Isotopic Disequilibrium for Assessment of Radionuclide Transport in Peat Lands

Uranium-Thorium Series Nuclides in a Core from Klarebäcksmossen, Oskarshamn, Sweden

Fredrik Lidman

Abstract

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Fredrik Lidman

Teknisk- naturvetenskaplig fakultet
UTH-enheten

Besöksadress:
Ångströmlaboratoriet
Lägerhyddsvägen 1
Hus 4, Plan 0

Postadress:
Box 536
751 21 Uppsala

Telefon:
018 – 471 30 03

Telefax:
018 – 471 30 00

Hemsida:
http://www.teknat.uu.se/student

In order to assess the risks that are associated with a deep repository of nuclear waste, it is important to know how different radionuclides behave in different environments. Since some of the most critical radionuclides in nuclear waste such as Ra-226 occur naturally in the environment, it is possible to study their behaviour directly. Peat lands are thought to be one of the most critical ecosystems due to their capability of accumulating large amounts of radioactivity and the possible exposure pathways to man.

Klarebäcksmossen is a peat land situated close to the nuclear power plant in Oskarshamn, which is one of two areas in Sweden where site investigations for a future deep repository are being conducted. In this study a complete peat-gyttja-clay profile from Klarebäcksmossen has been analysed for a large number of both natural and artificial radionuclides using gamma spectrometry. The degree of isotopic disequilibrium between different nuclides in the uranium-thorium series has been used to assess radionuclide migration and accumulation throughout the core.

The measurements indicate that uranium has been accumulated in the gyttja, but mobilised from the clay. Radium, on the other hand, has been leached from the gyttja layers, and the strikingly low Ra-226/Pb-210 ratios show that it might have been very recently. Alternatively, there is a very extensive migration of Rn-222.

In the peat low levels of radioactivity were found for most radionuclides, but with clear differences between minerotrophic and ombrotrophic peat. This may indicate that the uptake of radionuclides by peat mainly is passive. The accumulation rate for the peat has also been determined using Pb-210 dating.

PREFACE

Like most environmental studies this thesis work is a truly multidisciplinary project. Prof. Farid El-Daoushy, who has been the one of the supervisors of this thesis work, once described environmental research as the heptathlon of science. I guess that the point was that it is not enough to be good at javelin in order to win a gold medal in heptathlon – one must master all the events. Likewise environmental research requires deep multidisciplinary knowledge in order to produce credible results. I do not claim to possess all that knowledge and, therefore, I am also very grateful for comments from various specialists that may take interest in the findings of this work.

I am also indebted to Prof. El-Daoushy for his support. His genuine interest in the proceeding of the measurements and the interpretation thereof has been of unquestionable importance for the quality of this work.

I must also thank Dr. Ulrik Kautsy, not only for supervising my work, but also for many important contributions along the way. I am also grateful to many of his colleagues working for SKB, above all Karin Aquilonius, who helped me with the work at the Äspö Laboratory.

Finally, I must express my gratitude to Dr. Emil Rydin at the Department of Ecology and Evolution for helping me to dry the samples from Klarebäcksmossen.

To some extent the methods used in this thesis work coincide with the ones that were used in my earlier project work at the Department of Physics. Some parts of this report will therefore be similar to certain parts of my report *Reliable Determination of Spatio-Temporal Scales in Paleolimnological Studies* (Lidman, 2004). This concerns the background theory of low-level gamma spectrometry and the description of the facilities of the Environmental Physics Group at the Ångström laboratory.

This M. Sc. thesis work was co-funded by the Swedish Nuclear Fuel and Waste Management Company (Svensk kärnbränslehantering AB).

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1. BACKGROUND

1.1 INTRODUCTION

1.1.1 Deep Repository of Nuclear Waste

The Swedish Nuclear Fuel and Waste Management Company, SKB, is responsible for taking care of Sweden's nuclear waste. Much of this waste comes from the use of nuclear power, but also to some extent from research and health care. It is estimated that if the operating time of the existing nuclear power plants is 40 years, Sweden will have produced 9,500 tonnes of nuclear waste before they are closed (SKB, 1999). Since nuclear waste can be dangerous to both man and the environment, it is essential that the waste is taken care of in a proper way. As yet there is no method to render spent nuclear fuel harmless, the nuclear waste must be prevented from entering any ecosystem until the radionuclides have decayed to harmless levels.

Although the radioactivity declines fast to begin with, the nuclear waste will remain hazardous for a long time to come. It is estimated that it will take 100,000 years before the radiotoxicity (on ingestion) of 1 tonne of nuclear fuel will equal the radiotoxicity of the 8 tonnes of enriched natural uranium used to fabricate the fuel (SKB, 1999). Since there are no guarantees that there will be any institutional control of the nuclear waste for such a long span of time, it is necessary to find a repository that is safe even if there will be no monitoring of it in the future. SKB's proposal to solve this problem is that the nuclear waste should be encapsulated in special copper canisters and embedded in bentonite clay at a depth of approximately 500 meters in the bedrock somewhere in Sweden. Presently, SKB is focusing on the Oskarshamn and Forsmark areas, where two of Sweden's nuclear power plants are situated.

However, before any deep repository can be taken in use, it must be shown that this really is a safe solution. Then the question is – what is meant by "safe"? Like most human activities handling of nuclear waste involves a risk, which has to be assessed in some way. The authority that primarily controls matters concerning radiation is the Swedish Radiation Protection Agency, SSI. SSI has stipulated that the annual risk of harmful effects after closure must be no more than 10^{-6} for a representative individual in the group that is exposed to the greatest risk. If there is a 100 % certainty of exposure, this would correspond to 0.015 mSv/yr. Alternatively, SSI has defined an acceptable annual risk of 10^{-5} for especially exposed individuals, which – under the same conditions as above – would imply 0.15 mSv/yr (SKB, 1999). This could be compared to the average radiation dose in Sweden, which is approximately 4 mSv/yr (SSI, 2005). Main sources of nuclear radiation include radon in buildings (2 mSv/yr), background radiation (1 mSv/yr), medical treatment (0.7 mSv/yr) and radionuclides such as ^{14}C and ^{40}K in the human body (0.2 mSv/yr), although these figures may vary considerably for different persons.

SKB's strategy for assuring that these limits are not exceeded involves the use of multiple barriers – the copper canisters, the bentonite clay and, finally, the bedrock. If a copper canister would somehow fail, for instance due to corrosion or bedrock movements, the bentonite clay is thought to delay the release of radionuclides both by sorption of radionuclides and reduction of groundwater movements in the vicinity of the canisters. Finally, the rock would delay the transport of radionuclides even further, but eventually it cannot be excluded that radionuclides will reach the surface. In that case, the final risk assessments would depend on how these radionuclides behave in the different ecosystems that they may enter.

1.1.2 Critical Radionuclides and Ecosystems

Nuclear fuel contains a wide variety of radionuclides (Håkansson, 2000). Some of them are more likely than others to escape from a deep repository in the case of a canister failure, for instance because of different geochemical properties. Calculations of the radionuclide transport from a deep repository show that above all two radionuclides tend to dominate in the scenarios where significant doses are predicted. These radionuclides are ^{129}I and ^{226}Ra (SKB, 1999). ^{129}I does not occur naturally, but its long-term behaviour in ecosystems could be studied via a stable iodine isotope, ^{127}I. For radium there are no stable isotopes, but several naturally occurring radioactive ones, among which ^{226}Ra is the most abundant. Yet other radionuclides belong to elements that do not naturally occur, such as plutonium and curium, and their environmental behaviour is therefore harder to assess.

There are also certain critical ecosystems, in which the release of radionuclides could lead to particularly high doses. Above all, this can be expected in ecosystems that tend to accumulate different types of material, such as sediments, wetlands and peat lands. However, the radiation dose will not only depend on how much radioactivity that is accumulated, but also on what the exposure pathways are. Since peat lands can be used as source of fuel or for agricultural purposes, peat lands are considered to be one of the most critical ecosystems for the exposure to man. In the safety assessment project SR 97 mires were identified as the ecosystem that potentially could cause the highest doses to man (SKB, 1999). Mires are also a type of ecosystem that most likely will be common in both the Oskarshamn and Forsmark areas due to the land rise. Furthermore, they tend to be located in areas where one could expect an outflow of deeper groundwater, which potentially could carry radionuclides from a deep repository. Therefore, mires and wetlands were pointed out as especially important ecosystems to study in last year's research programme from SKB (2004). Indeed, high activities for various radionuclides have been reported from peat lands. For instance, specific activities for ^{226}Ra well above 8 Bq/g have been reported in peat close to radioactive springs in northern Sweden (Ek et al.,1982).

However, the attempts to model the behaviour of radionuclides in mires tend to be quite simple. One example is the mire model presented by Karlsson et al. (2001), which has only two compartments, the soluble fraction and the solid fraction. According to the authors there is no data available to support a more complex model. Hence, there seems to be a need for more information about the behaviour of radionuclides in the peat lands in the Oskarshamn and Forsmark areas.

1.1.3 This Study

By studying naturally occurring radionuclides in critical ecosystems close to a possible future deep repository it should be possible to acquire a good understanding of how these radionuclides would behave in case of a release from a deep repository. This would in turn lead to more reliable assessments of the risk connected to a deep repository.

In this work, a core from Klarebäcksmossen, a bog in the Oskarshamn area, has been analysed using gamma spectrometry in order to quantify the content of some radionuclides, above all the uranium-thorium chain nuclides, which include among all ^{226}Ra. These decay chains also represent many other long-lived nuclides that are found in spent nuclear fuel, for instance uranium, thorium and protactinium isotopes. It has also been proposed that actinides of the same oxidation state behave similarly. For instance, artificial elements such as neptunium as plutonium occur as tetravalent ions,

Np^{4+} and Pu^{4+}, and could therefore be expected to behave in a similar manner as other tetravalent actinide ions such as U^{4+} according to Airey *et al.* (1986).

The fact that these radionuclides occur in decay chains makes them particularly interesting to study, because of a concept called secular equilibrium, which implies that in a closed system all radionuclides in a certain decay chain eventually will acquire the same activity. Accordingly, there are possibilities to decide whether certain radionuclides have been mobilised or accumulated. Since the time to reach secular equilibrium is dependent on the half-lives of the involved radionuclides, it is sometimes even possible to draw conclusions about on what time-scales these possible movements have taken place. As the investigated core encompasses both sediments and peat, it is possible to follow the evolution of the landscape from the lake stage to the bog stage, which thought to represent a typical development in the area. For the Forsmark area the development of lakes has been extensively studied by Brunberg and Blomqvist (1999), but the development in the Oskarshamn area is hardly dramatically different.

The purpose of this thesis work is to investigate and interpret the distribution of radionuclides in a peat bog in the Oskarshamn area. One reason is that it is important to make a survey of the radioactivity in the area before a possible deep repository of nuclear waste is taken in use. Secular equilibrium (or the degree of disequilibrium) will be used to interpret the radionuclide profiles, as this provides a way to find evidence of transport of accumulation processes in different layers of the core. In the ideal case, this will even allow an estimation of removal or accumulation rates. Thus, this thesis work will contribute to a better understanding of the behaviour of radionuclides during the development of peat lands.

1.2 RADIOACTIVITY IN THE ENVIRONMENT

1.2.1 The Naturally Occurring Decay Chains

The radioactive substances that are encountered in the environment can be of three principally different origins. The first group does not naturally belong in the environment and are found there because of human activities such as testing of nuclear weapons or accidents in nuclear power plants. For instance, the cesium isotopes ^{137}Cs and ^{134}Cs that were released in the Chernobyl accident belong to this group of radionuclides. Hence, this group is referred to as anthropogenic or artificial radionuclides. Secondly, there are radionuclides that continuously are being produced in the upper atmosphere. These are called cosmogenic radionuclides and include among all ^{14}C and ^{3}H. Finally, there are radionuclides that have been present on earth since its formation; these are the so-called primordial radionuclides. In order to stay around for so long, they would seemingly have to be very long-lived. This is indeed the case for some of them, but far from all. The reason is that many of the primordial radionuclides occur in decay chains, which are characterised by the fact that the decay of a radionuclide often leads to the formation of another radionuclide according to a certain decay pattern. Because of the significance of these decay chains in applied radioactivity, the naturally occurring decay chains will be briefly presented here.

In the beginning 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 in includes isotopes of interesting elements such as radium and thorium. The thorium chain looks like this:
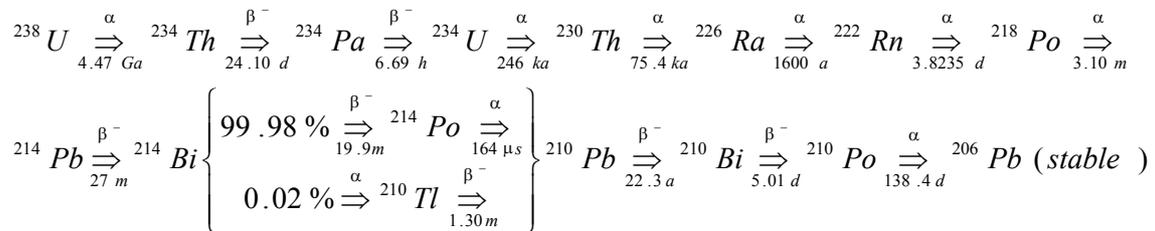
$$^{232}Th \underset{14.0\,Ga}{\overset{\alpha}{\Rightarrow}} {}^{228}Ra \underset{5.76\,a}{\overset{\beta^-}{\Rightarrow}} {}^{228}Ac \underset{6.15\,h}{\overset{\beta^-}{\Rightarrow}} {}^{228}Th \underset{1.913\,a}{\overset{\alpha}{\Rightarrow}} {}^{224}Ra \underset{3.36\,d}{\overset{\alpha}{\Rightarrow}} {}^{220}Rn \underset{5.56\,s}{\overset{\alpha}{\Rightarrow}} {}^{216}Po \underset{0.145\,d}{\overset{\alpha}{\Rightarrow}} {}^{212}Pb \underset{10.64\,h}{\overset{\beta^-}{\Rightarrow}}$$

$$^{212}Bi \begin{cases} 64.1\% \underset{1.009\,h}{\overset{\beta^-}{\Rightarrow}} {}^{212}Po \underset{0.298\,\mu s}{\overset{\alpha}{\Rightarrow}} \\ 35.9\% \underset{25\,m}{\overset{\alpha}{\Rightarrow}} {}^{208}Tl \underset{3.053\,m}{\overset{\beta^-}{\Rightarrow}} \end{cases} {}^{208}Pb\,(stable)$$
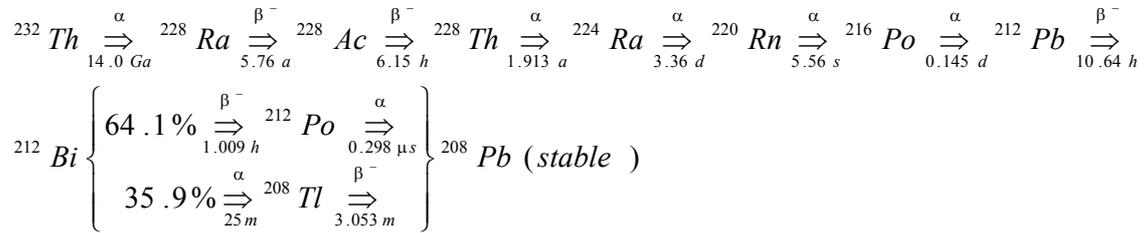
The radionuclides that can be of any interest in studies of the long-term migration of radionuclides are ^{232}Th, ^{228}Ra and, to some extent, ^{228}Th. The remaining radionuclides are too short-lived to be capable of migrating any longer distances in soil.
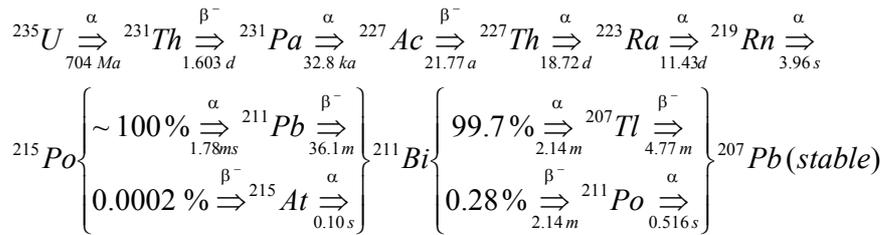
The neptunium chain (A=4n+1) should not really be referred to as a naturally occurring decay chain anymore, since it has decayed to negligible amounts by now. Its most long-lived member, ^{237}Np, has a half-life of only 2.14 million years, which is very little compared to the age of the earth for instance. 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 ^{241}Pu daughter ^{241}Am in recent deposits in some environments, but they should then be regarded as artificial radionuclides.

