cm) and GR1 (445–449 cm), result in even younger ages, 1,260 ± 290 years and 1,080 ± 370 years respectively. These measurements are also shown in Figure 3-7.

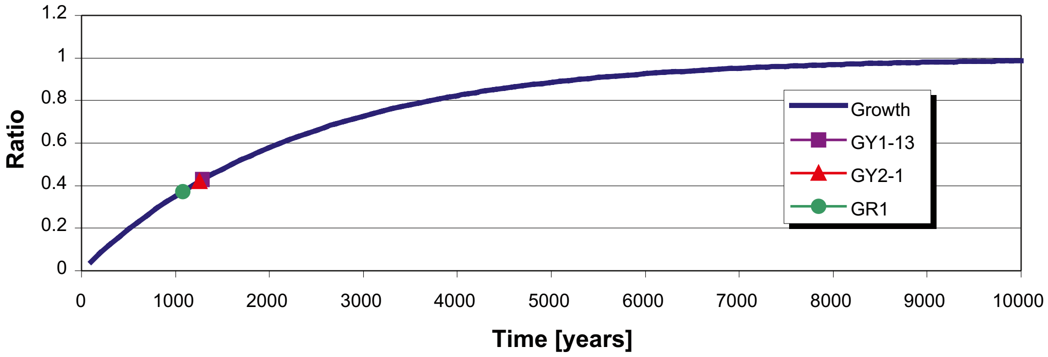


Figure 3-7. *The growth of the Ra-226/Th-230 ratio with time when no Ra-226 is assumed to be present at t = 0. The Ra-226/Th-230 ratios in some gyttja samples are also marked indicating their age calculated from these initial conditions.*

Obviously, these ages seem very low. The average growth rate of the peat would have to be well above 2 mm/yr (with compaction) and the net production would have to exceed 160 g/m^2/yr. These figures are not unrealistic /Franzén 1985/, but it should be noted that they represent absolute minima. More realistic assumptions would lead to even higher growth rates. Furthermore, the Pb-210 dating shows that the present growth rate is much lower than what is required. Hence, it must have been appreciably higher in the past.

This discussion should not be understood as an attempt to convince anyone that these ages are correct or that the suggested dating method is sensible in this case. On the contrary, one should expect at least some Ra-226 to have been present in the deposited material and this would then result in even lower ages. Similarly, accumulation of radium in the gyttja would also lead to lower ages in these calculations. Since the assumption that there has not been any leakage of Ra-226 leads to unreasonable conclusions, it cannot be valid. Hence, the alternative hypothesis, namely that there has been a leakage of Ra-226, must be accepted.

The weakness of this argument is obviously the quality of the Th-230 measurements. The uncertainty of these analyses is unsatisfying, but all acquired spectra from the gyttja, whose measuring time has been long enough to allow quantification of the Th-230, indicate a distinct disequilibrium with Ra-226. The weighted average for the Ra-226/Th-230 ratio in the gyttja is 0.43 ± 0.16, which is unexpectedly low. Elsewhere in the profile, the Th-230 activities agree well with the Ra-226 and Pb-210 activities, which indicates that the Th-230 activities probably are reliable – although they remain very inaccurate.

There are no signs in the core of where the leached Ra-226 has gone. The groundwater flow that probably was responsible for the radium transport was – or is – most likely directed more or less vertically, upwards or, possibly, downwards through the gyttja. It seems less probable that there has been any extensive horizontal redistribution of radium in the gyttja due to its relatively low hydraulic conductivity. Much higher conductivity can be expected both in the peat and the gravel, which suggest that the radium has reached one of these layers and then been transported away.

3.3.3 Leakage of Radium and the Ra-226/Pb-210 Ratio

Having established the fact that radium is leached from the gyttja, the question that needs to be addressed is the extent and the rate of the leakage. With better understanding of the hydrology in Klarebäcksmossen, C-14 dating and better Th-230 analyses it should be possible to make much better estimations, but with the available data it is still possible to draw some conclusions.

It has also been observed that there is a pronounced disequilibrium between Ra-226 and Pb-210 in the gyttja. As it is known that Ra-226 has been lost from the gyttja, it could be that the Ra-226/Pb-210 ratio also is affected. Since the half-life of Pb-210 is relatively short, this would, however, require a rapid loss of radium. If radium currently is being lost from the gyttja, it would appear as if the half-life of Ra-226 is shorter than the physical half-life. In radioecology, this apparent half-life is often referred to as the effective half-life. If it is assumed that the removal of radium is proportional to the number of nuclei, the process could mathematically be described as

$$\frac{dN}{dt} = -\lambda N - rN = -\lambda_{eff} N \,, \qquad \text{Equation 3-1}$$

where N denotes the number of nuclei and λ the decay constant. r is a constant, analogous to λ, which describes the how large fraction of the nuclei that is removed – by other processes than physical decay – per time unit. Apparently, λ and r could be substituted by a single decay constant, λ_{eff}, the effective decay constant, which also is done in Equation 3-1. This effective decay constant is related to the effective half-life mentioned above by $T_{eff} = \ln(2)/\lambda_{eff}$. Similarly, r can be associated with a "removal half-life" or an environmental half-life, T_{rem}. The half-lives will be related as

$$T_{eff} = \frac{1}{\frac{1}{T_{1/2}} + \frac{1}{T_{rem}}} \,. \qquad \text{Equation 3-2}$$

In order to see what implications this will have for the Ra-226/Pb-210 ratio it is necessary to turn to the equation describing the relation between the activity of a parent and its daughter. The Bateman equation is derived in Appendix A, where it is described how secular equilibrium is established. If the parent in this case is identified with Ra-226 and the daughter is identified with Pb-210, we can write

$$A_{Pb} = \frac{\lambda_{Pb}}{\lambda_{Pb} - \lambda_{Ra}} A_{Ra} \left(1 - e^{-(\lambda_{Pb} - \lambda_{Ra})t}\right), \qquad \text{Equation 3-3}$$

where A_{Pb} and A_{Ra} denote the activities of Pb-210 and Ra-226 respectively and λ_{Pb} and λ_{Ra} their decay constants. Under normal circumstances, when there is no removal of radium, $\lambda_{Pb} - \lambda_{Ra} \approx \lambda_{Pb}$. However, if there is a removal of radium, λ_{Ra} must be substituted by $\lambda_{Ra} + r$ according to Equation 3-1. Obviously, the mentioned approximation is not valid, if r is comparable in size to λ_{Pb}. The situation probably becomes more evident if the decay constants are substituted by half-lives and the Ra-226/Pb-210 ratio isolated. This will result in the following expression:

$$\frac{A_{Ra}}{A_{Pb}} = \left(1 - \frac{T_{Pb}}{T_{eff}}\right)\left(\frac{1}{1 - e^{-\ln 2\left(\frac{1}{T_{Pb}} - \frac{1}{T_{eff}}\right)t}}\right). \qquad \text{Equation 3-4}$$

The expression within the second parenthesis only shows how fast the ratio will approach the asymptote when no Pb-210 is present at t = 0. It is clear that if the effective half-life of Ra-226 is decreased, this factor will approach unity much slower. However, the time dependent factor will look different if Pb-210 and Ra-226 were at secular equilibrium when the removal began, which probably was the case in the gyttja. Having recognized this, we can for now focus on the Ra-226/Pb-210 ratio by assuming that t is great enough to make the expression within the second parenthesis approximately equal to unity. Hence, the equation simplifies to

$$\frac{^{226}Ra}{^{210}Pb} = 1 - \frac{T_{Pb}}{T_{eff}}. \qquad \text{Equation 3-5}$$

Equation 3-5 shows that if there is no removal of radium, e.g. the effective half-life of Ra-226 is equal to the physical half-life of Ra-226, the Ra-226/Pb-210 ratio will be 0.986. This is the classical secular equilibrium between these two radionuclides. The actual Ra-226/Pb-210 ratios in the gyttja sample are, however, as low as 0.5 and in some samples even less than that. Using Equation 3-5, it can be calculated that the half-life of Ra-226 in the gyttja must be 45.9 years. This corresponds to a removal rate of approximately 0.015 per year. In other words, to support a Ra-226/Pb-210 ratio of 0.5, 1.5% of the total Ra-226 has to be removed annually. Evidently, Equation 3-5 does not include the effects of Th-230 decay, but it can be shown that they are negligible on these short time-scales.

The only process that possibly could cause such a rapid removal of radium is advection. Thus, there are two central factors that must be examined are the amount of radium dissolved in the pore water and the size of the groundwater flow through the gyttja.

3.3.4 The Amount of Radium in the Pore Water

Unfortunately, this project did not include any analyses of elements and radionuclides in the aqueous phase, but there are good reasons to believe that the dissolved fraction is small in comparison with the solid fraction. If radium is comparable to other alkaline earths (in this case magnesium, calcium and barium) in terms of distribution between pore water and peat, less than 0.1% of the radium could be expected to occur in the pore water /Steinmann and Shotyk 1997b/.

Another way to estimate the amount of radium in the pore water is to use distribution coefficients, so-called K_d values. The K_d value for radium in organic soils is 2,400 L/kg (with no specified range) according to the /IAEA 1994/ and 500 (200–1,000 L/kg) for sediment and suspended particles in freshwater systems. /Karlsson and Bergström 2002/ give an expected value of 2,000 L/kg in organic soils with a range of 200–20,000 L/kg. The fraction of radium in the pore water will vary significantly depending on what value of the distribution coefficient that is chosen, as is shown in Figure 3-8, where the measured water content and dry weights of the samples have been used in

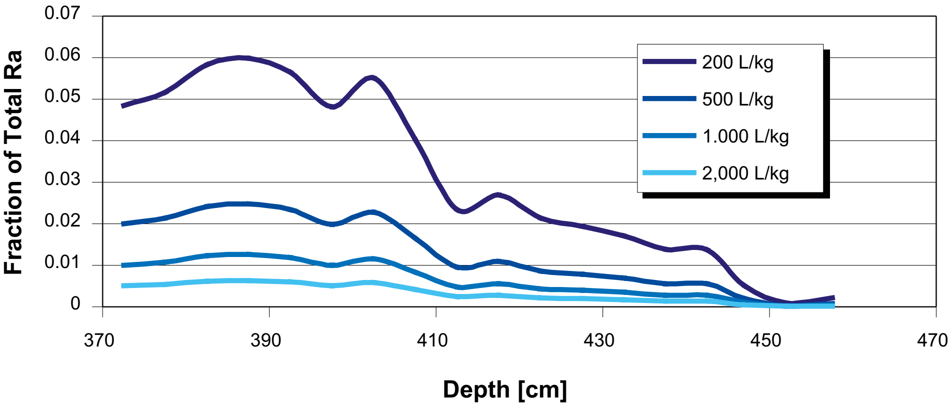


Figure 3-8. *The dissolved fraction of radium for some different distribution coefficients.*

the calculations. Although the K_d values can hardly be expected to be constant throughout the core, this should at least give a hint of what the actual fraction in the aqueous phase might be. It is clear that if a rather low value is assumed, quite much of the radium could be found in the aqueous phase, perhaps as much as 1% or even more. It seems unlikely, however, that more than 2% of the radium is found in the pore water.

These estimations are also supported by measurements from the Simpevarp area included in a report by /Tröjbom and Söderbäck 2006a,b/. This data set includes analyses of Ra-226 and Rn-222 in pore water, which should be possible to use in order to make a crude estimation of what fraction of the total Ra-226 that is dissolved in the pore water. Rn-222 is produced in the decay of Ra-226, but as an inert gas it should mainly be present in the pore water, although it has been suggested that it so some extent can be sorbed by sediments /Wong et al. 1992/. Hence, we can assume that the Rn-222 activities gives an idea about the Ra-226 in the solid phase, which then can be compared to the Ra-226 in pore water. Applying these simple assumptions on the 22 samples presented by /Tröjbom and Söderbäck 2006a, b/ suggests that the amount of radium in solution is somewhere in the range 0.13–1.8%, which agrees well with the figures presented above. The conclusion must be that hardly more than 2% of the radium under no conditions can be found in the pore water of the gyttja.

3.3.5 The Groundwater Flow through the Gyttja

The next step is to assess the groundwater flow in the through the gyttja, but unfortunately not very much is known about the hydrological conditions in Klarebäcksmossen. This makes it hard to estimate what volumes of water that possibly may pass the gyttja layers in a year. It is not even clear in what direction the water flows. The Cs-137 profile indicates, however, that the groundwater flow has a significant downward component, at least in the upper 2 m of the profile, but it is unclear what happens further down. Considering the fact the Klarebäcksmossen was drained in the late 19th or early 20th century, the best guess is probably that there is a horizontal flow in the deeper parts of the peat, where most of the discharge takes place.

If the effective half-life of Ra-226 really is as low as 50 years, this would require very high radium levels in the case that the removal has been going on for a while. Therefore, it seems likely that the losses would be related to a fairly recent event in the history of the bog. The draining could possibly be that event, since the draining of a bog will result in a lowered groundwater level, which in turn will decrease the hydraulic pressure so that the inflow of groundwater from below generally could be expected to increase. /Kellner 2003/ writes that "an increased component of upward flow (…) often is experienced after drainage" and refers to a study by /Lundin 1993/.

A problem with this explanation is, however, that the water flowing through the gyttja must be relatively pure in order to accomplish leaching. From this point of view it would be easier to explain the leakage if there was a downward flow of rainwater through the gyttja, but it seems harder to imagine that this would be the case. On the other hand, if there were a comparatively rapid upward transport of radium, it should be possible to detect enhanced levels of radium immediately above the gyttja. This is, however, not the case. It would be easier to imagine the radium disappearing through the gravel layer below the gyttja without leaving any traces in the isotopic ratios.

Quantitatively, it also seems rather hard to argue that there is such a rapid transport of radium in the gyttja. No data is available for Klarebäcksmossen, but according to measurements in the catchment area of Forshultesjön in the Oskarshamn area /Larsson-McCann et al. 2002/ the average discharge is 5.7 L/s/km^2, which equals approximately 180 mm or 18 ml/cm^2 annually. If the discharge in Klarebäcksmossen is assumed to be of equal size, this figure could be compared to the amount of water in the gyttja, which is approximately 36 ml/cm^2 (400–445 cm). Thus, if the groundwater flow through the gyttja were equal to the expected discharge in Klarebäcksmossen, the turnover time for the pore water would be two years. Viewed as one compartment, this would allow no more than 1% of the radium to be removed annually. More accurate estimations are evidently possible, but that would require some more detailed modelling of the transport processes in the gyttja.

However, the gyttja is not very likely to play an important role in the discharge from Klarebäcksmossen, especially since it was drained in the late 19th or early 20th century. Considering that the hydraulic conductivity of gyttja can be quite low, it seems much more reasonable that there is a horizontal discharge in the lower parts of the peat. If there were a rapid removal of radium from the gyttja, a Darcy velocity of $7\cdot10^{-7}$ cm/s or more is needed, and it seems hard to bring about sufficiently high gradients to support such a flow. Hence, when the amount of radium in the pore water and the possible groundwater flow through the gyttja is taken into account, it seems hard to explain the Ra-226/Pb-210 ratios by a very rapid transport of radium.

3.3.6 Isotopic Ratios Involving Ra-228

The hypothesis that there is a rapid removal of radium from the gyttja is also contradicted by the isotopic ratios of other radium isotopes than Ra-226. Ra-223 and Ra-224 both have very short half-lives, 11.4 and 3.66 days respectively, so they will not be affected by any leakage of radium. Ra-228, on the other hand, has a half-life of 5.76 years, which makes it interesting to study in more detail. Both the Ra-228/Th-232 and the Ra-228/Th-228 ratios could be influenced by removal of radium, provided that it is rapid enough. Along with the Ra-226/Pb-210 and the Th-232/Th-228 ratios, these isotopic ratios are shown in Figure 3-9.

Ra-228 and Th-228 have similar half-lives (5.76 and 1.91 years respectively) and will not occur in secular equilibrium unless both of them are in secular equilibrium with Th-232. Without Th-232 the Th-228 activity would be roughly 1.5 times the Ra-228 activity. In other words, the Ra-228/Th-228 ratio would be 0.67. As can be seen in Figure 3-9, the Ra-228/Th-228 ratios seem to be close to unity in the gyttja. Despite some minor deviations, it seems as if Ra-228 and Th-228 occur in secular equilibrium with Th-232.

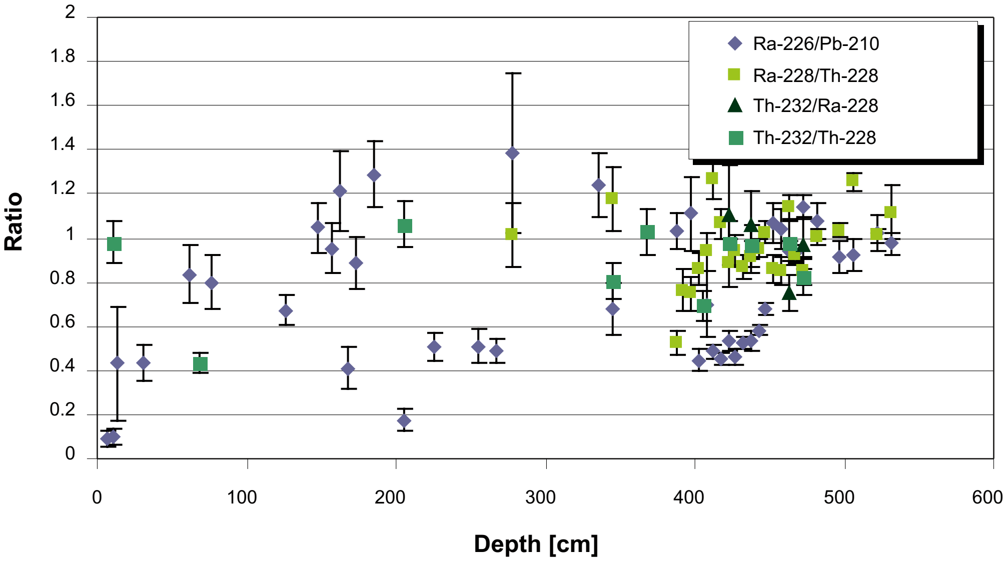


Figure 3-9. *Isotopic ratios for Ra-226, Ra-228 and some related radionuclides.*

The most interesting ratio in the thorium chain is probably the Th-232/Ra-228, which directly could be used to calculate the transport of radium. If radium is lost, one should expect Ra-228/Th-232 ratios lower than unity or more exactly:

$$\frac{^{228}Ra}{^{232}Th} = \frac{\lambda_{Ra-228}}{r + \lambda_{Ra-228}}, \qquad \text{Equation 3-6}$$

where r is the removal constant of radium and $\lambda_{Ra\text{-}228}$ the decay constant of Ra-228. Since the exact ratio will depend on the removal rate of radium, this is a way to directly quantify any possible removal of radium during the last years. Another advantage is that there cannot be any influences of radon on this ratio. However, since the half-life of Ra-228 is fairly short, the removal must be rather high to cause any effect on the Ra-228/Th-232 ratio. For instance, if 1.5% is lost by leaching each year, the expected ratio would be 0.89. If the Ra-228/Th-232 ratio, on the other hand, would be close to unity, it can be concluded that the transport of radium is limited in comparison with the decay of Ra-228, which is approximately 12% annually. In Figure 3-9 the uncertainties are rather large, but the general impression is that the Ra-228/Th-232 ratios are greater than 0.89, which implies that there cannot be annual losses of radium in the order of 1.5%.

Yet there seems to be a tendency of slightly lowered Ra-228 activities in the gyttja. Unfortunately, the measurements are too uncertain to allow reliable determination of the Ra-228/Th-228 ratio in the gyttja. Just above the gyttja, however, there is a pronounced disequilibrium between Ra-228 and Th-228. As this is indicated by several independent measurements, it suggests that Ra-228 and Th-228 are not in secular equilibrium with Th-232 in this region. On the contrary, the ratios seem to agree well with what could be expected, if the ratio is governed by the decay of Ra-228 and Th-228 without the involvement of Th-232. Hence, this could support the idea that there is an appreciable water flow in the lower parts of the peat.

3.3.7 Estimation of the Leakage of Radium from the Gyttja

It seems safe, however, given the uncertainties of the measurements, to assume that the actual ratios are greater than 0.9. In that case, the removal rate of radium cannot be greater than 1.4% annually according to Equation 3-6. In this manner, the Ra-228/Th-232 ratios provide a maximum limit for the loss of radium from the gyttja. Hypothetically, it would of course be possible to imagine much higher removal rates during a short period of time, but it is hard to imagine what could cause that. Considering the possible groundwater flow and the fraction of radium in the pore water, even 1.4% per year seems much. The actual losses are probably less. However, because of the high amounts of sulphur in the gyttja, it is possible that $RaSO_4$ plays an important role in the radium transport as was suggested by /Beneš 1982/.

In a similar manner, the Ra-226/Th-230 ratios can be used to estimate a minimum value for the removal rate. Provided that the gyttja is old enough, one can argue that at least 57 ± 16% of the radium must be lost by leaching instead of radioactive decay, because the average isotopic ratio is 0.43 ± 0.16. This implies that the removal rate must be at least 0.057 ± 0.0375% per year, if Equation 3-6 is rewritten for Ra-226 and Th-230.

Hence, this leaves an interval of 0.02–1.4% per year for the leakage of radium, which is not very precise. Yet the uncertainty is not higher than what could be expected from a model, and an important advantage in comparison with model calculations is that these figures are based on actual observations. Better measurements of above all Th-230 and C-14 dating are also likely to substantially improve the accuracy of the estimation. More importantly, this also provides evidence about the long-term fate of radium in sediments.

3.3.8 Migration of Rn-222

Before the hypothesis that the low Ra-226/Pb-210 ratios are caused by rapid leakage of radium is finally discarded, it should be investigated whether there is some other process that satisfactorily may explain the observations. The only reasonable alternative hypothesis seems to be migration of Rn-222, which occurs between Ra-226 and Pb-210 in the uranium decay chain. Being a noble gas, radon is chemically inert and, consequently, very mobile. /Wong et al. 1992/ have proposed that radon can be sorbed by sediments to some extent, but despite this, the general impression is still that radon is conservative in its behaviour. According to /Kadko 1980, p. 370/, “molecular diffusion through pore water and radioactive decay far outweigh mechanical mixing and advection for Rn-222", which seems like a reasonable statement. In particular, the water flow through the gyttja would have to be very fast in order to transport Rn-222 any considerable distances before it decays. Hence, molecular diffusion of Rn-222 seems to be an interesting explanation.

The hypothesis becomes even more attractive, if one considers the Pb-210 and Ra-226 profiles in Figure 3-10. The graph is essentially identical to Figure 3-1, but the unit on the y-axis has been converted so that activity per volume unit is shown, since the diffusive transport is governed by the concentration gradient. Mathematically, the diffusive transport is described by Fick's first law:

$$\bar{j} = -D\nabla C . \qquad \text{Equation 3-7}$$

Here **j** is the diffusion flow, D the (effective) diffusivity and C the particle concentration. A remarkable thing about Figure 3-10 is that the Pb-210 profile between 400 and 450 cm appears to have been translated approximately 5 cm upwards in relation to the Ra-226 profile. Hence, it is possible that the Pb-210 on a certain depth is not in secular equilibrium with the Ra-226 on the same depth, but rather with the Ra-226 some centimetres below. This is exactly what one should expect, if there was a sufficiently fast diffusive transport of Rn-222. It must then be investigated whether the given concentration gradient is enough to produce the observed pattern, if a reasonable value of the effective diffusivity is used.

/Etiope and Martinelli 2002/ have made an overview of the literature on the migration of carrier and trace gases in the geosphere and present a value of $2 \cdot 10^{-6}$ cm^{-2}/s for the efficient diffusivity of radon in saturated soil. Higher values of the efficient diffusivity can, however, be encountered elsewhere in literature. For instance, /Kadko 1980/ says the effective diffusivity of radon in sediments is $5 \cdot 10^{-6}$ cm^2/s, while /Benoit et al. 1991/ have used an even higher value, $6 \cdot 10^{-6}$ cm^2/s, in their model.

However, preliminary modelling of the diffusive transport in the gyttja indicates that diffusion alone cannot account for the much more than a Ra-226/Pb-210 ratio of 0.9 – even if the highest value of the effective diffusivity is used. More thorough investigations may be required, since the effective diffusivity might vary appreciably, but by considering the diffusion length one can acquire a sense of what values that are needed. The diffusion length, Z_d, is the average distance that a single atom will travel during the time t. Formally, the diffusion length is defined as

$$Z_d = \sqrt{Dt} , \qquad \text{Equation 3-8}$$

where D is the diffusivity. In the case radionuclides the diffusion is limited not only by the diffusivity, but also by its lifetime. For Rn-222 the mean lifetime is roughly 5.5 days, which means that the diffusion length is in the order of 0.97–1.7 cm, if the values presented in literature are used for the effective diffusivity.

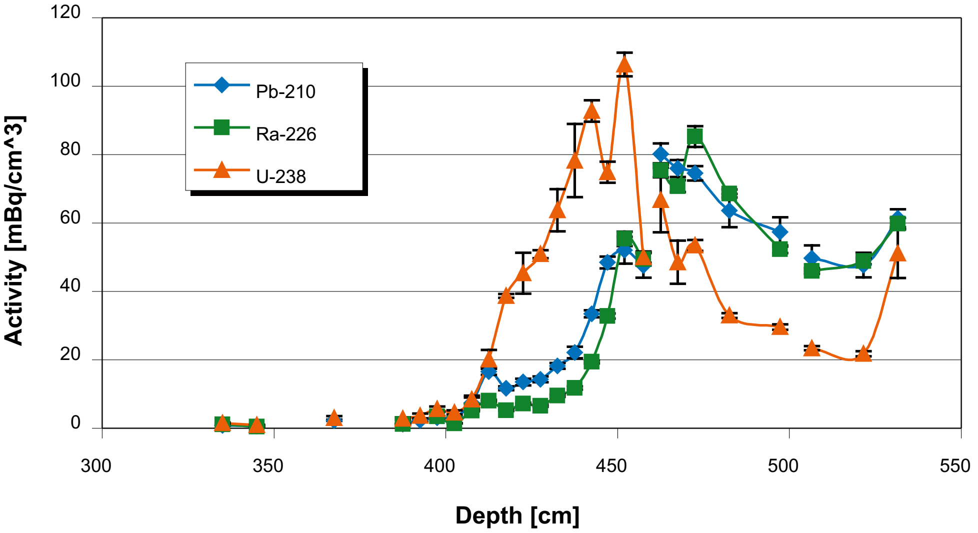


Figure 3-10. *Uranium chain nuclides measured in activity per volume unit.*

Since the diffusion length is proportional to the square root of the effective diffusivity, values greater than $5 \cdot 10^{-5}$ cm^2/s are required to produce a diffusion length of 5 cm, which is an absolute minimum. This does not seem reasonable, when compared to what has been published.

Even if diffusion appears to be insufficient to explain the observed disequilibria, this does not mean that the radon hypothesis can be discarded. /Etiope and Martinelli 2002/ refer to several studies, where diffusion has been unsuccessful in explaining large-scale radon transport. Therefore, it has been suggested that there also are other important mechanisms that can cause a significant transport of radon. According to the geogas hypothesis, the explanation is bubble transport, which really is a kind of advection with gas instead of water as medium. These carrier gases could for instance be carbon dioxide or methane that is produced in the soil. Radon and other trace gases are then thought to move together with these bubbles and this would allow a much more rapid transport. The geogas hypothesis is supported by the fact that radon and carbon dioxide are very well correlated above fault zones /Etiope and Martinelli 2002/. Although, there are no possibilities to decide how large this transport may be in the case of Klarebäcksmossen based on these data, the geogas hypothesis should be regarded as a very likely explanation to the Pb-210/Ra-226 disequilibrium. It is a well-documented process that most certainly takes place in this core, although it cannot be determined whether the transport is rapid enough to explain the observed ratios. For instance, /Culbert and Leighton 1981/ write that "Ra-226/Pb-210 disequilibrium may almost always be considered as a measure of radon mobility". Excess of Pb-210 was also found by /Zielinski et al. 1986/ in a peat-sediment core. Although they observed low Ra-226/Th-230 ratios in some samples, they claimed that the most probable explanation to their data is input of intervening Rn-222. The conclusion in this case must be that transport of Rn-222 is a more plausible explanation to the observed Pb-210/Ra-226 ratios than rapid transport of Ra-226. There are of course ways to test the hypothesis that the low ratios are caused by migration of Rn-222, but it does not appear as a very relevant task at this stage.

3.3.9 Conclusions Concerning the Transport of Radium

As far as the Th-230 measurements can be trusted, there is clear evidence that radium is being leached from the gyttja. Based on the Ra-228/Th-232 and Ra-226/Th-230 ratios it can be concluded that the annual losses must be between 0.02 and 1.4%. It is suggested that more reliable and accurate measurements of Th-230 are made and that the age of the gyttja is determined by C-14 dating in order to enhance the reliability and accuracy of the figures. This could be very useful information for validation of radionuclide models of peat lands.

The low Ra-226/Pb-210 ratios observed in the gyttja are, however, probably not caused by leakage of radium. Considering the groundwater flow in the gyttja and the amount of radium in the pore water, it seems difficult to explain how there could be such rapid transport of radium. Instead migration of Rn-222 seems to be the most likely explanation to the observed pattern. Diffusion of Rn-222 alone seems insufficient to explain the observed ratios, but according to the geogas hypothesis radon can be transported by bubbles of carbon dioxide and methane in the soil.

3.4 Uranium and Thorium

3.4.1 Interpretation of Isotopic Ratios Involving Uranium Isotopes

Unlike radium, the natural uranium isotopes and their relevant daughters are all comparatively long-lived in comparison with the age of the investigated samples. This makes the interpretation of the isotopic ratios more difficult in one way, but it may also be advantageous in the sense that it may allow some conclusions concerning the formation of the different layers.

Two of the three natural uranium isotopes, U-238 and U-235, are the first radionuclides in their respective decay chains. Hence, there are no parents, with which they can be compared. Among their daughters all radionuclides either have so short half-lives that they are uninteresting in this context or so long half-lives – 75,400 years for Th-230, 32,800 years for Pa-231 and 246,000 years for U-234 – that secular equilibrium cannot be expected in this kind of relatively young deposits even if there has been a closed system. Consequently, isotopic disequilibria can reflect either the composition of the original deposits or post-depositional processes. This of course makes their meaning more ambiguous.

As regards the U-234/Th-230 and U-235/Pa-231 ratios, the interpretation must be based on the geochemical behaviour of the involved elements. Both protactinium and thorium are considered to be less mobile than uranium and, therefore, isotopic disequilibria are generally attributed to mobilisation or accumulation of uranium. Uranium is considered to be fairly mobile in the oxidised hexavalent state, but under reducing conditions it will be reduced to the more immobile tetravalent state. The U-234/U-238 ratio may appear quite useless from this point of view, since it involves two isotopes of the same element. Geochemically, one might expect them to behave similarly, which then would make the U-238/U-235 equal to unity in all samples. Nevertheless, it is a well-established fact the U-234/U-238 ratios in environmental samples often do not equal unity. It is generally agreed that this is due to effects related to the alpha recoil in the decay of U-238, although there seems to be no consensus concerning the exact mechanisms. Somehow the alpha recoil facilitates the mobilisation of U-234 relative to U-238, which often results in an enrichment of U-234 relative to U-238 in groundwater. The implications and usefulness of this phenomenon have been thoroughly described by /Osmond et al. 1983/. The mobilisation process has also been studied in detail by /Suksi 2005/. Moreover, /Bonotto 1998/ has shown that the level of U-238 is enhanced in borehole samples, while the level of U-234 is enhanced in the groundwater. In this manner it is often possible to tell whether there has been a mobilisation or an accumulation of uranium.