Probably, 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 ^{226}Ra, which has been identified as a particularly critical radionuclide, but also two long-lived uranium isotopes, ^{238}U and ^{234}U, the long-lived parent of ^{226}Ra ,^{230}Th, and the granddaughter of ^{226}Ra, ^{210}Pb. The uranium decay chain looks like this:

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

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

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 ^{222}Rn. Being a noble gas it is inert and can migrate considerable distances despite its comparatively short half-life. In Sweden, intrusion of ^{222}Rn in buildings and wells stands for half of the average annual radiation dose.

The actinium chain (A=4n+3) is interesting because it begins with ^{235}U, which is the uranium isotope that is used to generate electricity in nuclear power plants. Therefore, ^{235}U is enriched in nuclear fuel in comparison with the natural levels. In applied radioactivity, the protactinium isotope ^{231}Pa with a half-life of 32,400 years is also of interest.

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

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

1.2.2 The Importance of Secular Equilibrium

What makes the decay chains so interesting to study is the phenomenon called secular equilibrium that was mentioned earlier. This basically depends on the dynamics of the decay and production of the decay chain radionuclides. It can be shown, which is done in appendix A, that if the parent has a much longer half-life than the daughter, the daughter will eventually acquire the same activity as the parent in a closed system. They are then said to be in secular equilibrium. Once that secular equilibrium is established between two radionuclides, the activity of daughter will decrease at the same rate as the parent. Thus, it will essentially behave as if it had the same half-life as its parents. This makes it possible to establish secular equilibrium throughout the whole decay chain, as the radionuclides in the beginning of the natural decay chains always have much longer half-lives than the rest.

As is shown in appendix A, the time to reach secular equilibrium is primarily dependent on the half-life of the daughter. If the activity of the daughter is zero to begin with, it will take between approximately 5-7 half-lives of the daughter before they can be considered to be more or less in secular equilibrium. Thus, different spans of time are required to establish secular equilibrium between different radionuclides. Very short-lived radionuclides can always be expected to occur in secular equilibrium with their parents or grandparents, while more long-lived radionuclides sometimes may have either higher or lower activity than their parent. One must then draw conclusion that there has been a movement of either the parent or the daughter. Depending on the half-life of the daughter, it may even be possible to tell on what time-scales this mobilisation or accumulation has taken place. Accordingly, secular equilibrium or the degree of disequilibrium provides a unique way to assess the mobility of the decay chain elements, which has no counterpart in common ecological studies.

1.2.3 The Geochemistry of the Key Elements

The interpretation of an isotopic disequilibrium must also involve some understanding of the geochemical properties of the elements in question. For example, if the activity ratio between the parent and the daughter exceeds unity, this could be interpreted either as an accumulation of the parent or as a removal of the daughter. In order to decide which alternative that is most likely, the behaviour of the involved elements must be considered.

In the going-over of the naturally occurring decay chains a few radionuclides belonging to a very limited number of elements were identified as particularly relevant in studies of the long-term behaviour of the decay chain nuclides. Elements such as bismuth, polonium and thallium do not have to be considered, since their representatives in the decay chains are so short-lived, while the behaviour of elements such as uranium, thorium and radium in peat land and sediments require some attention.

Uranium occurs in two oxidation states 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 shown to be very mobile in comparison with U^{4+}. Because reducing conditions can be expected

below the water table in any peat land (Shotyk *et al.*, 1989), there is a great risk of uranium being 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. It is not unlikely that there are even higher activities elsewhere in published literature. Indeed this behaviour of uranium makes it special, since it easily can be mobilised and transported by both surface and groundwater under oxidizing conditions, but also enriched to very high concentrations when the redox conditions change. More thorough descriptions of the geochemistry of uranium are provided by, for example, Zielinski and Meier (1988) and Halbach *et al.* (1980).

Thorium, on the other hand, only occurs as a tetravalent ion, Th^{4+}. Similar to U^{4+} it is very immobile, both in 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 concentrations are 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". 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.* also indicate that there has been little thorium mobilization in the peat-rich soils in their study.

Radium is an alkaline earth metal and occurs as Ra^{2+} when dissolved in water. It has also been reported that the $RaSO_4$ complex sometimes might be important in radium migration (Beneš, 1982). This makes radium mobile in most environments, which also explains why ^{226}Ra is regarded as a critical radionuclide in dose assessments. However, the amounts of radium found in different waters appear to vary considerably. For instance, Plater *et al.* (1995) write that "river concentrations of radium are extremely variable, depending upon the type of terrain in the catchment and climate".

Other elements with relatively long-lived isotopes in the decay chains tend to be more or less immobile. Protactinium is sometimes described as comparable to thorium in terms of solubility (Karlsson and Bergström, 2002), although it seems to differ somewhat between different environments (IAEA, 1985 and 1994). A recent study, however, indicate that thorium may be more particle reactive than protactinium (Geibert and Usbeck, 2004) in most cases. Likewise, lead is known to be very immobile in most environments. For instance, a comparative study of uranium and lead in soils and swamps has shown demonstrated that lead is relatively immobile (Granier, 1979). This is also supported by data from the IAEA (1985, 1994).

The conclusion is that one above all should suspect migration of radon, radium or – provided that there are or have been oxidizing conditions – uranium, when isotopic disequilibrium is observed.

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 1, where the red dots correspond to different sampling sites in a survey by SKB. The dot indicated by the black arrow in the upper left corner, between European highway 22 and Misterhult, represents Klarebäcksmossen (PSM 006562).

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 about three or four times as big as the bog itself. Based on its elevation is has been estimated that what was to become Klarebäcksmossen was isolated from the Baltic Sea 11,250 years ago (Nilsson, 2004). As will be apparent from the analysis of the cores from Klarebäcksmossen, the site has developed from some kind of aquatic system to a peat land.
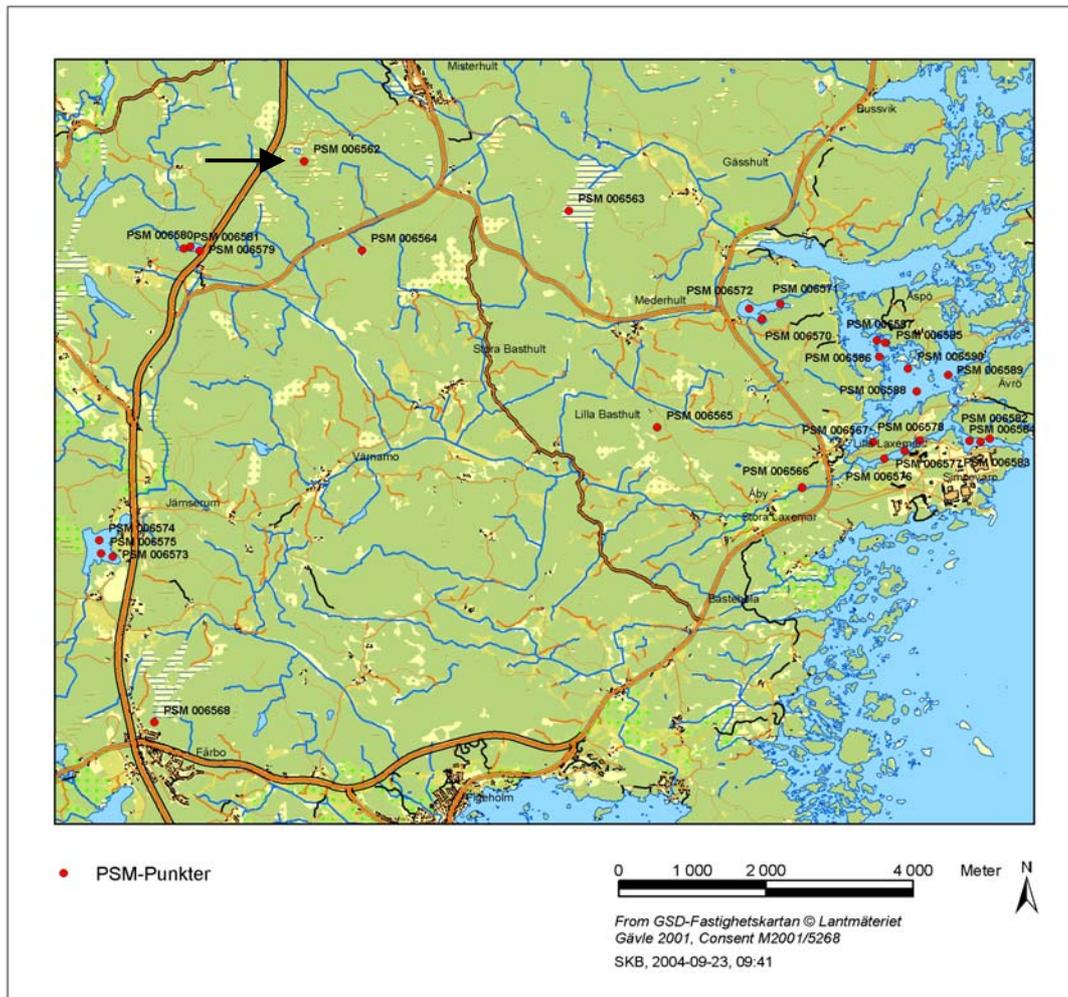

Figure 1: Map of the Oskarshamn area with the sample sites marked. The point PSM 006562 indicated by the black arrow in the upper left corner is Klarebäcksmossen.

Nowadays Klarebäcksmossen is a wooded bog. The pines growing on it are not very tall, partly due to the poor nutrient status, but possibly also due to low ages. Possibly, this is related to the drainage of the south-western parts of the bog, which probably occurred in the late 19th or early 20th century. To the extent that this can be judged from this appearance of 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 *Ledum palustre* [eng. wild rosemary, sv. skvattram], and *Sphagnum* [eng. bog moss, sv. vitmossa]. The core from Klarebäcksmossen was chosen because of the *Sphagnum*, which thanks to its comparatively vertical growth pattern it particularly suitable for ²¹⁰Pb dating. (This method will be described in section 2.2.)

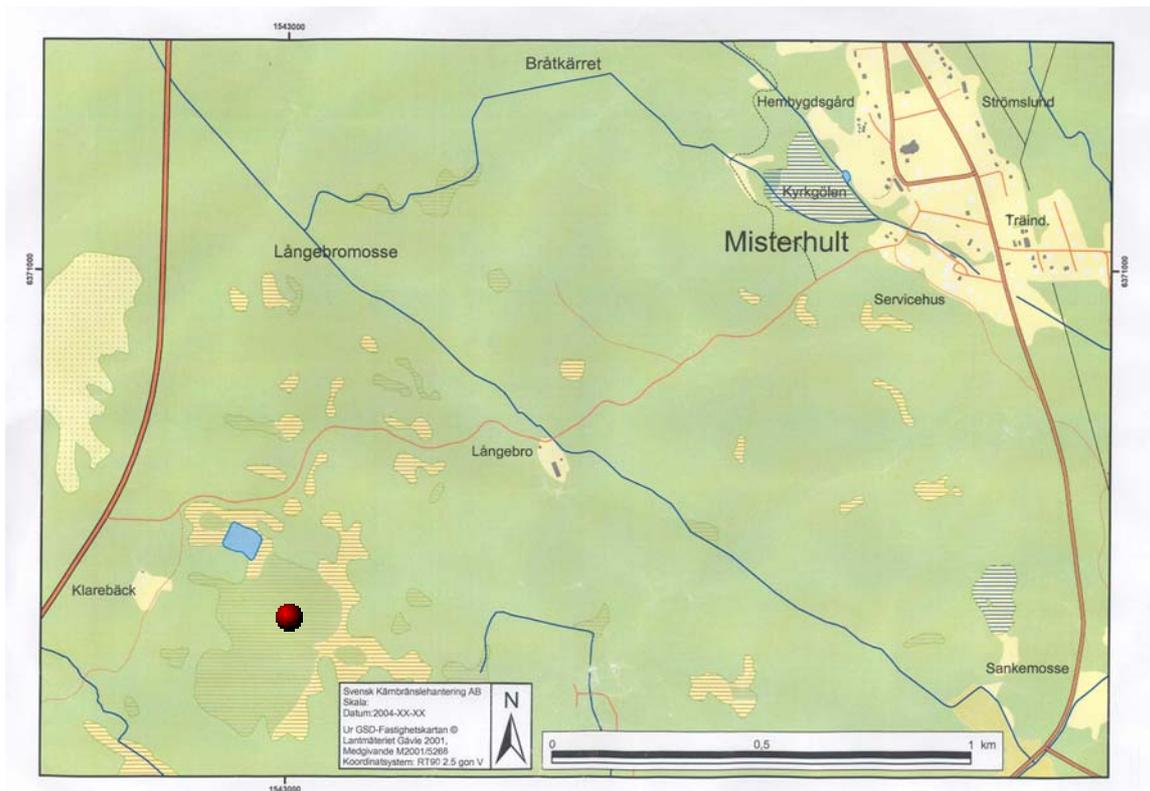A more detailed map of Klarebäcksmossen is shown in figure 2.

Figure 2: A map of Klarebäcksmossen and its vicinity. Klarebäcksmossen is the striped area in the lower left corner and the red point marks the approximate sampling site.

2.1.2 The Core

During August and September 2004 cores from the samples sites shown in figure 1 were collected by Geosigma AB using a Russian peat corer. Two cores were sampled from 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 interpretations of the soil layers in the different cores are presented in an SKB report (Nilsson, 2004). According to this soil layer interpretation, the core from Klarebäcksmossen has the following composition:

0-130 cm: **Peat:** *Sphagnum,* H3-4 [sv. vitmosstorv] (S)
130-160 cm: **Peat:** *Sphagnum/Eriophorum,* H3-4 [sv. vitmosstorv/tuvdun] (ERS)
160-170 cm: **Peat:** *Lignidi/Carex,* H4-5 [sv. lövkärrtorv] (LC)
170-310 cm: **Peat:** *Sphagnum/Carex,* H4-5 [sv. starrtorv] (SC)
310-370 cm: **Peat:** *Sphagnum/Carex,* H3-4 (SC2)
370-437 cm: **Gyttja:** brownish (GY1)

437-462 cm: **Gyttja:** olive green (GY2)
462-470 cm: **Gravel:** diameter <3 cm, wave-washed (GR)
470-524 cm: **Clay:** greyish, probably till below (LE)

Photographs of the cores that were analysed in this study are found in appendix B. It is evident that there is a disagreement between the description above and the photographs. For instance, the gravel layer in the core on the photograph is not found between 462 and 470 cm. This is because the cores were taken a few meters apart. Hence, the interpretation presented above is not strictly valid for the core that was analysed in this study when it comes to the precise depths of the different layers.
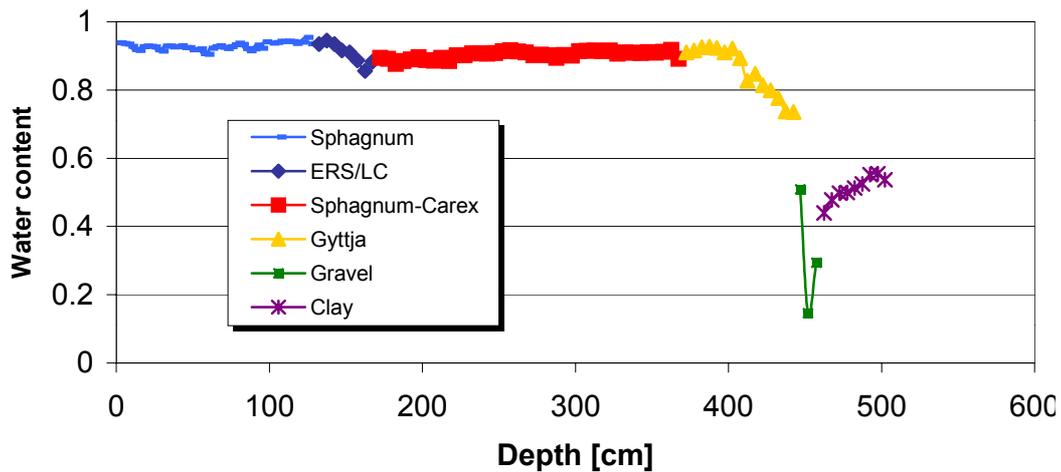

Figure 3: Water content by weight for the different layers in the analysed profile.

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

It is also clear from the picture of the cores in appendix B that there is a distinct change in colour just below 400 cm, although nothing is said about this is the interpretation of the soil layers above. Again, this only goes to show that the analysed cores do fully agree as regards the layer sequence. T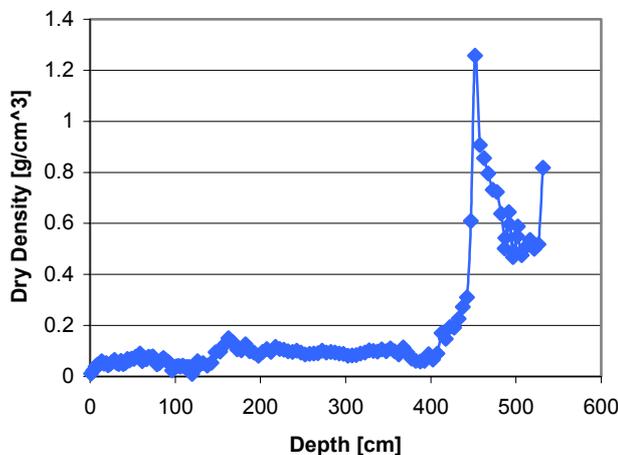he colour coincides with changes in both dry density and water content, which is shown in figures 3 and 4. All these factors suggest that there is a change in the type of material just below 400 cm, which probably should be identified as the transition from gyttja to peat.

Figures 3 and 4 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)

Figure 4: The dry density of the profile.

Carex species are to be connected with 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 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 rather a recharge area.

2.2 DETECTION OF GAMMA RADIATION

2.2.1 Gamma Spectrometry

Gamma radiation is emitted when atomic nuclei de-excite, which sometimes may occur as a consequence of alpha or beta decay. The gamma particles, which are photons, can be detected via their interaction with matter and their energies can be determined. Two common types of gamma detectors are scintillation detectors and semiconductor detectors. The detectors at the Ångström Laboratory in Uppsala are of the latter type.

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 this minimal induced current 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 after a while. 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 numbers 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 calculate the activity of radionuclide, whose decay causes the peak in the gamma spectrum.

Since the energy resolution of gamma detectors generally is very good and the gamma peaks often are well separated, it possible to simultaneously determine the activity of several radionuclides. This is one of the main advantages of gamma spectrometry. It does not only make the measurements very effective, but it also renders any chemical preparation of the samples to be measured superfluous. The only requirements are generally that the samples are homogeneous and that they contain enough radioactivity. 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 be encapsulated in certain containers, for whose geometry the detector has been calibrated. Otherwise advanced calculations are required to determine the efficiency of the geometry. Since gamma spectrometry generally does not require anything more than this, it should also be clear that gamma spectrometry is a non-destructive method. This implies that the samples can be used for other purposes when the measurements are through.

2.2.2 The Low-Level Gamma Detection Laboratory in Uppsala

The quality of measurements by the use of gamma spectrometry for environmental analyses depends to a large extent on the equipment and the environment, in which the measurements are performed. In order to decrease the uncertainties to an acceptable level it is important that the background radiation is low in comparison with the radiation from the sample that one wishes to analyse. Because environmental samples do not tend to be very radioactive, this criterion is not so readily met. Essentially, environmental samples are often nothing more than what commonly is referred to as "background". Things are complicated further by the fact that gamma radiation is very hard to stop. It can be significantly lowered by shields of dense elements such as lead, but it can never be completely absorbed by any material.

The measurements presented in this work have been performed in the low-level gamma laboratory of Uppsala University, which was constructed some years ago with the sole purpose of creating a good environment for low-level gamma spectrometry. It is located two floors below ground in the Ångström Laboratory in Uppsala and its walls and ceiling are covered by copper plates, acting as a Faraday shield. In this manner, disturbance from electromagnetic fields outside the laboratory is limited. The environment inside the laboratory is strictly controlled and kept at constant humidity and temperature. Only authorised personnel have access there. In order to prevent intrusion of ^{222}Rn the room is constantly kept at over-pressure by radon free air. Hence, when doors are opened, the air will always flow out from the room. Likewise, intrusion of ^{222}Rn through crannies is impossible, as the pressure is higher inside the laboratory. All detectors are surrounded by thick walls of lead to protect them from background radiation inside the laboratory. The lead parts closest to the detector materials are made of particularly old lead, which is especially pure with respect to radioactive isotopes such as ^{210}Pb.

The low-level gamma spectrometry laboratory presently houses four different detector systems, consisting of seven gamma detection units – five HPGe (high purity germanium) detectors and two NaI(Tl) detectors (NaI crystals doped with thallium). The detectors have been designed to allow measurements of variable sample masses, activities and volumes. The smallest samples are analysed in well detectors, where the sample is almost entirely surrounded by the detector material. Hence, the solid angle is close to 4π, which significantly increases the efficiency of well detectors. One of the well detectors also has two NaI(Tl) detectors connected to it, acting as a anti-coincide shield. That means that they surround the HPGe detector, which is used to acquire the gamma spectrum, and notify it when there are photons coming from outside the sample. Accordingly, these gamma particles are not included in the spectrum, which significantly decreases the background radiation. In this way, it is possible to reduce the background level to approximately 0.06 counts per second integrated over an energy range from 25 to 1600 keV. Since the accuracy of low-level measurements depends on the ratio between sample radiation and background radiation, this well detector is

particularly useful for measuring small samples with very low activities. In these measurements, this well detector has been used for pure peat samples with masses as low as 0.25 g. The other well detector has no anti-coincidence shield, and, accordingly, its background radiation is much higher: 0.5 counts per second. However, it allows larger samples, which to some extent compensates for this. Indeed, when larger sample quantities are available, increasing the amount of radioactivity in the detector can compensate for a higher level of background radiation. In such cases, the two systems consisting of planar detector are especially suitable. One of them is a simple planar detector with an integrated background of 0.2 counts per seconds, whereas the other one is sandwich detector, consisting of two oppositely directed planar detectors, with an integrated background level of 0.55 counts per second for each detector. In this study, sample masses as large as 80 g have been used in the sandwich detector. Thus, the detectors in the low-level gamma laboratory are capable of handling very different kinds of samples. Two of the detectors are more thoroughly presented in an article by El-Daoushy and García-Tenorio (1994). They have also been described in some detail by Hernández (2003).

2.2.3 Analysis of the Gamma Spectra

All detector systems are connected to a computer, which registers each detected photon. This allows the operator to follow the development in real-time and to finish the measurements whenever acceptably low uncertainty levels have been reached. For low-active samples, such as most environmental samples, this will generally require at least some days of measurements.

When the measurement of a sample is finished, the gamma spectrum can be analysed directly in the computer using special software, in this case a programme called Genie 2000. However, the identification of gamma peaks by Genie 2000 requires a nuclide library with information about the peak energies for all relevant radionuclides. Furthermore, calculation of activities requires emission probabilities for all relevant peaks. This information has to be provided by the operator. In the course of this work an updated nuclide library has been compiled based on decay data from Laboratoire National de Henri Becquerel (2004). The new library includes all major gamma-emitting nuclides from the naturally occurring decay chains plus many other radionuclides that can be suspected to occur in environmental samples.

The analysis of gamma spectra also requires information on the background radiations. Such measurements were performed before the measurements of the samples were begun and evaluated with respect to earlier background measurements. Available efficiency calibrations for the different detector systems has been used.

Finally, the determination of activities for different radionuclides must also involve knowledge about what peaks in the spectra that are reliable and how one should act in order to achieve accurate measurements for as many relevant radionuclides as possible.

2.2.4 Measuring ^{238}U by Gamma Spectrometry

^{238}U is the first radionuclide in the important uranium chain and it has been used for a wide scale of applications in environmental studies. However, because ^{238}U is a very poor gamma-emitter, direct measurements of it are impossible in environmental samples. The emission probability for the most intense gamma line (49.5 keV) is only 0.070 %. Yet gamma spectrometry can be used to measure ^{238}U thanks to secular equilibrium. ^{238}U will be in secular equilibrium with its daughter, ^{234}Th, within four months at the very most, and therefore ^{234}Th can be addressed instead. El-Daoushy and

Hernández (2002) have shown how it is possible to make accurate absolute determinations of the [234]Th activities in environmental samples. As they conclude, the 92.5 keV doublet peak is often disturbed by X-rays, which in most cases makes it unreliable for absolute measurements. However, by using Monte Carlo simulation techniques, they have shown how it is possible to control the self-absorption for the 63 keV peak. Thus, the 63 keV of [234]Th peak provides a way to determine the [238]U activity using gamma spectrometry. The only risk may be disturbance from [232]Th in samples with high thorium content, but low uranium content.

In this study, the 63 keV peak has been used to determine the [238]U activities. However, no corrections for self-absorption have been performed, which could lead to an underestimation of the [238]U activities in samples with a high mineral content.

2.2.5 Measuring [226]Ra by Gamma Spectrometry

[226]Ra is a gamma emitter with its main gamma line at 186.1 keV. Although the emission probability is fairly low, 3.516 %, this line would in many cases be sufficient to measure the activity directly, if it not were for the fact that [235]U has an overlapping gamma line at 185.7 keV with emission probability 57.25 %. In general, one can expect both [226]Ra and [235]U to be present in environmental samples, so these lines cannot straight off be used for absolute measurements.

In order to measure [226]Ra in a more proper way, one has to turn to its daughters. However, the daughter [222]Rn is a very mobile gas with a half-life of 3.8235 days. When preparing the sample it is inevitable that at least some [222]Rn is lost, which means that any possible secular equilibrium is disturbed. Therefore, it is necessary to leave the samples for approximately four weeks before measurements are made in order to assure that the secular equilibrium is re-established in the sample. In cases where the sample does not completely fill the container that is used in the measurements, the sample is covered by a plastic film in order to prevent the radon from gathering in the air-gap between the sample and the lid, since this would change the spatial distribution of the radiation not only from [222]Rn, but also from its short-lived daughters, for instance [218]Po, [214]Pb and [214]Bi. This would in turn affect the efficiency of the measurements in an uncontrolled way, which makes it impossible to draw any conclusions concerning their absolute activities either. This is important because the radon daughters provide the best way to accurately measure the [226]Ra activity in a sample. The best choice is [214]Pb that has a gamma line at 351.9 keV with a high branching ration (35.14 %). An obvious drawback with this approach is of course that the sample has to be prepared at least some weeks prior to the measurements in order to assure that [214]Pb really is in secular equilibrium with [226]Ra. On the other hand, this allows correction for the interference in the 185/186 keV peak so that the [235]U activity can be accessed.

2.2.6 Measuring Other Uranium Chain Nuclides by Gamma Spectrometry

[210]Pb can be measured using its 46.5 keV peak, but requires corrections for self-absorption in some cases. However, no such corrections have yet been made for these measurements, which could lead to a slight underestimation of the ^{210}Pb activities, above all in the gravel and clay samples.

Measurements of two other important members of the uranium chains have also been attempted, but these measurements are uncertain and their reliability remains to be tested. [230]Th has a small peak (0.376 %) at 67.67 keV, where there seems to be no interference from any other radionuclide in environmental samples. In the more radioactive samples, a distinct peak has been observed in this region and identified as [230]Th. Because of the low emission probability the accuracies will not be very good

even if fairly long measuring times are used. If better measurements are required, alpha spectrometry must be used.

The other radionuclide is ^{234}U, which has a small peak with emission probability 0.123 % at 53.20 keV. Moreover, it is overlapped by a much more intense (1.07 %) peak from ^{214}Pb, whose energy is 53.23 keV. However, samples where there is a significant enrichment of uranium in comparison with radium, ^{234}U can be expected to contribute considerably to this peak. Since ^{214}Pb is easy to determine via other gamma lines, the interference in this peak can be corrected for an approximate ^{234}U activity be calculated. However, no examples where these methods have been employed to determine the ^{230}Th and ^{234}U activities have been encountered in literature. Therefore, their reliability is questionable until a proper validation has been performed.

2.2.7 Measuring Thorium Chain Nuclides by Gamma Spectrometry

As was described earlier, there are essentially only three radionuclides in the thorium chain that are interesting in this kind of studies, ^{232}Th, ^{228}Ra and ^{228}Th. ^{232}Th has a small gamma line (63.81 keV), which, however, is overlapped by the 63.28 keV gamma line of ^{234}Th. This can cause some uncertainties in the measurement of ^{238}U, since it is hard to compensate for the contribution from ^{232}Th. As the other major gamma line of ^{234}Th cannot be trusted due to influences from X-rays, it seems more or less impossible to indirectly determine the ^{232}Th activity by gamma spectrometry.

^{228}Ra cannot be measured directly either, but thanks to its daughter ^{228}Ac, it is possible to measure it indirectly. ^{228}Ac 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.

^{228}Th, finally, has a small peak in the X-ray region (84.37 keV), which makes it impossible to measure it directly. Thanks to the short half-lives of the remaining thorium chain nuclide, it is, however, possible to access the ^{228}Th activity by daughters such as ^{212}Pb and ^{208}Tl, of which the former probably is the best one. Accordingly, ^{212}Pb is the radionuclide that has been used to determine the ^{228}Th activities in these measurements. Its 238.63 keV peak has a very high emission probability (43.6%), which allows accurate determination even in relatively small and pure samples.

2.2.8 Measuring Actinium Chain Nuclides by Gamma Spectrometry

Among the actinium chain nuclides it is mainly ^{235}U and ^{231}Pa that are of interest in this kind of studies. They are comparatively hard to measure, partly because of low emission probabilities for useful peaks and interference, and partly because of their low abundance in environmental samples. As was mentioned earlier, there is actually a gamma line with very high emission probability for ^{235}U (57.2 %), but often this peak is risky to use due the interference from ^{226}Ra. By determining the ^{226}Ra activity via its daughter ^{214}Pb it is, however, possible to correct for the interference from ^{226}Ra and in this manner indirectly determine the ^{235}U activity. In stronger samples other peaks can also be used. The 143.76 keV peak is the peak with the second highest emission probability (10.96 %), but then one has to be careful about interference from the 144.23 keV peak of ^{223}Ra (3.22 %).

When it comes to ^{231}Pa, the situation is even more complicated. The best way to access ^{231}Pa is probably via ^{227}Th, ^{223}Ra or ^{219}Rn, but no evaluation of these possibilities has been encountered in literature. ^{227}Th has a gamma line at 235.96 keV with emission probability 12.6 %, which is dangerously close to the intensive 238.63 keV gamma line of ^{212}Pb, but with good energy resolution it should be possible to make reliable measurements. ^{223}Ra 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 [228]Ac (270.24 keV) and – unfortunately – also the best gamma line of [219]Rn at 271.23 keV. If the activities are high, it should be possible to use interference correction and even smaller peak to determine the [231]Pa activities. It is also possible to test the reliability of the [231]Pa measurements by intercomparison between these three radionuclides.

2.2.9 [210]Pb Dating of Peat

Since large amounts of [222]Rn are able to escape to the atmosphere, there will be a production of [222]Rn daughters in the atmosphere. The most long-lived among these daughters is ^{210}Pb with a half-life of 22.3 years. Since lead is very particle reactive, the ^{210}Pb that is produced in the atmosphere will be attached to aerosols, which sooner or later will be deposited on the ground. In this manner, there is a continuous atmospheric flux of [210]Pb. If ^{210}Pb is deposited in some environment where there is an ordered build-up of some kind of material, such as sediments or peat, this can provide a geochronology. In peat lead will be very immobile and can be expected to stay in the peat layer, in which it is deposited. As the peat grows and new peat layers are added, the atmospherically deposited ^{210}Pb will decay and eventually reach undetectable levels. However, by measuring the ^{210}Pb 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 ^{210}Pb is known.

There are different ways to do these calculations and they are all based on different assumptions. The most straightforward model for ^{210}Pb 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 ^{210}Pb in the upper layer always is constant. If this is true, it can easily be shown that the time t that has passed since deposition, in other word the age of the peat layer, must be

$$t = \frac{1}{\lambda} \ln(\frac{A_0}{A}),$$ **Eq. 1**

where λ is the decay constant of ^{210}Pb, A the specific activity at some depth and 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 ^{210}Pb 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 an good choice anyway.