U-234/U-238 ratios can also be used to assess groundwater mixing, since there are differences between older groundwater and younger groundwater. The older the groundwater is, the more pronounced isotopic disequilibrium could be expected. One example of this has been published in an article by /Ivanovich and Alexander 1987/. In the oceans /Koide and Goldberg 1963/ have found that the U-234/U-238 ratios are more or less constant – the average ratio in their experiments was 1.14 with no apparent variations outside experimental error. This was explained by the long residence time of uranium, which is estimated to be roughly 500,000 years, in comparison with the mixing time of the water, which hardly is more than a couple of thousands of years. However, they remark that variations may occur in isolated basins. In this case, it is not fully clear in what environment the sediments were deposited, but under all circumstances it should have been an isolated basin of some kind.

Unfortunately, U-234, Th-230 and Pa-231 are very hard to measure accurately with gamma spectrometry and the accuracy and reliability of the analyses are not very satisfying. For the peat, where such information would be very valuable, no activities at all could be determined for these radionuclides. Even in the clay it was not possible to determine even approximate U-234 activities due to the low emission probability of U-234 and the relatively high Pb-214 activities in these samples. In the gyttja, however, there were significant contributions from U-234 to the 53 keV peak, which allowed indirect determination of the U-234 activities in some samples. These measurements are shown in Figure 3-1. According to these analyses the mean U-234/U-238 ratio in the gyttja is 1.63 ± 0.17, which strongly indicates that this uranium once has been dissolved. This would also explain the low amounts of Th-230 in relation to U-238 and U-234 that can be seen in the gyttja samples in Figure 3-1. In the clay, on the other hand, there is an excess of Th-230 in relation to U-238, which shows that uranium has been preferentially mobilised. These interpretations agree with the U-235 and Pa-231 profiles in Figure 3-2, where the U-235/Pa-231 ratios are greater than unity in the gyttja and less than unity in the clay.

In literature, there are several papers that have reported similar results. /Plater et al. 1992/, for instance, have reported Th-230/U-238 ratios greater than unity in river sediments. Measurements published by /Scott 1968/ show the same pattern. In these cases, the sediments appear to be very young so there can have been no significant post-depositional migration. Furthermore, the ratios in sediments are reported to agree very well with the ratios found in the suspended particles in the studied river /Plater et al. 1992/. In the river water, however, the Th-230/U-238 ratios were much lower than unity (roughly 0.03–0.04). That would indicate that thorium in this case mainly is brought to these sediments in particulate form.

It does not seem unlikely that the Th-230/U-238 ratios in the clay underlying Klarebäcksmossen were caused by similar processes. The weighted mean of the Th-230/U-238 ratio in the clay layers is 2.19 ± 0.13, which indicates preferential mobilisation of uranium. If it is assumed that Ra-226 is in secular equilibrium with Th-230 in the clay, the weighted mean will be somewhat lower: 1.87 ± 0.03. This latter figure is probably more likely, since the quantification of Ra-226 activities is much more accurate and Th-230 probably is in secular equilibrium with Ra-226 in the clay. These ratios are somewhat higher than those reported by /Plater et al. 1992/, but probably only reflect the environment and the composition of the material.

The alternative explanation would be that there has been a post-depositional leakage of uranium from the clay. Although the available time for such leakage is rather long, it still seems like a rather far-fetched hypothesis in comparison with the one described above. The thickness of the clay is more than 0.5 meters and the hydraulic conductivity of clays is known to be very low. Although there is an enrichment of uranium above the clay (in the gyttja) of approximately the same size as the deficit in the clay, there are no signs in the U-238 profile in the clay that there would have been an upward transport of uranium. Instead it is C-shaped, indicating that there might have been a post-depositional intrusion of uranium into the clay rather than a loss. Finally, it is hard to imagine why the conditions for leaching would be better in the clay than when the particles were suspended in water. Therefore, the most probable explanation to the low Th-230/U-238 ratios observed in the gyttja is that the clay particles were depleted of uranium before they were deposited.

3.4.2 Accumulation of Uranium in the Gyttja

In the gyttja, the Th-230/U-238 ratios are greater than unity – opposite to what was observed in the gyttja. Compared to the clay, however, the gyttja has a much higher content of organic material, which should favour sorption of both uranium and thorium from the aqueous phase.

Since uranium often tends to be more common in the aqueous phase, that would increase the U/Th ratio. Another factor that would favour the accumulation of uranium is connected to changes in the redox potential, since the mobility of uranium decreases as U^{6+} is reduced to U^{4+}. /Bonatti et al. 1970/ have investigated uranium profiles in deep-sea sediments and found that the upper sediment layers often contain less uranium than the deeper layers. By measuring Eh they have concluded that there is a steady increase in the uranium content in the reduced part of the core. The fact that there is no sharp change in the uranium concentration is interpreted by /Bonotti et al. 1970/ as a sign of “slow, gradual reduction and fixation of U upon burial in the reduced zone”. /Halbach et al. 1980/ have studied the sorption of uranium in sediments from a more chemical perspective. They state that the main reasons for uranium fixation in sediments are “flocculation and sedimentation of uranyl-bearing humates” and “precipitation caused by reduction”. If hexavalent U is taken up by ion exchange, it can later be reduced and immobilised “due to degradation of humic substances under anaerobic conditions”. In the case of Klarebäcksmossen, it does not seem unlikely that there were reducing conditions rather shortly after the deposition, since there is a tendency of lamination at some depths. (See Figure 2-4.)

Obviously, it is impossible to know what circumstances that were prevailing when these sediments were deposited, but there are no special reasons to assume that it is dramatically different from today as regards activities of uranium and thorium in the surface waters. In lack of better data, recent measurements could serve as a reference. Measurements of uranium and thorium isotopes have been attempted in the Simpevarp area, but unfortunately the measuring technique that was used did not allow quantification of a single uranium or thorium isotope /Tröjbom and Söderbäck 2006a, b/. More successful measurements of uranium and thorium have, however, been made in the Forsmark area /Sonesten 2005/. The highest activities that were encountered in these analyses were 28.2 ppb or roughly 350 mBq/kg for U-238 and 0.315 ppb or roughly 1.3 mBq/kg for Th-232. In many samples the Th-232 levels were below detection limit, while the lowest level of U-238 was 0.267 ppb or roughly 3.3 mBq/kg. As no adequate measurements are available from the Simpevarp area, these figures, representing lake water, seawater and streaming water, will be used as an estimate. Based only on the samples were Th-232 was above detection limit, the U/Th mass ratio ranges from 7.6–240 with an arithmetic mean of 68. This corresponds to an activity ratio of almost 210 (23–730) between U-238 and Th-232.

Since the aqueous phase has high U/Th ratios, incorporation of dissolved uranium and thorium in the sediments would lead to high U/Th ratios there too – unless sorption of thorium is strongly favoured. However, given the redox chemistry of uranium, it seems much more likely that sorption of uranium would be favoured instead. This would lead to even higher U/Th ratios.

The enrichment of uranium in the gyttja in Klarebäcksmossen is consistent with uranium data from peat cores published by /Shotyk et al. 1992/. Their data is based on measurements in 35 peat lands throughout eastern Canada and summarized as a constructed composite *Sphagnum* bog profile with underlying *Carex* peat, ooze (limnic sediments such as gyttja or dy) and clay. What is especially interesting in this context is that the highest uranium levels were found in the ooze layers immediately overlying the mineral sediments. This would then indicate that the high uranium levels in ooze might be related to the underlying material. Consequently, Shotyk et al. have stated that the mineral sediments (clays) represent the "main source of inorganic materials during the initial stages of the formation of the peat profile". Similarly, the highest uranium activities in Klarebäcksmossen are found in the deepest gyttja layers, although the organic content of these samples appears to be lower than further up. A crucial difference between the Canadian peat lands and Klarebäcksmossen could, however, be the presence of the gravel layer. While it seems likely that the gyttja could have provided the peat with various elements, the situation is more unclear for the relation between the gyttja and the clay. One uncertainty here is the direction of the groundwater flow during different periods in the history of Klarebäcksmossen.

3.4.3 Stocksjön

Stocksjön is a lake in the Forsmark area, which is interesting in this context because it represents an earlier stage in the natural development of a peat land. It is a small and shallow lake that to a large extent has been covered by peat. Therefore, it is not unlikely that the gyttja layers in Klarebäcksmossen once were formed under fairly similar conditions. As data is available from a core in Stocksjön (PSM004509) this can give some indications concerning the behaviour of various during the transition from lake to wetland.

Figure 3-11 shows the uranium and thorium profiles in Stocksjön. The upper 10–15 cm of the sediments consists of an organic slush of mainly cyanobacteria. Red sulphur-reducing bacteria occur at approximately 10 cm indicating the absence of oxygen /Brunberg 2005/. Hence, there are good reasons to expect reduction of uranium to the tetravalent state.

Apparently, no high concentrations of uranium are found in the upper 10 cm of the profile, while there is a gradual increase with depth in the true sediments below the organic slush. Around 20 cm the concentrations are comparable with the gyttja from Klarebäcksmossen. Despite the increasing concentrations of uranium, the concentrations of thorium remain fairly constant down to 30 cm, where there is a significant increase. This supports the assumption that there is no extensive post-depositional accumulation of thorium in the sediments. Evidently, the U/Th ratios, shown by the green line, are high in some parts of the core. Compared to the sediments from Klarebäcksmossen, where the U/Th ratio never exceeds 2.8, the accumulation of uranium seems to be much more substantial here, although this partly may be explained by different background concentrations rather than differences in accumulation mechanisms.

No analyses are available of the surface water in Stocksjön, but several measurements have been made at the outlet of Eckarfjärden (PFM000070) a few hundred meters upstream from Stocksjön /Sonesten 2005/. Uranium and thorium have not been reported for all samples, but it is clear that the water carried more uranium than thorium, although the U/Th mass ratios seem to vary appreciably with time. On January 14th 2004 the ratio was 28.1, while it was 51.6 on April 20th 2004 for instance. In the other samples thorium has been below detection limit, but based on the uranium concentrations and the detection limit, the U/Th ratio has not on any sampling occasion been below 13.3. The lowest U/Th that actually has been measured is 28.1. The stream between Eckarfjärden and Stocksjön is approximately 300 m long, and it is hard to imagine how any significant changes in the U/Th ratio could arise during that time. Hence, one should expect very high U/Th ratios in Stocksjön too, as this stream is the major inflow to Stocksjön.

Judging from Figure 3-11 the U/Th ratio is low in the upper 10 cm. This suggests that there is no appreciable accumulation of uranium there. Below that the U/Th ratio increases rapidly, which suggest that there has been a preferential accumulation of uranium from the water. It seems likely that something similar is the explanation to the high uranium activities in the sediments from Klarebäcksmossen.

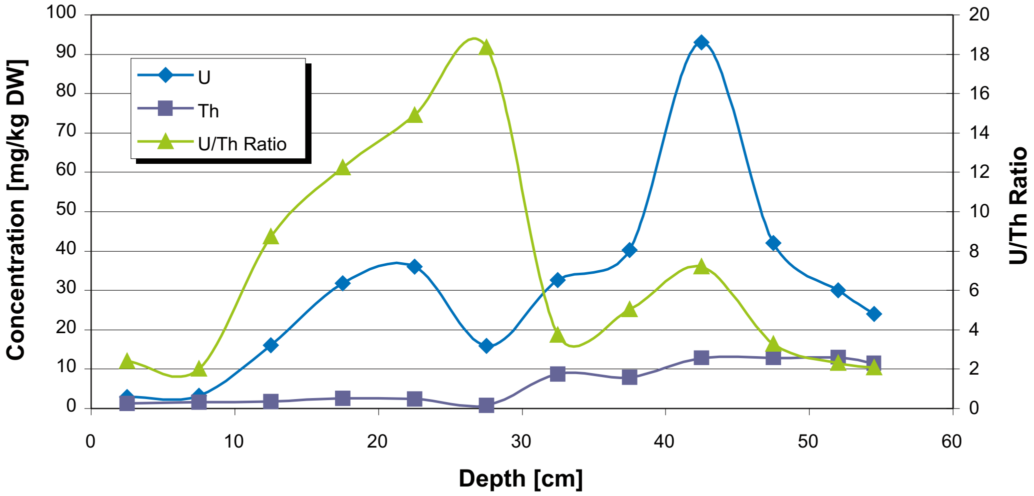


Figure 3-11. *Uranium and thorium concentrations in the sediments of Stocksjön. The U/Th ratio is shown on the secondary y-axis.*

3.4.4 Thorium and Protactinium

A comparison of the ratio between the thorium isotopes Th-232 and Th-230 shows that the Th-230/Th-232 ratio differs between the gyttja and the clay. The weighted average for the gyttja samples including a gyttja/gravel sample (GR1) is 2.8 ± 0.4, while the weighted average for the clay samples is 1.4 ± 0.1. This anomaly can partly be explained by decay of Th-230 in the clay and production of Th-230 in the gyttja due to excess of U-234, but it seems impossible that these ratios could have been produced during the comparatively short period of time after the deposition. /Plater et al. 1992/ have reported high Th-230/Th-232 ratios (approximately 4–12) from the ion-exchangeable and organic phases of river sediments, while Th-230/Th-232 ratios of 1 ± 0.5 have been reported in detrital matter. Accordingly, /Plater et al. 1992/ have concluded that there has been a sorption of radionuclides in the ion-exchangeable and organic fractions in their sediments. Indeed, it does not seem improbable that Th-230 is enriched relative to Th-232 in natural waters, since the former can benefit from alpha recoil effects.

Although no speciation experiments have been performed for the samples from Klarebäcksmossen, it does not seem unlikely that a similar pattern might be found here. The ratios in the gyttja from Klarebäcksmossen are lower than those reported by /Plater et al. 1992/, but they are not directly comparable, as the ratios for Klarebäcksmossen refer to the total samples and not just fractions of them. Consequently, there are signs that thorium too has been sorbed from solution in the gyttja layers.

The weighted mean for the Pa-231/U-235 ratio in the gyttja is 0.38 ± 0.03, indicating an enrichment of uranium relative to protactinium as well. In the clay, on the other hand, the ratio is 1.17 ± 0.07, which indicates that uranium might have been leached from the clay to some extent, possibly prior to the deposition. In that sense, protactinium appears to behave similar to thorium. The ratio is, however, much lower than the Th-230/U-238 ratio in the clay, which is close to 2. The actual value depends on whether Ra-226 is assumed to be in secular equilibrium with Th-230 or not. However, if thorium and protactinium had behaved similarly, the initial Pa-231/U-235 and Th-230/U-238 should be equal. Because Pa-231 has a shorter half-life than Th-230, the former ratio would decrease faster, but it would require a long time to reach differences that are observed in the clay. Accordingly, it appears as if protactinium – at least under certain circumstances – is more mobile than thorium. The most reasonable explanation is probably that protactinium was mobilised to a higher degree than thorium, while the clay particles were suspended in water.

Generally, distribution coefficients for protactinium tend to be similar to those of thorium or in some cases even higher /Karlsson and Bergström 2002, IAEA 1985/, but this does not necessarily imply that there is a disagreement, since the published K_d values represent a much wider range of environments. One important difference between the two elements is that protactinium preferentially occurs as pentavalent ions, whereas thorium occurs in the tetravalent state. Generally, pentavalent actinide ions are considered to be more mobile than tetravalent ones. Moreover, experiments by /Geibert and Usbeck 2004/ indicate that thorium in most cases is more particle reactive than protactinium, which agrees with the observations from Klarebäcksmossen. However, final conclusions concerning the relative mobilisation of protactinium from the clay particles would require validation of the method used to determine the Pa-231 activity. If alpha spectrometry is used to measure other isotopes such as Th-230, this would hopefully also give information on the Th-227 activities, which then could be used for such validation.

3.5 ICP-AES Data

3.5.1 Concentrations in Relation to Dry Weight, Ash and Volume

The results from the ICP-AES measurements and additional chemical analyses are shown in Figure 3-12. The results are also shown in a table in Appendix B.

The general picture agrees well with what was observed in the radiometric measurements. The concentrations for most elements are considerably higher in the gyttja and clay layers than in the peat just like for the analysed radionuclides. However, there are a few important exceptions.

Not unexpectedly, carbon is more abundant in peat, while other biologically important elements such as nitrogen and phosphorus have fairly similar concentrations in peat and gyttja. Among the metals, calcium is the only element, for which there is a significant increase in the peat in relation to the dry weight. However, fairly high concentrations are also found for some of the other alkaline earth elements as well as yttrium, lanthanum and most lanthanides.

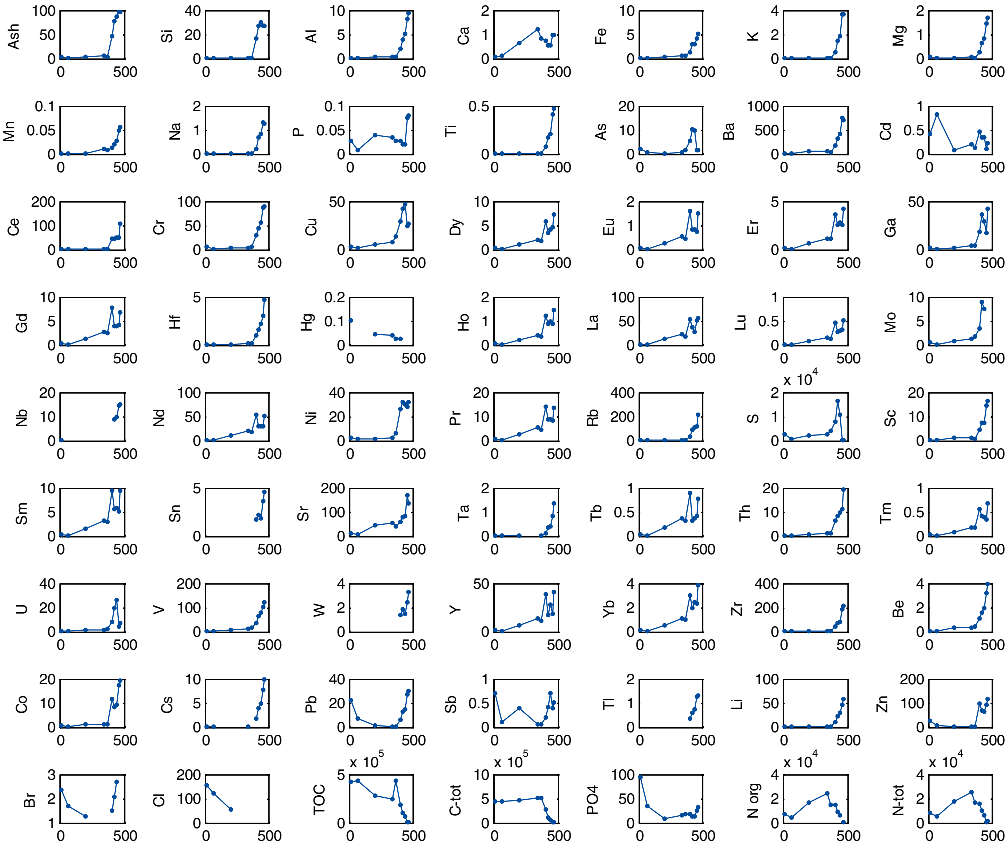


***Figure 3-12.** Results from ICP-AES and other chemical analyses. The vertical axes represent depth (in cm) and the horizontal axes represent concentration. Ash content and the elements Si-Ti are given in percent dry weight. The rest is given in ppm dry weight.*

The concentrations are generally higher in the minerotrophic peat, although there are several exceptions. Elements such as cadmium, antimony and lead are strongly enriched near the surface.

One way to try to explain the distribution of various elements is to compare their abundance to the ash content, since the ash content should correspond to the mineral content of the samples. Elements that mainly occur in minerals should generally follow the ash content closely. Figure 3-13 shows normalised concentrations in ash.

Some of the elements shown in Figure 3-13, e.g. tungsten, thallium and tin, could not be detected in the peat samples and will therefore not be commented further in this report.

Another way to present the data is to relate to the concentrations to volume. It is not relevant to compare the peat with the gyttja and the clay in this manner, as the density of the latter is much higher. Therefore, Figure 3-14 only contains the peat samples.

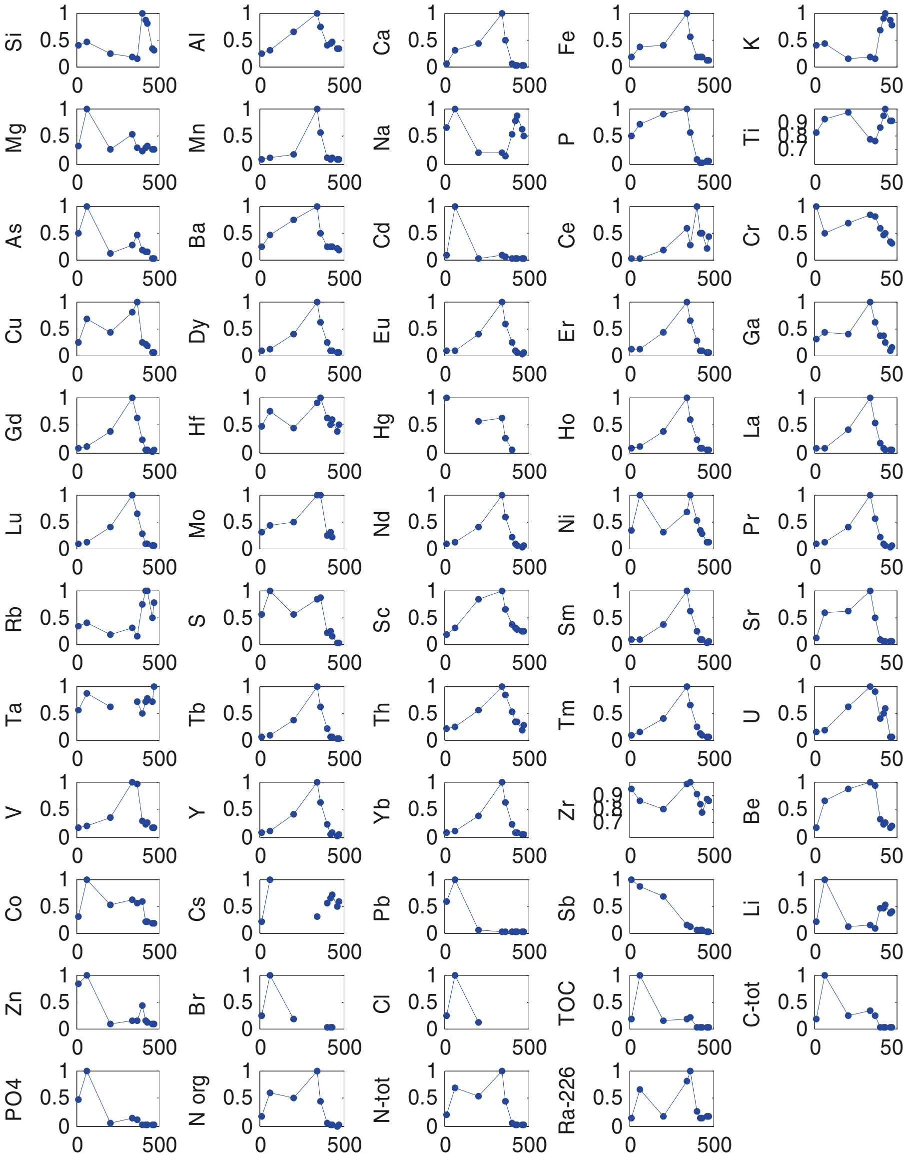


__Figure 3-13.__ Normalised concentration in ash. The concentrations have normalized so that the maximum concentration equals unity. Ra-226 has been included for comparison.

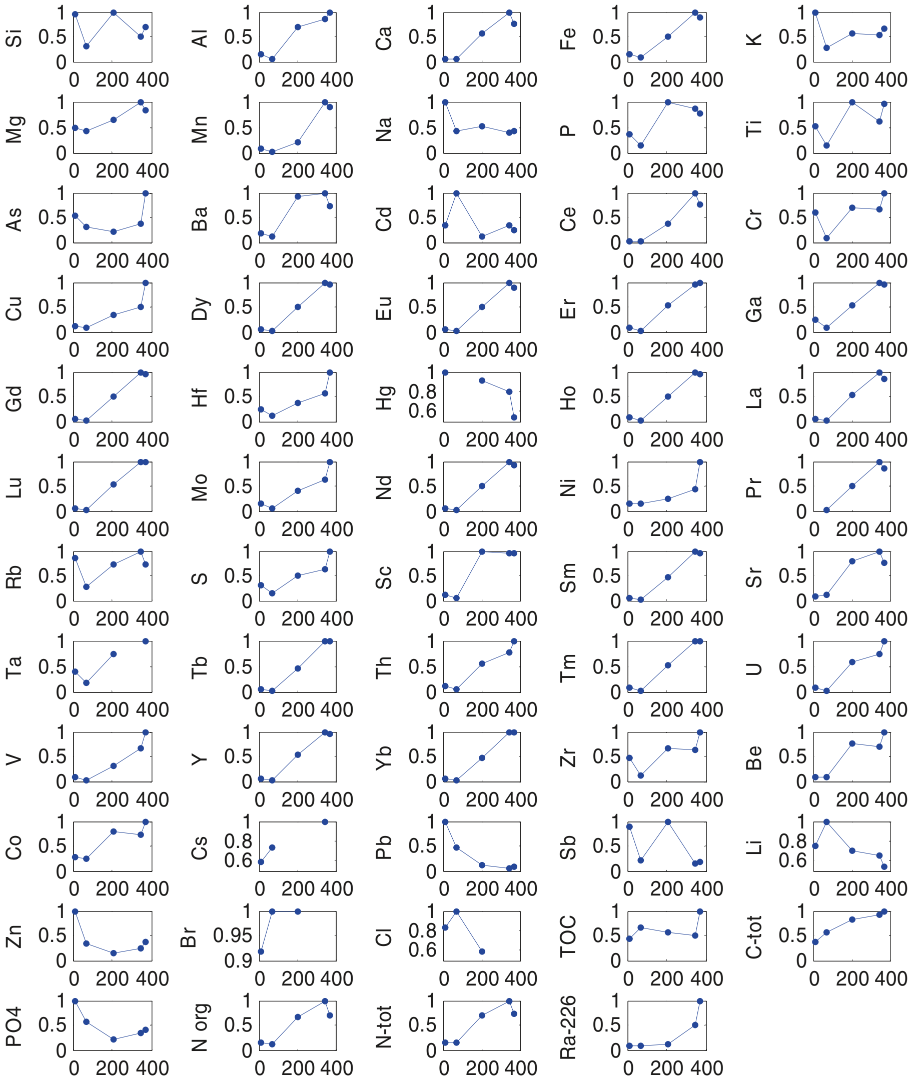


__Figure 3-14.__ Normalized concentration per volume unit in the peat samples.

As the differences in density for the deeper peat samples are accounted for, it becomes clear that there is concentration gradient from the deeper peat and upwards for many elements. This may be of importance for diffusion, but that will ultimately depend on the concentration in the pore water. Since so little is known about the hydrology of the mire, it is hard to know how important diffusive transport is.

TOC is fairly constant with depth, while C-tot increases with depth. This could indicate compaction and decomposition of the peat, but intrusion of inorganic carbon with groundwater is also possible. With exception of the surface sample, sodium and potassium have quite constant concentrations in the peat with respect to volume. Scandium has a constant concentration in the minerotrophic peat.

3.5.2 Correlation Analysis

One way to get a sense of what elements that related to one another is to perform a correlation analysis. Figure 3-13 indicates that all lanthanides except cerium are well correlated to one another. Yttrium and lanthanum also have very similar profiles. This observation is confirmed by the correlation analysis, which is shown in Table 3-1. The correlation analyses are based on the concentrations in relation to ash content.

Table 3-1. Correlation coefficients for yttrium, lanthanum and all analysed lanthanides except cerium.

	Dy	**Eu**	**Er**	**Gd**	**Ho**	**La**	**Lu**	**Nd**	**Pr**	**Sm**	**Tb**	**Tm**	**Y**	**Yb**
Dy	1.0000													
Eu	0.9976	1.0000												
Er	0.9976	0.9954	1.0000											
Gd	0.9993	0.9984	0.9983	1.0000										
Ho	0.9995	0.9982	0.9982	0.9996	1.0000									
La	0.9933	0.9952	0.9898	0.9935	0.9938	1.0000								
Lu	0.9986	0.9963	0.9990	0.9989	0.9983	0.9905	1.0000							
Nd	0.9989	0.9992	0.9965	0.9993	0.9992	0.9965	0.9974	1.0000						
Pr	0.9968	0.9986	0.9930	0.9971	0.9977	0.9976	0.9935	0.9990	1.0000					
Sm	0.9992	0.9980	0.9973	0.9994	0.9994	0.9923	0.9986	0.9988	0.9967	1.0000				
Tb	0.9997	0.9964	0.9972	0.9992	0.9992	0.9921	0.9982	0.9984	0.9961	0.9990	1.0000			
Tm	0.9981	0.9945	0.9990	0.9981	0.9983	0.9879	0.9985	0.9962	0.9927	0.9975	0.9983	1.0000		
Y	0.9990	0.9981	0.9983	0.9991	0.9993	0.9923	0.9982	0.9987	0.9966	0.9984	0.9983	0.9980	1.0000	
Yb	0.9985	0.9933	0.9961	0.9971	0.9975	0.9883	0.9979	0.9959	0.9925	0.9981	0.9987	0.9976	0.9966	1.0000

The lowest correlation coefficient in Table 3-1, 0.9879, is found between lanthanum and thulium. In other words, the degree of correlation between these elements is exceptionally good. Consequently, as regards the analyses in Klarebäcksmossen, yttrium, lanthanum and all lanthanides except cerium can be considered as more or less interchangeable. Hence, in order to save space yttrium, lanthanum and all lanthanides except for cerium are represented by europium in Table 3-2, were the correlation coefficients for the remaining elements and parameters are shown. Radium has also been included from the radiometric analyses.

Cells shaded in green in Table 3-2 are those pairs with the highest positive correlation ($0.9 < r < 1$), while cells shaded in yellow have $0.75 < r < 0.9$. Those cells indicating strong negative correlation ($r < -0.75$) are shaded in red.

The correlation coefficients say something about the distribution of various elements in the profile with respect to other elements. However, it does not imply that two strongly correlated elements necessarily are governed by the same processes. For instance, lead and phosphate are well correlated, but to a large extent this probably depends on the high concentrations in the ombrotrophic peat. However, phosphate is probably enriched due to biological uptake, while lead is enriched due to anthropogenic emissions to the atmosphere.

Table 3-2 does not show any strong clusters of elements like the lanthanides, which could contribute to a more generalized picture of the elemental behaviour of elements in peat lands. There are some, however, some trends that are worth noticing.

The alkali metals are fairly well correlated to one another, particularly potassium-rubidium and lithium-ceasium. The alkali metals are also fairly well correlated to titanium.

Strong correlation can also be found among the alkaline earth metals, particularly between calcium and strontium, but the correlation with beryllium and barium is also fairly good. Calcium shows good agreement with europium, iron and nitrogen. Radium shows better correlation with elements like copper, nickel and vanadium, but the distribution of radium is likely to be influenced by radioactive decay and production of Ra-226. Hence, it does not imply that radium behaves very different from other alkaline earth elements. The distribution of magnesium is, however, different from that of the other alkaline earth metals, and this can clearly not be attributed to radioactivity decay.

Table 3-2. Correlation coefficients.

	Al	As	Ba	Be	Ca	Cd	Ce	Co	Cr	Cs	C-tot	Cu	Eu	Fe	Ga	Hf	K	Li	Mg	Mn	Mo	N org	Na	Ni	N-tot	P	Pb	PO4	Ra	Rb	S	Sb	Sc	Si	Sr	Te	Th	Ti	TOC	U	V	Zn	Zr
Al	1,000	-0,473	0,533	0,550	0,391	-0,488	0,175	-0,202	0,069	0,348	-0,342	0,171	0,493	0,458	0,159	0,503	0,143	-0,259	-0,252	0,571	0,803	0,204	-0,261	-0,136	0,057	0,084	-0,537	-0,512	0,330	0,070	-0,153	-0,322	0,808	-0,535	0,257	0,524	0,792	0,359	-0,400	0,332	0,671	-0,562	0,391
As	-0,473	1,000	0,082	0,193	0,170	0,793	-0,726	0,743	0,458	-0,079	0,851	0,571	-0,042	0,243	0,477	0,195	-0,403	0,183	0,584	-0,040	0,206	0,468	0,181	0,778	0,576	0,610	0,930	0,958	0,411	-0,416	0,862	0,761	-0,328	-0,183	0,360	-0,241	-0,269	-0,183	0,873	-0,145	-0,041	0,870	-0,040
Ba	0,533	0,082	1,000	0,846	0,830	0,122	-0,506	0,416	0,124	-0,114	0,373	0,498	0,679	0,778	0,539	-0,004	-0,500	-0,367	0,084	0,503	0,573	0,849	-0,479	0,180	0,786	0,782	0,028	0,102	0,290	-0,579	0,465	0,263	0,853	-0,864	0,893	0,023	0,491	-0,128	0,255	0,353	0,432	-0,113	-0,111
Be	0,550	0,193	0,846	1,000	0,854	0,208	-0,437	0,563	0,012	0,133	0,448	0,797	0,745	0,817	0,613	0,231	-0,597	-0,357	0,068	0,584	0,786	0,786	-0,603	0,544	0,778	0,688	-0,018	0,087	0,646	-0,630	0,588	0,104	0,810	-0,892	0,883	-0,099	0,679	-0,249	0,359	0,551	0,676	-0,167	-0,194
Ca	0,391	0,170	0,830	0,854	1,000	0,156	-0,465	0,414	-0,057	-0,432	0,407	0,768	0,914	0,961	0,793	-0,027	-0,776	-0,560	-0,057	0,799	0,756	0,897	-0,770	0,470	0,871	0,691	-0,046	0,071	0,591	-0,784	0,596	0,054	0,708	-0,971	0,939	-0,311	0,629	-0,560	0,292	0,638	0,699	-0,175	-0,459
Cd	-0,488	0,793	0,122	0,208	0,156	1,000	-0,529	0,851	-0,080	0,265	0,948	0,387	-0,193	0,144	0,170	0,083	-0,231	0,541	0,872	-0,182	-0,052	0,462	0,256	0,656	0,554	0,387	0,778	0,835	0,359	-0,250	0,593	0,432	-0,302	-0,144	0,393	-0,089	-0,431	-0,139	0,974	-0,329	-0,265	0,598	-0,149
Ce	0,175	-0,726	-0,506	-0,437	-0,465	-0,529	1,000	-0,536	-0,413	0,277	-0,701	-0,593	-0,224	-0,464	-0,497	0,153	0,546	0,193	-0,391	-0,139	-0,443	-0,743	0,076	-0,526	-0,729	-0,800	-0,650	-0,692	-0,267	0,692	-0,826	-0,709	-0,094	0,474	-0,633	0,399	0,151	0,284	-0,659	-0,176	-0,115	-0,529	0,205
Co	-0,202	0,743	0,416	0,563	0,414	0,851	-0,536	1,000	0,078	0,215	0,920	0,619	0,151	0,379	0,367	0,193	-0,444	0,256	0,691	0,022	0,259	0,663	-0,052	0,766	0,729	0,634	0,664	0,739	0,522	-0,490	0,733	0,486	0,098	-0,425	0,634	-0,147	-0,036	-0,166	0,908	-0,139	0,030	0,523	-0,106
Cr	0,069	0,458	0,124	0,012	-0,057	-0,080	-0,413	0,078	1,000	-0,224	0,071	0,148	0,022	0,094	0,343	0,330	-0,044	-0,203	0,118	0,017	0,300	0,123	0,227	0,127	0,120	0,515	0,522	0,457	-0,008	-0,110	0,448	0,783	0,005	-0,053	0,014	0,104	0,073	0,318	0,069	-0,128	0,096	0,665	0,518
Cs	0,348	-0,079	-0,114	0,133	-0,432	0,265	0,277	0,215	-0,224	1,000	0,112	-0,291	-0,659	-0,368	-0,592	0,698	0,752	0,947	0,540	-0,455	-0,432	-0,291	0,730	0,004	-0,296	-0,363	0,010	0,001	0,230	0,710	-0,313	-0,206	0,023	0,267	-0,265	0,792	-0,141	0,732	0,178	-0,665	-0,393	-0,109	0,574
C-tot	-0,342	0,851	0,373	0,448	0,407	0,948	-0,701	0,920	0,071	0,112	1,000	0,599	0,072	0,395	0,421	0,088	-0,458	0,291	0,765	0,018	0,190	0,694	0,042	0,751	0,773	0,649	0,785	0,858	0,465	-0,483	0,793	0,557	-0,066	-0,399	0,633	-0,177	-0,217	-0,244	0,991	-0,122	-0,052	0,604	-0,205
Cu	0,171	0,571	0,498	0,797	0,768	0,387	-0,593	0,619	0,148	-0,291	0,599	1,000	0,688	0,795	0,794	0,261	-0,755	-0,389	0,141	0,627	0,903	0,753	-0,562	0,888	0,787	0,659	0,263	0,371	0,842	-0,761	0,849	0,235	0,368	-0,775	0,760	-0,371	0,522	-0,514	0,549	0,594	0,721	0,162	-0,343
Eu	0,493	-0,042	0,679	0,745	0,914	-0,193	-0,224	0,151	0,022	-0,659	0,072	0,688	1,000	0,893	0,784	0,005	-0,740	-0,777	-0,390	0,882	0,787	0,677	-0,893	0,341	0,651	0,531	-0,284	-0,188	0,537	-0,718	0,434	-0,088	0,733	-0,882	0,748	-0,343	0,817	-0,566	-0,041	0,757	0,835	-0,310	-0,413
Fe	0,458	0,243	0,778	0,817	0,961	0,144	-0,464	0,379	0,094	-0,368	0,395	0,795	0,893	1,000	0,860	0,191	-0,676	-0,505	0,024	0,884	0,852	0,860	-0,654	0,524	0,836	0,682	0,028	0,135	0,698	-0,688	0,633	0,100	0,655	-0,980	0,876	-0,102	0,679	-0,431	0,293	0,579	0,786	-0,082	-0,275
Ga	0,159	0,477	0,539	0,613	0,793	0,170	-0,497	0,367	0,343	-0,592	0,421	0,794	0,784	0,860	1,000	0,150	-0,789	-0,572	0,001	0,726	0,867	0,798	-0,607	0,604	0,781	0,736	0,261	0,339	0,578	-0,676	0,788	0,364	0,384	-0,771	0,728	-0,282	0,557	-0,529	0,339	0,561	0,655	0,234	-0,317
Hf	0,503	0,195	-0,004	0,231	-0,027	0,083	0,153	0,193	0,330	0,698	0,088	0,261	0,005	0,191	0,150	1,000	0,346	0,341	0,380	0,259	0,741	-0,039	0,300	0,362	-0,035	-0,004	0,143	0,145	0,595	0,343	0,128	0,015	0,103	-0,164	-0,054	0,703	0,421	0,559	0,130	-0,163	0,417	0,153	0,692
K	0,143	-0,403	-0,500	-0,597	-0,776	-0,231	0,546	-0,444	-0,044	0,752	-0,458	-0,755	-0,740	-0,676	-0,789	0,346	1,000	0,674	0,174	-0,471	-0,732	-0,797	0,802	-0,563	-0,790	-0,694	-0,164	-0,257	-0,364	0,915	-0,736	-0,287	-0,333	0,646	-0,764	0,785	-0,343	0,853	-0,370	-0,676	-0,434	-0,113	0,743
Li	-0,259	0,183	-0,367	-0,357	-0,560	0,541	0,193	0,256	-0,203	0,947	0,291	-0,389	-0,777	-0,505	-0,572	0,341	0,674	1,000	0,754	-0,573	-0,517	-0,298	0,827	-0,018	-0,291	-0,364	0,372	0,341	-0,072	0,644	-0,249	-0,002	-0,501	0,480	-0,378	0,608	-0,586	0,593	0,386	-0,805	-0,598	0,281	0,465
Mg	-0,252	0,584	0,084	0,068	-0,057	0,872	-0,391	0,691	0,118	0,540	0,765	0,141	-0,390	0,024	0,001	0,380	0,174	0,754	1,000	-0,241	-0,032	0,311	0,600	0,434	0,337	0,275	0,786	0,801	0,272	0,108	0,393	0,460	-0,301	-0,028	0,185	0,371	-0,441	0,327	0,830	-0,612	-0,329	0,636	0,320
Mn	0,571	-0,040	0,503	0,584	0,799	-0,182	-0,139	0,022	0,017	-0,455	0,018	0,627	0,882	0,884	0,726	0,259	-0,471	-0,573	-0,241	1,000	0,815	0,556	-0,654	0,355	0,506	0,320	-0,272	-0,182	0,691	-0,490	0,330	-0,226	0,554	-0,830	0,573	0,013	0,781	-0,388	-0,065	0,611	0,905	-0,303	-0,195
Mo	0,803	0,206	0,573	0,786	0,756	-0,052	-0,443	0,259	0,300	-0,432	0,190	0,903	0,787	0,852	0,867	0,741	-0,732	-0,517	-0,032	0,815	1,000	0,632	-0,543	0,610	0,600	0,548	-0,055	0,022	0,811	-0,758	0,654	0,043	0,632	-0,833	0,643	0,269	0,834	-0,164	0,127	0,644	0,925	-0,102	0,222
N org	0,204	0,468	0,849	0,786	0,897	0,462	-0,743	0,663	0,123	-0,291	0,694	0,753	0,677	0,860	0,798	-0,039	-0,797	-0,298	0,311	0,556	0,632	1,000	-0,474	0,557	0,995	0,872	0,337	0,438	0,525	-0,814	0,793	0,380	0,533	-0,885	0,974	-0,258	0,285	-0,421	0,593	0,303	0,425	0,177	-0,302
Na	-0,261	0,181	-0,479	-0,603	-0,770	0,256	0,076	-0,052	0,227	0,730	0,042	-0,562	-0,893	-0,654	-0,607	0,300	0,802	0,827	0,600	-0,654	-0,543	-0,474	1,000	-0,237	-0,491	-0,339	0,440	0,347	-0,322	0,709	-0,280	0,240	-0,609	0,653	-0,605	0,625	-0,683	0,763	0,145	-0,848	-0,653	0,452	0,691
Ni	-0,136	0,778	0,180	0,544	0,470	0,656	-0,526	0,766	0,127	0,004	0,751	0,888	0,341	0,524	0,604	0,362	-0,563	-0,018	0,434	0,355	0,610	0,557	-0,237	1,000	0,643	0,491	0,518	0,609	0,840	-0,568	0,831	0,298	-0,019	-0,484	0,528	-0,304	0,210	-0,396	0,756	0,247	0,449	0,425	-0,224
N-tot	0,057	0,576	0,786	0,778	0,871	0,554	-0,729	0,729	0,120	-0,296	0,773	0,787	0,651	0,836	0,781	-0,035	-0,790	-0,291	0,337	0,506	0,600	0,995	-0,491	0,643	1,000	0,883	0,427	0,530	0,533	-0,804	0,842	0,448	0,453	-0,843	0,964	-0,315	0,282	-0,492	0,683	0,353	0,392	0,270	-0,396
P	0,084	0,610	0,782	0,688	0,691	0,387	-0,800	0,634	0,515	-0,363	0,649	0,659	0,531	0,682	0,736	-0,004	-0,694	-0,364	0,275	0,320	0,548	0,872	-0,339	0,491	0,883	1,000	0,540	0,592	0,303	-0,729	0,858	0,746	0,466	-0,701	0,836	-0,249	0,242	-0,257	0,563	0,257	0,283	0,463	-0,139
Pb	-0,537	0,930	0,028	-0,018	-0,046	0,778	-0,650	0,664	0,522	0,010	0,785	0,263	-0,284	0,028	0,261	0,143	-0,164	0,372	0,786	-0,272	-0,055	0,337	0,440	0,518	0,427	0,540	1,000	0,990	0,132	-0,198	0,685	0,851	-0,422	0,016	0,200	-0,057	-0,488	0,058	0,817	-0,441	-0,333	0,958	0,152
PO4	-0,512	0,958	0,102	0,087	0,071	0,835	-0,692	0,739	0,457	0,001	0,858	0,371	-0,188	0,135	0,339	0,145	-0,257	0,341	0,801	-0,182	0,022	0,438	0,347	0,609	0,530	0,592	0,990	1,000	0,235	-0,288	0,753	0,818	-0,362	-0,093	0,310	-0,097	-0,425	-0,030	0,882	-0,365	-0,251	0,921	0,069
Ra	0,330	0,411	0,290	0,646	0,591	0,359	-0,267	0,522	-0,008	0,230	0,465	0,842	0,537	0,698	0,578	0,595	-0,364	-0,072	0,272	0,691	0,811	0,525	-0,322	0,840	0,533	0,303	0,132	0,235	1,000	-0,415	0,569	-0,081	0,256	-0,668	0,516	0,027	0,549	-0,233	0,453	0,341	0,761	0,034	-0,047
Rb	0,070	-0,416	-0,579	-0,630	-0,784	-0,250	0,692	-0,490	-0,110	0,710	-0,483	-0,761	-0,718	-0,688	-0,676	0,343	0,915	0,644	0,108	-0,490	-0,758	-0,814	0,709	-0,568	-0,804	-0,729	-0,198	-0,288	-0,415	1,000	-0,741	-0,317	-0,371	0,700	-0,792	0,766	-0,278	0,749	-0,397	-0,570	-0,454	-0,135	0,617
S	-0,153	0,862	0,465	0,588	0,596	0,593	-0,826	0,733	0,448	-0,313	0,793	0,849	0,434	0,633	0,788	0,128	-0,736	-0,249	0,393	0,330	0,654	0,793	-0,280	0,831	0,842	0,858	0,685	0,753	0,569	-0,741	1,000	0,689	0,130	-0,595	0,715	-0,385	0,152	-0,414	0,753	0,285	0,349	0,606	-0,239
Sb	-0,322	0,761	0,263	0,104	0,054	0,432	-0,709	0,486	0,783	-0,206	0,557	0,235	-0,088	0,100	0,364	0,015	-0,287	-0,002	0,460	-0,226	0,043	0,380	0,240	0,298	0,448	0,746	0,851	0,818	-0,081	-0,317	0,689	1,000	-0,105	-0,083	0,287	-0,140	-0,277	0,081	0,547	-0,229	-0,233	0,870	0,183
Sc	0,808	-0,328	0,853	0,810	0,708	-0,302	-0,094	0,098	0,005	0,023	-0,066	0,368	0,733	0,655	0,384	0,103	-0,333	-0,501	-0,301	0,554	0,632	0,533	-0,609	-0,019	0,453	0,466	-0,422	-0,362	0,256	-0,371	0,130	-0,105	1,000	-0,756	0,657	0,115	0,776	-0,026	-0,176	0,508	0,605	-0,492	-0,020
Si	-0,535	-0,183	-0,864	-0,892	-0,971	-0,144	0,474	-0,425	-0,053	0,267	-0,399	-0,775	-0,882	-0,980	-0,771	-0,164	0,646	0,480	-0,028	-0,830	-0,833	-0,885	0,653	-0,484	-0,843	-0,701	0,016	-0,093	-0,668	0,700	-0,595	-0,083	-0,756	1,000	-0,917	0,084	-0,682	0,370	-0,291	-0,556	-0,759	0,145	0,246
Sr	0,257	0,360	0,893	0,883	0,939	0,393	-0,633	0,634	0,014	-0,265	0,633	0,760	0,748	0,876	0,728	-0,054	-0,764	-0,378	0,185	0,573	0,643	0,974	-0,605	0,528	0,964	0,836	0,200	0,310	0,516	-0,792	0,715	0,287	0,657	-0,917	1,000	-0,275	0,432	-0,463	0,526	0,463	0,488	0,032	-0,402
Te	0,524	-0,241	0,023	-0,099	-0,311	-0,089	0,399	-0,147	0,104	0,792	-0,177	-0,371	-0,343	-0,102	-0,282	0,703	0,785	0,608	0,371	0,013	0,269	-0,258	0,625	-0,304	-0,315	-0,249	-0,057	-0,097	0,027	0,766	-0,385	-0,140	0,115	0,084	-0,275	1,000	0,119	0,930	-0,149	-0,532	-0,041	-0,070	0,866
Th	0,792	-0,269	0,491	0,679	0,629	-0,431	0,151	-0,036	0,073	-0,141	-0,217	0,522	0,817	0,679	0,557	0,421	-0,343	-0,586	-0,441	0,781	0,834	0,285	-0,683	0,210	0,282	0,242	-0,488	-0,425	0,549	-0,278	0,152	-0,277	0,776	-0,682	0,432	0,119	1,000	-0,135	-0,292	0,660	0,895	-0,464	-0,002
Ti	0,359	-0,183	-0,128	-0,249	-0,560	-0,139	0,284	-0,166	0,318	0,732	-0,244	-0,514	-0,566	-0,431	-0,529	0,559	0,853	0,593	0,327	-0,388	-0,164	-0,421	0,763	-0,396	-0,492	-0,257	0,058	-0,030	-0,233	0,749	-0,414	0,081	-0,026	0,370	-0,463	0,930	-0,135	1,000	-0,185	-0,652	-0,290	0,098	0,944
TOC	-0,400	0,873	0,255	0,359	0,292	0,974	-0,659	0,908	0,069	0,178	0,991	0,549	-0,041	0,293	0,339	0,130	-0,370	0,386	0,830	-0,065	0,127	0,593	0,145	0,756	0,683	0,563	0,817	0,882	0,453	-0,397	0,753	0,547	-0,176	-0,291	0,526	-0,149	-0,292	-0,185	1,000	-0,200	-0,114	0,645	-0,150
U	0,332	-0,145	0,353	0,551	0,638	-0,329	-0,176	-0,139	-0,128	-0,665	-0,122	0,594	0,757	0,579	0,561	-0,163	-0,676	-0,805	-0,612	0,611	0,644	0,303	-0,848	0,247	0,353	0,257	-0,441	-0,365	0,341	-0,570	0,285	-0,229	0,508	-0,556	0,463	-0,532	0,660	-0,652	-0,200	1,000	0,723	-0,471	-0,610
V	0,671	-0,041	0,432	0,676	0,699	-0,265	-0,115	0,030	0,096	-0,393	-0,052	0,721	0,835	0,786	0,655	0,417	-0,434	-0,598	-0,329	0,905	0,925	0,425	-0,653	0,449	0,392	0,283	-0,333	-0,251	0,761	-0,454	0,349	-0,233	0,605	-0,759	0,488	-0,041	0,895	-0,290	-0,114	0,723	1,000	-0,343	-0,101
Zn	-0,562	0,870	-0,113	-0,167	-0,175	0,598	-0,529	0,523	0,665	-0,109	0,604	0,162	-0,310	-0,082	0,234	0,153	-0,113	0,281	0,636	-0,303	-0,102	0,177	0,452	0,425	0,270	0,463	0,958	0,921	0,034	-0,135	0,606	0,870	-0,492	0,145	0,032	-0,070	-0,464	0,098	0,645	-0,471	-0,343	1,000	0,237
Zr	0,391	-0,040	-0,111	-0,194	-0,459	-0,149	0,205	-0,106	0,518	0,574	-0,205	-0,343	-0,413	-0,275	-0,317	0,692	0,743	0,465	0,320	-0,195	0,222	-0,302	0,691	-0,224	-0,396	-0,139	0,152	0,069	-0,047	0,617	-0,239	0,183	-0,020	0,246	-0,402	0,866	-0,002	0,944	-0,150	-0,610	-0,101	0,237	1,000

Uranium, which was discussed earlier, shows no strong correlation with any other element. Most significant is the correlation with the lanthanides and vanadium. Thorium shows better correlation with other elements than uranium does; particularly interesting are elements like vanadium, molybdenum, europium and aluminium, although the correlation is not very strong.

TOC is well correlated with cadmium, cobalt and some other elements. The role of carbon and organic matter will be discussed in section 3.5.16.

Silicon is negatively correlated to many elements, e.g. calcium, strontium, europium and iron, probably due to its comparatively low concentrations in the peat. However, to some extent this negative correlation is necessary, since both silicon and calcium, for instance, are major elements in mineral fraction. If one major element increases its share of the total mass, some other major elements must inevitably decrease. In this manner, accumulation or depletion of major elements may significantly alter the concentration of other major and trace elements. Hence, the variations in the composition of the mineral fraction deserve some extra attention.

3.5.3 The Composition of the Mineral Fraction

Silicon is depleted out of proportion with all other analysed elements in the transition from sediments to peat. This indicates that there is a much lower abundance of silicates in the peat. In comparison with the average abundance of silicon in Earth's crust the concentrations in the gyttja are not remarkably high, but rather quite typical for granites.

A problem with the ash content is that accumulation or mobilisation of the major elements significantly may alter the amount of ash. The abundance of the major elements that were analysed is shown in Figure 3-15.

According to Figure 3-15 the transition from gyttja to peat is accompanied by a dramatic change in the composition of the mineral fraction. Silicon decreases, while elements such as iron, sulphur, aluminium and – above all – calcium become more important. As was noted, the decrease of one element is inevitably connected to an increase of another or several other elements, and drastic changes in the concentration of a major element like silicon must have an impact on the concentration of other elements.

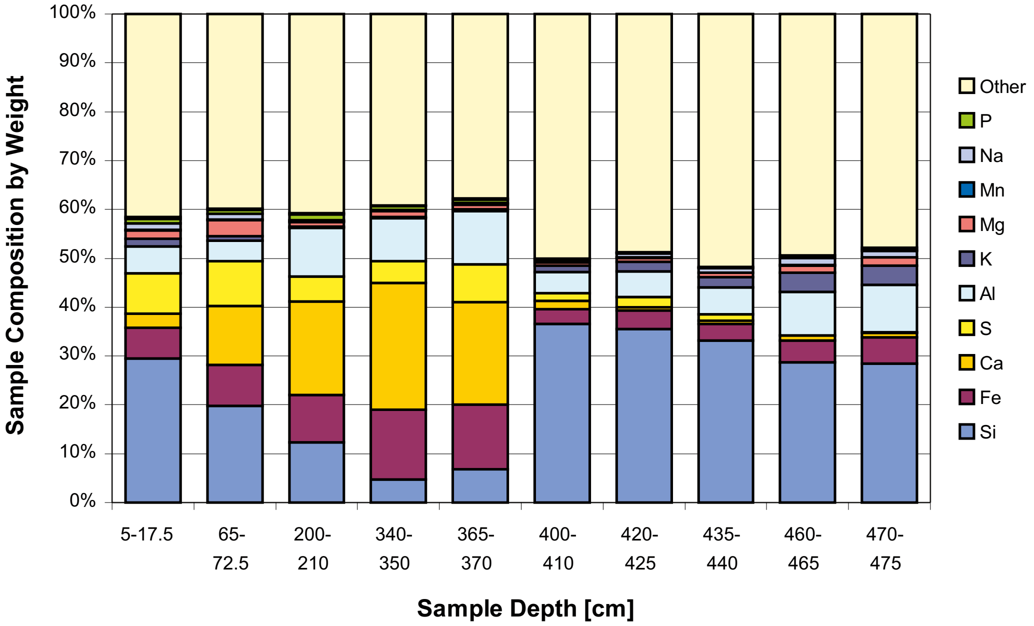


Figure 3-15. Elemental composition by weight for the ash content of the analysed samples.

Silicon decreases from approximately 38% to only 8%. This implies that there is almost 80% less silicon in the lower peat samples than in the sediments. However, depletion of silicon in the peat cannot alone explain why elements like calcium and sulphur increase. Enrichment of sulphur, calcium and other major elements in the peat will counteract the effects of the silicon depletion by suppressing the relative increase of other elements. Since silicates are known to be resistant to weathering, it is possible that a large portion of the silicon found in the sediments was transported there as suspended particles. When the lake started to grow into a wetland, this should have limited the particulate transport, which in turn would lead to low silicon concentrations.

Since the composition of the mineral fraction has changed so much, it is hard to know to what extent it is representative for the original mineral fraction. If the possible loss of silicon dominates, even an element that has not moved with respect to the mineral fraction will appear to have been enriched. On the other hand, if the accumulation of calcium is more extensive, an immobile element will appear to have been leached, since its concentration has decreased in relation to the ash content. This makes the ash content less useful when trying to understand the behaviour of various elements.

3.5.4 Normalization of the Chemical Profiles to Titanium and Zirconium

Since variations among the major elements are likely to influence the relative abundance of other elements by changing the ash content, elements with strong association to the mineral fraction are sometimes used instead of ash content to study accumulation and leakage processes. Several elements have been suggested as conservative reference elements for such normalizations, most frequently titanium, zirconium, hafnium, rare earth metals and scandium /Steinmann and Shotyk 1997b, Frontasyeva and Steinnes 2004, Shotyk et al. 2001/.

In other studies all these elements have been well correlated to one another, which makes the choice of reference element quite unimportant. In Klarebäcksmossen, however, the elements are not very well correlated. For instance, scandium and most rare earth metals are strongly enriched in the minerotrophic peat in relation to the ash content, while elements like titanium and zirconium follow the ash content fairly well. This makes the choice of reference metal crucial.

However, since titanium and zirconium follow the ash content much better than scandium and the lanthanides, it is reasonable to assume that they will represent the original mineral content better. Few elements are enriched to the same degree as the lanthanides (except for cerium) in the transition from gyttja to peat, which suggests that they in fact could be quite mobile in this environment. This is supported by the fact that the enrichment is limited to the minerotrophic peat. If they would represent the original mineral content, there would have been a massive leakage of most elements from the peat. Hence, there are clear signs that these elements would not be suitable as reference elements in this case.

Instead elements like titanium and zirconium will be used to represent the original mineral content. A problem is that titanium and zirconium are not as well correlated as one would wish ($r = 0.866$), but their general agreement with the ash content indicate that it is not crucial whether titanium or zirconium is used. This also implies that the differences compared to using the ash content will not be very dramatic. However, as it seems hard to judge which one of the two that is more suitable for representing the original mineral fraction, an average of both is used.

It could be noted that both titanium and zirconium are enriched out of proportion with the ash content in the clay according to Figure 3-13. This most likely reflects a different mineral composition of the clay, an assumption that also is confirmed by Figure 3-15. However, since the clay, which represents a stage long before the wetland was formed, is not very interesting in this context, this does not constitute a big problem. The major focus will be on the distribution and transport processes between gyttja, minerotrophic peat and ombrotrophic peat.

The deviations between titanium and zirconium do not necessarily mean that one of them is more mobile than the other; it could reflect variations in the mineral composition of the samples. Titanium mainly occurs as TiO_2, $FeTiO_3$ and $CaTiSiO_5$ in Earth's crust, while zirconium mainly occurs as $ZrSiO_4$. All these minerals are considered to be stable and very resistant to chemical weathering even in very acidic environments /Shotyk et al. 2001/.

Figure 3-16 shows the normalized concentrations in relation to the weighted average of titanium and zirconium.

A comparison between Figure 3-13 and Figure 3-16 shows that the general patterns are the same, although there has been a substantial shift in some cases, above all in the deeper parts of the peat.

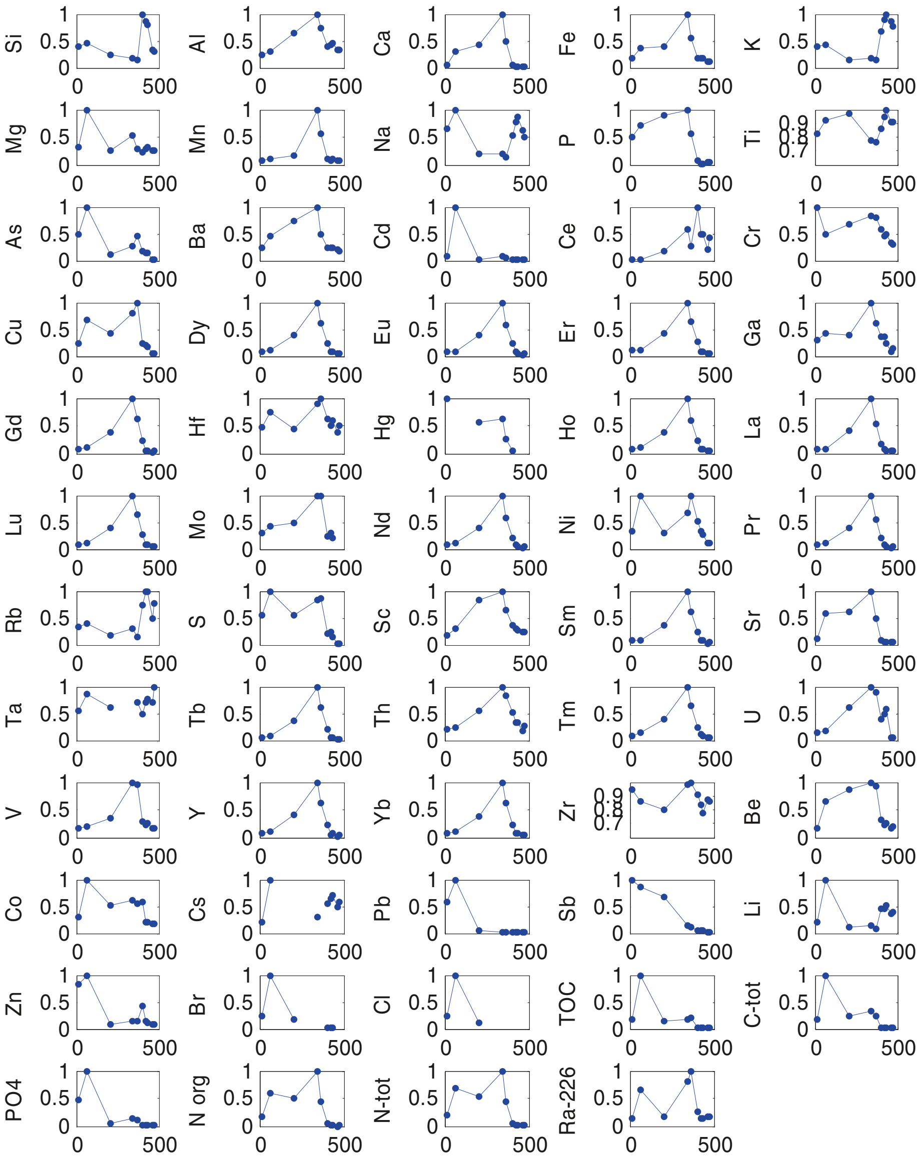


Figure 3-16. *Normalized concentrations for analysed parameters in relation to the weighted average of titanium and zirconium.*

3.5.5 Transport Processes

Figure 3-16 shows that there the mineral content is not enough to understand the distribution of most elements; there must be processes other than transport of mineral grains. For instance, elements could be transported by groundwater advection as free ions, organic or inorganic complexes or colloids. Elements that are enriched in peat by processes related to groundwater movements should be enriched mainly in the minerotrophic peat, since the ombrotrophic peat has not been in contact with mineralised groundwater. The enrichment in the peat could take place in several ways, e.g. precipitation and co-precipitation, cation exchange and complexation, preferentially to organic matter. Depending on the direction and chemical composition of the groundwater, mobile elements can also be lost from the peat. If the groundwater movement is slow, other processes such as diffusion may also contribute significantly to the transport.