Some questions regarding the reliability of the ^{210}Pb dating method for peat were raised by Shotyk (1988) in an article, where he 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 are, however, comparative studies by El-Daoushy *et al.* (1982) on Finnish *Sphagnum* hummocks, where the ^{210}Pb dating method shows excellent agreement with the moss increment method.

2.2.10 Sample Preparation

One of the advantages with gamma spectrometry is that very little sample preparation is needed. As was mentioned earlier, the cores were sampled in August or September 2004 and kept in a cold-storage room at the Äspö Laboratory. In October the cores were sliced in 2.5-5 cm thick pieces and put in plastic containers. They were then transported

to Uppsala where they were freeze-dried at the Department of Ecology and Evolution. The samples were weighted before and after the freeze-drying in order to determine the water content.

The samples were then encapsulated in the special containers that are used in the gamma detectors at the Ångström Laboratory. Some of the peat and clay samples were integrated in order to increase the sample masses. Moreover, in a few cases peat samples were ashed at a temperature of $550^{o}C$ in order to increase the density of the material so that more radioactivity could be compressed in the containers.

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

3. RESULTS AND DISCUSSION

3.1 RADIONUCLIDE PROFILES

3.1.1 Uranium Chain Nuclides

The most relevant radionuclides from the uranium chain in a study like this one are shown in figure 5 below. There are several things in this diagram that calls for an explanation. The first striking thing is of course the high ^{210}Pb activities in the uppermost peat layers. This is due to the atmospheric deposition of ^{210}Pb and is

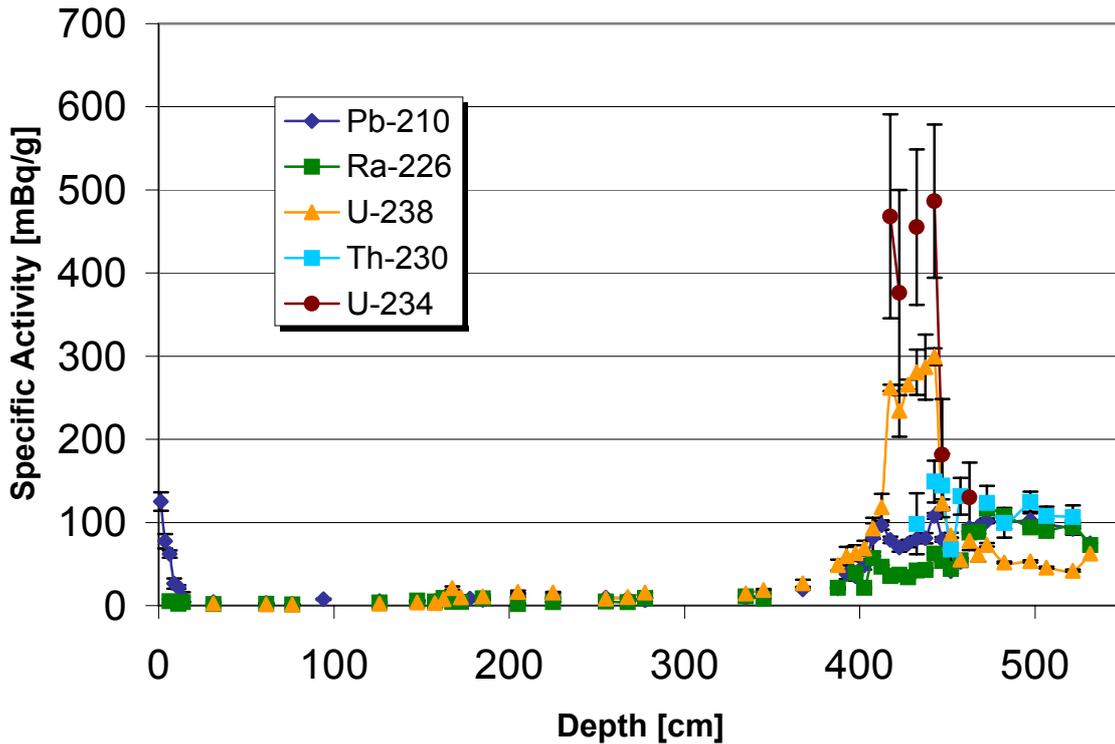*Figure 5: Specific activity for uranium chain nuclides including ^{234}U and ^{230}Th where measured. The gyttja is found between 400 and 450 cm.*

expected. In section 4.2.1 this will be used to date the peat layers and to calculate the recent growth rate of the peat. However, apart from this accumulation of ^{210}Pb, the levels of radioactivity in the rest of the peat are very low, although there are some differences in the distribution of radioactivity throughout the peat that are not very obvious in figure 5 (See section 4.2.2.). The highest specific activities are, however, encountered in the gyttja layers, which are thought to start just below 400 cm. Especially uranium reaches very high activities in the gyttja, and there are several interesting disequilibria in this region involving radionuclides such as [238]U, [234]U, [230]Th, [226]Ra and [210]Pb. Above all the [210]Pb-[226]Ra disequilibrium is interesting because of the comparatively short half-life of [210]Pb. The consequences of these disequilibria for radium is discussed in chapter 4.3, while uranium is discussed in chapter 4.4.

In the gravel zone below the gyttja, the specific activities for all the radionuclides presented in figure 1 drop, while it increases again in the clay for most radionuclides. Here the ^{210}Pb, [226]Ra and [230]Th activities appear to agree well, which

indicates that they are in secular equilibrium. The ^{238}U activities, on the other hand, are significantly lower, which of course calls for an explanation (See section 4.4.4.).

It is clear from figure 5 that the profiles for ^{230}Th and ^{234}U are not complete. This is because they are very difficult to measure using gamma spectrometry, as was mentioned earlier. ^{234}U could be detected and quantified in some samples in the gyttja thanks to the low ^{226}Ra content and the high uranium content. This implied that there was a significant contribution from ^{234}U to the 53.2 keV peak, which in normal samples is totally dominated by ^{214}Pb. Likewise, long measuring times and large sample masses has allowed determination of ^{230}Th in some samples, above all in the clay. It must be emphasized once again, however, that the uncertainties of the ^{234}U and ^{230}Th activities are very high, and there is no validation of the reliability of these peaks. Because of their importance for the interpretation of the other radionuclide profiles and lack of better data, the inclusion of these measurements is, however, motivated.

3.1.2 Actinium Chain Nuclides

The relevant actinium chain nuclides are presented in figure 6 below. Clearly, the ^{235}U profile shows an obvious resemblance with the ^{238}U profile in figure 5. The ^{235}U activities in the peat are very low, while there is a dramatic increase in the gyttja. In the gravel layer, the specific activity drops sharply and does not increase considerably in the clay samples.
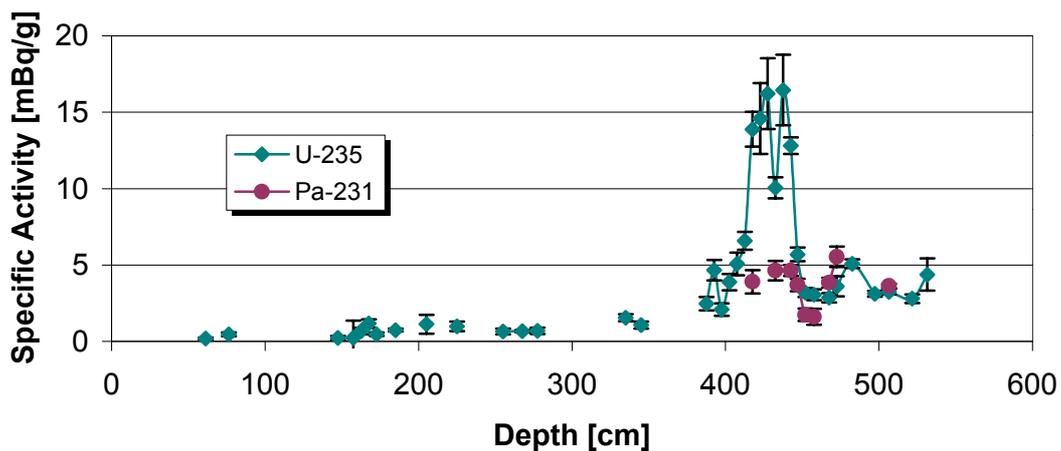

Figure 6: Actinium chain nuclides.

It is also clear that ^{231}Pa is not in secular equilibrium with ^{235}U in the gyttja layers, while the discrepancy is much smaller in the clay. As was discussed earlier, the peaks that were used to measure ^{231}Pa appear to be insufficiently tested, which of course raises some questions regarding the reliability of the ^{231}Pa profile. As for ^{234}U and ^{230}Th there are limitations in the measurements due to a combination of low activities and emission probabilities, but because all acquired spectra have not yet been analysed for ^{231}Pa, the ^{231}Pa profile could be made more complete without further measurements.

The independent measurement of two uranium isotopes, ^{235}U and ^{238}U, provides an easy way to test the reliability of the 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 ^{234}U, which could affect the ^{235}U/^{238}U ratio. Consequently, one would expect a fairly constant ^{235}U/^{238}U ratio throughout the core, provided that the measurements are correct. It should be obvious from figure 7 that this indeed is the case. The few exceptions are mainly among the

clean peat samples, where the ^{235}U obviously cannot be accurately determined because the ^{235}U activities are too low.

Since the ^{235}U content has been found to be constant in natural material, it is even possible to compare the measured ^{235}U/^{238}U ratio with a theoretically expected value: 99.2745 % of the natural uranium is ^{238}U, while the abundance of ^{235}U only is 0.7200 % According to Handbook of Chemistry and Physics (1974), the ^{235}U content may, however, vary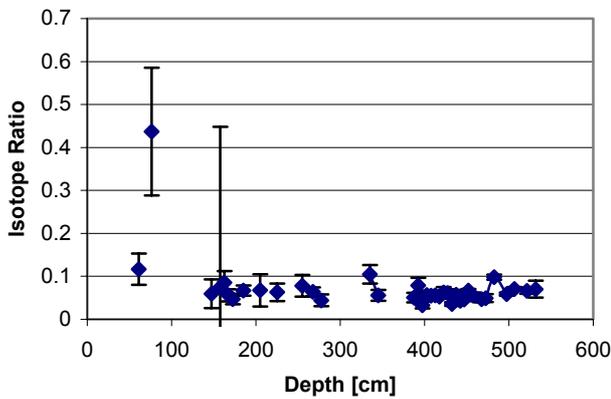 with 0.1 % depending on the source. This means the expected ^{235}U/^{238}U activity ratio is 0.046±0.07. In these measurements the weighted average of the ^{235}U/^{238}U ratios is 0.054, which is slightly high. This may indicate that the ^{235}U activities are overestimated or that the ^{238}U activities are underestimated. Since the ^{238}U have not been corrected for self-absorption, it is likely that the true ^{238}U activities, above all in the clay samples, are higher.

Figure 7: The ^{235}U/^{238}U ratio for the samples where quantification of ^{235}U has been attempted.

Moreover, the measurement of ^{235}U is very uncertain in some samples due to the very low activities. Often it is only possible to assess the ^{235}U activity via the 185-186 keV line, which is dominated by ^{226}Ra. It cannot be excluded that this in some way causes a slight overestimation of the ^{235}U activity, but it should be emphasized that this is not vital to the conclusions presented in this report, where ^{235}U is of minor interest.

3.1.3 Thorium Chain Nuclides
There are two interesting radionuclides in the thorium chain that can be measured by gamma spectrometry, ^{228}Ra and ^{228}Th. Their activity profiles are shown in figure 8 below. Evidently the ^{228}Th and ^{228}Ra activities agree very well throughout the core, which is not very surprising due to the comparatively short half-lives of these radionuclides, 5.76 years for ^{228}Ra and 1.91 years for ^{228}Th. Unfortunately, it is hard to
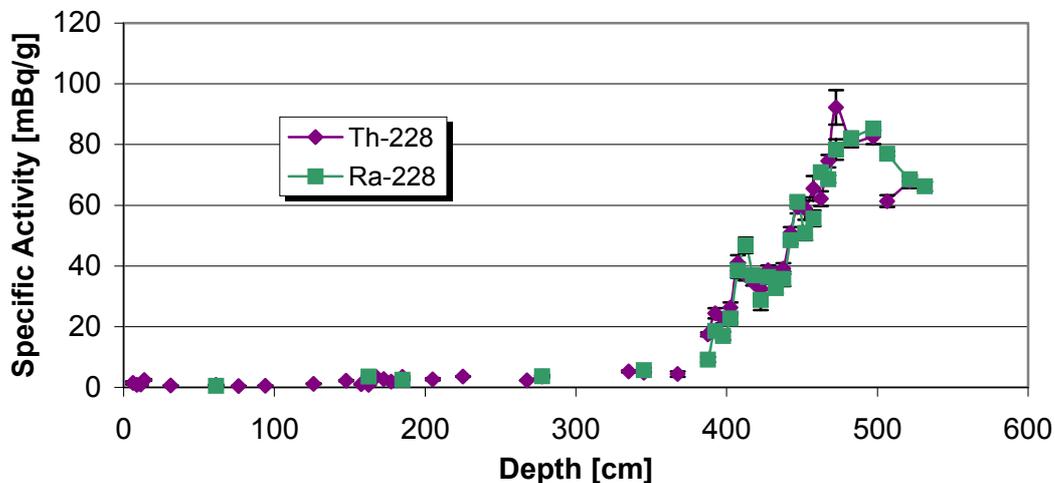

Figure 8: The relevant thorium chain nuclides accessible by gamma spectrometry.

measure the ^{232}Th activity, but if there has been only a limited transport of the ^{232}Th daughters, these profiles may reflect the ^{232}Th activity profile very well. The importance of these two measured profiles and the consequences of a possible disequilibrium with ^{232}Th for assessment of radium migration is discussed in section 4.3.5.

As for the radionuclide profiles presented above, there seems to be very low levels of thorium chain nuclides in the peat, while the levels sharply increase 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. Thus, it is clear that the behaviour of uranium significantly differs from the behaviour of many of the other elements that have been measured.

3.1.4 Miscellaneous Radionuclides

Apart from the nuclides of the naturally occurring decay chains, there are mainly three radionuclides that often are encountered in gamma spectrometry measurements of environmental samples: ^{40}K, ^{137}Cs and the ^{241}Pu daughter ^{241}Am. Traces of ^{241}Am were observed in the uppermost centimetres of the peat moss, but the activities were too low to allow reliable quantification with the available sample masses.
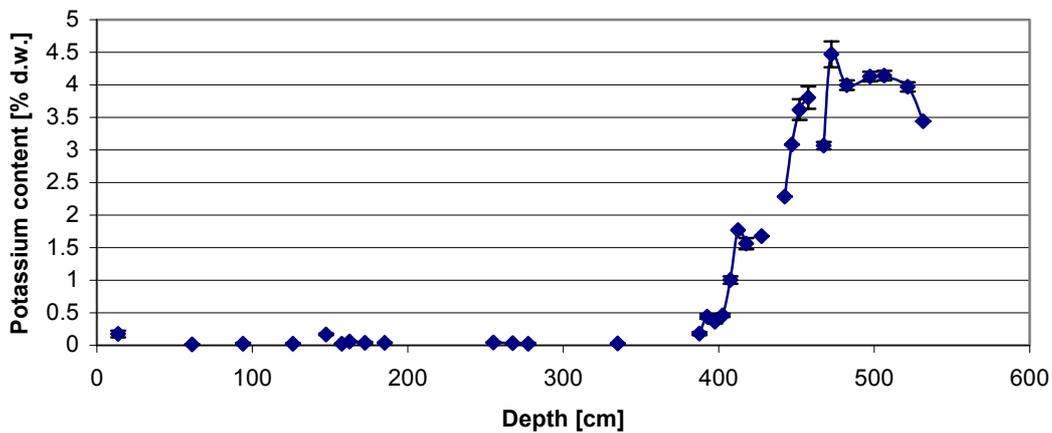

Figure 9: Potassium content by mass (dry weight) based on ^{40}K activities.