The hydrology of Klarebäcksmossen has not been investigated yet, but by definition bogs are recharge areas. Hence, there is a downward movement of water in the upper parts of the peat. Although lateral flow is likely to play an important role for the discharge from Klarebäcksmossen, traces of anthropogenic Cs-137 as deep as 200 cm indicate that the groundwater flow also has a significant downward component, at least to this depth.

During the minerotrophic stage, Klarebäcksmossen (then a fen) was a discharge area by definition. Hence, there should have been an upward movement of groundwater, at least during some parts of the year. This could lead to a transport of more or less mobile elements from the underlying gyttja sediments to the peat. In other words, the gyttja constitutes a possible source for many of the elements that are enriched in the peat.

This assumption is supported by the fact that the enrichment often is concentrated to the lower parts of the peat for those elements that are enriched in the minerotrophic peat. It does not occur that an element is enriched in the upper parts of the minerotrophic peat, but not in its lower parts. Furthermore, it is very rare that there is more accumulation in the upper parts of the minerotrophic peat than in the lower parts; the concentrations tend to be higher in the deeper parts of the peat.

An alternative could be that deeper parts of the peat were more influenced by the surrounding catchment. The more peat the groundwater has to pass through, the more likely it is that elements will be lost from the aqueous phase. Groundwater that already has passed through large volumes of peat could already have lost certain elements, above all such elements that bind strongly to organic matter. However, the measurements from this single core do not provide any possibilities to test the importance of such processes.

Biological processes may also be important for certain elements. For these elements one would expect enrichment above all in the living moss near the surface. However, higher concentrations may be found in the minerotrophic peat, since the supply of nutrients often is better there. Anthropogenic emissions to the atmosphere may also result in enrichment of certain elements near the surface. As the impact from mineralised groundwater ceases in connection with the transition to the ombrotrophic stage, the relative importance of atmospheric deposition will increase.

Obviously, variation in the composition of the original mineral fraction may also occur further down in the core. However, there are reasons to believe that the original mineral fraction in the gyttja and the peat respectively should be fairly similar. Most of the minerals found in the gyttja could be expected to originate from the catchment of Klarebäcksmossen. When the lake was transformed into a wetland, there is no reason why this would have changed the hydrology of the catchment as such. Consequently, the minerals reaching Klarebäcksmossen by lateral flow could still be expected to have approximately the same composition as before. However, the transport of these particles to the central parts of Klarebäcksmossen, which was possible during the lake stage, must have been severely hampered when the lake turned into a wetland. Now that the water had to pass through large volumes of organic material its chemical composition and, not least, its content of suspended particles could have changed considerably before it reached the central parts of the mire.

3.5.6 Overview of the Relative Elemental Distribution

If the assumption that the original mineral content in the gyttja and the peat are of similar origin is valid, a comparison between the concentration in the minerotrophic peat and the gyttja should say something about the mobility and the relative inclination to accumulate in peat for the different elements. In a similar way it should be possible to assess the importance of different transport processes by comparing the concentration in minerotrophic peat to the concentration in ombrotrophic peat.

Therefore, Figure 3-17 is suggested as a tool to help interpret the collected data. It is also an attempt to give an overview of the behaviour of various elements and as a complement to the correlation analysis in order to group the analysed elements. In Figure 3-17 the concentrations in relation to the titanium-zirconium content has been used, but the general pattern will be the same even if the ash content is used instead.

The y-axis in Figure 3-17 shows the ratio between the average concentration in the minerotrophic peat and the average concentration in the underlying gyttja. Based on the assumption that there can be an exchange between the gyttja and the peat, the y-axis generally indicates the tendency of various elements to accumulate in peat. Elements below the horizontal line are depleted in the peat in comparison with the gyttja, while elements above the horizontal line are enriched in peat in comparison with the gyttja.

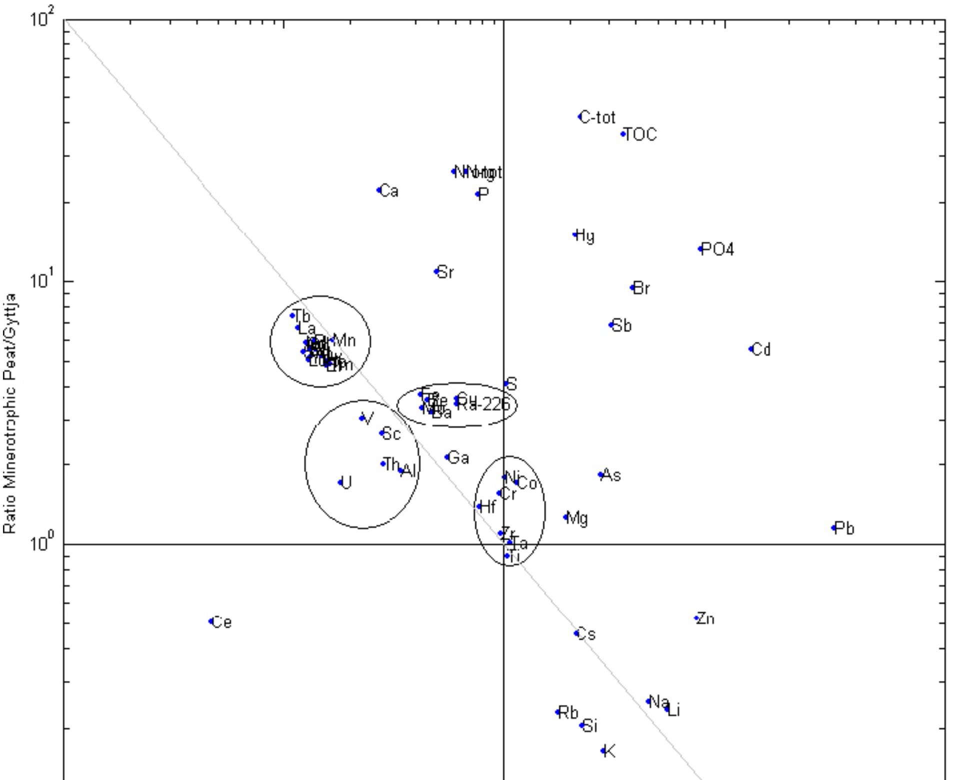


Figure 3-17. The ratio between ombrotrophic peat and minerotrophic peat versus the ratio between minerotrophic peat and gyttja for various elements. The ratios are based on the abundance of each parameter in relation to the weighted average of titanium and zirconium.

The x-axis shows the ratio between the concentration in ombrotrophic peat and the concentration in minerotrophic peat. Hence, it should say something about what transport processes that are most important for the different elements. Elements to the left of the vertical line are enriched in the minerotrophic peat in relation to the ombrotrophic peat. This would generally indicate that the groundwater plays an important role for these elements. Elements to the right of the vertical line are enriched in the ombrotrophic peat in relation to the minerotrophic peat, which indicates that there must be other transport mechanisms than groundwater advection that are important, e.g. bioaccumulation or atmospheric deposition.

Unfortunately, it is hard to see all elements in Figure 3-17. The small circle in the upper left part contains yttrium, lanthanum, manganese and all lanthanides except cerium. The horizontal ellipse contains iron, molybdenum, beryllium and barium to the left and copper and radium to the right, while the vertical ellipse in the centre contains titanium, tantalum, zirconium, hafnium, chromium, cobalt and nickel. Organic nitrogen and total nitrogen are found near the vertical line in the upper parts of the graph, just above phosphorus. All other elements should be possible to read directly in the graph.

Based on Figure 3-17 it is possible to identify some important groups of elements with fairly similar behaviour. Close to where the two lines cross (both ratios equal unity) we would expect to find the most immobile elements that follow the mineral fraction closely. Here we find titanium, tantalum, zirconium and, a bit further up, hafnium, chromium, cobalt and nickel. The fact the titanium and zirconium occur here is not surprising, since they were used for normalization with the mineral fraction. If the assumption that titanium and zirconium closely follow the mineral fraction is valid, the same seems to be true for tantalum, which occurs between titanium and zirconium in the graph. It must be emphasized that there might be other reasons why tantalum is found in this part of the graph, but based only on these measurements, the most plausible explanation is that tantalum is closely related to the mineral fraction. Hafnium, chromium, cobalt and nickel are found above the horizontal line, indicating that they are slightly enriched in the peat. The higher ratios are caused by a peak in the deepest peat sample (see Figure 3-13). This indicates that hafnium, chromium, cobalt and nickel could be capable of migrating independently of mineral particles, e.g. by forming organic complexes. The question of whether this is a fair picture of the behaviour of these element will be discussed more thoroughly later on.

The elements in the upper left quadrant are thought to be enriched in peat mainly due to groundwater transport. This is suggested by the fact the enrichment mainly is limited to the minerotrophic peat, which has been influenced by mineralised groundwater. The role of the groundwater is particularly evident for the elements close to the diagonal line, since these elements have approximately the same concentration in the ombrotrophic peat as in the gyttja. (The ratio between minerotrophic peat and gyttja is equal to the ratio between minerotrophic peat and ombrotrophic peat. Thus, the concentrations in ombrotrophic peat and gyttja must be equal.)

The lanthanides are clumped together with manganese, yttrium and lanthanum in this region. They are strongly enriched in peat in comparison with the gyttja and the proximity to the diagonal line suggests that groundwater advection is responsible for their enrichment in the minerotrophic peat.

Vanadium, scandium, thorium and aluminium are also enriched in the minerotrophic peat, but not to the same extent as the lanthanides. This group is also found close to the diagonal line, which suggests that groundwater is important for the migration of these elements too. Uranium is the only element in this quadrant, which is found far below the diagonal line. This means that the concentration in the gyttja is higher than in the ombrotrophic peat. The U-234/U-238 and Th-230/U-234 ratios indicate that this is caused by substantial accumulation of uranium in the gyttja.

Beryllium, barium, molybdenum, iron, copper and radium are all found above the diagonal line. All are clearly enriched in the minerotrophic peat in relation to the gyttja, but the enrichment is not limited to the minerotrophic peat, but extends to the ombrotrophic peat. This suggests that there could be additional transport processes that are important for these elements, e.g. biological uptake or anthropogenic emissions. Probable explanations will be discussed as the profiles are examined in more detail. Gallium is also found above the diagonal line, but it is not enriched in the peat to the same extent as the other elements.

Calcium and strontium are strongly enriched in the peat, and unlike many other elements the amount in the peat is of similar size as or even greater than the amount in the gyttja. Knowing that radium has been leached from the gyttja, one might expect the same to be true for calcium and strontium. This would push these elements upwards in the graph. The distance from the centre of the graph shows that both calcium and strontium must be considerably mobile and that they are accumulated in peat.

The elements in the upper right quadrant are also enriched in the peat, but here the dominating process behind the accumulation seems not to be groundwater advection. For all these elements the concentrations are higher in the ombrotrophic peat than in the minerotrophic peat. Possible explanations include bioaccumulation, anthropogenic emissions and high abundance in atmospherically deposited material.

The fact that TOC and C-tot are found here is not surprising, since the ash content in ombrotrophic peat is lower. Nitrogen and sulphur are found close to the vertical line, which indicates that the discrimination between ombrotrophic and minerotrophic conditions is not very important for these elements. However, nitrogen is somewhat more abundant in minerotrophic peat, which probably reflects the nutrient status of the peat.

Phosphate is likely to be accumulated in the ombrotrophic peat by biological uptake, while the enrichment of elements like lead, arsenic and cadmium seems more likely to be affected by anthropogenic emissions. These possibilities will be investigated more thoroughly later on.

In the lower right quadrant we find all the alkali metals – lithium, sodium, potassium, rubidium and caesium – together with silicon and zinc. They are all characterised by low concentration is the peat in comparison with the underlying gyttja. This could be interpreted either as accumulation in the gyttja or as leakage from the peat. Generally, these measurements suggest that these elements do not have any potential for accumulation in peat lands.

In the case of zinc the explanation is probably accumulation in the gyttja, since there is a peak in the uppermost gyttja sample. As it seems, zinc was somehow accumulated out of proportion with titanium and zirconium during the late lake stage. Zinc is also strongly enriched in the ombrotrophic peat, but this is likely to be related to atmospheric deposition of anthropogenic emissions. The alkali metals and silicon on the other hand appear to have been lost from the peat.

Cerium is the only element found in the lower left quadrant. This means that it does not seem inclined to accumulate in peat and that groundwater transport is the dominating transport mechanism. It is not easy to imagine how a pattern like this could arise, but possible alternatives will be discussed later on.

The various profiles will now be studied in more detail and compared to one another in order to investigate the results of the correlation analysis and the approach in Figure 3-17. To facilitate these comparisons normalized concentrations will be used in most cases. Unless nothing else is stated, concentrations normalized to the weighted average of titanium and zirconium are used.

3.5.7 Alkali Metals and Silicon

Together with silicon the alkali metals are the elements that have the lowest concentrations in the minerotrophic peat in comparison with the underlying gyttja. The concentrations in the minerotrophic peat are probably suppressed by accumulation of calcium and some other major elements, which makes the differences even more dramatic.

Among the alkali metals there seem to be two major groups: lithium, sodium and caesium that are enriched in the lower sample from the ombrotrophic peat and potassium and rubidium that have a smoother profile in the peat. The enrichment in the lower parts of the ombrotrophic peat show that lithium, sodium and caesium probably are not found in the mineral fraction to the same extent as potassium and rubidium. As will be shown in Figure 3-31 they seem to follow TOC very well in this region, which suggest that biological processes may play an important role for controlling the abundance of these elements. Figure 3-4 showed that the highest activities of Cs-137 still are found in the surface sample, which could indicate that there has been significant biological uptake of caesium. However, if the dating of the peat is correct, it is not impossible that the Chernobyl peak could occur in the uppermost 2.5 cm of the profile, although it most likely was deposited somewhat deeper. It is possible that higher concentrations of come elements could be seen if the uppermost 5 cm of the core had been analysed by ICP-AES too.

The correlation analysis showed no good agreement between silicon and potassium for the core as a whole. However, in the peat both potassium and rubidium follow silicon very well, which suggests that much of the potassium in the peat might occur as potassium feldspar, $KAlSi_3O_8$, or some other silicate mineral.

The idea that the alkali metals mainly occur in minerals is also supported by the fact that they also follow the titanium-zirconium content quite well, at least in parts of the peat. However, they are strongly depleted with respect to titanium and zirconium in the transition from gyttja to peat, which suggests that there is a more mobile fraction of these elements that may be leached from the peat. Hence, it seems likely that the alkali metals generally are quite mobile in peat and that they do not sorb very strongly to peat. Instead the alkali metals could be present in various silicates. The high mobility of alkali metals is also supported by the Cs-137 profile in Figure 3-4, since the artificial Cs-137 is found deep in the profile despite the comparatively short period of time that has elapsed since the first emissions.

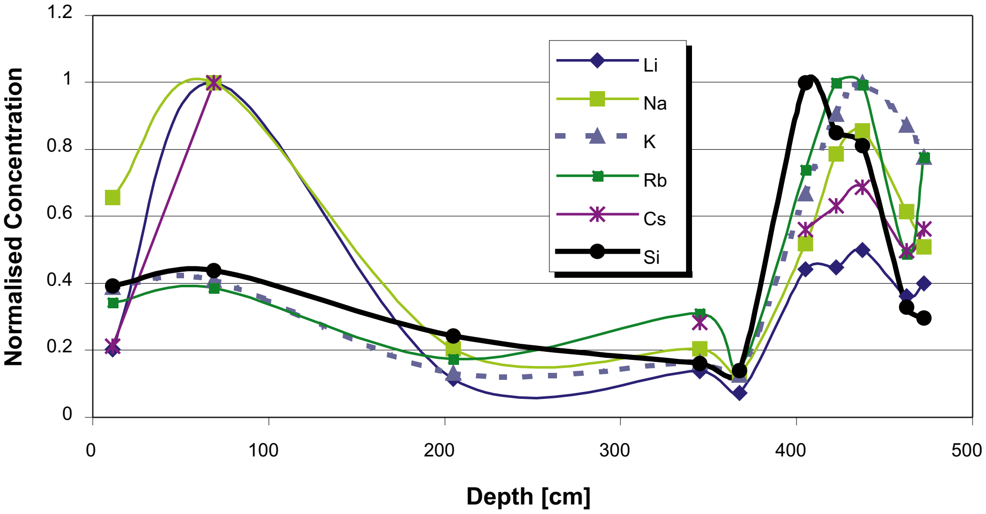


Figure 3-18. *Normalized concentrations for alkali metals and silicon.*

3.5.8 Alkaline Earth Metals

There are considerable differences among the alkali metals. Calcium is enriched out of proportion with any other metal in the minerotrophic peat. It is followed by strontium, which also is strongly enriched in the minerotrophic peat. Hence, they clearly demonstrate that they are capable of being accumulated in peat. Barium and beryllium also remain high throughout the peat, although they are not accumulated to the same degree as calcium and strontium.

Magnesium is the only alkaline earth metal that is not strongly enriched in the minerotrophic peat. According to Figure 3-19 the concentrations are about the same in minerotrophic peat and gyttja. The highest concentrations of magnesium are found in the ombrotrophic peat. Generally, magnesium follows titanium and zirconium rather well, which suggests association to the mineral fraction, but the enhanced levels in the ombrotrophic peat also indicate that there probably are other important transport mechanisms for magnesium.

Judging from Figure 3-19, radium might seem quite different from the other alkaline earth metals, but this is not necessarily the case. Radium is initially enriched in the minerotrophic peat in a similar manner as barium and beryllium, and their behaviour in the ombrotrophic peat seems to coincide. The explanation to the comparatively low concentrations in the upper parts of the minerotrophic peat might be radioactive decay. Since the half-life of Ra-226 is only 1,600 years, the distribution of Ra-226 in the core is most likely affected by the distribution of Th-230 even at these depths. Hence, the differences in comparison with other alkaline earth metals cannot be taken as indications of a very different biogeochemical behaviour. It in order to understand the behaviour and distribution of radium better it is necessary to also take a closer look at Th-230.

Knowing that there is – or has been – a leakage of radium from the gyttja, it is not unlikely that other alkaline earth metals are lost as well. This might be one reason behind the differences between peat and gyttja for elements like calcium and strontium.

An important question is how the different elements are fixed in the peat. There is very little data available to discuss such matters, but measurements of calcium carbonate, $CaCO_3$, have been made in the other core from Klarebäcksmossen /Nilsson 2004/. This is interesting, since calcium is so strongly enriched in the peat. The results of the analyses are presented in Table 3-3.

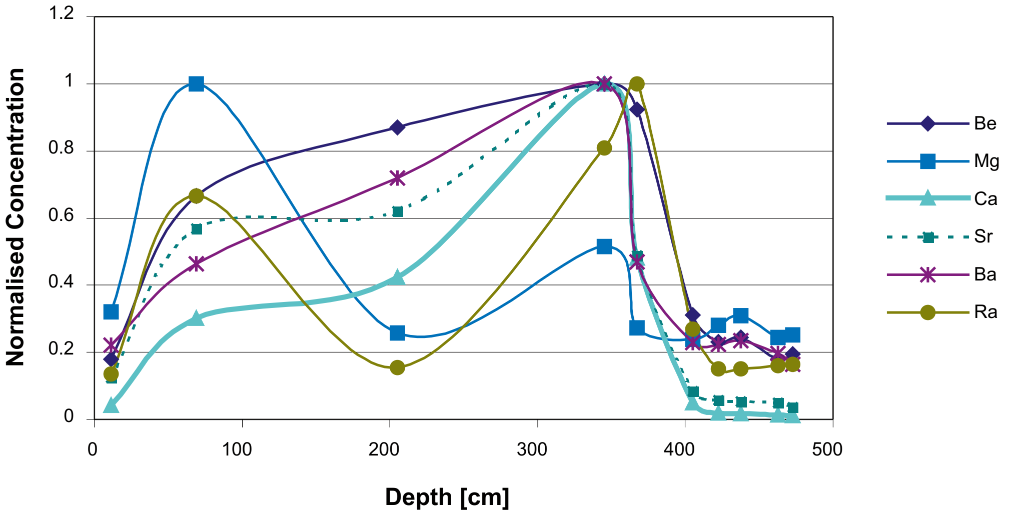


Figure 3-19. Alkaline earth metals.

Table 3-3. Concentration of calcium carbonate in the other core from Klarebäcksmossen /Nilsson 2004/.

Depth [cm]	Type	$CaCO_3$ [% DW]
60–90	Peat	0
320–370	Peat	0.2
440–460	Gyttja	0.2

Since the two cores were sampled only a few meters apart, it is reasonable to assume that they have approximately the same content of calcium, calcium carbonate and ash. If this is true, it implies that not very much of the calcium occurs as calcium carbonate. In the ombrotrophic peat, there is no calcium carbonate at all. Accordingly, calcium must occur in some other form in the ombrotrophic peat. In the deeper parts of the minerotrophic peat, where calcium is the dominating metal (approximately 23–29% in ash), calcium in calcium carbonate only contributes with 1.7% to the ash content. In other words, only 5.8–7.2% of the calcium is found as carbonate, while the rest of the calcium, more than 90%, must occur in some other form. In the gyttja, where calcium only makes up 0.6% of the ash, calcium carbonate contributes more to the total calcium content. Here, roughly 15% of the calcium can be expected to occur as calcium carbonate, which is more than twice as much as in the peat.

Hence, it is clear that calcium cannot be enriched in peat due to precipitation of calcium carbonate. For stoichiometric reasons, the only possibility seems to be that the vast majority of the calcium in the peat somehow is bound to the organic fraction. Calcium outnumbers all other analysed elements (in numbers of atoms) except for carbon in the minerotrophic peat. Since calcium does not occur as a pure metal, association to organic matter appears to be the most reasonable possibility.

By analogy, one would expect strontium and possibly also beryllium, barium and radium to behave similarly. The idea that these elements are associated with the organic matter is consistent with the fact that they occur above the diagonal line in Figure 3-17. Leakage from the gyttja is one process that would push them upwards in the graph, but there may also be some other processes that accumulate these elements in the ombrotrophic peat. For instance, calcium and magnesium are important nutrients, which also could have consequences for the other alkaline earth metals.

The impression from the profiles in Klarebäcksmossen is that alkaline earths generally must be rather mobile in peat, above all calcium and strontium. Otherwise it will be hard to explain why they are so strongly enriched in the peat. However, the enrichment also requires that they can be fixed in the peat so the mobility cannot be too high.

3.5.9 Titanium, Zirconium, Hafnium, Chromium, Nickel, Cobalt, Tantalum

According to Figure 3-17 hafnium, chromium, nickel, cobalt and tantalum should be the most immobile elements in peat. Titanium and zirconium have already been assumed to follow the mineral fraction, and since they were used for normalization, the profiles are fairly constant. However, Figure 3-20 shows that this is not the case for the other elements. Hence, they are probably capable of migrating independently of the mineral fraction, at least to some extent.

In order to evaluate the behaviour of titanium and zirconium too, the concentrations in relation to the ash content has also been plotted in Figure 3-21 for these elements.

Hafnium has been enriched out of proportion with ash in the lower parts of the peat and to some extent in the ombrotrophic peat. The enrichment in lower parts of the peat suggests that there has been a transport of hafnium from the gyttja. In comparison with zirconium, hafnium appears to be more mobile.

Nickel is also enriched out of proportion with as well titanium and zirconium as the ash content in the lower parts of the peat. Hence, nickel is evidently capable of migrating independently of the mineral fraction too. Nickel is also enriched in the deeper sample in the ombrotrophic peat along with cobalt. This is another sign that nickel does not always follow the mineral fraction. However, the enrichment is limited to a few samples.

Cobalt is enriched in throughout peat and in the uppermost gyttja sample, although the concentrations are in no way exceptional. In combination with the peak in the ombrotrophic peat, this indicates that cobalt is not as immobile as Figure 3-17 suggests.

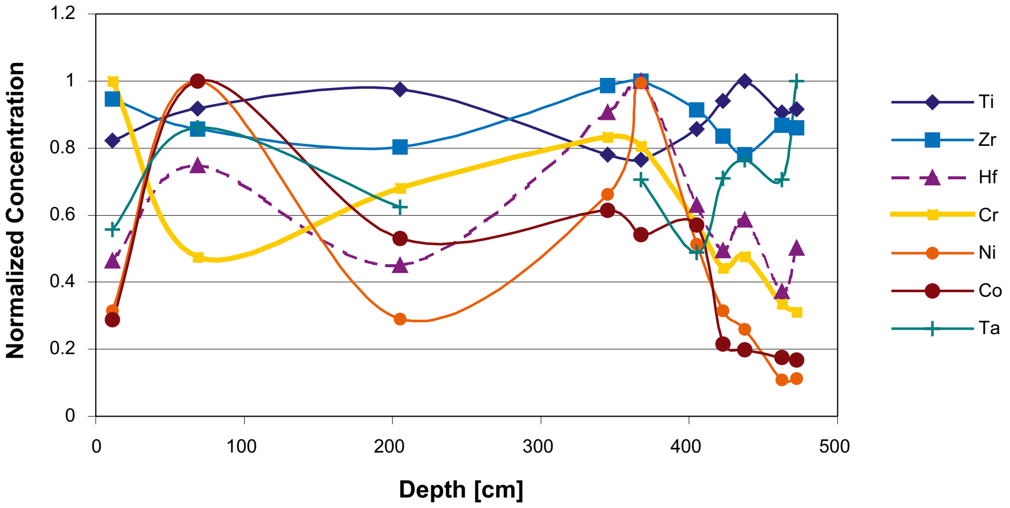


Figure 3-20. *More or less immobile elements according to Figure 3-17. Concentrations are normalised using the weighted average of titanium and zirconium.*

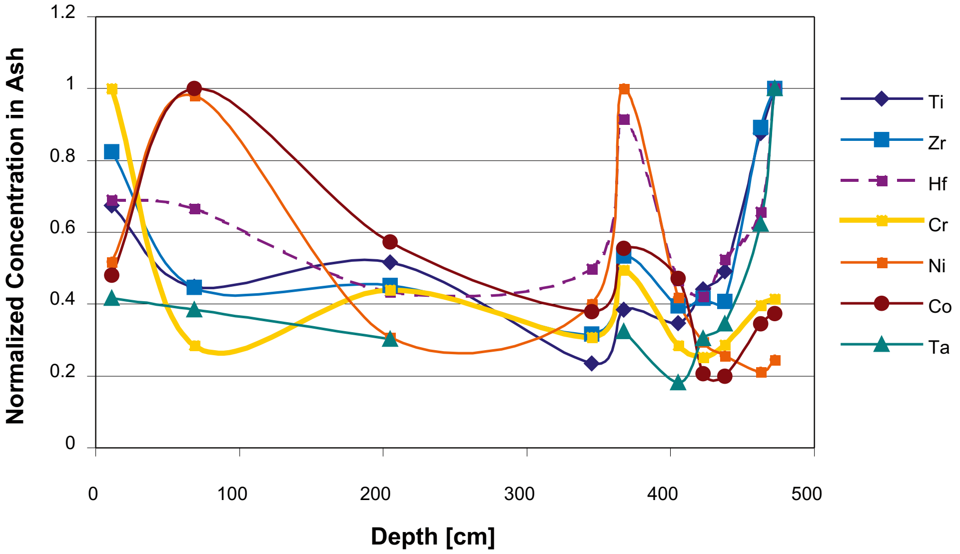


Figure 3-21. *Normalised concentrations for titanium, zirconium, hafnium, chromium, nickel, cobalt and tantalum in relation to ash content.*

Since titanium and zirconium were chosen as immobile elements, the smallest variations are expected for these elements. This is indeed the case, but it is noteworthy that the differences are as big as they are. Evidently, titanium and zirconium are not particularly well correlated. Unless one wishes to explain this as variations in the composition of original mineral fraction, this indicates that at least of the two is mobile to some extent.

Chromium is slightly enriched in the peat in comparison with titanium and zirconium, but the differences are generally so small that this could depend on minor variations in the mineral composition. The only major difference is the enrichment in the surface sample, where chromium is enriched out of proportion with titanium and zirconium. Hence, there is some process that affects chromium neat the surface. However, the general impression from these measurements is that chromium indeed seems to be a very immobile element in peat.

Tantalum follows the titanium-zirconium content very well, at least in those samples where it could be detected. Thus, it seems clear that its abundance in peat is determined by the mineral content.

3.5.10 Lanthanides and Related Elements

Compared to the average abundance in Earth's crust, all lanthanides are enriched in the peat except for cerium, whose concentration is somewhat lower than its average crustal abundance in the minerotrophic peat. In the gyttja, on the other hand, the concentrations are generally close to the average crustal abundance for all lanthanides, including cerium. This suggests that the observed differences between cerium and the other lanthanides are caused by enrichment of the latter in minerotrophic peat. This would imply that cerium is less mobile than other lanthanides.

On the other hand, the cerium concentrations observed in the ombrotrophic peat are low in comparison with the average abundance in Earth's crust. Figure 3-17 showed that cerium is the only element that was not only depleted in the ombrotrophic peat in comparison with the minerotrophic peat, but also depleted in the minerotrophic peat in comparison with the gyttja. If cerium was very immobile, one would expect it to follow the titanium-zirconium content, which it obviously does not. For instance, there is distinct peak in the upper parts of the gyttja and very low concentrations in the ombrotrophic peat. As for uranium, accumulation in the gyttja may be a contributing factor to the relatively low concentration in the ombrotrophic peat. Possibly, variations in the mineral content may also explain the apparent depletion in the ombrotrophic peat. An alternative hypothesis is that cerium, on the contrary, is very mobile in peat. Thus, it has been leached from all parts of the peat, but to a greater extent in the ombrotrophic peat. Cerium will be discussed more thoroughly later on in the light of other investigations, but based only on the measurements in Klarebäcksmossen it is hard to provide a good explanation to its distribution in the core. Possibly fractionation of cerium occurred in connection with the formation of the minerals.

The heavy lanthanides, shown in Figure 3-23, are well correlated to the light lanthanides as was shown earlier. There can be no doubt that yttrium, lanthanum and all lanthanides except for cerium and, possibly, promethium, which was not analysed, are very similar in their geochemical behaviour.

Manganese was found in the same region as the lanthanides in Figure 3-17. As Figure 3-23 shows, its profile is quite similar to those of the lanthanides. The major difference is that manganese is not enriched in the upper parts of the minerotrophic peat. One possible explanation could be the redox chemistry of manganese.

In comparison with the concentrations in the gyttja, manganese is not enriched to the same extent as the lanthanides and the actual differences between ombrotrophic and minerotrophic peat are much smaller. Manganese is enriched throughout the peat in comparison with the concentrations in the gyttja, but in comparison with the average abundance in Earth's crust, the concentrations are low. The only exception is the lower parts of the peat. In this sense, manganese appears to have more in common with elements like iron and gallium.

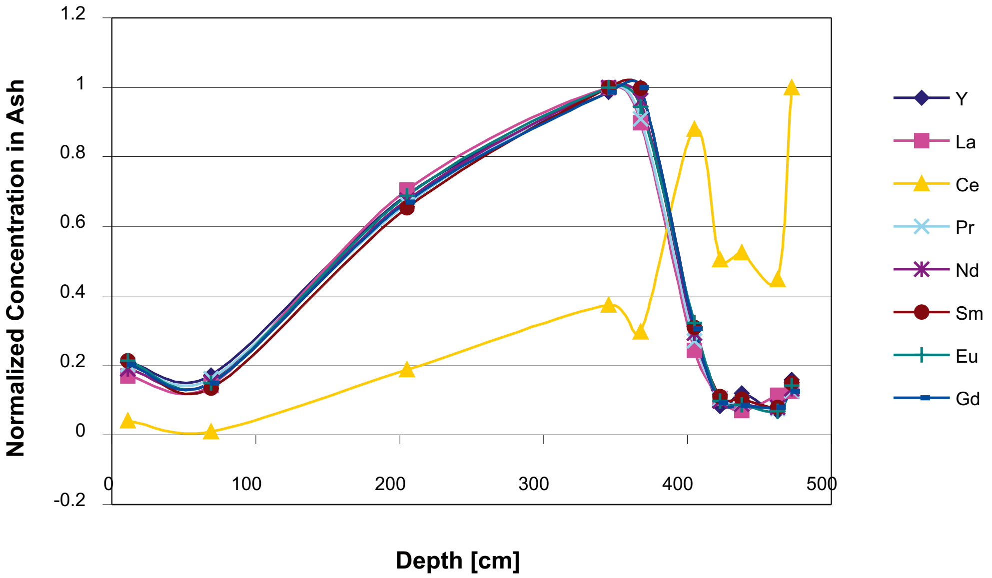


***Figure 3-22.** Normalised concentrations for yttrium, lanthanum and the light lanthanides.*

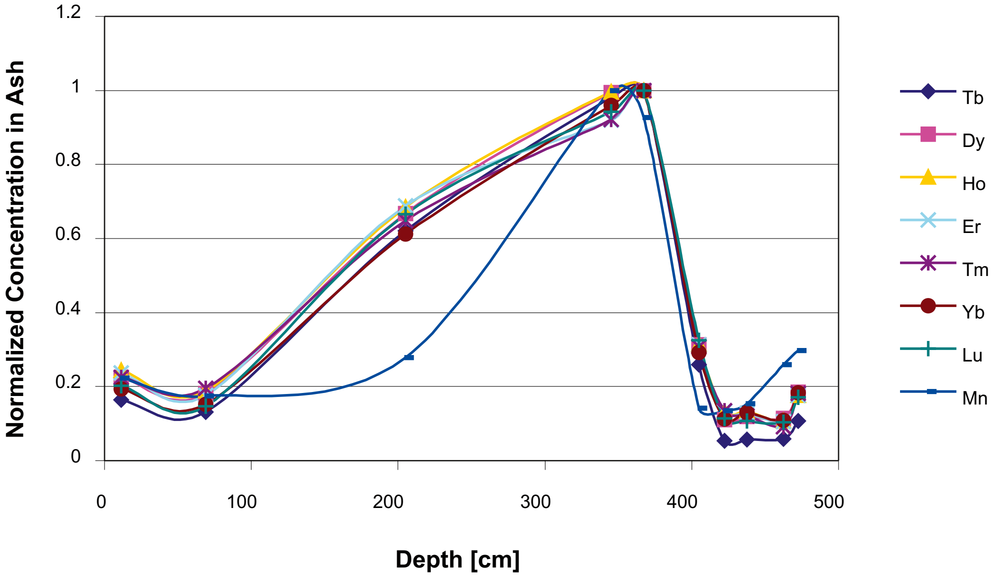


Figure 3-23. Normalised concentrations for the heavy lanthanides and manganese.

3.5.11 Iron, Molybdenum, Gallium, Copper and Radium

All elements in Figure 3-24 occur above the diagonal line, which indicates that there generally are higher concentrations in peat – both ombrotrophic and minerotrophic – than in gyttja. This could indicate that there are some other processes than only groundwater advection that influence their distribution in the profile.

The affinity for peat is most apparent for sulphur, which seems to be rather independent of whether the peat is ombrotrophic or minerotrophic. Accordingly, it could be associated with biological uptake.

Iron, molybdenum and gallium have pronounced peaks in the bottom layers of the peat, possibly indicating transport from the underlying gyttja, but there are no considerable differences in the transition from minerotrophic to ombrotrophic peat – at least not with the resolution provided by these analyses. Above all molybdenum occurs in concentrations much higher than the average concentration in Earth's crust. Unless there has not been a change in the composition of the mineral fraction, these elements appear to have been influenced either by biological processes or by leakage from the gyttja.

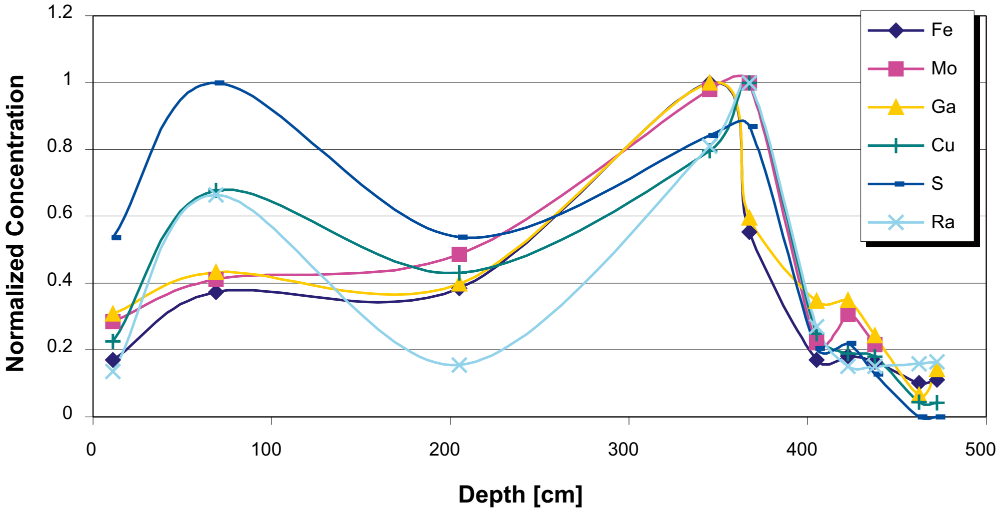


Figure 3-24. Normalised concentrations for iron, molybdenum, gallium, copper, sulphur and radium.

Radium has been included in this graph too, since the correlation analysis showed a fairly high correlation between radium and copper. Furthermore, it occurred in the same region as the other elements in Figure 3-17. Indeed, radium follows copper quite well despite the dip in the upper parts of the minerotrophic peat. However, the similarities may not mean very much in terms of biogeochemistry, since the radium profile is affected by radioactive decay.

3.5.12 Uranium, Thorium, Scandium, Vanadium, Aluminum and Gallium

All elements in Figure 3-25 are enriched in the minerotrophic peat, but not in the minerotrophic peat, which indicates that their presence primarily is controlled by groundwater advection. Just like for the lanthanides the concentrations in the ombrotrophic peat are of fairly equal to the concentrations in the gyttja. The major difference is that the enrichment in minerotrophic peat is stronger for the lanthanides, which suggests that they are more mobile in these environments.

Exceptions from this pattern are uranium and gallium. Uranium clearly occurs in lower concentrations in the ombrotrophic peat than in the gyttja, while it is the other way around for gallium. In the case of uranium, it was shown earlier that there has been accumulation in the gyttja, which also is indicated by the peak below 400 cm in Figure 3-25. If it is assumed that accumulation in the gyttja is the only explanation why uranium does not occur on the diagonal line like the other elements in this group, it would imply that roughly 70% of the uranium in the gyttja would have been sorbed from solution.

Gallium, on the other hand, occurs above the diagonal line in Figure 3-17, which indicates that it is less dependent on the groundwater for its transport than the other elements. As was shown in Figure 3-24, gallium is similar to molybdenum and iron in the peat samples.

3.5.13 Zinc, Lead, Mercury, Cadmium, Antimony and Arsenic

All elements in Figure 3-26 are strongly enriched in the peat in relation to the gyttja. In the case of mercury, cadmium and antimony, the enrichment occurs throughout the peat, while it mainly is limited to the ombrotrophic peat for zinc, lead and arsenic. It can be suspected that all these elements are influenced by atmospheric deposition.

Compared to the average abundance in Earth's crust, the concentrations of mercury in the gyttja are normal. The enrichment of mercury appears to be closely related to the increase in carbon (both total carbon and total organic carbon), which indicates that that mercury probably is connected to the organic fraction. Cadmium is also strongly enriched in the transition from gyttja to minerotrophic peat, which suggests that it too might be closely associated with organic matter.

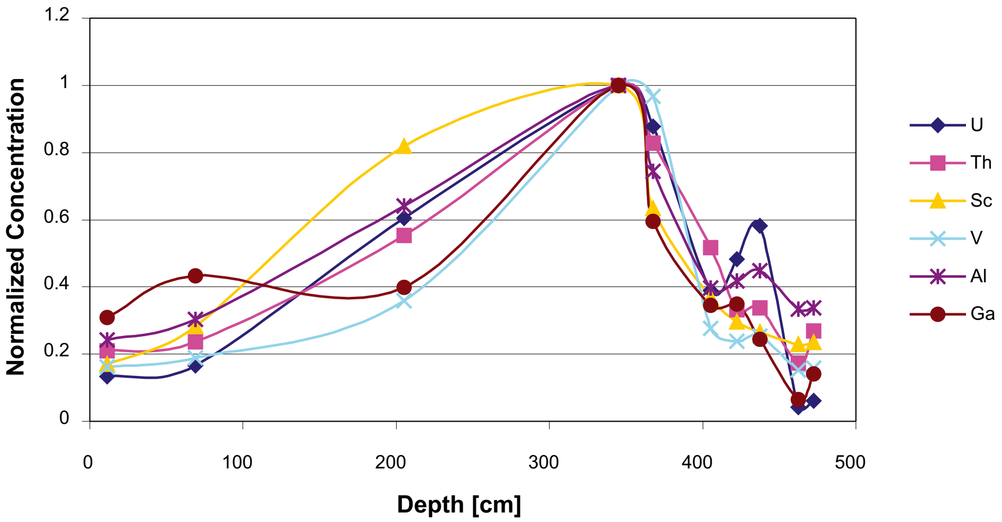


Figure 3-25. *Normalised concentrations for uranium, thorium, scandium, vanadium, aluminium and gallium.*

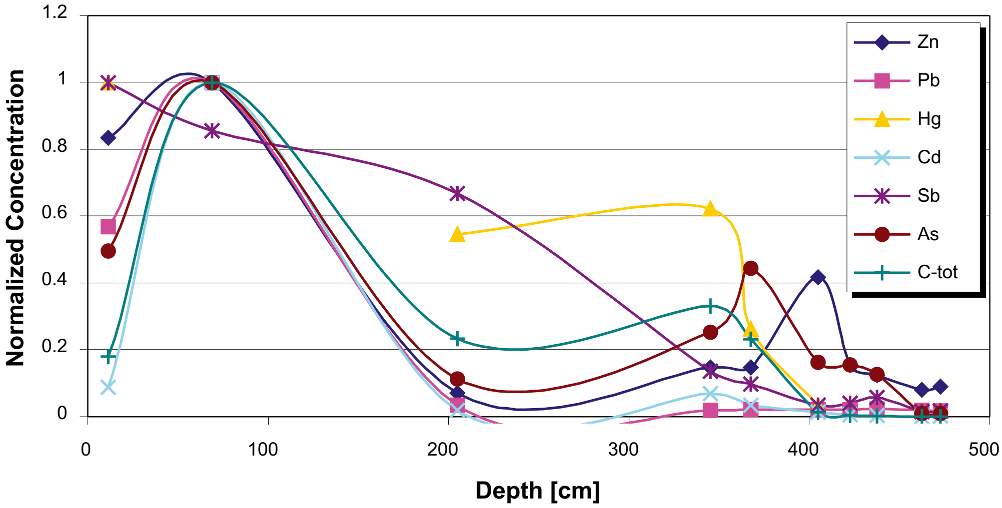


***Figure 3-26.** Normalised concentration for zinc, lead, mercury, cadmium, antimony and arsenic. Total carbon has been included for comparison.*

The concentrations of antimony in the gyttja are not exceptional in relation to the average abundance in Earth's crust, but the increase in the peat is not as dramatic as that for mercury. A reasonable explanation would be that there is an extensive atmospheric deposition of antimony and that the mobility of antimony is rather high.

For zinc, lead and arsenic the concentrations in the minerotrophic peat are normal. Up to 200 cm these profiles look very much like many other metals. All of them seem to be quite immobile in relation to the mineral fraction. Lead has approximately the same abundance in minerotrophic peat as in gyttja, which makes it comparable to titanium and zirconium. Arsenic has a peak in the lower peat samples, and zinc has a peak in the upper gyttja samples. This is probably the major explanation why they do not occur on the horizontal line in Figure 3-17. Hence, judging from the measurements in Klarebäcksmossen, lead, arsenic and zinc seem to be rather immobile in peat.

However, they are all more or less strongly enriched in the ombrotrophic peat. The most probable explanation is that there has been extensive – most likely anthropogenic – atmospheric deposition of these elements. The role of anthropogenic emissions to the atmosphere will be evaluated in Chapter 4, where the pattern is compared to data for atmospheric depositions from other studies.

3.5.14 Carbon, Nitrogen and Phosphorus

The amount of carbon is fairly constant throughout the peat, but the relative amount of organic carbon decreases successively from almost 100% at the top to 50% in the deeper parts of the minerotrophic peat. This could be related to humification of the peat, although /Nilsson 2004/ says that the degree of humification is lower in this region.

In the lowest parts of the peat there is a rather sharp peak in the TOC content. This peak occurs for many other elements as well, which could mean that those elements have been transported by dissolved organic carbon. The concentration of various elements in relation to TOC is shown in Figure 3-32.

In the gyttja, and subsequently in the clay, the amount of carbon decreases rapidly. It is clear that the sediments gradually became richer in organic material, which agrees well with the theory that Klarebäcksmossen was a lake that was invaded by plants.

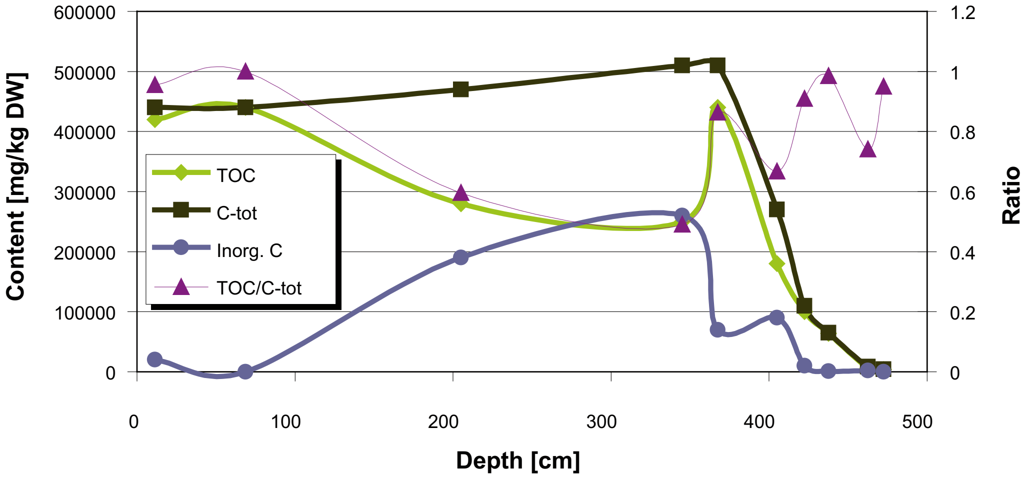


Figure 3-27. *Total organic carbon (TOC), total carbon and inorganic carbon (calculated) with respect to dry weight throughout the core. The ratio between organic and total carbon is shown on the secondary axis.*

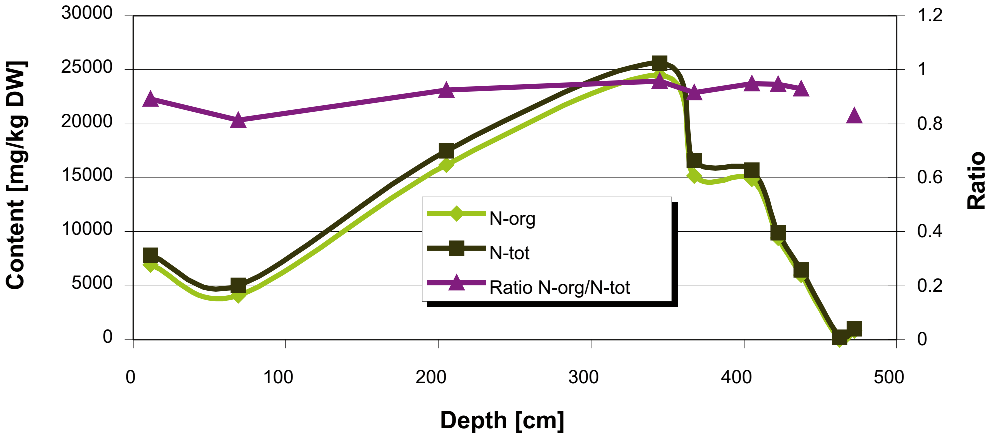


Figure 3-28. *Organic and total nitrogen throughout the core. The ratio between organic ant total nitrogen is shown on the secondary axis.*

As for carbon the levels of nitrogen decrease significantly in the gyttja and reach their lowest levels in the clay. It is noteworthy that the organic nitrogen was below detection limit (5 ppm DW) in one clay sample. The nitrogen levels from these measurements are, however, fairly well correlated with those from the other core from Klarebäcksmossen that was analysed by /Nilsson 2004/. Nitrogen is almost entirely present in organic forms, which is demonstrated by an almost constant ratio between organic and total nitrogen.

The amount of nitrogen is significantly lower in the ombrotrophic peat, which shows that the nutrient status during the bog stage is much poorer than during the fen stage. This is also shown by the C/N ratios in Figure 3-30.

The phosphorus inventory is dominated by the mineral fraction; in the lower parts of the profile there are only a few percent of bioavailable phosphorus. Only in the ombrotrophic peat the concentrations become more equally sized. Here, as much as 50% of the phosphorus is biologically available.

According to Figure 3-17 both total phosphorus and phosphate are strongly enriched in the peat as compared to the gyttja. However, total phosphorus is not enriched in the ombrotrophic peat, but seems to follow the mineral fraction quite well, whereas phosphate is strongly enriched in the ombrotrophic peat. This suggests that there is a pronounced bioaccumulation of phosphate in the ombrotrophic peat. Figure 3-12 clearly shows that there is an increase of phosphate in relation to the dry weight towards the bog surface.

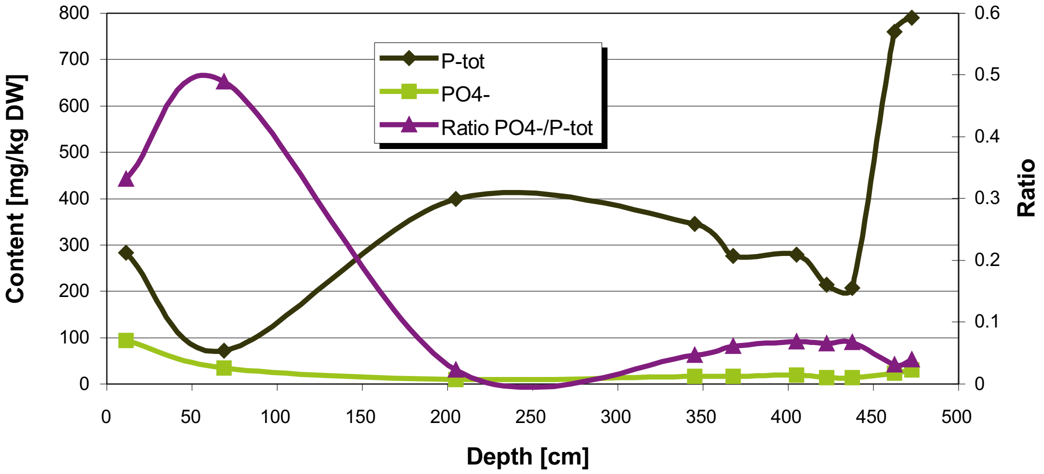


Figure 3-29. *Bioavailable (PO_4^-) and total phosphorus throughout the core. The ratio between bioavailable and total phosphorus is shown on the secondary axis.*

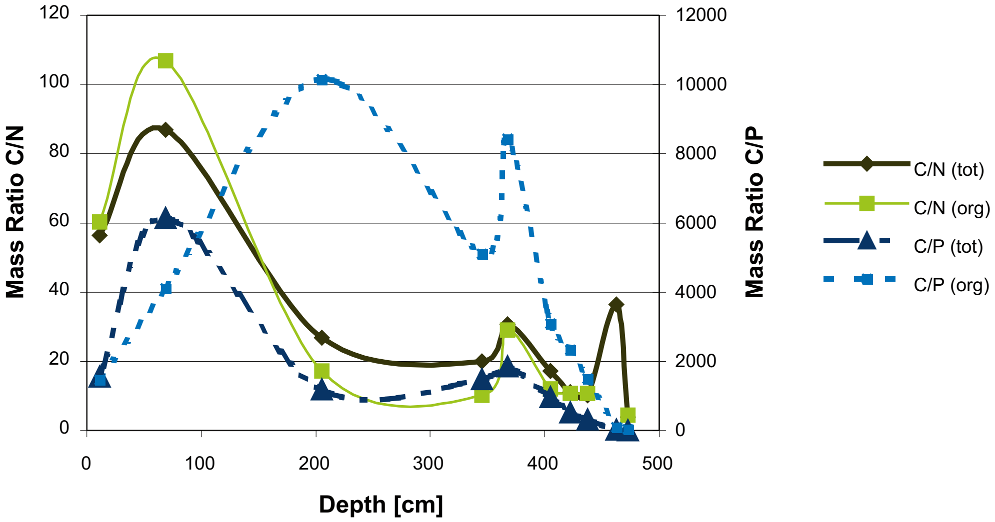


Figure 3-30. *C/N and C/P ratios for the total content and the organic/bioavailable fraction respectively.*

Figure 3-30 shows the C/N both for the total content of carbon and nitrogen as well as for the organic fraction. Both graphs show similar patterns. The C/N ratios are fairly similar in the gyttja and in the minerotrophic peat, except for the peak at in the lowest peat sample. Considerably higher C/N ratios are encountered in the ombrotrophic peat, which signifies that the nutrient status is poorer there.

The C/P ratio for the total content in Figure 3-30 resembles the C/N ratios. This ratio may not be very interesting, however, since only a small portion of the phosphorus is biologically available outside of the ombrotrophic peat according to Figure 3-29. Hence, the abundance of phosphorus below 200 cm is not primarily related to biological processes, although phosphorus seems to have a high affinity for environments with high organic content. However, it might be more interesting to study the C/P ratio for the biologically available fraction.

Figure 3-30 shows that the C/P ratio, unlike the C/N ratio, is lower in the ombrotrophic peat. There might be several explanations to this phenomenon. For instance, phosphate could be leached from decomposing peat and either accumulated by living moss or lost with the groundwater.

3.5.15 Halogens, TOC, Lithium and Magnesium

Unfortunately, both bromine and chlorine were below detection limit in several samples. Chlorine was only detected in the three uppermost samples, while bromine also was detected in the gyttja. However, being the best analogues for iodine, which could not be detected at all, it is worth to give these halogens some attention, since I-129 is thought to be one of the most critical radionuclides in nuclear waste.

Both bromine and chlorine are enriched out of proportion with their average abundance in Earth's crust in the peat. The concentration of chlorine in some samples is more than 100 times higher than the average in Earth's crust. Both chlorine and bromine appear to follow TOC quite well, which suggests that their distribution mainly is governed by biological processes. By analogy, one might suspect that iodine also could be strongly enriched in peat.

Lithium and magnesium are also included in Figure 3-31 to illustrate the trend the several elements other than the halogens seem to follow TOC more or less closely at least in parts of the peat. It seems like the distribution of lithium in the peat can be entirely explained by TOC.

3.5.16 The Role of TOC

It seems clear from Figure 3-13 that the abundance of most elements in various layers to a large extent can be explained by the mineral fraction. However, there are also several deviations from the titanium-zirconium content for many elements. One likely explanation in an environment with such high organic content as peat is that TOC also plays an important role for the distribution of various elements. The concentrations in relation to TOC in the peat samples are shown in Figure 3-32.

If an element (or compound) follows the TOC closely, one might expect that the distribution of these elements somehow is related to TOC. A problem, however, is that TOC is rather constant in peat in comparison with the ash content according to Figure 3-13. Essentially, the only major difference in the peat is the second sample from the top, which is ombrotrophic peat with very low ash content. However, in comparison with the titanium-zirconium content, which has been shown in most of the graphs, Figure 3-16 shows that TOC is strongly enriched in the deeper ombrotrophic sample. This leads to the characteristic peak shown in Figure 3-31.

Sodium, potassium, chlorine, bromine, phosphate, zinc, lead and some other elements appear to be enriched in the living moss in relation to TOC. In many cases it is not unlikely that bioaccumulation plays an important role, while anthropogenic emission might seem more likely to be the major mechanism in other cases.

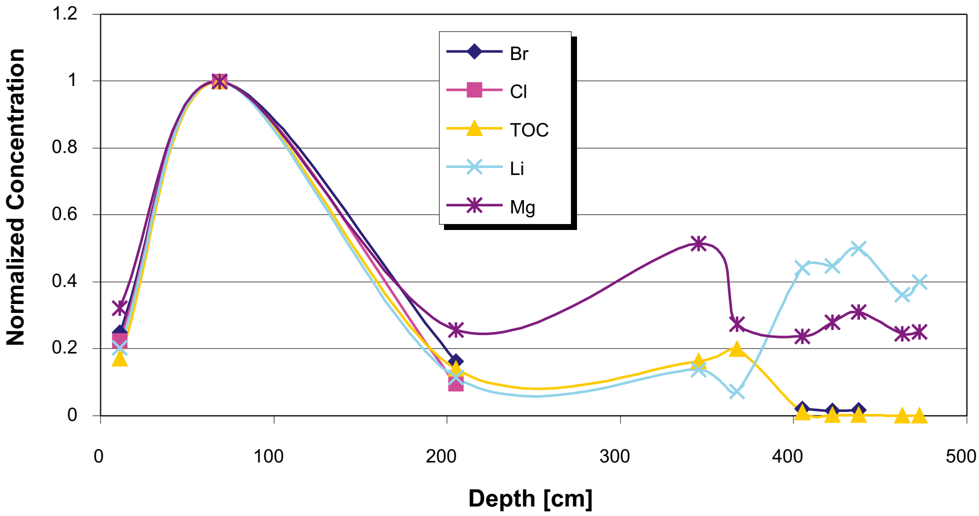


Figure 3-31. *Normalized concentrations for bromine, chlorine, TOC, lithium and magnesium.*

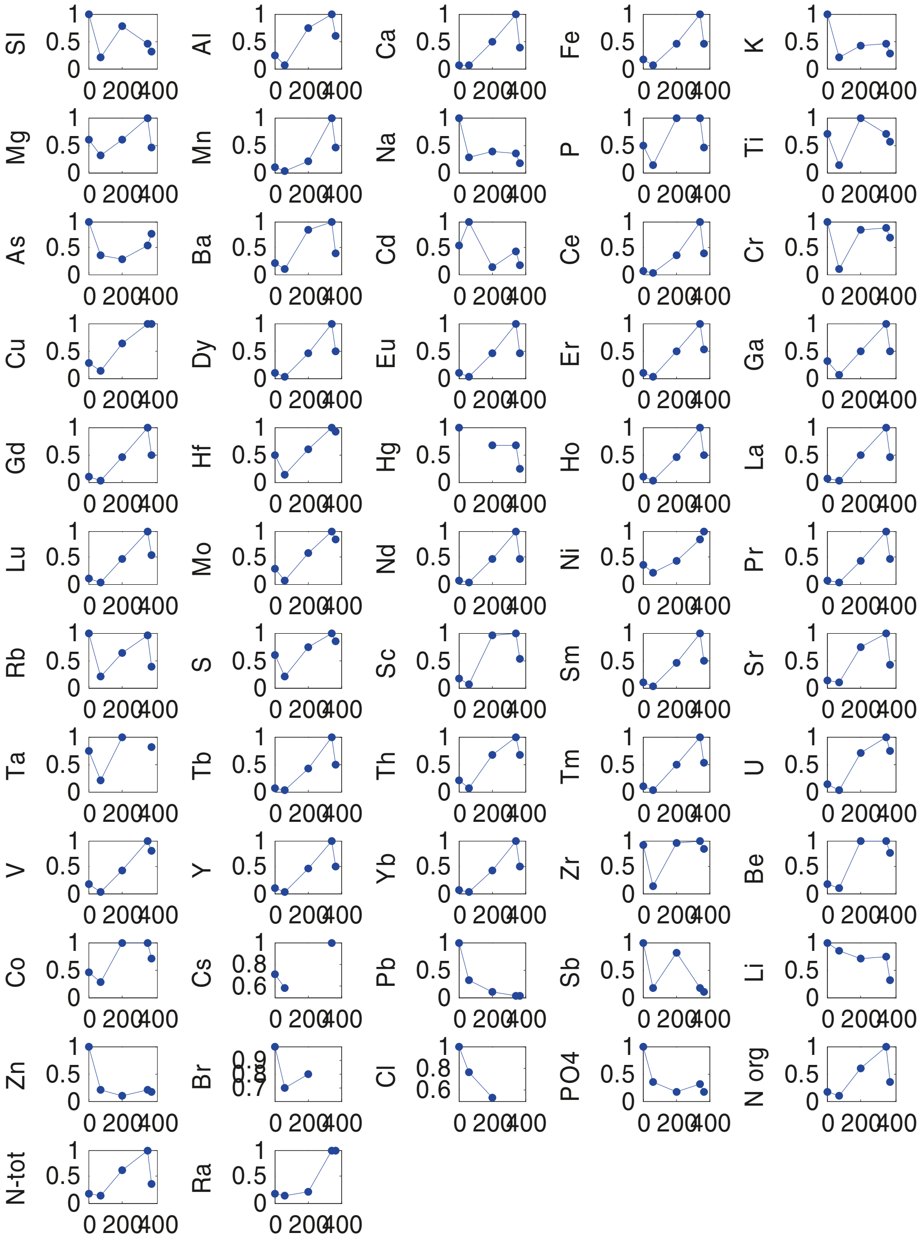


Figure 3-32. *Normalised concentration for the analysed parameters in relation to TOC. Only peat samples are included, since the low TOC content and high mineral content in the gyttja and clay samples would make it impossible to see the patterns in the peat otherwise.*

It is also interesting to see the peak that some elements have in Figure 3-13 and Figure 3-16 in the second sample from the top disappears in Figure 3-32. Nickel, radium and lithium are examples of elements that seem to follow TOC very closely at least in the uppermost samples, although the number of observations is low. They are not enriched in the living peat, however, which suggests that they mainly are passively bound to organic matter.