^{40}K can be used as an indicator of the total potassium content, because it is chemically equivalent to other potassium isotopes. Most of the natural potassium occurs as ^{39}K (93.26 %) or ^{41}K (6.73 %), while ^{40}K makes up only 0.0117 % of the total potassium inventory. The total potassium content can be calculated from the ^{40}K activity by multiplication by a conversion factor of 0.003234, if the potassium content is measured in percent and the ^{40}K activity is measured in mBq/g. Since the total potassium content probably is more interesting than the ^{40}K activity, this has been done for the data presented in figure 9. Figure 9 reveals that there is very little potassium in the peat, but as much as 4 % potassium in the clay. The potassium content increases sharply with depth in two steps: first to 2 % at the top of the gyttja and then to 4 % just below the gyttja. Further down the potassium stays close to 4 % with the exception of a temporary dip in the gravel. A comparison of figures 8 and 9 reveals that ^{40}K profile very much resembles the profiles of the thorium chain nuclides. The correlation becomes even more obvious, if the ^{40}K activities are plotted against the ^{228}Th activities. This is shown in figure 10. The lower peat samples, which are coloured in green in figure 10, clearly deviate from the general trend and if the were excluded, the agreement would of course be even better. One plausible explanation to this correlation is that both of these

radionuclides to a large extent could be connected to the mineral content of the samples. Thorium is generally considered more or less immobile in most environments. Rowe *et al.* (1997) write that thorium only is incorporated in peat in detrital mineral matter.

One thing that is not apparent in figure 10 due to the large variations in activity between different layers is that the correlation is not valid for the peat. In figure 11 only
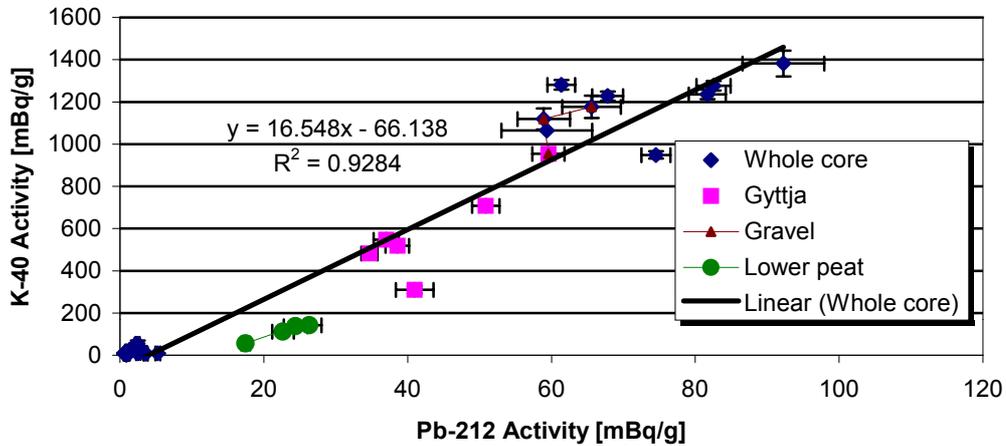

Figure 10: ^{40}K vs. ^{212}Pb throughout the entire core, but with special regions marked. The linear regression refers to the entire core.

the activities for the peat samples have been included, and this reveals a more or less constant potassium content throughout the peat. The only two anomalies are two samples with very high potassium content, but these samples also differ in other ways from the rest of the samples; one of them contains a piece of wood and the other one is

the most superficial of the samples analysed for ^{40}K, only about 10 cm below the surface. Thus, these deviations are probably explained by biological uptake of potassium. Accordingly, ^{40}K is probably not a good indicator of mineral content in peat, whereas the reliability of ^{212}Pb (in secular equilibrium with ^{228}Th) remains to be tested.

The specific activity for ^{137}Cs, finally, is shown in figure 12. Due to its comparatively short-half life
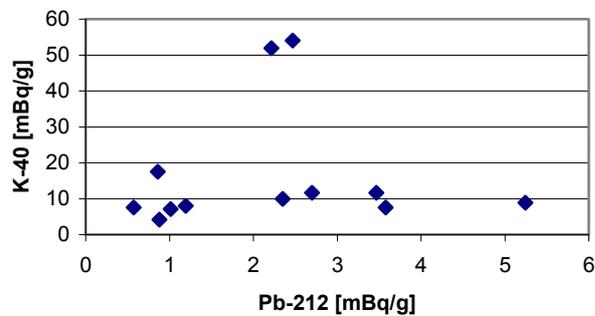
Figure 11: ^{212}Pb vs. ^{40}K in peat layers. The two points with ^{40}K activities above 50 mBq/g represent a sample close to the surface and a sample containing a piece of wood.

^{137}Cs is not very interesting in the assessment of radionuclide transport from a deep repository. Yet ^{137}Cs may be of some interest in this study because it can give some hints concerning the direction of the water flow. As no ^{137}Cs could possibly have been present in the core before the late 1950s, it is clear that a maximum of 45 years is available for the transport. The highest specific activities are found in the upper peat layers. This indicates that there has been a post-depositional redistribution of cesium and that there probably is a significant biological uptake of cesium, since the highest levels are found in the living moss. Had there been no redistribution of ^{137}Cs, one would

expect to see two peaks, the first one representing the atmospheric testing of nuclear weapons in the late 1950s and early 1960 and the second one representing the Chernobyl accident in 1986.

Despite the fact that much ^{137}Cs appears to be caught in the uppermost peat layers, parts of the ^{137}Cs has been transported surprisingly deep. Apparently cesium must be transported downwards at speed of at least 4 cm/yr. Maybe it is possible that the root systems of the pines on the bog are partly responsible for this, but it seems likely that the major explana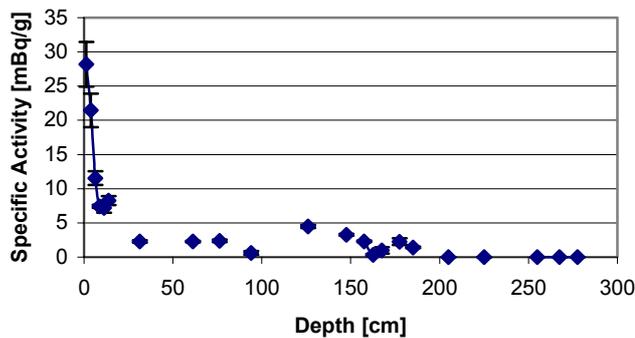tion is groundwater transport. Landström and Sundblad (1986) also found ^{137}Cs very deep in a peat (150-180 cm) and suggested that this could be the result of an upward migration through the fracture zones in the bedrock below. No ^{137}Cs could be detected in samples below 200 cm in Klarebäcksmossen, however, so it seems clear that it hardly has come from below, but that there rather has been a transport from the surface. There is extensive literature showing that cesium indeed is very mobile and affected by both biological uptake and advection (Turetsky, 2004). This would not only imply that cesium is very weakly sorbed by peat, but also that there has to be a considerable downward movement of water. No hydrological measurements are available for Klarebäcksmossen, but measurements from the area have shown that the average discharge in the area is 180 mm/yr (Larsson-McCann *et al.*, 2002). If this is representative for Klarebäcksmossen, it can be estimated the it would take the groundwater 7-8 years to reach a depth of 180 cm, provided that it flows vertically. Cesium will of course be retarded by sorption, but it must be realized that the more horizontal the water flow is, the longer the ^{137}Cs must have been transported. At some depth there ought to be a predominately horizontal flow in order to drain the bog and its drainage area, but whether this is above or below the gyttja seems hard to decide without relevant observations. It will be apparent that this question is absolutely central in the discussion of the isotopic disequilibria in the gyttja.

Figure 12: [137]Cs activity profile. No ^{137}Cs could be detected below 200 cm.

It can also be mentioned that all major peaks in the gamma spectra have been identified with a reasonable accuracy and that no gamma-emitting artificial nuclides except for ^{137}Cs and [241]Am appears to be present in detectable levels.

3.2 THE PEAT LAYERS

3.2.1 [210]Pb Dating and Determination of Peat Growth Rates

As was described earlier, the accumulation of ^{210}Pb 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 ^{210}Pb, especially in the somewhat deeper samples. As the accuracy of the unsupported ^{210}Pb in the deeper samples is very important in the CRS model, this model is not very suitable in this case. Therefore, it was decided that the CIC model

would be used for the dating. The result of this dating is shown in figure 13. It should be noted that the linear regression in figure 13 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.

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 moss 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 very careful about such extrapolations. A much more reliable approach in this case would be to use the ^{14}C method.
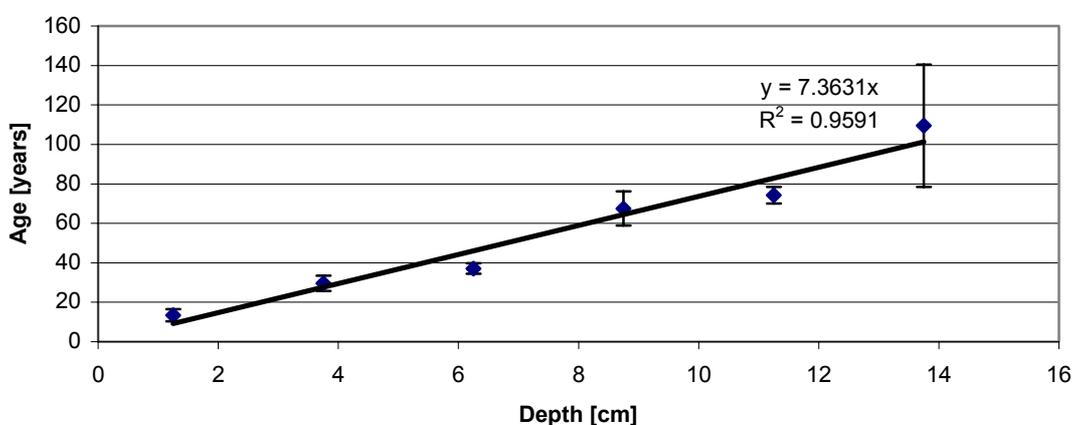

Figure 13: Peat age as a function of depth as determined by the CIC model.

However, 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 ^{210}Pb dating of *Sphagnum* peat in central Småland by El-Daoushy and Franzén (See Franzén, 1985). Since the ^{210}Pb 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.

3.2.2 Differences Between Minerotrophic and Ombrotrophic Peat
Figure 14 shows the specific activity of some important radionuclides in the peat. It is to a large extent only a part of the profiles in figure 5, but ^{228}Th has been included together with the uranium chain nuclides, because it is thought to be closely correlated to the mineral content as was described earlier. The fluctuations that some profiles show in the region between 150 and 200 cm, could possibly be related to small pieces of wood that were present in some of the samples. As can be seen from the soil interpretation, there are also some different kinds of peat in this region, which represents the transition from minerotrophic to ombrotrophic conditions.

It seems clear from figure 14 that above all ^{238}U, but also ^{210}Pb and ^{228}Th, are more abundant in the minerotrophic sedge peat, whereas the behaviour of ^{226}Ra is

somewhat more complex, but with increasing levels towards the bottom of the peat profile. There is also a tendency that the upper bog peat layers have higher specific activities than the lower bog peat layers, which possibly could be an indication of active biological uptake of radium. Unfortunately, the sample masses for the upper 10 cm of the peat were to small to reliably determine ^{226}Ra and ^{238}U activities in the living moss. This would be possible, if more material could be introduced in the detectors.
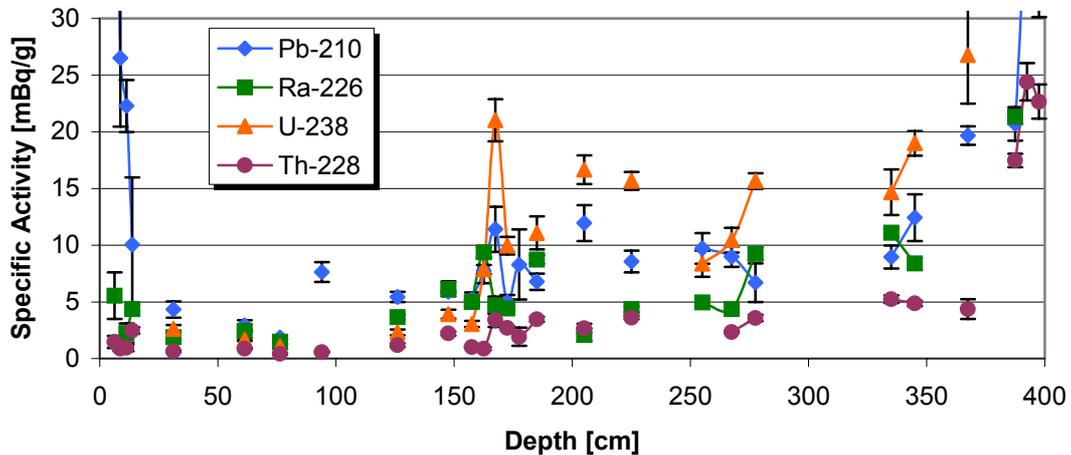

Figure 14: Some uranium chain nuclides and ^{228}Th in the peat.

Since the increase in activity for radionuclides such as ^{238}U, ^{228}Th and ^{210}Pb coincides with the transition from ombrotrophic to minerotrophic conditions, it seems very probable that there is a causal connection between these things. It could mean either that sedge (*Carex*) accumulates these elements more effectively than bog moss *(Sphagnum)* or that the transport of these radionuclides in peat primarily is controlled by the groundwater. However, since the pattern is similar for several elements, the latter hypothesis seems more likely. There is little support in these measurements for the idea that bog moss actively would transport large amounts of radioactivity from below. In the case of ^{238}U, which is the radionuclide in figure 14 that increases most in the sedge peat, there are studies indicating little or no enrichment of uranium in plants. Greger (2004) refers to several investigations of uranium uptake in her report. Dunn (1981) has investigated uranium levels in plants above a uranium ore 150 m beneath the surface. Uranium is mineralised and transported through fracture zones and increased uranium levels have indeed been observed in these areas. It was concluded that the uranium content of different species and even plant parts varies greatly. Both spruce and pine wood contained less than 1 ppm in average (roughly 12.4 mBq/g ^{238}U), while spruce twigs had an average of 84 ppm or more that 1,000 mBq/g ^{238}U. Although these levels are very high, Dunn emphasizes that even the highest concentrations in plants are only slightly higher than those found in the soil (compared on a dry-weight basis). The situation could of course be different for bog or fen communities and this could be investigated further, but it is hard to see any strong tendency of enrichment of uranium by living organisms in these measurements. Figure 15 also shows that there is a deficit of uranium in comparison with radium in the ombrotrophic peat, which may indicate that radium is more easily taken up that uranium. This would then agree with results published by Greeman *et al.* (1998), who claim that radium is preferentially is incorporated in vegetation relative to uranium.
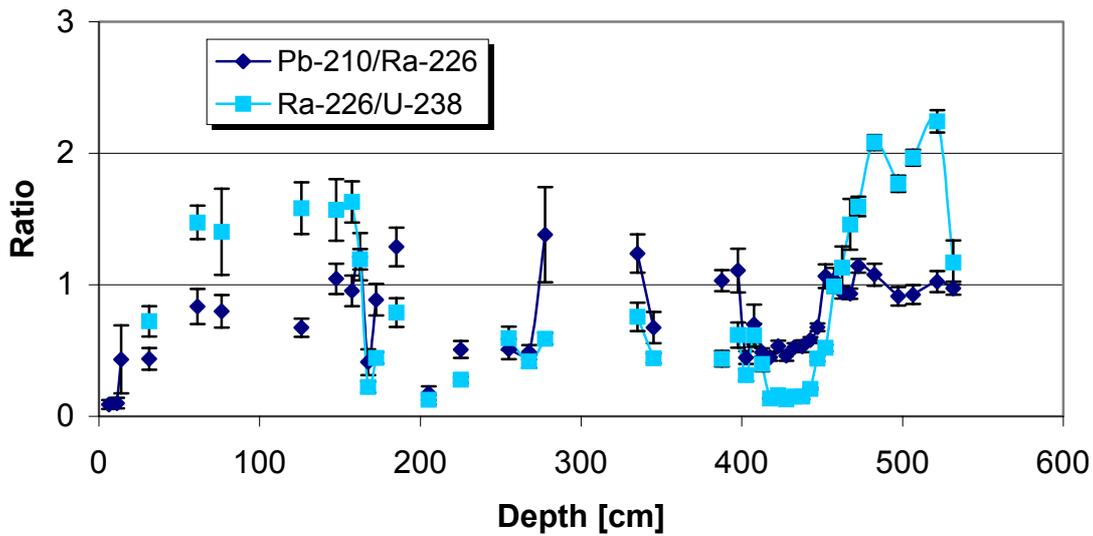
Figure 15: Key isotopic ratios for the uranium chain.