Conversely, elements with a clear dip in the second sample from the top could generally be assumed to be rather independent of TOC. Here we find elements such as titanium, zirconium, silicon and chromium.

3.6 Evaluation of the Measuring Techniques

3.6.1 U-235 and U-238

U-235 and U-238 provide an easy way to test the reliability of the radiometric measurements, since both isotopes are known to behave similarly and occur in a fairly constant ratio in most natural materials. There are for instance no alpha recoil effects for any of them as for U-234, which could affect the U-235/U-238 ratio. Consequently, one would expect a constant U-235/U-238 ratio throughout the core, provided that the measurements are correct. It should be obvious from Figure 3-33 that this indeed is the case. The few exceptions are mainly among the peat samples, where the U-235 activities obviously cannot be accurately determined due to the low activities.

Since the U-235 content has been found to be constant in natural material, it is possible to compare the measured U-235/U-238 ratio with a theoretically expected value: 99.2745% of the natural uranium is U-238, while the abundance of U-235 only is 0.7200%. According to /Weast 1974/, the U-235 content may, however, vary with 0.1% depending on the source. This means the expected U-235/U-238 activity ratio is 0.046 ± 0.07. In these measurements the weighted average of the U-235/U-238 ratios is 0.054, which is somewhat high. This may indicate that the U-235 activities are overestimated or that the U-238 activities are underestimated. Since the U-238 have not been corrected for self-absorption, it is likely that the true U-238 activities, above all in the clay samples, are slightly higher. Moreover, the measurement of U-235 is uncertain in some samples due to the low activities. Often it is only possible to assess the U-235 activity via the 185–186 keV line, which is dominated by Ra-226. It cannot be excluded that this in some way causes a slight overestimation of the U-235 activity, but it should be emphasized that this is not vital to the conclusions presented in this report, where U-235 is of minor interest.

3.6.2 Uranium and Thorium

It is also possible to compare gamma spectrometry and ICP-AES for a few elements: uranium, thorium and potassium. Both uranium and thorium occur only as radioactive isotopes with varying abundances. For uranium, there are three natural isotopes: U-238, U-235 and U-234. As was described above 99.27% is U-238 and 0.72% is U-235 as viewed by mass, while only 0.0055% is U-234.

Figure 3-34 shows that the agreement between gamma spectrometry and ICP-AES is satisfying for uranium. Only in the gyttja there seems to be a small deviation, but it is within the uncertainty limits. The fact that the both methods are so well correlated even for the clay samples indicates that there is no urgent need to correct for self-absorption in these samples.

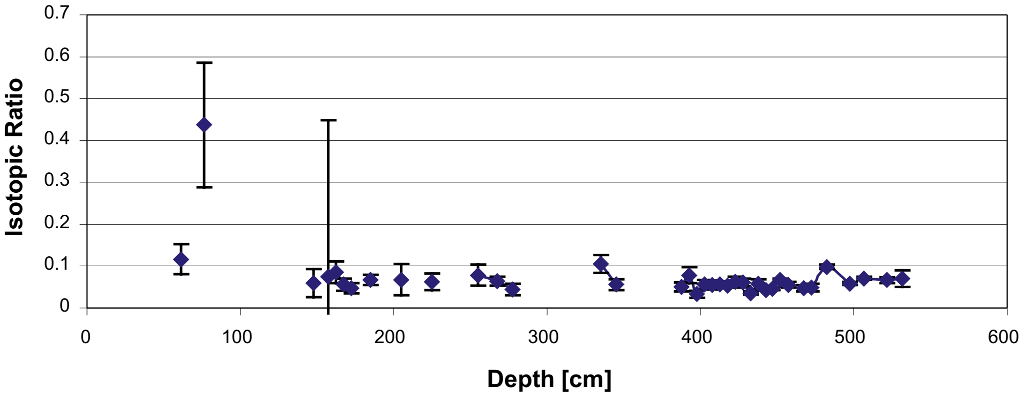


Figure 3-33. *U-235/U-238 ratios for samples where quantification of U-235 activities has been attempted.*

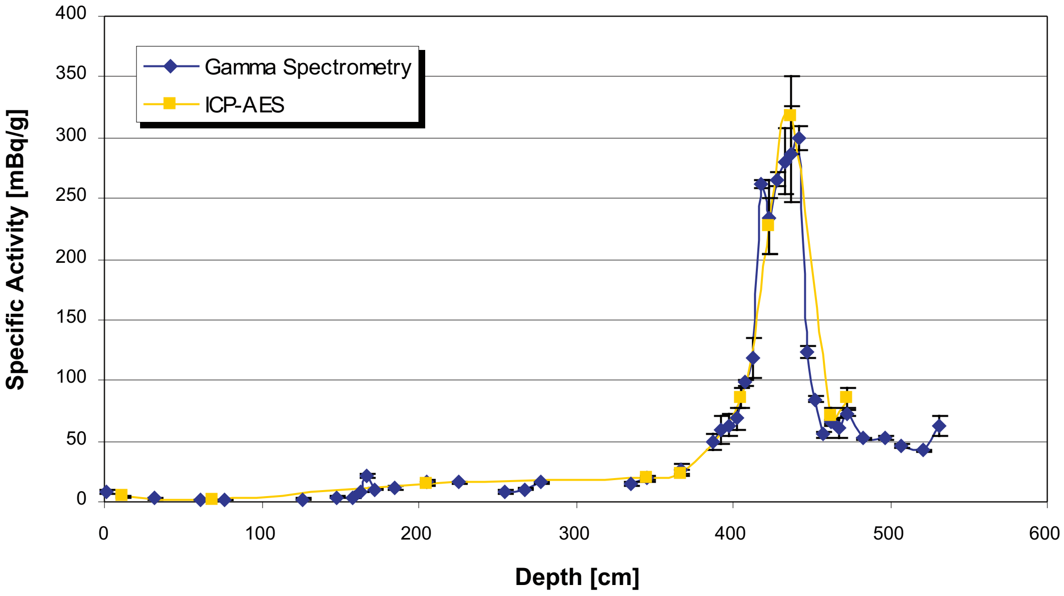


Figure 3-34. Comparison of the measurements of uranium by ICP-AES (converted to activity of U-238) and the measurements of Th-234 by gamma spectrometry. The uncertainty of ICP-AES has been assumed to be 10%.

A similar comparison can be made for thorium, which in terms of mass is completely dominated by Th-232. Hence, it is possible to convert concentration of thorium to activity of Th-232, which has been made in Figure 3-3. It was shown that the Th-232 profile agrees very well with the Ac-228 and Ra-228 profiles. Provided these radionuclides actually are in secular equilibrium, which most likely is the case, this means that there is a good agreement between gamma spectrometry and ICP-AES as regards thorium as well. Minor deviations may prise due to migration of Ra-228, but all and all the agreement between gamma spectrometry and ICP-AES is convincing for thorium.

3.6.3 Potassium

Whereas the measurements of uranium and thorium have given satisfying results, the situation is unfortunately more problematic for potassium. By gamma spectrometry potassium can be measured via its long-lived primordial isotope, K-40. It constitutes only 0.0117% of the total amount of potassium, which is dominated by the stable isotopes K-39 (93.26%) and K-41 (6.73%). However, since these isotopes are relatively heavy, no extensive fractionation is expected.

In Figure 3-35 the total content of potassium as measured by gamma spectrometry and ICP-AES respectively is shown. The agreement seems to be good, except for the clay samples, where there apparently is some problem with the radiometric measurements. Possibly, there has been some mistake in the analysis of the spectra, e.g. bad peak fitting.

However, by zooming in on the peat samples it becomes obvious that there are severe problems with the measurements of potassium in the peat, which are not visible in Figure 3-35. Figure 3-36 shows the percentage of the potassium concentrations as determined by ICP-AES in relation to the potassium concentrations determined by gamma spectrometry. Generally, there seems to be an underestimation of the potassium content by ICP-AES or an overestimation by gamma spectrometry. In clay and gyttja samples, where the mineral content is high, the deviations mainly appear to be within the uncertainty intervals, but in the peat gamma spectrometry in some cases detects more than four times as much potassium as ICP-AES.

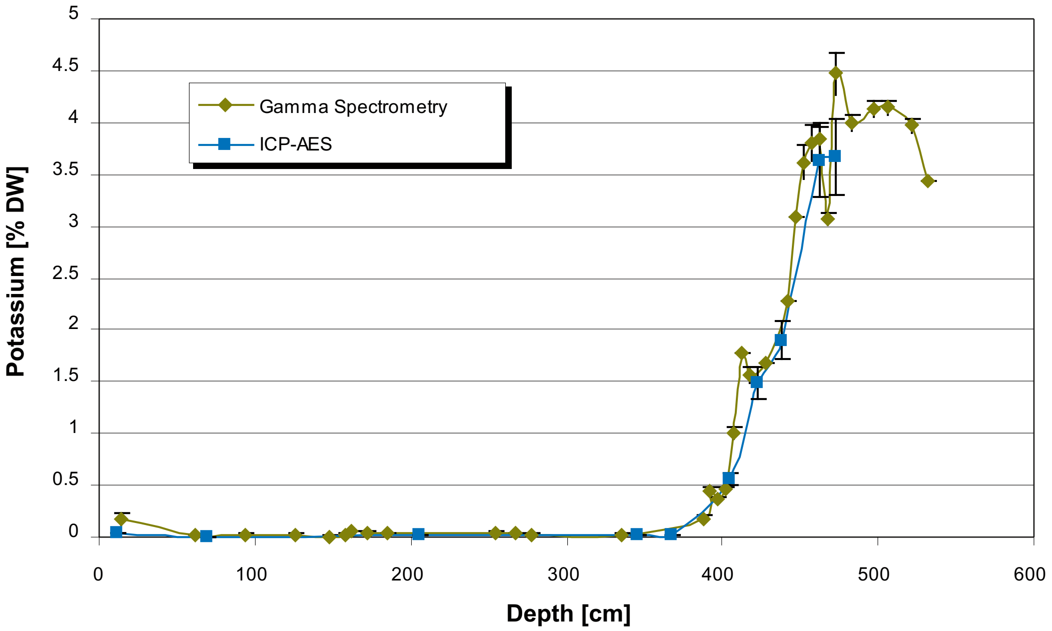


Figure 3-35. Content of potassium in percent dry weight throughout the core as determined by gamma spectrometry and ICP-AES. For gamma spectrometry the total content of potassium has been calculated from K-40. The uncertainty for ICP-AES has been assumed to be 10%.

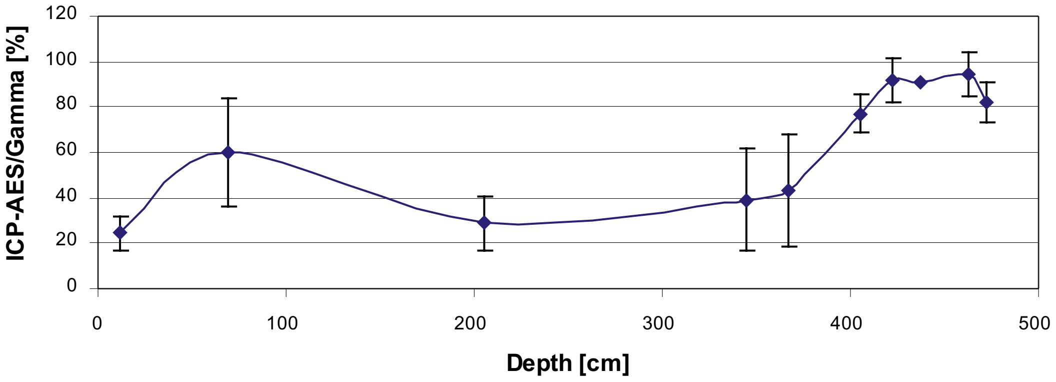


Figure 3-36. Concentration of potassium as measured by ICP-AES as percentage of the concentration of potassium measured by gamma spectrometry.

The disagreement between ICP-AES and gamma spectrometry for the peat samples is unsatisfactory and indicates a problem with either of the two measuring techniques. The problem has been discussed with Analytica who are responsible for the ICP-AES measurements and with expertise at the Swedish Geological Survey (SGU), but no satisfactory explanation has been found. Some of the samples have been remeasured by ICP-AES, but with similar results. For gamma spectrometry no new measurements have been made, but the number of analysed samples is high and different detector systems have been used in the measurements. Thus, there seems to be some kind of systematic error.

One possibility is that potassium was lost or not fully dissolved in the chemical preparation of the samples. A common method is extraction by a strong acid, e.g. concentrated nitric acid. The leachability of major elements in strong acids has been investigated by /Snäll and Liljefors 2000/ for various types of samples. Their conclusion concerning potassium is that it is very hard to extract from certain minerals such as feldspar, while it is much easier to extract from biotite. Therefore, "leachable potassium largely reflects the content of biotite in the samples" according to /Snäll and Liljefors 2000/. In Analytica's analyses, however, lithium metaborate was used to fuse the samples, and it is then thought that everything will be dissolved and that ICP-AES with this extraction method will give the total content in the samples. It seems strange that peat would be the most difficult matrix to extract potassium from.

Further analyses, preferably by some independent technique, would be needed to fully resolve the problems. However, this does not appear as an urgent task at this stage. Although it is disturbing that one of few elements, where validation of the results is possible, showed such disagreement, it must be emphasised that the deviations do not question the conclusions presented in this report. Regardless of whether one chooses to trust ICP-MS or gamma spectrometry the conclusions about potassium will remain more or less the same.

Another possibility is that the K-40 activities somehow were overestimated. The most plausible explanation would then be that there was some problem with the background correction. If the background radiation somehow was underestimated, that would lead to an overestimation of the activity in the sample. That would also explain why the problems only occured in the samples with low potassium concentrations, since the effects would be negligible with higher sample activities. However, it is not easy to see why two detectors independently would give coinciding but erroneous results unless there actually has been some change in the background levels.

4 Discussion

4.1 The Behaviour of Various Elements in Peat

4.1.1 Alkali Metals

The opinion that alkali metals generally are very mobile in peat finds much support in published literature. Sodium and potassium are generally considered to be highly soluble with low affinity for organic matter. They may form organic complexes, but they are often weak. Accordingly, both sodium and potassium are expected to be very mobile in peat. /Shotyk 1988/.

In one study where both the concentrations in peat and in the pore water were analysed showed that sodium followed by chlorine and potassium were the elements with highest concentrations in pore water in comparison with the concentrations in the peat. As much as approximately 15% of the sodium in peat samples has been found in the pore water. /Steinmann and Shotyk 1997b/.

While alkali metals are not strongly sorbed by organic matter, they are easily incorporated in clay minerals /Greger 2004/. This may very well be the explanation why they all are depleted in the peat in relation to the gyttja.

Potassium is a macronutrient and could therefore be expected to be accumulated by living moss. Lithium, sodium, rubidium and caesium can also be taken up by plants in the same way as potassium /Greger 2004/. No clear tendencies of near-surface bioaccumulation were observed in Klarebäcksmossen, but that might depend on the fact that the absolute peat surface was not included. Furthermore, the spatial resolution was not very good in this area. However, lithium, sodium and caesium followed TOC quite well in the ombrotrophic peat, which could indicate association to organic matter.

In other studies both sodium and potassium have been reported to follow the ash content fairly well, although they were enriched at the surface /Steinmann and Shotyk 1997b/. As was argued earlier, this observation does not have to be inconsistent with the statement that alkali metals are mobile in peat. The high mobility could lead to a loss of all potassium that is not bound in mineral particles, which then would explain the high degree of correlation with the ash content in peat.

Judging from the results from Klarebäcksmossen and published literature, it seems fair to treat the alkali metals as a group with fairly similar behaviour in peat. Rubidium is closely related to potassium when it comes to weathering, although it is reported to be more strongly bound to silicates. Caesium is similar to rubidium in its geochemical behaviour, but it is said to have a greater affinity for aluminosilicates /Greger 2004/.

Figure 4-1 shows the Rb/K ratio throughout the core. The ratio remains close to 0.006 in most samples, but there is a dip in the clay and a peak in parts of the minerotrophic peat. It is interesting the Rb/K ratio almost is constant throughout the gyttja and even in the deepest peat sample. First then the Rb/K ratio increases and remains high for the rest of the minerotrophic peat.

According to the information above, one process that could alter the Rb/K ratio is weathering. If this is the case in parts of the minerotrophic peat, this could mean that the material in the minerotrophic peat has been weathered to a higher degree than other parts of the core. This idea is consistent with the observation that all alkali metals are depleted above all in the minerotrophic peat with respect to the titanium-zirconium content. Apparently, there is some change in the composition of the peat in its lower regions, since there are sharps shifts in this area for elements like titanium and zirconium in relation to the ash content too.

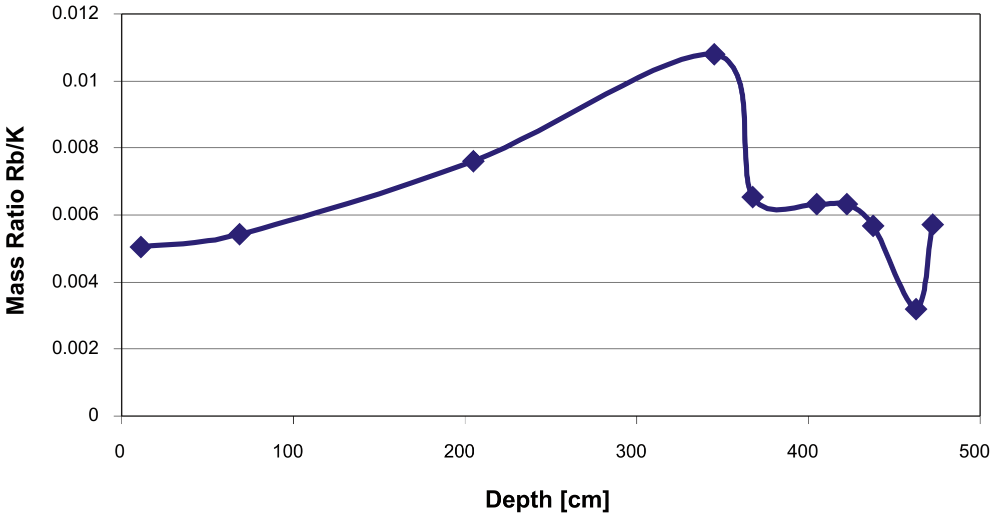


Figure 4-1. *Rb/K mass ratios throughout the core.*

4.1.2 Silicon

Other studies have shown high a relatively high correlation between silicon and ash, but this is clearly not the case in Klarebäcksmossen /Shotyk 1988/. It seems unavoidable to draw the conclusion the silicon has been leached from the peat, as all elements except for cerium and the alkali metals are enriched out of proportion with silicon in the transition from gyttja to peat.

There are two important types of silicon in peat: authigenic silicon and allogenic silicon. Authigenic silicon is formed by biological processes in the peat and is soluble. Allogenic silicon is not formed in the peat, but brought there from somewhere else. This could be different silicates and aluminosilicates. Quartz is an example of a highly insoluble silicate, while others are more soluble. /Shotyk 1988/.

Investigations of authigenic and allogenic silicon in peat lands have shown that insoluble, allogenic silicon tends to dominate in most cases /Shotyk 1988/. This could partly depend on leakage of the soluble, authigenic fraction. It is hard to tell what the proportions initially were in Klarebäcksmossen. The same differentiation between authigenic and allogenic silicon can probably be made in the gyttja, but there are no special reasons why the proportions would be similar. Moreover, the authigenic silicon in the gyttja may be different in terms of leachability and so may the conditions for silicon mobilisation. Hence, this does not provide many clues to why silicon was lost from the peat.

The concentration of silicon increases towards the bog surface. One reason could be that less authigenic silicon has been leached, but it has also been shown in other studies that the increase in silicon in surface peat is attributable to recent increases in wind-blown materials /Shotyk 1988/. This is not unlikely to be the case in Klarebäcksmossen too.

4.1.3 Alkaline Earth Metals

Judging from literature and the measurements in Klarebäcksmossen, the alkaline earth metals constitute a more disparate group that the alkali metals. Alkaline earth metals like calcium and magnesium are considered to be soluble and not capable of forming particularly stable organic complexes or bind strongly to organic matter /Shotyk 1988/. Thus, one would expect these elements to be lost from peat.

Despite the expected losses, calcium is one of the elements that are most strongly enriched in the peat in relation to the underlying gyttja. One factor that could enhance the enrichment in peat is that calcium and other alkaline earth metals by analogy with radium could be lost from the gyttja. This would increase the peat/gyttja ratio and make them seem more inclined to accumulate in peat. However, this cannot explain the whole enrichment.

Accumulation of calcium in minerotrophic peat has been also observed elsewhere /Steinmann and Shotyk 1997b/. They explained it as mobilisation of inorganic calcium from underlying sediments and subsequent fixation in peat. This explanation is consistent with the observations from Klarebäcksmossen, since there is so much calcium that it cannot be associated to anything else than organic matter. Furthermore, the enrichment of calcium seems to be connected to the presence of mineralised pore water, which often is enriched in calcium in relation to rainwater. The enrichment of calcium in the minerotrophic peat in relation to the ombrotrophic peat is consistent with other observations / Shotyk 1988/.

Ca/Mg ratios have sometimes been used to discriminate between ombrotrophic and minerotrophic peat, since considerably higher Ca/Mg ratios are expected in freshwater than in seawater. The Ca/Mg ratios for Klarebäcksmossen shown in Figure 4-2 confirm the validity of the separation between ombrotrophic and minerotrophic peat, although the spatial resolution of the measurements is too bad to follow the transition from minerotrophic to ombrotrophic conditions more closely. The Ca/Mg ratios in Klarebäcksmossen are, however, remarkably high in comparison with those presented in a review of the inorganic chemistry in peat lands /Shotyk 1988/.

Unlike the other alkaline earth metals, magnesium is not very strongly enriched in the minerotrophic peat. Instead in follows the titanium-zirconium content, which could imply that it mainly is found in the mineral fraction in the minerotrophic peat. Hence, it would be more mobile than the other alkaline metals. On the other hand, magnesium is the only alkaline earth metal that is clearly enriched in the ombrotrophic peat in relation to the minerotrophic peat. Magnesium could be favoured by the proximity to the Baltic Sea, since magnesium generally is more abundant in seawater than in soil water. However, both magnesium and calcium are important nutrients in plans so biological uptake is also a possibility /Greger 2004/.

Due to chemical similarities, other alkaline earths could also be influenced by bioaccumulation. The near-surface-enrichment of the alkaline earths has been reported to occur in the order Mg > Ba > Ca > Sr /Steinmann and Shotyk 1997b/, which supposedly should reflect the importance of biological uptake for the different metals. The concentrations in ombrotrophic peat are higher than in the gyttja for all alkaline earth metals, but it is hard to tell whether this mainly is due to bioaccumulation in the ombrotrophic peat or leakage in the gyttja. For Ra-226, for which the spatial resolution is better than for the other elements, no enrichment in the surface layers could be observed in the radiometric measurements where the spatial resolution of the samples was better. Unfortunately, the ash content was not measured for these samples so the statement that radium is not enriched in living moss is only valid in relation to the dry weight. Thus, the possibility that the biological uptake of radium is camouflaged by variations in the mineral content cannot be excluded.

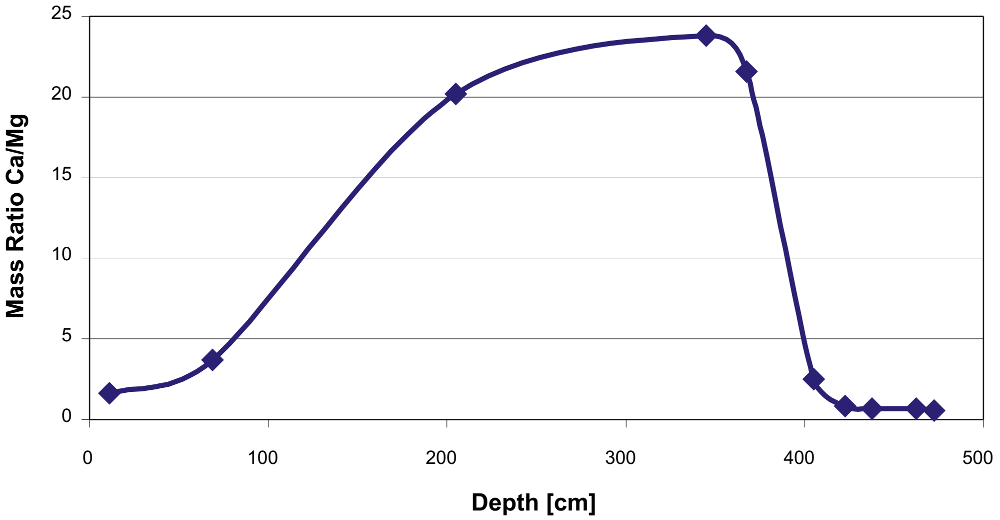


Figure 4-2. *Ca/Mg ratios throughout the core. High Ca/Mg ratios are characteristic for minerotrophic peat.*

However, other processes seem to dominate for all alkaline earth metals except magnesium. /Sjörs and Gunnarsson 2002/ write that peat substances tend to accumulate bivalent cations including Ca^{2+} and Mg^{2+}, whereas living cells tend to take up ions like K^+ and NH_4^+. The enrichment of strontium in peat is less than for calcium, but still substantial according to Figure 3-17. Strontium has been used to differentiate between present day ombrotrophic and minerotrophic peat in contrast to the botanical or original limit between ombrotrophic and minerotrophic conditions /Shotyk et al. 2001/. This supports the idea that the accumulation of strontium not mainly is connected to biological uptake by living moss, but rather to sorption of strontium by organic matter.

While calcium and strontium are strongly enriched in minerotrophic peat and magnesium hardly enriched at all, beryllium, barium and radium seem to be somewhere in between. Beryllium has been described as being similar to calcium and magnesium in terms of sorption /Greger 2004/. However, magnesium and calcium seem to behave quite differently in this environment. Barium has been geochemically associated to potassium, since they have similar ionic radii, but barium is divalent and not considered to be very mobile /Greger 2004/. The analyses from Klarebäcksmossen do not show any striking similarities between barium and potassium in peat. While barium is enriched in peat, potassium is depleted. Hence, it seems to have more in common with beryllium. Both elements are enriched in peat, although not to the same extent as calcium and strontium.

Radium often occurs as Ra^{2+} when dissolved in water, but the $RaSO_4$ complex may sometimes also be important in radium migration /Beneš 1982/. Radium is more strongly enriched in the lower parts of the minerotrophic peat than beryllium and barium, but it is not enriched in the upper parts of the minerotrophic peat. However, radioactive decay may significantly alter the distribution of radium in the profile. The upper layers of the minerotrophic peat are so old that large amounts of radium could have decayed by now. Given that the mobility of thorium seems to be much more modest than that of radium, one should not expect an excess of Th-230 that could produce Ra-226, but rather an initial excess of Ra-226. Until Ra-226 can be compared to Th-230 in the peat samples and role of radioactive decay be determined, it is advisable to consider radium to have the same capability to accumulate in peat as calcium and strontium.

4.1.4 Lanthanides, Lanthanum and Yttrium

The most stable oxidation state for the elements in the lanthanide series is + 3. Under natural conditions there are two exceptions: cerium, which may be oxidized to Ce^{4+}, and europium, which under reducing conditions may occur as Eu^{2+} /Krupka and Serne 2002/. The fact that europium in this profile is strongly correlated with the other lanthanides shows that the trivalent oxidation state, Eu^{3+}, has dominated during the development of Klarebäcksmossen. That makes sense, as the conditions hardly have been oxidizing at any stage. For cerium, on the other hand, it seems likely that the tetravalent state has played an important role.

The lanthanides are interesting not only because there are several important radionuclides from the lanthanide series in nuclear waste, but also because they often are used as geochemical analogues of some important artificial actinides in nuclear waste, e.g. americium and curium, which also occur as trivalent ions, Am^{3+} and Cm^{3+} /Krupka and Serne 2002/.

Judging from literature, yttrium, lanthanum and lanthanides are often rather immobile. For instance, lanthanides were considered as conservative reference elements by /Shotyk et al. 2001/ and compared to elements like titanium, zirconium, hafnium, yttrium and scandium. They also found that yttrium was well correlated with titanium and zirconium /Shotyk et al. 2001/ in the peat profile they investigated. In that context, the strong enrichment of yttrium and lanthanides in Klarebäcksmossen is remarkable. No similar enrichment has been encountered in published literature. On the other hand, lanthanide profiles in peat appear to be very rare.

The big differences between ombrotrophic and minerotrophic peat suggest that their abundance in the peat mainly is controlled by the groundwater. Hence, there must be some process that mobilises these elements and some chemical form that allow them to be transported and enriched in peat. Since lanthanum, yttrium and all lanthanides except cerium are almost perfectly correlated, it is unavoidable to draw the conclusion that they have been affected by the same processes. Therefore, the following discussion of europium is probably valid for all the other elements too.

In aqueous solution, europium may often occur as free ions in acidic environments, but it may also form various complexes. For instance, europium may form anionic or neutral carbonate complexes over a wide range of mainly alkaline pH values /Krupka and Serne 2002/. The presence of such complexes could greatly increase the mobility of europium in peat. This might possibly provide an explanation to the enrichment of lanthanides in Klarebäcksmossen, although binding to DOC is likely to be more important in these organic-rich environments.

It is also unclear how the lanthanides are accumulated in the peat. Generally europium is considered to be insoluble in environmental systems. The precipitation of $Eu(OH)_3$ is rapid and has been suggested to control the solubility of europium in slightly acidic and alkaline environments. Europium may also precipitate as $Eu_2(CO_3)_3 \cdot 2H_2O$, if the solution is not too acidic /Krupka and Serne 2002/. However, sorption to organic matter is probably the most likely mechanism here.

According to /Greger 2004/, the light lanthanides (Pr-Gd) are thought to be slightly more mobile than the heavy lanthanides (Tb-Lu). This can be used to test the hypothesis that lanthanides are transported to the peat. Figure 4-3 shows the average concentration for light and heavy lanthanides respectively based on the normalized concentrations in Figure 3-22 and Figure 3-23.

Figure 4-3 shows that the light lanthanides are more strongly enriched in the minerotrophic peat than the heavy lanthanides – at least when compared to the concentrations in the underlying gyttja. The curves have been normalized so that the average in the two deepest gyttja samples is unity in order to emphasise the differences between the light and the heavy lanthanides. Moreover, the gyttja is a likely source for the enrichment of lanthanides in the peat, which makes this normalisation sensible.

If the light lanthanides indeed are more mobile than heavy lanthanides, Figure 4-3 supports the hypothesis that the lanthanides have been enriched in the peat by transport from the gyttja. As one would expect, the more mobile lanthanides are enriched to a higher degree, and the differences increase with the distance from the source so that the biggest relative differences are found in the upper parts of the minerotrophic peat.

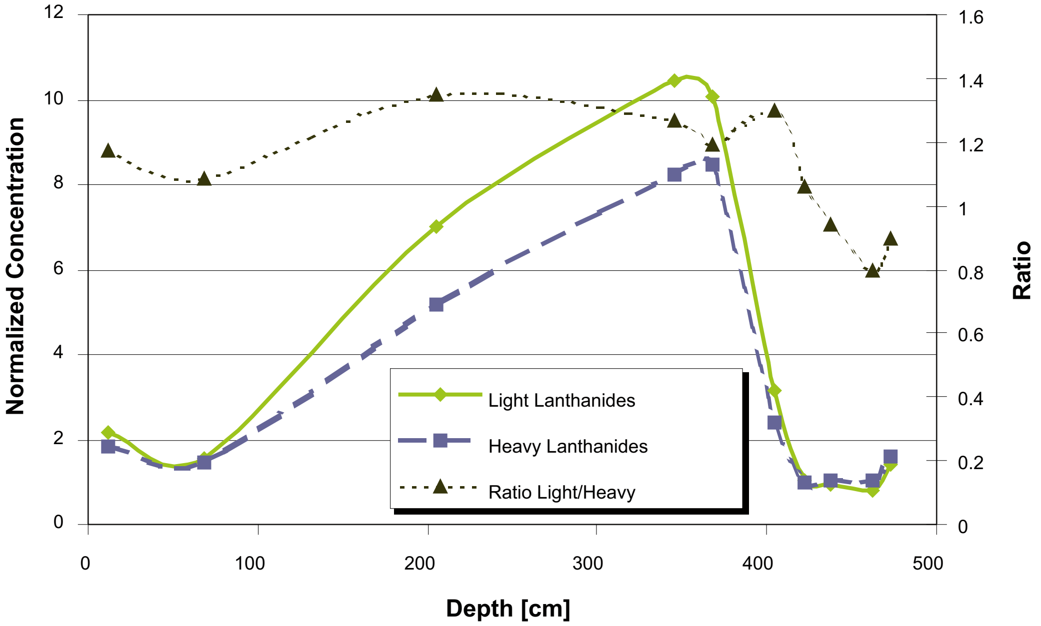


Figure 4-3. *Average normalised concentration for light and heavy lanthanides. The values have been normalized using the average content in the two deepest gyttja samples. The secondary axis shows the ratio between light and heavy lanthanides.*

If the lanthanides would have been enriched in the peat not by active transport to the peat, but by passive processes like weathering of other elements, one would expect the more immobile heavy lanthanides to be enriched with respect to the more mobile light lanthanides instead. However, this is not the case, which, again, points towards a significant mobility for lanthanides in peat.

Lanthanides are strongly excluded by plants, which suggests that biological uptake should be of little importance for these elements /Greger 2004/. This is consistent with the observations in Klarebäcksmossen, where groundwater advection appears to be the dominating transport process for lanthanides.

4.1.5 Cerium

As was mentioned earlier, cerium is different from other lanthanides, since it may occur as both Ce^{3+} and Ce^{4+} under natural conditions. Other studies of cerium in peat have shown that cerium often may be very well correlated with other lanthanides /Akagi et al. 2002, Shotyk et al. 2001/. Hence, it is very likely that the special redox chemistry of cerium has played an important role for the distribution of cerium in Klarebäcksmossen.

If would be tempting to suggest that Ce^{4+} is more mobile than Ce^{3+} in peat, since that would allow cerium to be leached from the peat, but according to /Akagi et al. 2002/ Ce^{4+} is less mobile than Ce^{3+}. Tetravalent cations are generally expected to be immobile, but yet other tetravalent cations such as Th^{4+} have managed to accumulate in the minerotrophic peat, while cerium is depleted. If Ce^{4+} is immobile, one would expect it to follow the mineral fraction.

One important factor for explaining the distribution of cerium could be possible accumulation in the gyttja. Figure 3-22 shows that there is a peak at the top of the gyttja, just before the transition to peat. This is an uncommon behaviour that cerium shares with zinc. Accumulation of cerium in the gyttja would lead to a lower ratio between minerotrophic peat and gyttja. However, this does not explain why even lower concentrations of cerium (1.6–7% of the average abundance in Earth's crust) are found in the ombrotrophic peat.

Hence, the situation is unclear for cerium. The overall pattern with depletion in both the ombrotrophic and minerotrophic peat could be interpreted as a sign of high mobility in peat. Unlike alkali metals, cerium is strongly excluded by plants so there would be no significant biological uptake /Greger 2004/. On the other, published literature claims that cerium is immobilized when oxidised to Ce^{4+}. The coming studies of cerium in other profiles will hopefully provide a better understanding of this element. In any case, this demonstrates that it is not advisable to use cerium as an analogue for trivalent transuranium elements.

4.1.6 Scandium

Scandium has been used as a conservative reference element in studies of peat cores /Shotyk et al. 2001/. This was justified by comparisons with other immobile elements such as titanium and zirconium.

Just like most lanthanides scandium only exists as trivalent ions. The geochemical properties of scandium have been described as mixture of aluminium and rare earth metals. Scandium forms insoluble oxides and hydroxides and is considered to be resistant to chemical weathering. /Shotyk et al. 2001/.

Given this description, the behaviour of scandium in Klarebäcksmossen is hard to explain. Judging from the observations in Klarebäcksmossen, scandium appears to have been transported and enriched in the minerotrophic peat out of proportion with titanium, zirconium and other lithogenic elements. Thus, it appears to be considerably mobile in peat, although not to the same extent as the lanthanides.

As for the lanthanides, the enrichment of scandium is limited to the minerotrophic peat, which suggests that scandium has been transported mainly by groundwater advection.

4.1.7 Titanium, Zirconium and Hafnium

Hafnium is though be geochemically similar to zirconium and occurs as Hf^{4+}. However, hafnium is much less abundant than zirconium. It mainly occurs in the same minerals as zirconium, where it may substitute for zirconium. Hence, a strong correlation is often observed between these elements. /Shotyk et al. 2001/.

The observations in Klarebäcksmossen, however, indicate that hafnium is somewhat more mobile than zirconium. The fact that hafnium has been able to migrate independently of zirconium suggests that there has been some weathering of the zirconium minerals. This may also be an explanation why zirconium does not agree very well with titanium.

4.1.8 Niobium and Tantalum

Niobium and tantalum are thought to resemble each other closely. According to /Greger 2004/ niobium easily forms complexes with organic matter, which makes it relatively mobile. The organic complexes of tantalum are less stable, and tantalum is also slightly less soluble than niobium. Hence, it should be somewhat less mobile. /Greger 2004/.

However, /Shotyk et al. 2001/ have mentioned tantalum together with elements such as titanium, zirconium and hafnium, which suggests that should be quite immobile. This does not agree very well with the description above.

A problem when interpreting these measurements is that similar patterns could be expected for both very immobile and very mobile elements. Immobile elements follow the mineral fraction, since they are immobile; mobile elements follow the mineral fraction, since they are leached from all other places. In this case, the concentrations of niobium and tantalum are somewhat low in comparison with the average abundance of these elements in Earth's crust, which suggests that they might have been leached. On the other hand, tantalum is one of the elements that follow the titanium-zirconium content most closely. The correlation is not limited to the peat as for the alkali metals.

Unfortunately, niobium was only detected in one peat sample, which makes it hard to draw any conclusions from the Nb/Ta ratios. Hopefully, coming studies can shed more light on these two elements. They are interesting not only because there are radionuclides like Nb-94 in nuclear waste, but also since they are among the few pentavalent elements that have been analysed.

4.1.9 Nickel, Vanadium, Chromium and Cobalt

Compounds of nickel are often highly insoluble and there is no redox chemistry for nickel in natural waters /Shotyk 1988/. Signs of post-depositional migration of nickel have, however, been reported from ombrotrophic peat in Finland
/Nieminen et al. 2002/.

Limited migration of nickel is also observed in Klarebäcksmossen, where it seems to have been enriched in the lower parts of the minerotrophic peat. However, comparison of nickel concentrations may be hazardous, since the abundance of nickel is very variable. For instance, basalt often contain as much as 150 ppp nickel, while granite generally contain 1 ppm /Shotyk 1988/.

However, nickel is also enriched out of proportion with the titanium-zirconium content in the second sample in the ombrotrophic peat (65–72.5 cm). Since nickel is a nutrient, biological uptake may be the explanation. The other possibility is anthropogenic emissions.

There is a paper by /Lantzy and Mackenzie 1979/, where the atmospheric interference factors for some elements have been estimated based on concentrations ombrotrophic peat. The atmospheric interference factor, AIF, is defined as

$$AIF(\%) = \frac{Total\ anthropogenic\ emissions}{Total\ natural\ emissions} \times 100 \qquad \text{Equation 4-1}$$

Although the anthropogenic emissions can be expected to vary in space and time, Table 4-1 should give some idea of what elements that can be expected to be enriched in the ombrotrophic peat due to atmospheric deposition.

Table 4-1. Anthropogenic deposition as percent of natural deposition /Lantzy and Mackenzie 1979/.

Element	AIF [%]	Element	AIF [%]	Element	AIF [%]
Pb	34,583	Cu	1,363	Mn	52
Hg	27,500	Sb	821	Fe	39
As	2,786	Ni	346	Ti	15
Zn	2,346	V	323	Al	15
Cd	1,897	Cr	161		

The five elements with the highest interference factors – lead, mercury, arsenic, zinc and cadmium – are all strongly enriched in the ombrotrophic peat in Klarebäcksmossen, although not necessarily in that order. It seems very likely that anthropogenic emissions are responsible for the high concentrations of these elements in the ombrotrophic peat.

According to Table 4-1 there could also be significant atmospheric input of nickel to Klarebäcksmossen. The highest concentrations are not found in the uppermost sample, however, which could indicate some redistribution of nickel or that the anthropogenic emissions of nickel are lower than suggested by Table 4-1. Anyway the mobility of nickel appears to be limited in peat.

Vanadium is said to be affected by anthropogenic emission to the same extent as nickel. In Klarebäcksmossen, however, vanadium follows the titanium-zirconium content very well in the ombrotrophic peat. There are no obvious signs of significant atmospheric deposition of vanadium.

Vanadium tends to form insoluble compounds and is generally expected to be immobile in peat. For instance, it is capable of forming hydroxides even at low pH values. Vanadium is redox sensitive in natural waters, however, which might affect its behaviour. /Shotyk 1988/.

In Klarebäcksmossen vanadium has clearly been accumulated in the lower parts of the peat, and the enrichment reaches higher in the minerotrophic peat than for nickel. This suggests that vanadium could be somewhat more mobile that nickel. However, is not enriched in the ombrotrophic peat as nickel is, but seems to follow the mineral fraction there. Hence, the distribution of vanadium seems to be controlled by the groundwater.

Chromium is expected to be immobile, but under highly oxidizing conditions it may be oxidized from the immobile Cr^{3+} to Cr^{6+}, which is more mobile and toxic /Shotyk 1988/. Possibly, this may contribute to an increased mobility of chromium, although the picture of chromium as an immobile element in peat is supported by the measurements in Klarebäcksmossen. Chromium follows the ash content and the titanium-zirconium content well, but there is slight tendency of chromium being accumulated throughout the minerotrophic peat.

Chromium is also clearly enriched in the surface sample, probably due to increased content of chromium in the atmospheric deposition according to Table 4-1. The general impression is, however, that chromium does not migrate much on its own in the peat, but follows the mineral content.

Cobalt mainly exists as Co^{2+} in natural waters, but Co^{3+} may occur under oxidising conditions. Its concentration in sediments and soil is thought to be controlled by adsorption and coprecipitation with manganese and iron oxides. The adsorption is generally thought to be moderate to high. /Krupka and Serne 2002/.

The measurements in Klarebäcksmossen indicate that cobalt clearly has been enriched in the peat and the uppermost gyttja sample, although not the same extent as iron or manganese. Just like iron there are small differences between minerotrophic and ombrotrophic peat, although cobalt has a significant peak in the second sample from the top. This suggests that cobalt might be associated with organic matter. Cobalt may also form strong complexes with organic ligands, which significantly increases the solubility of cobalt in aqueous solutions /Krupka and Serne 2002/. This could be the explanation to the enrichment that is observed in Klarebäcksmossen. However, given the half-life of the most important radioactive cobalt isotope, Co-60, is only 5.3 years, its mobility in peat is probably limited.

4.1.10 Uranium, Thorium, Copper, Lead and Zinc

As was discussed earlier, uranium occurs in two oxidation states in natural waters depending on the redox conditions, either as U^{4+} in reducing conditions or as U^{6+} in oxidizing conditions. This makes the mobility of uranium highly dependent on the redox conditions, as U^{6+} has been shown to be very mobile in comparison with U^{4+}. Because reducing conditions can be expected below the water table in peat land /Shotyk et al. 1989/, uranium can easily be accumulated in peat. For instance, wetlands have been described as efficient uranium filters by /Owen and Otton 1995/, who report very high enrichment factors between peat and uranium-bearing waters. They have found uranium concentrations as high as 3,000 ppm (dry weight), which corresponds to almost 37 Bq/g.

The combination of a mobile oxidation state, which allows extensive transport in both surface water and groundwater under oxidizing conditions, and an immobile oxidation state, which allows accumulation of large amounts of uranium under reducing conditions, makes uranium geochemically interesting. More thorough descriptions of the geochemistry of uranium are provided by, for example, /Zielinski and Meier 1988, Halbach et al. 1980/.

Thorium, on the other hand, only occurs as a tetravalent ion, Th^{4+}, in natural waters. Just like U^{4+} it is thought to be immobile, in both organic soils and clays. /Langmuir and Herman 1980/ have shown that the dissolved thorium in natural waters almost invariably exists as complexes, but that the concentrations rarely exceed 1 ppb. The concentration is probably not limited by solution equilibrium, but rather by the paucity and slow solution rate of thorium-bearing minerals. In natural sediments thorium is concentrated "largely either in detrital resistate […] or absorbed onto natural colloidal-sized materials" /Langmuir and Herman 1980/. Hence, it appears as if colloids may play an important role in the transport of thorium. The low mobility of thorium is consistent with several other studies, for instance /Bonotto 1998/. Data reported by /Read et al. 1993/ also indicate that there has been little thorium mobilisation in the peat-rich soils in their study.

However, in Klarebäcksmossen thorium has clearly been enriched out of proportion with titanium and zirconium, which implies that it most likely has migrated. The enrichment is limited to the minerotrophic peat, more specifically to its lower regions, so it is likely that thorium has been transported from the gyttja. In that case, colloids might have played an important role.

Thorium appears to have been accumulated in the peat to a larger extent than uranium in Figure 3-17, but as was commented earlier, this is probably due to accumulation of uranium in the underlying gyttja. The impression from the measurements in Klarebäcksmossen is that uranium is more mobile than thorium. This is also consistent with published literature.

Copper has a high affinity for organic matter and may form very strong organic complexes. Hence, copper is often enriched in peat. It may also form highly insoluble compounds with sulphides, which could contribute to its enrichment. /Shotyk 1988/.

Since copper is so easily accumulated in peat, it has been intensively studied. As much as 10% copper on a dry-weight basis has been encountered. However, no copper minerals were found in those samples, which indicates that copper mainly is associated to organic matter. /Shotyk 1988/.

Enrichment of copper has sometimes been observed in the surface samples, but sometimes not. Although copper is bioessential, it is more likely that the surface enrichment is caused by anthropogenic emissions (see Table 4-1). In Klarebäcksmossen no enrichment is observed in the surface sample, but some 70 cm below the surface, which suggests that the distribution of copper is not entirely controlled by groundwater movements. Anyhow, the strong enrichment of copper in the peat that is found in Klarebäcksmossen is consistent with other studies.

Despite the fact that zinc does not have any redox chemistry in natural waters, it is still a complicated element. It is infamous for its capricious behaviour in peat /Shotyk 1988/. Zinc has been described as fairly mobile by /Nieminen et al. 2002/, who studied two Finnish bogs. Zinc has also often been observed to accumulate in peat, and it is thought to have a high affinity for organic matter. For instance, zinc was reported to be enriched in peat ash by a factor of two in an investigation of 35 peat lands in Canada /Shotyk et al. 1992/, but then the concentrations were compared to the average crustal abundance. In cases where accumulation of zinc has been observed, contact with mineralised groundwater seems to be the explanation to the enrichment.

In Klarebäcksmossen, however, zinc appears to follow the titanium-zirconium content quite well – the major deviation being the enrichment near the surface. Such enrichment of zinc at the surface has been observed elsewhere /Shotyk et al. 1992/, and Table 4-1 suggests that the reason is anthropogenic emission. Hence, there are few signs of extensive migration or accumulation of zinc in Klarebäcksmossen. However, there has evidently been some accumulation of zinc in the upper regions of the gyttja, which explains the apparent depletion of zinc in the minerotrophic peat.

Lead is the element that shows the biggest differences between ombrotrophic and minerotrophic peat. This is probably entirely due to anthropogenic emissions and agrees well with observations elsewhere /Shotyk 1988/. The fact that enhanced concentrations of lead only are found in the ombrotrophic peat suggests that lead is not very mobile in peat. In the parts of the peat that have not been affected by anthropogenic emissions lead seems to follow the titanium-zirconium content. For instance, Figure 3-17 shows that there only are minor differences between the content in the peat and the underlying sediments.

However, there are observations indicating that lead is more mobile in the near-surface zone in peat profile. The vertical distribution of lead near the surface and the enrichment of Pb-210 in hollows in relation to hummocks indicate that redistribution of lead in peat may occur /Shotyk 1988/. This is mainly alarming for Pb-210 dating as downward migration of Pb-210 would lead to an underestimation of the age of the peat layers.

Lead may precipitate as $PbCO_3$ for pH values above approximately 7, but in less alkaline environments like Klarebäcksmossen it may be mobilised as Pb^{2+}. In peat, however, complexation with organic matter is probably the most important mechanism, although there are indications that lead sometimes is unexpectedly mobile in peat. /Shotyk 1988/.

/Shotyk et al. 1992/ have discussed how uranium, copper, zinc and lead are transported and accumulated in peat. They have proposed that the dominating process behind the enrichment of uranium and copper in peat is precipitation of inorganic solids rather than sorption to organic matter. They argue that if organic processes alone were responsible for the enrichment of metals like uranium, copper, lead and zinc, the order of relative enrichment should follow the order of cation selectivity, which is $UO_2^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+}$. Since lead and zinc were not enriched in the peat samples they investigated, they think that processes such as ion exchange and surface complexation by organic matter do not control the behaviour of these metals in peat. /Shotyk et al. 1992/.

Instead they argue that the redox potential of the pore water is the factor that may explain the behaviour of these elements. Their predominance area diagrams indicate that uranium and copper mainly occur as solid species in reducing solutions in pH from strongly acidic to alkaline, whereas lead and zinc do not form solids until the pH is approximately 7. This would then explain why enrichment of lead and zinc “almost always” is limited to alkaline fens in areas of lead and zinc bedrock mineralization. /Shotyk et al. 1992/.

4.1.11 Aluminium and Gallium

Aluminium is not expected to be very soluble, and it has been shown to be relatively immobile in peat in other studies. Just like scandium and most lanthanides it only occurs in the trivalent oxidation state. However, some leakage of aluminium has been reported from ombrotrophic peat. /Steinmann and Shotyk 1997b/.

Gallium is considered to have similar geochemical properties as aluminium /Shotyk et al. 2001/. As regards the enrichment in minerotrophic peat in relation to gyttja, aluminium and gallium are indeed very similar. A major difference is, however, the fact that aluminium, unlike gallium, is not enriched in the ombrotrophic peat.

According to /Greger 2004/, there is a selective uptake of gallium by plants, causing higher Ga/Al ratios in plants than in soils. This might be the explanation why the concentration of gallium does not decrease as much in transition between minerotrophic and ombrotrophic peat.

Aluminium is said to be enriched relative to scandium during chemical weathering /Shotyk et al. 2001/. However, scandium is enriched in the minerotrophic peat relative to aluminium, which is yet another indication that weathering is not the explanation to the enrichment of scandium in the minerotrophic peat.

4.1.12 Iron and Manganese

Iron and manganese are both thought to be strongly affected by redox processes. Precipitation is favoured by oxidizing conditions and increasing alkalinity, while mobilisation is favoured by reducing conditions and increasing acidity. Hence, one might expect both iron and manganese to be leached from peat. Considerable depletion of iron and manganese has also been reported from an investigation of 35 Canadian peat profiles /Shotyk 1992/.

In Klarebäcksmossen, however, there are no signs that iron and manganese have been lost from the peat. On the contrary, both elements have been enriched in the peat in comparison with the underlying sediments. Possibly, manganese and iron may appear to be enriched in the peat due to leakage from the underlying gyttja.

However, both iron and manganese show the highest concentrations at the bottom of the peat with successively decreasing levels towards the surface, which suggests that there has been transport from the gyttja to the peat. Manganese decreases faster than iron and reaches the same concentrations as in the gyttja in the ombrotrophic peat and the upper parts of the minerotrophic peat, while the concentration of iron remains high throughout the peat.

Enrichment of iron in minerotrophic peat has also been observed elsewhere and explained as release of inorganically bound iron from underlying sediments to the pore water and subsequent fixation in peat /Steinmann and Shotyk 1997b/.

/Steinmann and Shotyk 1997a/ have investigated the occurrence of iron in peat and pore water. According to them, the formation of iron sulphide, iron carbonate and iron phosphate is not possible in ombrotrophic peat, while it may occur in minerotrophic peat under special conditions. Hence, it appears as if precipitation does not control the concentration iron in the pore water and, accordingly, not the mobility of iron in ombrotrophic peat. Since iron has been reported to from very stable complexes with organic ligands, this may be a more plausible mechanism. That would also explain why iron is not leached from the peat. /Steinmann and Shotyk 1997a/.

4.1.13 Arsenic and Antimony

Antimony occurs as Sb^{3+} or Sb^{5+} under natural conditions. It is considered to be comparatively mobile, less under reducing conditions, however, than under oxidizing conditions. According to /Krupka and Serne 2002/ the concentration of antimony in pore water is controlled by adsorption, but there are several factors that counteract adsorption. Their thermodynamic calculations of antimony complexation also indicate that antimony should be mobile. /Krupka and Serne 2002/.

This is consistent with the antimony profile from Klarebäcksmossen. Apparently, anthropogenic emission has caused high concentrations of antimony in the near-surface region (see Table 4-1). An investigation of a peat core from Switzerland has shown that the emissions of arsenic and antimony increased dramatically in the late 19th and early 20th century /Shotyk et al. 1996/. That is probably fairly representative for southern Sweden too. The fact that the atmospherically deposited antimony appears to have reached as deep down in the profile as at least 2 m indicates a fairly high mobility.

4.1.14 Sulphur

Along with nitrogen and phosphorus, sulphur is thought to be a growth-limiting nutrient in bogs according to /Steinmann and Shotyk 1997a/. They refer to several studies showing that organic forms of sulphur account for most of the sulphur in freshwater peat lands. Likewise, analyses of sulphur in pore water from a bog have shown that most dissolved sulphur (90–99%) occurs in an organic form /Steinmann and Shotyk 1997a/. These observations seem to agree well with the situation in Klarebäcksmossen, where sulphur is strongly enriched in the peat.

Since most of the sulphur probably is present in organic forms, less sulphur is available for precipitation with various metals in the pore water. In marine sediments, precipitation of iron sulphides is a major sink for both iron and sulphur, but according to /Steinmann and Shotyk 1997a/, this is not possible in bogs due to low availability of sulphate and iron.

Unlike some other sampling sites in the Simpevarp area, no smell of H_2S was encountered during the sampling in Klarebäcksmossen /Nilsson 2004/.

4.1.15 Halogens

I-129 has been identified as one of the most critical radionuclides in nuclear waste, but unfortunately iodine was below detection limit in all samples. Chlorine and bromine could be measured, however, and Cl-36 is also an important radionuclide in nuclear waste.

The profiles for chlorine and bromine are not complete, but it can be concluded that they both are strongly enriched in the peat, whereas as the abundance of at least bromine in the gyttja corresponds to the average concentrations in Earth's crust. This is consistent with other studies of halogens in peat /Biester et al. 2006/. Based on their study it seems as if bromine is a better analogue for iodine than chlorine. Iodine and bromine seem to be more strongly related to the organic fraction in the pore water, whereas chlorine mainly occurs as free ions. This reflects the fact that the release of iodine and bromine from peat is more closely related to the decomposition of the peat. However, iodine was found in organic forms to an even larger extent than bromine. /Biester et al. 2006/.

According to /Biester et al. 2006/ the advection and diffusion of halogens are generally low, since there are sharp gradients in the halogen concentrations in pore water. Hence, they suggest that the halogen concentrations in the pore water predominately reflect the release from the peat.

4.2 Conclusions

4.2.1 Summary

The discussion of the elemental distribution in Klarebäcksmossen has shown that the results from these analyses in most cases are consistent with results from published literature, although there important differences too. One should be careful not to draw too far-reaching conclusions from a study like this. After all it only represents a single core form a single bog. Hence, much more work is needed to achieve reliable and general results concerning radionuclide transports in peat lands. Nevertheless, this first attempt to describe the behaviour of various elements in a mire in the Simpevarp area may prove useful in coming studies of other profiles.

As it seems, Figure 3-17 is a good summary of the analyses in Klarebäcksmossen in most aspects. The vertical axis gives a picture of tendency to accumulate in peat as compared to gyttja for various elements, while the horizontal axis provides some information on what the important processes may be. Being a generalization, there are, however, elements whose behaviour is not fairly described in the graph.

Some general conclusions that are worth noticing are the following:

- Alkali metals are thought to be highly mobile and leached from the peat along with silicon.
- All alkaline earth metals except magnesium are enriched in peat. The enrichment is strongest for calcium, strontium and possibly radium.
- Lead, cadmium, zinc, arsenic, antimony and mercury are enriched in the near-surface zone due to anthropogenic emissions.
- Lanthanides, yttrium and lanthanum are very well correlated to one another and strongly enriched in minerotrophic peat by groundwater advection.
- Manganese, uranium, vanadium, scandium, thorium and aluminium are also enriched mainly by groundwater advection.
- Copper, molybdenum, iron, gallium, nickel and cobalt are more or less enriched in the peat, but probably not only by groundwater advection. Bioaccumulation, atmospheric deposition or extensive leakage from the peat are may contribute.
- Above all titanium and zirconium, but also hafnium, chromium and – probably – tantalum are thought to be rather, but not completely, immobile in peat.
- The distribution of sulphur, nitrogen, phosphorus and halogens is thought to be strongly affected by biological processes.
- For many elements, the sediments constitute a likely source for the accumulation in the minerotrophic peat
- Significant differences are observed between ombrotrophic and minerotrophic peat.

Although it has been possible to identify the most important transport mechanisms in some cases, this study does not contribute to a better understanding of how the transport and accumulation takes place, i.e. what chemical processes that are involved. This may be key factors, when trying to predict the behaviour of various elements under various conditions. A likely mechanism behind much of the accumulation in peat is binding to organic matter. This implies that the affinity for organic matter would be a key property for controlling to what extent different elements are accumulated in mires. Binding to dissolved organic carbon may also increase the mobility of otherwise immobile elements substantially so that they can be transported longer distances.

4.2.2 Implications for the Safety Assessment

Measurements in Klarebäcksmossen and elsewhere have shown that there are significant differences between minerotrophic and ombrotrophic peat. Most elements are only or mainly enriched in minerotrophic peat. This emphasises the role of groundwater advection for the transport of radio-nuclides in wetlands. Since radionuclides released from a deep repository will not reach the peat from the atmosphere, it seems clear that the risks for accumulation in peat for most elements are limited to fens. For hydrological reasons, they will never reach the ombrotrophic peat in a bog. However, some elements seem to be affected by biological uptake to a large extent, which could lead to significant accumulation in ombrotrophic peat too.

This study has strengthened the suspicions that mires may be critical ecosystems for radionuclide accumulation. Most elements are at least to some extent enriched in peat in relation to more immobile elements like titanium and zirconium. The two most critical radionuclides, I-129 and Ra-226, both represent elements that potentially could be enriched in peat. Since the role of radioactive decay and production could not be fully evaluated for Ra-226, it most be considered as potentially capable of accumulation at the same level as calcium and strontium. Iodine was below detection limit, but by analogy with chlorine and bromine it could be expected to accumulate in high concentrations in peat. Hence, there are good reasons to continue the investigations on radionuclide behaviour during peat land formation and development.

Earlier SKB studies of radionuclide accumulation in mires have been based on ecosystem modelling. The measurements in Klarebäcksmossen indicate that the distribution coefficients compiled by /Karlsson and Bergström 2002/ that were used in the biosphere models in SR 97 and SAFE do not describe the actual behaviour of various elements during the development of a mire very well. Apparently, it is hard to make comparisons, but it seems reasonable to expect some kind of relationship between the distribution between peat and pore water, on one hand, and the actual degree of accumulation that is observed in the peat, on the other hand.

Figure 4-4 shows the distribution coefficients for organic soil that were used in SR 97 and SAFE versus the observed enrichment in the minerotrophic peat in relation to the underlying gyttja.

Figure 4-4 does not show any clear relationship between the actual distribution of elements in the peat profile and the distribution coefficients that have been used for organic soils. However, some elements coincide very well: samarium-holmium, nickel-cobalt and europium-cadmium respectively.

In order to get a high accumulation in peat an element must not be too easily leached. Generally, one would expect that from elements to the left in Figure 4-4. However if an element binds too strongly to peat, it will not be able to migrate very long distances. In that case, one might expect that the accumulation is limited to the edges of the mire. The highest degree of accumulation could be expected for elements that can be highly mobile under certain conditions, but immobilised in peat. Uranium is an example of an element with such properties.