It is also noteworthy (see figure 15) that ^{210}Pb is not in secular equilibrium with ^{226}Ra in many of the peat samples. Generally there seems to an excess of ^{210}Pb throughout he core This suggests either that the peat is supported with ^{222}Rn from below or that there has been a recent removal of radium from parts of the peat. Similar patterns are found in the gyttja, but there the difference is even more striking. However, there is also more data available for the gyttja, which makes it somewhat easier to discuss the reasons behind the ^{210}Pb-^{226}Ra disequilibrium.

3.3 RADIUM IN THE GYTTJA LAYERS

3.3.1 The Reliability of the ^{226}Ra and ^{210}Pb Measurements

The half-life of ^{210}Pb is 22.3 years, which means in a closed system it would more or less be in secular equilibrium with ^{226}Ra after 100-150 years, unless there initially was extremely much ^{210}Pb in comparison with ^{226}Ra. In material as old as the gyttja, which undoubtedly is at least 1,000 years old, it seems improbable that the disequilibrium would reflect the initial conditions of the deposited material. Because of the comparatively short half-life of ^{210}Pb, the ^{226}Ra/^{210}Pb ratios strongly indicate that there is recent or even on-going migration of some radionuclide in the uranium chain. Before any conclusions are drawn, it is, however, important to make sure that the results really reflect the true conditions in the gyttja.

As regards the measurements, there should be little doubt about the reliability of the data. ^{210}Pb and ^{226}Ra are the most frequently used radionuclides by the Environmental Physics Group at the Ångström Laboratory. They have been measured in numerous studies and the ways to quantify them are well established. Furthermore, there are no apparent disequilibrium in other parts of the core, such as the clay, which would indicate a systematic error in the measurements. Most of the gyttja samples were measured in the planar detector, while some were measured in the new well detector (well 2). However, there is no significant difference between the ^{226}Ra/^{210}Pb ratios in these measurements. The planar detector was also used to measure other samples, where no disequilibrium were detected. Thus, these measurements can be considered to

be reliable; there is nothing indicating that the results from the measurements would not reflect the actual situation of these radionuclides in the containers.

However, this does not automatically imply that the samples in the containers correctly reflect the *in situ* conditions in the gyttja. It seems impossible, however, that the sampling significantly would have altered the radium-lead balance in the samples. If significant volumes of water were lost in connection with the sampling, although this was not the case according to those who collected the cores (Nilsson, private communication), the fraction of radium is the pore water is expected to be very low, a few percent at the very most, if one uses the K_d values presented by the IAEA (1994). Hence, there is no way that as much as half of the radium could have been lost because of this. Likewise, it seems impossible that the radium-lead balance would have changed while the cores were stored in the freezer at the Äspö Laboratory. The half-life of ^{210}Pb is too long to allow any significant change in the ^{210}Pb activities during this time. A hypothesis that is worth to investigate closer, however, is the possibility of sorptive uptake of radium in the plastic containers, in which the samples were transported from Oskarshamn to Uppsala. Unfortunately, the samples could not be transported in the frozen state. Thus, radium could have moved through the water and attached to the walls of the plastic containers. However, measurements have been performed on one of these containers and no detectable amounts of radium were found. Hence, this hypothesis must be rejected. Furthermore, none of the gyttja samples have been ashed so radium cannot have volatilised during heating, if it would exist in a chemical form that would allow this to happen. Hence, the bottom line is that it is very hard to explain the measured ^{226}Ra/^{210}Pb ratios in any other way than that they do reflect the true conditions in the gyttja from Klarebäcksmossen. Accordingly, one must try to find processes in the gyttja that may explain the observed disequilibrium.

3.3.2 Migration of ^{222}Rn

The first hypothesis that must be investigated is migration of ^{222}Rn, which occurs between ^{226}Ra and ^{210}Pb in the uranium decay chain. This hypothesis will be referred to as the radon hypothesis. 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 very mobile. According to Kadko (1980, p. 370), "molecular diffusion through pore water and radioactive decay far outweigh mechanical mixing and advection for ^{222}Rn", which seems like a reasonable statement under most conditions. In particular, the water flow through the gyttja would have to be extremely fast in order to move ^{222}Rn any considerable distances before it decays. Would it then be possible to explain the ^{226}Ra/^{210}Pb ratios observed in the gyttja by diffusion of ^{222}Rn?
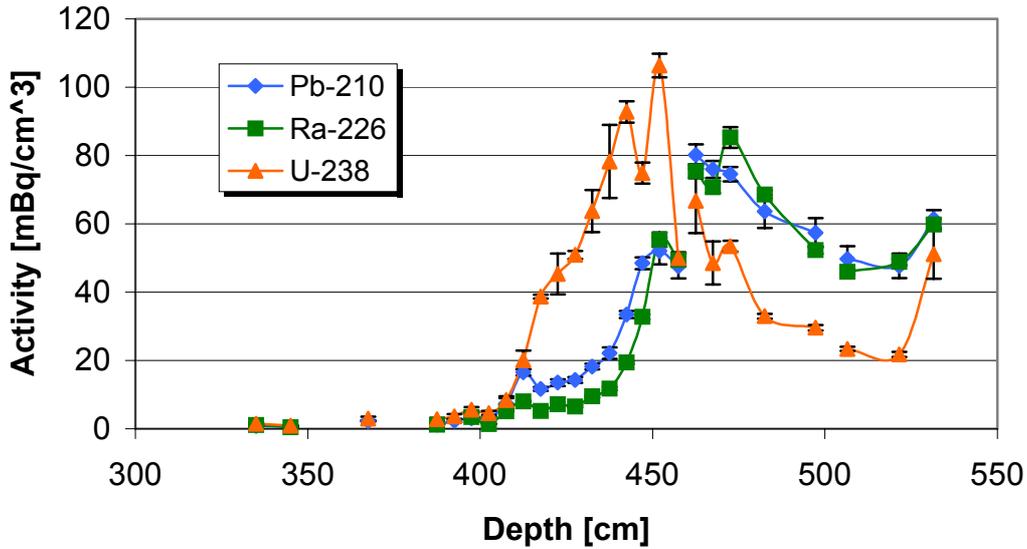
Figure 16: Uranium chain nuclides measured in activity per volume unit.

The hypothesis becomes even more attractive, if one considers the ^{210}Pb and [226]Ra profiles in figure 16. The figure essentially shows the same as figure 5, but the unit on the y-axis has been converted so the activity per volume unit is shown. If it is assumed that [222]Rn only to a small extent is connected to the solid material, this picture would better describe the concentration gradient, which governs the size of the diffusive transport according to Fick's first law:

$$\overline{j} = -D\nabla C.$$ **Eq. 2**

Here **j** is the diffusion flow, D the (effective) diffusivity and C the particle concentration. A rather conspicuous thing in figure 16 is that the ^{210}Pb profile between 400 and 450 cm appears to have been translated approximately 5 cm upwards in relation to the [226]Ra profile. Hence, it is possible that the ^{210}Pb on a certain depth is not in secular equilibrium with the [226]Ra on the same depth, but rather with the [226]Ra some centimetres below. Indeed, one could expect such a phenomenon, if there is a sufficiently fast diffusive transport of [222]Rn.

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 for the effective diffusivity of radon in saturated soil 2×10^{-6} cm^{-2}/s. Higher values of the effective diffusivity can, however, be encountered in literature. For instance, Kadko (1979) says the effective diffusivity of radon in sediments is 5×10^{-6} cm^{2}/s, while Benoit *et al.* (1991) have used an even higher value, 6×10^{-6} cm^{2}/s, in their model. The distance that a single [222]Rn atom can cover is limited both by its half-life and the effective diffusivity. Formally, this is described by the diffusion length, Z_d, which is defined as

$$Z_d = \sqrt{Dt},$$ **Eq. 3**

where D is the diffusivity and t the time. In the case of radionuclides, the most relevant time is often the mean life. In the case of [222]Rn the mean life is roughly 5.5 days, which means that the diffusion length for [222]Rn should be in the order of 0.97-1.7 cm. This

may indicate the diffusion is too slow to explain the low ^{226}Ra/^{210}Pb ratios in the gyttja. A thorough investigation of the migration of radon in the gyttja would, however, require more detailed calculations involving the concentration gradient. Preliminary modelling of the diffusion process has been performed indicating that diffusion alone cannot account for much more than a ^{226}Ra/^{210}Pb ratio of 0.9, but this has to be investigated further before any definitive answer can be given.

Even if diffusion would turn out 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 the carrying medium. These carrier gases could for instance be carbon dioxide and methane. Radon and other trace gases are then thought to move together with these bubbles and this would allow a much more rapid movement. The geogas hypothesis is, for example, supported by the fact that radon and carbon dioxide are strictly correlated above fault zones (Etiope and Martinelli, 2002). However, there seem to be small possibilities to decide how large this transport may be in the case of Klarebäcksmossen based on these data. Hence, it is not possible to reject the hypothesis that migration of ^{222}Rn causes the ^{226}Ra/^{210}Pb disequilibrium at this stage.

On the contrary, migration of radon should be regarded as a very likely explanation. Migration of radon 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 "^{226}Ra/^{210}Pb disequilibrium may almost always be considered as a measure of radon mobility". Excess of ^{210}Pb was also found by Zielinski *et al.* (1985) in a peat-sediment core. Although they observed low ^{226}Ra/^{230}Th ratios in some samples, they concluded that the most probable explanation to their data is input of intervening ^{222}Rn.

There are ways to experimentally test the radon hypothesis, but it probably requires much work. At this stage such attempts can hardly be justified, since there also may be other ways to explain the ^{226}Ra/^{210}Pb ratios. For instance, the ^{226}Ra/^{230}Th ratios in the gyttja, suggest that migration of ^{222}Rn cannot be the whole truth.

3.3.3 ^{226}Ra/^{230}Th Ratios in the Gyttja

One of the advantages of gamma spectrometry it that it allows simultaneous determination of all gamma-emitting radionuclides with reasonably high emission probabilities. This results in a rather impressive set of data, which can be very valuable in this kind of studies. Since ^{226}Ra is one of the radionuclides in the nuclear waste that possibly could reach the surface in appreciable amounts, it would be interesting if any conclusions can be drawn concerning the behaviour of radium in this core. In this case, it is possible to study the levels of ^{226}Ra in relation to its granddaughter ^{210}Pb, but also in relation to its parent, ^{230}Th. Generally, ^{226}Ra could be expected to reach secular equilibrium with ^{230}Th after at least 6,000-8,000 years. Hence, if the gyttja has behaved as a closed system with respect to radium, one would expect ^{226}Ra/^{230}Th close to unity.

Once again it must be underlined that the reliability of the [230]Th measurements is unsatisfying, but all acquired spectra from the gyttja, whose measuring time has been long enough to allow quantification of the [230]Th activity, indicate a distinct disequilibrium between [226]Ra and [230]Th. As it appears, the [226]Ra/[230]Th ratio is only 0.43±0.16 based on a weighted average. This is unexpectedly low. For instance, if it is assumed – rather unrealistically – that no [226]Ra at all was imbedded in the gyttja during its formation and that everything that is found there today can be attributed to *in situ* production, it is possible to estimate a maximum age for the sediments. Provided that no radium has been lost from the gyttja and that the estimated [230]Th activity is fairly correct, the age of sample GY1-13 (430-435 cm) should be 1,290±650 years. Similar calculations for the even deeper samples, GY2-1 (440-445 cm) and GR1 (445-449 cm), results in even younger ages, 1,260±290 years and 1,080±370 years respectively. The points are also shown in figure 17 together with the expected growth curve of the [226]Ra/[230]Th ratio with time.

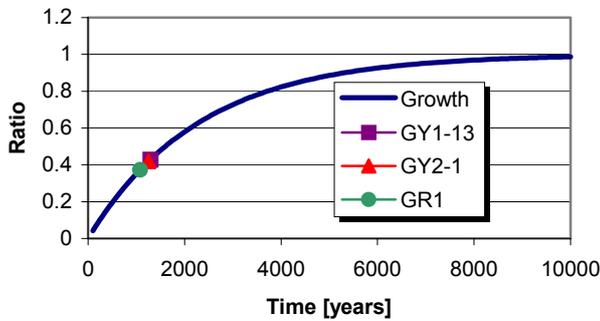*Figure 17: The exponential growth of the [226]Ra/[230]Th ratio with time and the ratios found in some gyttja or gyttja-gravel samples.*

Clearly, these estimated ages seem very low. The average growth rate of the peat would have to be well above 2 mm/yr and the net production more than 160 g/m^2/yr. These figures are not completely unrealistic (Franzén, 1985), but it should be remembered that they represent absolute minima and that the calculations, on which they are based, are quite unrealistic. Now, this discussion should not be understood as an attempt to convince anyone that these ages are correct or even that the suggested dating method is sensible. On the contrary, one should expect at least some [226]Ra 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. The point is that the only way to explain these low [226]Ra/[230]Th ratios and, thus, to allow the gyttja to be older is to assume that there has been a post-depositional removal of radium.

Hence, if the determination of the [230]Th activities in the gyttja is correct – which it appears to be – there are strong indications of removal of radium from the gyttja. Removal of radium would not only affect the activity ratio for [226]Ra with respect to its parent, [230]Th, but also with respect to its daughters, among them [210]Pb. The question is then whether it is possible to explain the low [226]Ra/^{210}Pb ratios in the gyttja in this way instead, since there after all are signs that radium is or has been moving in the gyttja.

3.3.4 Removal of Radium from the Gyttja

If removal of radium is the explanation to the low [226]Ra/^{210}Pb ratios observed in the gyttja, it is clear that this must be a relatively recent and rapid removal. In order to assess the credibility of this hypothesis, the radium hypothesis, some basic calculations can be done. If radium really is disappearing from the gyttja in some way, it would appear as if the half-life of [226]Ra is shorter than the physical half-life. In radioecology,

this apparent half-life is often referred to as the effective half-life. Mathematically, the process could be described as

$$\frac{dN}{dt} = -\lambda N - rN = -\lambda_{eff} N \, ,$$ **Eq. 4**

where N denotes the number of nuclei and λ the decay constant. r is a removal constant, analogous to λ, which describes the how large fraction of the nuclei that is removed – by other processes than physical decay – in a time unit. Obviously, λ and r could be substituted by a single decay constant, λ_{eff}, the effective decay constant. 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

$$T_{eff} = \frac{1}{\dfrac{1}{T_{\frac{1}{2}}} + \dfrac{1}{T_{rem}}} \, .$$ **Eq. 5**

In order to see what implications this will have for the ^{226}Ra/^{210}Pb ratio it is necessary to go to the equation describing the relation between the activity for a parent and a daughter. This equation is derived in appendix A, where it is described how secular equilibrium is established. If the parent in this case is identified with ^{226}Ra and the daughter is identified with ^{210}Pb, we can write

$$A_{Pb} = \frac{\lambda_{Pb}}{\lambda_{Pb} - \lambda_{Ra}} A_{Ra} \left(1 - e^{-(\lambda_{Pb} - \lambda_{Ra})t}\right),$$ **Eq. 6**

where A_{Pb} and A_{Ra} denote the activities of ^{210}Pb and ^{226}Ra respectively and λ_{Pb} and λ_{Ra} their decay constants. Under normal circumstances, where 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 4. 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 ^{226}Ra/^{210}Pb ratio isolated. This will result in the following expression:

$$\frac{A_{Ra}}{A_{Pb}} = \left(1 - \frac{T_{Pb}}{T_{eff}}\right) \left(\frac{1}{1 - e^{-\ln 2 (\frac{1}{T_{Pb}} - \frac{1}{T_{eff}})t}}\right) \, .$$ **Eq. 7**

The expression within the second parenthesis only tells us how fast the ratio will approach steady state. It is clear that if the effective half-life of ^{226}Ra is decreased, this factor will approach unity much slower. However, the time dependent factor will look somewhat different if ^{210}Pb and ^{226}Ra 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 ^{226}Ra/^{210}Pb 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

$$\frac{^{226}Ra}{^{210}Pb} = 1 - \frac{T_{Pb}}{T_{eff}}.$$

Eq. 8

Equation 8 shows that if there is no removal of radium, i.e. the effective half-life of ^{226}Ra is equal to the physical half-life of ^{226}Ra, the ^{226}Ra/^{210}Pb ratio will be 0.986. This is the classical secular equilibrium between these two radionuclides under laboratory conditions. The actual ^{226}Ra/^{210}Pb ratios in the gyttja sample are, however, as low as 0.5 and even less. We are now in position to determine how fast ^{226}Ra must be removed in order to accomplish such ratios. For instance, if the ratio is exactly 0.5, the effective half-life must apparently be twice the half-life of ^{210}Pb – that is 44.6 years. Using equation 8, it can then be calculated that the environmental half-life for ^{226}Ra must be 45.9 years. This corresponds to a removal rate r of approximately 0.015 per year. In other words, to support a ^{226}Ra/^{210}Pb ratio of 0.5, 1.5 % of the total ^{226}Ra has to be removed annually. Evidently, equation 8 does not include the effects of ^{230}Th decay, but it can be shown that they are negligible on these short time-scales.