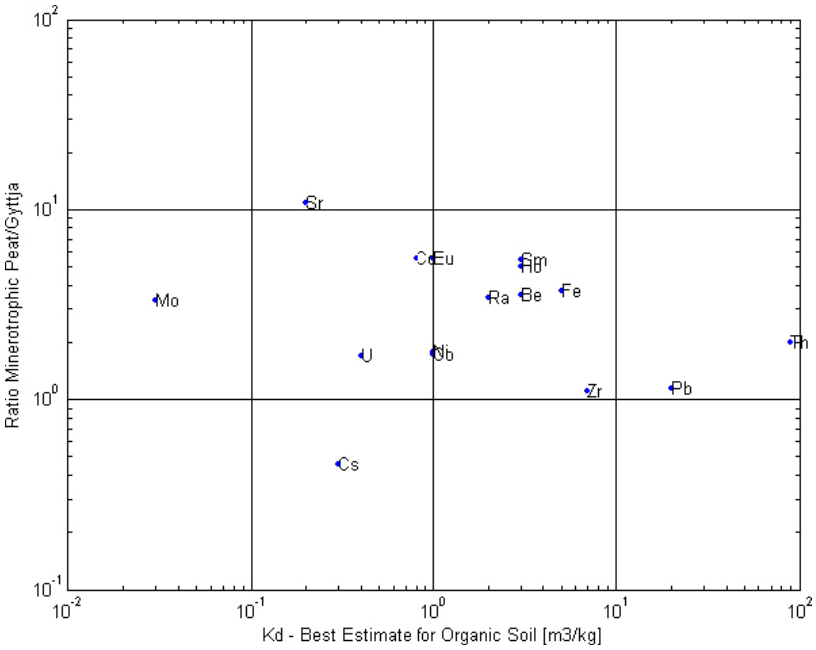


***Figure 4-4.** Comparison of the enrichment in peat and the distribution coefficients for organic soil used in safety assessments SR 97 and SAFE.*

The most mobile elements, judging from distribution coefficients, are found to the left and the most immobile to the right. Apparently, there is little correlation between distribution coefficients and the distribution between gyttja and peat in this sense. Most remarkable is probably the big difference between caesium and strontium, where the distribution coefficients completely fail in predicting the contrasting behaviour of these two elements. According to the distribution coefficients, strontium is somewhat more mobile than caesium. Yet strontium has apparently been accumulated in the peat, while caesium has been depleted in the peat. Thorium, on the other hand, has a very high distribution coefficient, but yet it is enriched almost to the same degree as molybdenum, which has the lowest distribution coefficient among the elements in Figure 4-4.

As there is a lack of data for many of the lanthanides, distribution coefficients from the same group in the periodic table has sometimes been used for organic soil. For instance, the distribution coefficient for neptunium has been used for promethium, since they belong to the same group. Judging from the observations in Klarebäcksmossen, it could be wiser to represent promethium by some other lanthanide, for which there are available distribution coefficients.

In the safety assessments SR 97 and SAFE distribution coefficients for cerium have been used to represent several other lanthanides in both brackish water and organic soil, since the values for cerium are reported to be the highest /Karlsson and Bergström 2002/. Based on these observations it does not seem very wise to use cerium to represent the other lanthanides – at least in mire models.

A problem with distribution coefficients is that the uncertainty intervals often are very wide. It would probably be possible to create a reasonable relationship in Figure 4-4 by changing the distribution coefficients within the uncertainty intervals. However, it is not clear what importance sorption-desorption processes have for the distribution of various elements in peat. To a large extent it remains unclear how the various elements are transported and accumulated, although organic matter is likely to play an important role for many elements. Since all processes like cation exchange, organic and inorganic complexation, precipitataion and so forth vary with the chemical conditions it may be very hard to predict the behaviour of an element using only one parameter. Moreover, elements may not only be transported in solution. It is likely that many elements are bound to dissolved organic carbon (DOC), since high DOC concentrations should be expected in mires.

No measurements of the chemical composition of the pore water were performed in this project, but that would probably shed some light on these questions. However, a comparison between the concentration in peat and pore water respectively has been made for ombrotrophic peat samples from the Jura Mountains in Switzerland /Steinmann and Shotyk 1997b/. The affinity for peat, which should correspond to the distribution coefficient, was approximately in the following order:

Al > Mn > Ba > Si > P > S > Br > Ca > Zn > K > Cl > Na

Both magnesium and iron had rather wide ranges, but they should be found somewhere between phosphorus and zinc.

If this order is assumed to be representative for Klarebäcksmossen, we see that sodium and potassium have a low affinity for peat. This is consistent with the observation that they seem to be leached from the peat. Chlorine, however, most likely strongly enriched in peat, probably by biological processes. Calcium that also is strongly enriched in peat does not have a particularly high affinity for peat. Silicon, which has been lost from the peat, appears to be more readily fixed in peat.

On the left-hand side we find aluminium that has the highest affinity for peat. This seems consistent with the observations from Klarebäcksmossen, but manganese seems to be less soluble than barium, although it is enriched in the peat to a higher degree.

If this order indeed is representative for Klarebäcksmossen, it implies that the affinity for peat not is the only factor controlling the actual enrichment that is observed in the peat. There may be several explanations to this phenomenon, but more careful analyses are undoubtedly needed in order to understand what goes on. However, it indicates that distribution coefficients may not be ideal for predicting radionuclide accumulation in peat. Future studies can hopefully provide a better understanding for elemental transport in peat, which then could be used to predict the behaviour of various radionuclides during the evolution of a wetland.

5 References

Akagi T, Feng-Fu F, Yabuki S, 2002. Absence of Ce anomaly in the REE patterns of peat moss and peat grass in the Ozegahara peatland *Geochemical Journal,* Vol. 36, pp. 113–118.

Bateman H, 1910. Solution of a system of differential equations occurring in the theory of radioactive transformations, Proc. Cambridge Philos. Soc. 15, pp 423–427.

Beneš P, 1982. Physico-Chemical Forms and Migration in Continental Waters of Radium from Uranium Mining and Milling *Environmental migration of long-lived radionuclides*, IAEA, Vienna, pp. 3–25.

Benoit J M, Torgersen T, O'Donell J, 1991. An advection/diffusion model for Rn-222 transport in near-shore sediments inhabited by sedentary polychaetes *Earth and Planetary Science Letters,* 105 pp. 463–473.

Biester H, Selimovič D, Hemmerich S, Petri M, 2006. Halogens in pore water of peat bogs – the role of peat decomposition and dissolved organic matter *Biogeosciences,* 3, pp. 53–64.

Bonatti E, Fisher D E, Joensuu O, Rydell H S, 1970. Postdepositional mobility of some transition elements, phosphorus, uranium and thorium in deep sea sediments *Geochimica et Cosmochimica Acta,* Vol. 35, pp 189–201.

Bonotto D M, 1998. Implications of groundwater weathered profile interactions to the mobilization of radionuclides *Journal of South American Earth Science,* Vol. 11, No. 4, pp. 389–405.

Bourdon B, Henderson G M, Lundstrom C C, Turner S P, (eds) 2003. *Uranium-Series Geochemistry* Mineralogical Society of America Reviews in Mineralogy and Geochemistry, Vol. 52.

Brunberg A, Blomqvist P, 1999. *Charachteristics and ontogeny of oligotrophic hardwater lakes in the Forsmark area, central Sweden*, SKB R-99-68, Svensk Kärnbränslehantering AB.

Brunberg A, 2005. Private communication, 12/12/2005.

Chapman N, McCombie C, 2003. *Principles and Standards for the Disposal of Long-Lived Radioactive Wastes,* Pergamon, The Netherlands.

Culbert R R, Leighton D G, 1981. Low energy gamma spectrometry in the geochemical exploration for uranium *Journal of Geochemical Exploration,* 14 pp. 49–68.

El-Daoushy F, Tolonen K, Rosenberg R, 1982. Lead 210 and moss-increment dating of two Finnish *Sphagnum* hummocks *Nature*, Vol. 296, No. 5856, pp. 429–431.

Etiope G, Martinelli G, 2002. Migration of carrier and trace gases in the geosphere: an overview *Physics of the Earth and Planetary Interiors* 129 pp. 185–204.

Franzén L, 1985. *Peat in Sweden*, Department of Physical Geography, University of Gothenburg, Gothenburg.

Frontasyeva M V, Steinnes E, 2004. *Distribution of 35 elements in peat cores from ombrotrophic bogs studied by epithermal neutron activation analysis*, Izdat'elskij otdel Objed'in'onnogo instituta jadernych issl'edovanij, Dubna, 2004.

Geibert W, Usbeck R, 2004. Adsorption of thorium and protactinium onto different particle types: Experimental findings *Geochimica et Cosmochimica Acta,* Vol. 68, No. 7, pp. 1489–1501.

Greger M, 2004. *Uptake of nuclides by plants,* SKB TR-04-14, Svensk Kärnbränslehantering AB.

Halbach P, von Borstel D, Gundermann K D, 1980. The Uptake of Uranium by Organic Substances in a Peat Bog Environment on a Granitic Bedrock *Chemical Geology,* 29 pp. 117–138.

IAEA, 1985. *Sediment K_ds and Concentration Factors for Radionuclides in the Marine Environment* International Atomic Energy Agency, Vienna.

IAEA, 1994. *Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Temperate Environments* International Atomic Energy Agency, Vienna.

Ivanovich M, Alexander J, 1987. Application of uranium-series disequilibrium to studies of groundwater mixing in the Harwell region, U.K. *Chemical Geology (Isotope Geoscience Section),* 66 pp. 279–291.

Kadko D, 1980. Th-230, Ra-226 and Rn-222 in Abyssal Sediments *Earth and Planetary Science Letters,* 49 pp. 360–380.

Karlsson S, Bergström U, Meili M, 2001. *Models for dose assessment: Models adapted to the SFR-area, Sweden,* SKB TR-01-04, Svensk Kärnbränslehantering AB.

Karlsson S, Bergström U, 2002. *Nuclide documentation: Element specific parameter values used in the biosphere models of the safety assessments SR 97 and SAFE*, SKB R-02-28 Svensk Kärnbränslehantering AB.

Kellner E, 2003. *Wetlands – different types, their properties and functions*, SKB TR-04-08, Svensk Kärnbränslehantering AB.

Kellner E, 2007. *Effects of variations in hydraulic conductivity and flow conditions on groundwater flows and transports in peatlands,* SKB R-07-41, Svensk Kärnbränslehantering AB.

Koide M, Goldberg E D, 1963. Uranium-234/Uranium-238 Ratios in Sea Water *Progress in Oceanography* Vol. 3, pp. 173–177.

Krupka K M, Serne R J, 2002. *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Sediments,* Pacific Northwest National Laboratory, Richland, Washington.

Laboratoire national de Henri Becquerel, 2004. http://laraweb.free.fr (2004-12).

Landström O, Sundblad B, 1986. *Migration of Thorium, Uranium, Radium and Cs-137 in till Soils and their Uptake in Organic Matter and Peat,* SKB TR 86-24, Svensk Kärnbränslehantering AB.

Langmuir D, Herman J S, 1980. The mobility of thorium in natural waters at low temperatures *Geochimica et Cosmochimica Acta* Vol. 44, pp 1753–1766.

Lantzy R J, Mackenzie F T, 1979. Atmospheric trace metals: global cycles and assessment of man's impact *Geochimica et Cosmochimica Acta* 43, pp. 511–525.

Larsson-McCann S, Karlsson A, Nord M, Sjögren J, Johansson L, Ivarsson M, Kindell S, 2002. *Meteorological, hydrological and oceanological information and data for the site investigation program in the community of Oskarshamn*, SKB TR-02-02, Svensk Kärnbränslehantering AB.

Lidman F, 2005. *Isotopic Disequilibrium for Assessment of Radionuclide Transport in Peat Lands,* M. Sc. Thesis Work at the Department of Physics, Uppsala University, Uppsala.

Lindgren M, Lindström F, 1999. SR 97: *Radionuclide transport calculations*, SKB TR-99-23 Svensk Kärnbränslehantering AB.

Lundin L, 1993. *Hydrologiska och hydrokemiska effekter av torvtäkt* Rapport torv-94/1, NUTEK, Stockholm.

Nieminen T M, Ukonmaanaho L, Shotyk W, 2002. Enrichment of Cu, Ni, Zn, Pb and As in an ombrotrophic peat bog near a Cu-Ni smelter in Southeast Finland *The Science of the Total Environment,* Vol. 292, pp. 81–89.

Nilsson G, 2004. *Oskarshamn site investigation – Investigation of sediments, peat lands and wetlands*, SKB P-04-273, Svensk Kärnbränslehantering AB.

Nilsson G, 2005. Private communication, February 2005.

Osmond J K, Cowart J B, Ivanovich M, 1983. Uranium Isotopic Disequilibrium in Ground Water as an Indicator of Anomalies *Int. J. Appl. Radiat. Isot.* Vol. 34, No. 1 pp. 283–308.

Owen D E, Otton J K, 1995. *Ecological Engineering* 5 pp. 77–93.

Plater A J, Ivanovich M, Dugdale R E, 1992. Uranium series disequilibrium in river sediments and waters: the significance of anomalous activity ratios *Applied Geochemistry,* Vol. 7, pp. 101–110.

Read D, Bennett D G, Hooker P J, Ivanovich M, Longworth G, Milodowski A E, Noy D J, 1993. The migration of uranium into peat-rich soils at Broubster, Caithness, Scotland, U.K. *Journal of Contaminant Hydrology,* 13 pp. 291–308.

Scott M R, 1968. Thorium and Uranium Concentrations and Isotope Ratios in River Sediments *Earth and Planetary Science Letters* 4 pp. 245–252.

Shotyk S, 1988. Review of the Inorganic Geochemistry of Peats and Peatland Waters *Earth-Science Reviews,* 25, pp. 95–176.

Shotyk W, Nesbitt H W, Fyfe W S, 1989. The behaviour of major and trace elements in complete vertical peat profiles from three *Sphagnum* bogs *International Journal of Coal Geology,* 15 pp. 163–190.

Shotyk W, Nessbitt H W, Fyfe W S, 1992. Natural and anthropogenic enrichments of trace metals in peat profiles *International Journal of Coal Geology,* 20, pp. 49–84.

Shotyk W, Cheburkin A K, Appleby P G, Fankhauser A, Kramers J D, 1996. Two thousand years of atmospheric arsenic antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland *Earth and Planetary Science Letters,* Vol. 145, E1–E7.

Shotyk W, Weiss D, Kramers J D, Frei R, Cheburkin A K, Gloor M, Reese S, 2001. Geochemistry of the peat bog Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ^{14}C yr BP *Geochimica et Cosmochimica Acta,* Vol. 65, No. 14, pp. 2337–2360.

Sjörs H, Gunnarsson U, 2002. Calcium and pH in north and central Swedish mire waters *Journal of Ecology,* 90, pp. 650–657.

SKB, 1999. *SR 97 – Post-closure safety*, SKB TR-99-06, Svensk Kärnbränslehantering AB.

SKB, 2004. *Fud-program 2004,* Svensk Kärnbränslehantering AB.

Snäll S, Liljefors T, 2000. Leachability of major elements from minerals in strong acids *Journal of Geochemical Exploration* 71, pp. 1–12.

Sonesten L, 2005. *Chemical Characteristics of Surface Waters in the Forsmark Area,* SKB R-05-41, Svensk Kärnbränslehantering AB.

Steinmann P, Shotyk W, 1997a. Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two *Sphagnum* bogs, Jura Mountains, Switzerland *Geochimica et Cosmochimica Acta,* Vol. 61, No. 6, pp. 1143–1163.

Steinmann P, Shotyk W, 1997b. Geochemistry, mineralogy, and geochemical mass balance on major elements in two peat bog profiles (Jura Mountains, Switzerland) *Chemical Geology,* Vol. 138, pp. 25–53.

Suksi J, 2005. *Natural Uranium as a Tracer in Radionuclide Geosphere Transport Studies,* Doctoral thesis, ethesis.helsinki.fi/julkaisut/mat/kemia/vk/suksi/naturalu.pdf (2005-02-01).

Tröjbom M, Söderbäck B, 2006a. *Chemical characteristics of surface systems in the Forsmark area. Visualisation and statistical evaluation of data from shallow groundwater, precipitation, and regolith,* SKB R-06-19, Svensk Kärnbränslehantering AB.

Tröjbom M, Söderbäck B, 2006b. *Chemical characteristics of surface systems in the Simpevarp area. Visualisation and statistical evaluation of data from surface water, precipitation, shallow groundwater, and regolith*, SKB R-06-18, Svensk Kärnbränslehantering AB.

Turetsky M R, Manning S W, Wider R K, 2004. *Dating recent peat deposits* Wetlands vol. 24 No.2 June 2004 pp. 324–356.

Vikström M, Gustavsson L G, 2006. Modelling transport of water and solutes in future wetlands in Forsmark R-06-46, Svensk Kärnbränslehantering AB.

Weast R C, (ed) 1974. *Handbook of Chemistry and Physics*, CRC Press, U.S.A.

Wong C S, Chin Y, Gschwend P M, 1992. Sorption of radon-222 to natural sediments *Geochimica et Cosmochimica Acta* Vol. 56 pp. 3923–3932.

Zielinski R A, Bush C A, Rosholt J N, 1986. Uranium series disequilibrium in a young surficial uranium deposit, north-eastern Washington, U.S.A. *Applied Geochemistry,* Vol. 1 pp. 503–511.

Zielinski R A, Meier A L, 1988. The association of uranium with organic matter in Holocene peat: an experimental leaching study *Applied Geochemistry,* Vol. 3, pp. 631–643.

Appendix A

Derivation of the Bateman equation:

The decay of a radioactive isotope is proportional to the number of atoms, N:

$$\frac{dN}{dt} = -\lambda N , \qquad \text{Equation A-1}$$

where the constant of proportionality, λ, is called the decay constant. Integration gives the exponential decay law:

$$N(t) = N_0 e^{-\lambda t} , \qquad \text{Equation A-2}$$

where N_0 denotes the number of atoms at t = 0. The exponential decay law is also applicable for activities, as the activity, A, is related to the number of atoms by

$$A = \lambda N . \qquad \text{Equation A-3}$$

In the decay chains the general situation is somewhat more complicated because atoms do not only decay – they are also continuously being produced by the decay of a parent. If we let N_1 denote the number of atoms of the parent and N_2 the number of atoms of the daughter the situation can be described by the differential equation:

$$\frac{dN_2}{dt} = -\lambda_2 N_2 + \lambda_1 N_1 \qquad \text{Equation A-4}$$

Equation A-4 is partly similar to Equation A-1, but it has an additional term that accounts for the production of new atoms. This term will be equal to the decay of the parent nuclide, whose variation in time is described by the exponential decay law. There are several ways to solve the differential equation, but the easiest way is probably to use Laplace transforms. If we let N_2^0 denote the number of atoms of the daughter at t = 0, the transformed equation will be

$$s\tilde{N}_2(s) - N_2^0 = -\lambda_2 \tilde{N}_2(s) + \lambda_1 \tilde{N}_1(s) \qquad \text{Equation A-5}$$

Solving for $\tilde{N}_2(s)$ gives

$$\tilde{N}_2(s) = \frac{N_2^0}{s+\lambda_2} + \frac{\lambda_1 \tilde{N}_1(s)}{s+\lambda_2} \qquad \text{Equation A-6}$$

$N_1(t)$ was said to decay exponentially according to Equation A-2. Hence, its Laplace transform will be

$$\tilde{N}_1(s) = \frac{N_1^0}{s+\lambda_1} \qquad \text{Equation A-7}$$

If $\tilde{N}_1(s)$ in Equation A-6 is substituted by this expression, we get

$$\tilde{N}_2(s) = \frac{N_2^0}{s+\lambda_2} + \frac{\lambda_1 N_1^0}{(s+\lambda_1)(s+\lambda_2)} \qquad \text{Equation A-8}$$

Transforming back to time-space will give

$$N_2(t) = N_2^0 e^{-\lambda_2 t} + \lambda_1 N_1^0 \left(\frac{e^{-\lambda_1 t} - e^{-\lambda_2 t}}{\lambda_2 - \lambda_1} \right) = \left(N_2^0 - \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} \right) e^{-\lambda_2 t} + \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^{-\lambda_1 t} \qquad \text{Equation A-9}$$

By using the fact that $A = \lambda N$ and multiplying both sides by λ_2, Equation A-9 can be rewritten in terms of activity

$$A_2(t) = \left(A_2^0 - \frac{\lambda_2}{\lambda_2 - \lambda_1} A_1^0 \right) e^{-\lambda_2 t} + \frac{\lambda_2}{\lambda_2 - \lambda_1} A_1^0 e^{-\lambda_1 t} \qquad \text{Equation A-10}$$

$A_1^0 e^{-\lambda_1 t}$ in the last term is simply $A_1(t)$. If the parent has a much longer half-life than the daughter, which is true for at least the two first radionuclides in all of the naturally occurring decay chains, it follows that $\lambda_2 >> \lambda_1$. If that is the case, it can be approximated that $\lambda_2 - \lambda_1 \approx \lambda_2$. If this approximation is made in Equation A-10, it will simplify to

$$A_2(t) = \left(A_2^0 - A_1^0 \right) e^{-\lambda_2 t} + A_1(t) \qquad \text{Equation A-11}$$

Evidently the activity of the daughter can be described as the sum of two terms. The first one is the difference in activity between the daughter and the parent, and the second one is simply the activity of the parent. Since $\lambda_2 >> \lambda_1$, the first term will approach zero much faster than the second one. This implies that the activity of the daughter will approach that of the parent. If there initially is an excess of the daughter, the excess will decay at a rate that is determined by the half-life of the daughter. Similarly, if there initially is more of the parent, there will be a build-up of the daughter so that the activity of the daughter becomes equal to that of the parent. This equilibrium between a parent and a much more short-lived daughter is commonly referred to as secular equilibrium or isotopic equilibrium.

The first term in the right-hand side of Equation A-11 shows that the time needed to establish secular equilibrium depends on the half-life of the daughter. It is often said that it takes 5–6 half-lives of the daughter to reach secular equilibrium, which is true under most – but not all – circumstances. If there is an initial deficiency of the daughter, the statement will indeed be true, since the most extreme case will be when the daughter is entirely absent. In that case the activity of the daughter will always be within a few percent of the activity of the parent within 5–6 half-lives. However, if there is an initial excess of the daughter, there is no limitation to how large that excess might be. As long as there is only twice as much or so of the daughter, there will be no problem, but in some situations the difference might be considerably bigger. One such example could be a natural water containing Ra-226 and its highly volatile daughter Rn-222, where there often may be large amounts of unsupported Rn-222. Imagine, for instance, that there are 5 mBq/l Ra-226 and 105 mBq/l Rn-222. The half-life of Rn-222 is 3.8 days so if the sample is conserved for six half-lives, a little more than three weeks, the activity will be $(100 \cdot 0.5^6 + 5)$ mBq/l = 6.56 mBq/l according to Equation A-11. Clearly, the Rn-222 activity is not within the a few percent of the activity of its parent. In fact, if Rn-222 in this case would have been used to measure the Ra-226 activity, it would have been overestimated by more than 30%. Evidently, a system may still be far from secular equilibrium, although it has been isolated for six half-lives – a fact that often is overseen.

The system could now be expanded and solved for the third and fourth members of the decay chains as a function of all the parents. These differential equations were first solved by /Bateman 1910/ and are therefore often called the Bateman equations. The general solution will not be derived here, but it can be shown that /Bourdon et al. 2003/:

$$N_i = \sum_{j=1}^{i} \left(\prod_{k=1}^{j} \lambda_k \right) a_j N_j^0 e^{-\lambda_j t} \qquad \text{Equation A-12}$$

Where

$$a_i = \prod_{j \neq i} \frac{1}{\lambda_j - \lambda_i} \qquad \text{Equation A-13}$$

In practice, however, one rarely needs more than three steps. The reason is that once a daughter has reached equilibrium with its parent, it will behave as if it had the same half-life as its parents, $A_2(t) = A_1(t)$. Hence, if the half-life of the next radionuclide in the decay chain also is very short in comparison with the original parent, the situation could again be reduced to Equation A-11, although in this case for $A_3(t)$, which then will turn out to be equal to $A_2(t) = A_1(t)$ within a limited amount of time that is determined by the half-life of the third radionuclide in the chain. In that manner, secular equilibrium can build up all throughout the decay chains if they are left alone for a sufficiently long time.

Since the radionuclides of the decay chains as a rule will strive to acquire the same activity as any of its more long-lived parents, this provides a good reference level for comparing activities. If there is secular equilibrium the activity ratio between the parent and the daughter will simply be equal to unity. Therefore, the delta notation that frequently is used for many isotope tracers is rarely used for the uranium-thorium chain nuclides even when the abundance of two isotopes is compared.

Appendix B

Raw data

Original data from ICP-AES and additional chemical analyses. Specific activities for Ra-226 have also been excluded. All values are in relation to dry weight.

Depth	cm	5–17.5	65–72.5	200–210	340–350	365–370	400–410	420–425	435–440	460–465	470–475
Ash	%	3	0.9	3.8	5.1	4.4	46.5	78.3	86.4	96.6	96.7
Sum	%	2.7	0.8	3.1	4.1	3.5	43.5	74.7	93.9	89.3	94.5
Si02	%	1.79	0.359	0.908	0.459	0.57	35.1	58.1	64.1	57.1	58.3
Al2O3	%	0.295	0.0662	0.641	0.765	0.817	3.73	7.62	9.45	15.5	17.7
CaO	%	0.114	0.144	0.924	1.67	1.15	1	0.777	0.785	1.38	1.34
Fe2O3	%	0.258	0.101	0.477	0.948	0.751	1.99	4.12	4.33	5.86	7.24
K2O	%	0.0513	0.0097	0.0142	0.0136	0.015	0.679	1.79	2.29	4.38	4.42
MgO	%	0.0828	0.0462	0.0542	0.0832	0.0632	0.471	1.08	1.38	2.39	2.78
MnO	%	0.0017	0.0004	0.0027	0.013	0.0104	0.0168	0.027	0.0339	0.0637	0.0735
Na2O	%	0.0501	0.0137	0.0128	0.0098	0.009	0.304	0.899	1.13	1.78	1.67
P2O5	%	0.065	0.0164	0.0916	0.0791	0.0634	0.0638	0.049	0.0475	0.174	0.181
TiO2	%	0.0165	0.0033	0.016	0.0098	0.0138	0.132	0.282	0.347	0.69	0.789
As	ppm	2.19	0.791	0.406	0.701	1.76	5.49	10.2	9.59	1.46	1.71
Ba	ppm	22.1	8.31	58.8	62.6	42.1	176	333	407	746	703
Cd	ppm	0.409	0.826	0.0753	0.2	0.139	0.458	0.349	0.336	0.115	0.228
Ce	ppm	0.137	0.010	0.807	2.159	1.479	46.272	44.755	51.284	48.926	109.405
Cr	ppm	6.73	0.574	3.75	3.52	4.88	29.7	44.5	55.5	85.9	90.1
Cu	ppm	3.38	1.81	5.26	7.44	13.4	28.6	42.1	46.5	24.8	27
Dy	ppm	0.2748	0.06678	1.0336	2.0706	1.7952	5.952	3.53916	4.18176	4.53096	7.27184
Eu	ppm	0.0696	0.01449	0.28272	0.5508	0.4488	1.6182	0.82215	0.819072	0.72384	1.48918
Er	ppm	0.1749	0.03933	0.646	1.1577	1.0868	3.5991	2.57607	2.73888	2.53344	4.21612
Ga	ppm	2.16	0.5436	2.2838	4.386	3.7444	18.6	36.4878	29.4624	17.2608	42.3546
Gd	ppm	0.333	0.07353	1.3946	2.7591	2.4112	7.812	3.94632	4.00896	4.20384	6.68197
Hf	ppm	0.1002	0.02898	0.0798	0.12291	0.19448	1.04625	1.59732	2.19456	3.0624	4.67061
Hg	ppm	0.103		0.046	0.0401	0.0243	0.0251				
Ho	ppm	0.0612	0.01413	0.21736	0.42483	0.36784	1.22295	0.8613	0.95904	0.86304	1.43116
La	ppm	2.35	0.594	12.4	23.6	18.3	52.4	37.9	28.4	51.5	55.9
Lu	ppm	0.01863	0.004068	0.0779	0.1479	0.13552	0.465	0.273267	0.286848	0.30972	0.508642
Mo	ppm	0.562	0.145	0.784	1.21	1.77	3.35	9.02	7.4		
Nb	ppm	0.274						8.78	9.78	14.5	14.9
Nd	ppm	2.247	0.5409	10.146	20.145	16.72	53.94	30.2238	30.4992	30.2064	50.4774
Ni	ppm	2.11	1.2	1.59	2.78	5.98	26.4	31.5	30.1	27.8	32.3
Pr	ppm	0.672	0.1602	2.7778	5.61	4.4	13.857	8.9262	8.64	8.1432	13.6347
Rb	ppm	2.148	0.4365	0.8968	1.2189	0.814	35.6655	93.96	108	116.232	209.839
S	ppm	2,630	879	2,160	2,590	3,830	7,680	16,200	10,900	160	129
Sc	ppm	0.278	0.0833	1.1	1.03	0.936	4.65	7.26	7.54	14.3	16.6
Sm	ppm	0.417	0.07884	1.615	3.3201	2.86	9.393	5.61411	5.79744	5.03904	9.38957
Sn	ppm						1.67	2.16	1.88	3.61	4.64
Sr	ppm	11.1	9.09	45.3	55.9	39.1	57.2	76.8	82.7	168	136
Ta	ppm	0.01764	0.004887	0.016188		0.020108	0.11904	0.33669	0.419904	0.84912	1.36347
Tb	ppm	0.0369	0.008811	0.17594	0.37332	0.32824	0.9021	0.315549	0.365472	0.42456	0.777468
Th	ppm	0.348	0.07029	0.7524	1.0404	1.2364	6.603	8.2215	9.6768	10.9968	19.1466
Tm	ppm	0.0260	0.0068	0.0946	0.1805	0.1690	0.5487	0.4079	0.4035	0.3431	0.6721
U	ppm	0.351	0.07839	1.3072	1.6575	2.0856	7.905	19.1052	26.6112	4.1412	7.01075
V	ppm	2.88	0.6	5.21	11.1	15.4	37.6	62.9	77.9	103	120
W	ppm						1.42	1.89	1.45	2.45	3.27
Y	ppm	1.71	0.419	7.09	13.6	11.9	39.1	17.7	28.1	18	41.5
Yb	ppm	0.1275	0.03015	0.5092	1.071	0.9636	2.976	1.94184	2.45376	2.2968	3.89701
Zr	ppm	5.4	0.877	3.75	3.53	5.13	40.1	71.3	77	188	211
Be	ppm	0.0835	0.0558	0.333	0.293	0.388	1.12	1.61	1.98	3.18	3.93

Depth	cm	5–17.5	65–72.5	200–210	340–350	365–370	400–410	420–425	435–440	460–465	470–475
Co	ppm	0.761	0.475	1.15	1.02	1.29	11.6	8.54	9.06	17.6	19.1
Cs	ppm	0.0871	0.0732		0.0726		1.76	3.85	4.86	7.72	9.89
Pb	ppm	22.1	6.97	1.11	0.457	0.713	6.09	12.6	15.1	27.5	29.9
Sb	ppm	0.71	0.109	0.388	0.0604	0.0625	0.191	0.428	0.694	0.402	0.51
Tl	ppm						0.335	0.612	0.745	1.28	1.29
Li	ppm	0.692	0.611	0.32	0.295	0.223	11.6	22.8	29.5	46.7	58.7
Zn	ppm	25.2	5.42	1.75	2.78	4.02	97	70.3	64.8	92.3	117
Br	ppm	2.35	1.69	1.25			1.48	2.05	2.68		
Cl	ppm	153	122	53.4							
TOC	ppm	420,000	440,000	280,000	250,000	440,000	180,000	100,000	64,000	6,300	3,800
C-tot	ppm	440,000	440,000	470,000	510,000	510,000	270,000	110,000	65,000	8,500	4,000
PO4	ppm	94	35	9	16	17	19	14	14	24	31
N org	ppm	6,960	4,120	16,200	24,500	15,200	14,900	9,400	5,990		855
N-tot	ppm	7,800	5,060	17,500	25,600	16,600	15,700	9,930	6,440	233	1,030
Ra-226	mBq/g	2.24	1.97	2.10	8.38	14.86	34.16	37.27	43.17	100.26	116.55

ISSN 1404-0344
CM Gruppen AB, Bromma, 2009