Is it then reasonable to expect such rapid removal of radium? Unless one does not want to claim that there is a significant uptake of radium by possible roots from the pines – which would seem strange, for instance because it appears to have been no uptake of potassium according to figure 10 – groundwater advection seems to be the only possibility. Hence, the answer to this question mainly depends on two factors: the fraction of radium dissolved in the water and the movement of water through the gyttja. The former of these factors could to some extent be estimated by the use of distribution coefficients, so-called K_d values. The best alternative would of course be to measure the ^{226}Ra activities in the aqueous phase, but in lack of such data, the available K_d values are better than nothing. 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 within 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 18, where the measured water content and dry weights of the samples have been used in 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
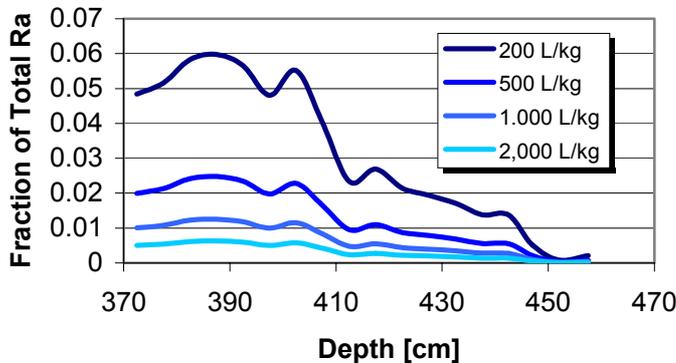

Figure 18: The dissolved fraction of the total Ra content for some different distribution coefficients.

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.

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 ^{137}Cs 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 below that. Although it might seem most natural to expect a flow upwards through the gyttja, since fens and bogs commonly are located in topographic depressions, such a flow can hardly explain the observed radionuclide profiles. If radium was transported upwards at the velocities described above, one might expect ^{226}Ra/^{210}Pb ratios higher than unity in the lower parts of the peat. Apparently this is not he case. If radium, on the other hand, was transported downwards, it seems more likely that it would be able to escape without leaving any traces, since there probably is relatively little sorption to the gravel due the low surface-volume ratio. Furthermore, the hydraulic conductivity of the gravel is most likely very high, which would allow a rapid removal. Another argument is that upwelling groundwater could be expected to have comparatively high concentrations of various soluble substances such as radium in comparison with rainwater from the peat above. In order to accomplish a leakage of radium from the gyttja, it is of course necessary that the groundwater entering it does not carry too much radium.

There are some signs that the sampling site is somewhat special, although very little data indeed is available. However, two cores were sampled from Klarebäcksmossen so it possible to draw some conclusions regarding the inclination of above all the wave-washed gravel zone and the gyttja. The exact distance between the two cores is not accessible at present, but it is estimated that the distance is approximately two or three meters. According to the analysis performed by Geosigma (Nilsson, 2004), the gravel is found on a depth of 462-470 cm in their core, while it is clear that in this core the gravel is found at a depth of 450-458 cm. This implies that the inclination of the gravel layer would be in the order of 4-6 %, which is rather steep. Moreover, if the interpretations of the gyttja layers are correct, the average inclination of the peat-gyttja interface could be as much as 10-18 %. This inclination would probably facilitate the movement of water into the gyttja, if the groundwater moves in a direction such that that the thickness of the more permeable peat layer decreases. In this manner the groundwater could be forced to flow through the gyttja, although it may seem somewhat awkward at first glance. It is hardly necessary to state that the situation would be much clearer, if some hydrological measurements were performed on the site.

Anyway, if it is assumed that there in some way is a flow through the gyttja directed downwards – how high could this flow possibly be? 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, it still remains unclear what volumes that pass the gyttja. It could be more, because the drainage area of the bog contributes with more water, or it could be less, because the bog mainly is drained by horizontal flow in the peat. The approximate amount of water in the gyttja (400-450 cm) is 30 g/cm^2 so if the flow through the gyttja would equal the discharge, for instance, the residence time for the pore water in the gyttja as a whole would be 1.7 years. Hence, it does not seem impossible that there is a rather fast circulation of water in the gyttja. More accurate estimations would require some modelling, where different gyttja layers can be distinguished, but with the limited

amount of time available for a thesis work, these attempts have not been finally evaluated. Preliminary results indicate, however, that it might be possible to obtain the ^{226}Ra/^{210}Pb ratios observed in the gyttja without assuming unreasonable K_d values or water velocities. However, a model would not prove anything anyway – the most important thing to do is to collect some supplementary hydrological data that may solve these problems once and for all.

Another aspect of the radium hypothesis that must be considered is that the removal cannot have been going on for very long. If the effective half-life is as low as 50 years, this would require extremely high radium levels in the case that the removal has been going on for while. Therefore, it seems likely that the losses are related to a fairly recent event in the history of the bog. One such event that possibly could have triggered the release of radium could be the draining of the south-western parts of the bog. However, it is yet unclear exactly when Klarebäcksmossen was drained, but most likely it must have been in the late 19th century or early 20th century. If a bog is drained, it seems sensible that the groundwater level would be lowered. After all, that is usually the reason why a bog is drained. This would in turn decrease the hydraulic pressure so that the inflow of groundwater from below would increase. Indeed, Kellner (2003) writes that "an increased component of upward flow (…) often is experienced after drainage" and refers to a study by Lundin (1993). Obviously, this does not support the hypothesis that radium is being transported down towards the gravel, but for various reasons there may of course be exceptions to this pattern.

3.3.5 Possible Clues from ^{228}Ra

If 1.5 % of the total ^{226}Ra content in a certain volume is removed every year, it seems reasonable to assume that all other radium isotopes are be removed at approximately the same speed. As there are three other radium isotopes in the naturally occurring decay chains, this could be used to test the radium removal hypothesis. ^{223}Ra and ^{224}Ra both have very short half-lives, 11.4 and 3.66 days respectively, so they are not very likely to be affected by any leakage of radium. ^{228}Ra, on the other hand, has a half-life of 5.76 years so, possibly, both the ^{228}Ra/^{232}Th and the ^{228}Ra/^{228}Th ratios could be influenced by removal of radium.

Figure 19: ^{226}Ra/^{210}Pb and ^{228}Ra/^{228}Th activity ratios.

[228]Th activities are unfortunately not available, but the [228]Ra/[228]Th ratios have been plotted in figure 19 together with the [226]Ra/^{210}Pb ratios. The most interesting region is 400-450 cm, where there is a clear excess of ^{210}Pb in relation to [226]Ra. Apparently there is also a slight excess of [228]Th in relation to [228]Ra, although the uncertainties here are so high that the difference hardly is significant for each individual sample. As the ratios in the gyttja seem to show a general trend, it may, however, be possible to show that there is a significant general discrepancy between [228]Th and [228]Ra. If it is assumed that the observations come from normal populations, this can be done with a matched pairs t test (See Johnson, 2000). Suppose that samples GY1-7 to GY2-1 (400-445 cm) make up the gyttja and let the null hypothesis be that there are equal activities of [228]Th and [228]Ra. The alternative hypothesis will be that the [228]Th activities are higher than the [228]Ra activities. The matched pairs t test then tells us that the null hypothesis must be rejected and that we can be at least 99.5 % confident that the measured [228]Th activities actually are higher.

This may signify that there either is an actual excess of [228]Th in the gyttja or that there is a systematic error in the measurement of at least either of the two isotopes. However, if the matched pairs t test is applied for the whole core with the same null hypothesis and the same alternative hypothesis, the null hypothesis cannot be rejected even on the 90 % confidence level. This may indicate either that there is no large systematic error or that the systematic error is disguised by an excess of [228]Ra in some samples so that the null hypothesis cannot be rejected for the core as a whole.

What pattern would then be expected for the [228]Ra/[228]Th ratios, if there was a removal of radium from the gyttja? If it is assumed that [228]Ra and [228]Th are in secular equilibrium with [232]Th when the removal begins, it is clear that the [228]Ra/[228]Th ratio initially will be affected. As long as the removal rate is in the order of 1 or 2 %, the [228]Ra/[228]Th ratio would not be affected more than by a few percent according to equation TTT. Furthermore, the effect would not last for very long, because [228]Th has a half-life of only 1.9 years and [228]Ra rather quickly will find a new steady state with [232]Th. Thus, the [228]Ra/[228]Th ratio cannot give many clues concerning the behaviour of radium in this specific case. If the small differences really indicate something, it must be that a small amount of radium has been lost very recently, possibly in connection with the sampling. Anyway, there is nothing about the [228]Ra/[228]Th ratios observed that contradicts the radium hypothesis, but, on the other hand, there appears to be nothing that supports it either.

Yet the thorium chain could provide positive proof of on-going radium removal, but this would require measurements of [232]Th, which cannot be accessed by gamma spectrometry. If radium is lost, one should expect [228]Ra/[232]Th ratios lower than unity. More exactly, one should expect

$$\frac{^{228}Ra}{^{232}Th} = \frac{\lambda_{Ra-228}}{r + \lambda_{Ra-228}},$$
<div align="right">**Eq. 9**</div>

where r is the removal constant of radium and λ_{Ra-228} the decay constant of [228]Ra. 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. The only risk may be that the removal rate is too low to cause any significant disequilibrium. For instance, if 1.5 % is lost annually by leaching, the expected ratio would be 0.89. If the [228]Ra/[232]Th ratio, on the other hand, would be close to unity, it can be concluded that the removal rate of radium is small in comparison to the decay of [228]Ra and that the [226]Ra/^{210}Pb ratios

observed in the gyttja accordingly hardly can be explained by the removal of radium. This would leave the radon hypothesis as the only reasonable explanation.

3.3.6 A Combination of Radon and Radium Transport

To summarise the discussion there are two hypotheses that have been forwarded to explain the low ^{226}Ra/^{210}Pb in the gyttja – either that it is caused by upward migration of ^{222}Rn or leaching of ^{226}Ra. The radon hypothesis is attractive because it would explain why the ^{210}Pb profile, as shown in figure FFF, is so beautifully correlated with the ^{226}Ra profile, although it seems to have been shifted some centimetres upwards. Furthermore, radon is known to be very mobile, and although diffusion alone might be insufficient to explain the observed ratios, there are suggestions in published literature that there are other processes that might increase the radon migration appreciably.

The radium hypothesis is attractive, because it would also explain the low ^{226}Ra/^{230}Th ratios in the gyttja. These measurements need to be confirmed in order to reach a scientifically acceptable standard, but they clearly indicate that radium has been leached from the gyttja. The problem with this hypothesis is that it seems somewhat hard to explain how the radium could be leached so rapidly. It requires quite low K_d values and a movement of relatively pure water through the gyttja, which may seem slightly unrealistic.

The most likely explanation at this stage may therefore be a combination of these two processes. If there indeed has been a removal of radium from the gyttja – which the measurements indicate – it is possible that the removal has been too slow to significantly affect the ^{226}Ra/^{210}Pb ratios. Then it would also seem more likely that the radium has been transported upwards. As was shown, quite high removal rates are required in order to bring about an appreciable influence on the ^{226}Ra/^{210}Pb ratio. Thus, migration of ^{222}Rn may be the main explanation to the observed ^{226}Ra/^{210}Pb ratios in the gyttja, while the ^{226}Ra/^{230}Th ratios are caused by a much slower leaching of radium, which then may have been going on for much longer periods of time.

There are, however, easy ways to test these hypotheses. Determinations of above all ^{232}Th and ^{230}Th in some strategic samples would increase the quality of this work considerably and most likely resolve most doubts concerning the behaviour of radium in the gyttja layers.

3.4 URANIUM IN THE GYTTJA AND CLAY LAYERS

3.4.1 The Solubility of Uranium and Thorium

The radioecological study of uranium differs somewhat from that of radium, because the naturally occurring uranium isotopes all have very long half-lives. Two of the isotopes, ^{238}U and ^{235}U, are the first ones in the their respective decay chains so there are no parents to compare them to. Among the daughters all radionuclides either have so short half-lives that they are uninteresting or so long half-lives – 75,400 years for ^{230}Th, 32,800 years for ^{231}Pa and 246,000 years for ^{234}U – 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 sediments or post-depositional influences, which makes their meaning more ambiguous. On the other hand, this may also be an advantage, as it may allow conclusions concerning the formation of the sediments.

Some interesting things in the uranium profiles that call for an explanation have already been mentioned. In figure 5 it was shown that there is a large difference

between the ^{238}U activities and the ^{230}Th/^{226}Ra activities in the clay. Apparently, ^{230}Th has been enriched in the clay relative to ^{238}U, either by accumulation of thorium or – more likely – by mobilisation of uranium. In the gyttja, the situation is the other way around; ^{238}U and to an even higher degree ^{234}U show much higher activities than ^{230}Th. The picture is similar for the actinium chain, where ^{235}U shows much higher activities than the daughter ^{231}Pa. It is of course obvious that uranium geochemically must behave in another way than thorium, for instance, but what implications would this have for the ^{230}Th/^{238}U ratio in different environments? One way to get a sense for this is to turn to the K_d values for uranium and thorium respectively.
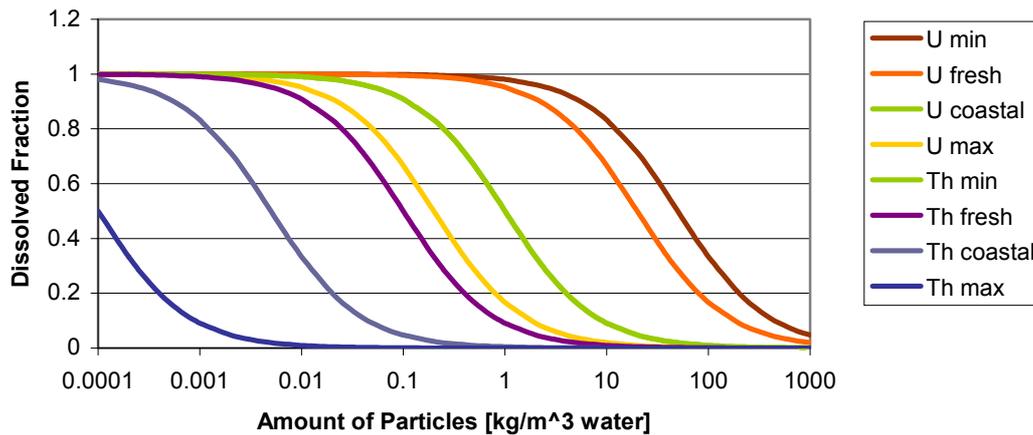

Figure 20: The fraction of soluble uranium and thorium in the water phase as a function of the amount of particles in water or sediments. The dissolved fraction is shown for the distribution coefficients presented by the IAEA for fresh water with emphasis on oxidizing conditions (1994) and coastal waters (1985): U_{min}(20 L/kg), U_{fresh}(50 L/kg), $U_{coastal}$(1,000 L/kg), U_{max}(5,000 L/kg), Th_{min}(1,000 L/kg), Th_{fresh}(500,000 L/kg), $Th_{coastal}$(2,000,000 L/kg), and Th_{max}(10,000,000 L/kg). The minimum and maximum values represent absolute minima/maxima.

Figure 20 shows the fraction of uranium and thorium respectively that can be expected in the aqueous phase based on K_d values presented by the IAEA (1994, 1985). The expected K_d value for uranium in sediments and suspended matter in aqueous systems with oxidizing conditions is 50 L/Bq and a range of 20-1,000 L/Bq, whereas thorium, for instance, has an expected value of 10,000 L/Bq and range of 1,000-1,000,000 L/Bq. The corresponding values for coastal systems are 1,000 (200-5,000) L/kg for uranium and 2,000,000 (500,000-10,000,000) L/kg for thorium. The x-axis in figure NNN shows the amount of particles relative to the water volume. It is important to realize that the difference between what commonly is referred to as water and sediments is rather vague. Sediments could theoretically be considered as water with high particle content, and water, on the other hand, could be thought of as sediments with a very high water content. Indeed, the water-sediment interface can in practice sometimes be hard to define strictly. Having recognized that there only is a quantitative difference between sediments and water in this sense, it should be clear that there is nothing strange about this approach. Thus, figure 20 should indicate the dissolved fraction of uranium and thorium in environments ranging from coastal or lake water to sediments.

The amount of suspended material in a lake or a bay can hardly be less than 0.0001 kg/m^3. As the gyttja generally contains an appreciable amount of organic material, one should expect that the lake or bay was fairly productive and that there, accordingly, could be expected to be more material than that suspended in the water. A

good estimation is probably between 0.001 and 0.01 kg/m^3 (El-Daoushy, 1986). Although the ranges for the K$_d$ values are very wide, figure 20 suggests that we should expect almost all soluble uranium to be in the aqueous phase before sedimentation, while the situation is more or less unclear for thorium, but as the particle concentration increases, it is obvious that thorium will be adsorbed before uranium. The present particle concentration in the gyttja is approximately 100 kg/m^3. Although figure 20 suggests that a substantial part of the uranium may be in solution, this is most likely not the case, since figure 20 only is valid for oxidizing conditions, while reducing conditions should be expected in the gyttja.

3.4.2 Deficiency of Uranium in the Clay

Figure 20 also suggests a way in which sediments can be enriched in thorium. If uranium is mobilised to a higher degree than thorium while the particles are suspended in the water, this may cause an excess of thorium in the settling material. There are also published articles that support this mechanism for thorium enrichment in sediments. Plater *et al.* (1992), for instance, have reported ^{230}Th/^{238}U ratios higher than unity in river sediments. Measurements published by Scott (1968) show the same pattern. In these cases, the sediments appear to 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). It can of course be argued that although uranium is more easily mobilized, one should still expect ^{230}Th/^{238}U ratios higher than unity in sediments, because ^{238}U can be expected to occur in much higher concentrations than ^{230}Th. However, there seems to be little empirical support for such arguments. Plater *et al.* (1992) also investigated the ^{230}Th/^{238}U ratios in the river water and concluded that they were much lower than unity (roughly 0.03-0.04).

This appears to be a very good way to explain the low ^{230}Th/^{238}U ratios in the clay. The weighted mean of the ^{230}Th/^{238}U ratio in the clay layers is 2.19±0.13, which clearly indicates leaching of uranium. If it is assumed that ^{226}Ra is in secular equilibrium with ^{230}Th in the clay, the weighted mean will be somewhat lower: 1.87±0.03. This figure is probably more likely, since the quantification of ^{226}Ra activities is much more accurate. 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 that described above. The thickness of the clay is more than 0.5 meters and the hydraulic conductivity of clays is know to be very low. Although there is an enrichment of uranium above the clay (in the gyttja) of approximately the same size as the deficiency in the clay, there are no signs in the ^{238}U 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 an intrusion of uranium both from below the clay (upwelling groundwater from the till) and from above it (possible uranium-rich water in the gravel layer). Had there been an upward migration of uranium, one would expect to find the lowest uranium levels in the deepest sample and higher levels in the upper samples. It is very 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 ^{230}Th/^{238}U ratios observed in the gyttja is that the deposited clay particles were depleted of uranium.

3.4.3 The Importance of the $^{234}U/^{238}U$ Ratio

More clues to the behaviour of uranium in the clay and elsewhere would be accessible if the ^{234}U activities also could be determined. At first glance it may seem quite surprising that the $^{234}U/^{238}U$ ratio could contribute with any useful information, since both isotopes could be expected to behave similarly. After all, no deviations can be expected in the $^{235}U/^{238}U$ ratios, at least in environmental samples. Nevertheless, it is a well-established fact the $^{234}U/^{238}U$ ratios often do not equal unity. For instance, groundwater often carries an excess of ^{234}U relative to ^{238}U, which is generally ascribed to selective mobilisation of ^{234}U due to effects related to the alpha recoil in the decay of ^{238}U. The implications and usefulness of this phenomenon has 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 ^{238}U is enhanced in borehole samples, while the level of ^{234}U 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.

However, $^{234}U/^{238}U$ ratios can also be used to assess groundwater mixing, since there are differences between older groundwater and younger groundwater, because in the older groundwater one should expect more pronounced disequilibria. One example of this is an article published by Ivanovich and Alexander (1987). In oceans, for instance, Koide *et al.* (1963) have found that the $^{234}U/^{238}U$ ratios are more or less constant – the average ratio in their experiments was 1.14 with no apparent variations outside experimental error. This is 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, which seems very reasonable. 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. Thus, $^{234}U/^{238}U$ ratios considerably higher than 1.14 could be expected in the water body.

3.4.4 Excess of Uranium in the Gyttja

Unfortunately, it was not possible to determine even approximate figures for the ^{234}U activities in the clay due to the low emission probability of ^{234}U and the relatively high ^{214}Pb activities. In the gyttja, however, there were significant contributions from ^{234}U to the 53 keV peak, which allowed indirect determination of the ^{234}U activities is some samples. According to these measurement the mean $^{234}U/^{238}U$ ratio in the gyttja is 1.63±0.17, which strongly indicates that uranium has been sorbed from solution. This would also agree with the low $^{230}Th/^{238}U$ ratios observed in the gyttja. However, the $^{234}U/^{238}U$ ratio does not indicate whether the solution in question was the water in which the gyttja was formed or groundwater moving through the gyttja causing a post-depositional accumulation of uranium.

According to the discussion above, one should generally expect sediments to have $^{230}Th/^{238}U$ ratios lower than unity, but it could be objected that the organic content of the gyttja is higher and that it therefore might accumulate uranium more efficiently. However, it has been observed that the ^{238}U activities in the upper sediment layers sometimes are lower than in deeper layers. Bonatti *et al.* (1970) have investigated uranium profiles in deep-sea sediments and found the same patterns there. However, they have also made Eh measurements and observed a steady increase in the uranium concentrations in the reduced part of the studied core. This should not come as a surprise as the solubility of uranium is strongly dependent on the redox conditions. As uranium is reduced from U^{6+} to U^{4+}, its mobility decreases dramatically and it gets

caught in the sediments. The fact that there is no sharp change in the uranium concentration is interpreted by Bonotti *et al.* as sign that there is a "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 point of view. 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 immobilized "due to degradation of humic substances under anaerobic conditions". In the case of Klarebäcksmossen, it does not seem unlikely that there were reducing conditions even shortly after the deposition, since there is a tendency of lamination at some depths. (See the photographs in appendix B.) Post-depositional accumulations also seem more likely because it would require much lower uranium concentrations in the water. Halbach *et al.* (1980) claim that significantly higher concentrations of uranium in the aqueous phase are needed in the case of accumulation in connection with the sedimentation. If the sediments, however, are in contact with uranium-bearing waters for a longer period of time, enrichment is possible without such high uranium concentrations in the water phase.

Evidently, it is hard to prove that there really has been a gradual build-up of uranium in Klarebäcksmossen by post-depositional sorption from pore water, but at this stage it seems to be the most likely explanation. The best way to find out how uranium is incorporated in gyttja is probably to try to find a site in the Äspö area, where gyttja currently is being formed. Such a profile has been analysed by Landström *et al.* (1994), but it is not possible to observe whether uranium is being gradually sorbed to the gyttja, as the uppermost sample is too thick (5-22 cm). The uppermost 5 cm have unfortunately not been analysed at all.

In the case that uranium has been accumulated by post-depositional sorption a central question would be whether the uranium has been accumulated from upwelling groundwater or from the lake or bay water in which the uranium was deposited. Although it is hard to prove anything, the best guess it probably upwelling groundwater. One reason is that peat lands tend to develop in local depressions, and thus one could generally expect inflow of groundwater through the bottom. Sundblad *et al.* (1990) have also reported enrichment of uranium in areas of groundwater seepage. The inflow of uranium to the gyttja must not necessarily have been mainly from the clay; instead the gravel with its high hydraulic conductivity seems like a more likely medium. Aggeryd *et al.* (1999) have also recognized the abundant gravel layers in the Äspö area as potentially important media for radionuclide transport. This is supported by the fact that the pore water in the gravel zones tends to have a quite different composition compared to the pore water in the surrounding layers. For instance, the highest concentrations of uranium and thorium were found in pore water from gravel layers. However, this does not automatically imply that there must be a similar situation in Klarebäcksmossen.

The enrichment of uranium in the gyttja in Klarebäcksmossen is also consistent with data published by Shotyk *et al.* (1991). Their data is based on measurements on 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 are 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. Hence, there are several empirical observations indicating that the uranium has been accumulated from upwelling groundwater.

3.5 THORIUM AND PROTACTINIUM

3.5.1 The Mobility of Thorium

A comparison of the ratio between the thorium isotopes ^{233}Th and ^{230}Th shows that the ^{230}Th/^{232}Th ratio appears to differ significantly 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 ^{230}Th in the clay and production of ^{230}Th in the gyttja due to excess of ^{234}U, 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 ^{230}Th/^{232}Th ratios (approximately 4-12) from the ion-exchangeable and organic phases of river sediments, while ^{230}Th/^{232}Th ratios of 1±0.5 have been reported in detrital matter. Accordingly, Plater *et al.* 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 ^{230}Th is enriched relative to ^{232}Th is natural waters, since the former can benefit from alpha recoil effect, but also be produced from mobilised uranium.

No speciation has been performed for the samples from Klarebäcksmossen, but it does not seem unlikely that a similar pattern might be found here. The ratios in the gyttja from Klarebäcksmossen are of course 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. It is hard to determine, however, whether the sorption has taken place in connection with the deposition or afterwards. Thus, these figures should not be interpreted as evidence of post-depositional migration of thorium in the gyttja layers.

3.5.2 The Mobility of Protactinium

The weighted mean for the ^{231}Pa/^{235}U ratio in the gyttja is 0.38±0.03, indicating an enrichment of uranium relative to protactinium. 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. In that sense, protactinium appears to behave similarly to thorium. The ratio is, however, much lower than the ^{230}Th/^{238}U ratio in the clay, which is close to 2. The actual value depends on whether ^{226}Ra is assumed to be in secular equilibrium with ^{230}Th or not. Anyhow, the difference seems significant. However, if thorium and protactinium had behaved similarly, the ^{231}Pa/^{235}U ratio should be expected to be higher than the ^{230}Th/^{238}U ratio because ^{231}Pa has a longer half-life than ^{230}Th. Accordingly, it appears as if protactinium – at least under certain circumstances – is more mobile than thorium. The most probably 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 be 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. The figures

published here only reflect a very limited number of measurements from different layers of the same deposits. On the other hand, 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 also require validation of the methods used to determine the ^{231}Pa activity. If alpha spectrometry is used to measure other isotopes (^{230}Th and ^{232}Th), this would probably also give information on the ^{227}Th activities, which then could be used for such validation.

3.6 CLOSING DISCUSSION

3.6.1 Recommendations for Future Research

^{230}Th is a key radionuclide, if one wishes to assess the mobility of radium. These measurements indicate that there has not been any large accumulation of radium in the core, but rather a leakage, at least from the gyttja layers. However, the measurements must be verified using some more conventional method in order to increase the scientific credibility of the conclusions. A good alternative would be to use alpha spectrometry for some strategic samples throughout the core.

Alpha spectrometry would not only give information about ^{230}Th, but also other important thorium isotopes. ^{232}Th would show whether migration of ^{222}Rn or ^{226}Ra is responsible for the low ^{226}Ra/^{210}Pb ratios in the gyttja, and thus that question could probably be settled too. Furthermore, ^{227}Th could be used to verify the ^{231}Pa measurements. Hence, these three thorium isotopes alone would solve three important problems and significantly increase the quality of this work. However, Gascoyne and Larocque (1984) have shown how both uranium and thorium could be extracted from granite for alpha spectrometry. A similar approach could probably be used for these samples, which thus would allow determination of not only the critical thorium isotopes, but of ^{234}U/^{238}U ratios outside the gyttja. In that case the uranium migration could probably be assessed much better. At least it would increase the reliability of the conclusions drawn concerning the accumulation and mobilisation of uranium in different layers to an acceptable level. Thus, the value of the alpha measurements would increase even more.

It is also obvious that there is a need to collect some more background information on Klarebäcksmossen. This should include above all hydrological measurements. It would also be of great interest to measure the activities of various radionuclides in the pore water from different layers in Klarebäcksmossen. That would open new possibilities to assess the mobility of key radionuclides. As the total activities and the water content already have been measured, this would also allow site-specific determination of distribution coefficients. This may prove very useful, if one decides to model the migration of radionuclides in peat lands in the Oskarshamn area in somewhat more complex ways than have been the case this far.

Another interesting experiment would be to apply a method that has been developed by Pr. El-Daoushy *et. al* to isolate specific fractions of the soil together with their respective content of radionuclides. In this manner, it would be possible to determined in what kind of material different elements are bound. Indirectly, it may also show how different radionuclides have been brought to where they are found today. Such measurements have a great potential to deepen the understanding of how different radionuclides behave during the development of a peat land.

Finally, there is of course the question of the representativity of the measurements. It is inevitable that the value of this study is limited by the fact that it only considers one single core. Evidently, it is far from clear, whether it describes any significant phenomena in peat lands in general or even in Klarebäcksmossen. As regards Klarebäcksmossen, it is very likely that very different profiles can be found closer to the edges of the bog. These measurements indicate that the activity in peat is highly dependent on groundwater transport, and it seems plausible that the water that reaches the edges of the bog could carry much more radionuclides. Thus, one might expect higher activities there. It may also be interesting to see whether the patterns from Klarebäcksmossen are repeated elsewhere. Studies from Canada (Shotyk *et al.*, 1989) have shown striking similarities between uranium profiles in several peat lands, and as the sequence of the layers in this profile seems to be very typical for peat lands in the Oskarshamn area, it would not be too surprising if such similarities could be identified there too. As sediments turned out to be especially effective in accumulating certain radionuclides, it would also be interesting to take a closer look at the gyttja as it is developing. This may give a good indication concerning the sources of the uranium. Furthermore, if it is true that radium has leached from the gyttja in Klarebäcksmossen, it is obvious that the radium activities must have been higher at earlier stages of the peat land development. However, it is hard to extract such information from these measurements only – that would require more work.

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APPENDIX A

Derivation of the Equation for Secular Equilibrium
The decay of a radioactive isotope is proportional to the number of atoms, N:

$$\frac{dN}{dt} = -\lambda N ,$$
Eq. 10

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

$$N(t) = N_0 e^{-\lambda t} ,$$
Eq. 11

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

$$A = \lambda N .$$
Eq. 12

In the decay chains the general situation is somewhat more complicated because atoms do not only decay, but may also continuously be produced by the decay of a parent. If we assume that the decay of a radionuclide leads to the production of another radionuclide and denote the number of atoms by N_1 and N_2 respectively, the change in N_2 is described by

$$\frac{dN_2}{dt} = -\lambda_2 N_2 + \lambda_1 N_1 .$$
Eq. 13

Suppose that the decay of the parent nuclide is governed by the exponential decay law. Insertion of equation 11 in equation 13 will then lead to a linear differential equation of the first order

$$\frac{dN_2}{dt} = -\lambda_2 N_2 + \lambda_1 N_1^0 e^{-\lambda_1 t} ,$$
Eq. 14

which can be solved by assuming that the solution can be written in the form

$$N_2(t) = f(t) e^{-\lambda_2 t} .$$
Eq. 15

Derivation of equation 15 gives

$$\frac{dN_2}{dt} = f'(t) e^{-\lambda_2 t} - f(t) \lambda_2 e^{-\lambda_2 t} .$$
Eq. 16

By comparison with equation 14 it is now possible to identify f(t) and f´(t). λ_2 clearly indicate which of the two that should be identified with f itself and which that should be associated with its derivative. Hence,

$$f(t) = N_2 e^{\lambda_2 t},$$ **Eq. 17**

$$f'(t) = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}.$$ **Eq. 18**

Now, by integrating the last of these equations, we find that

$$f(t) = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^{(\lambda_2 - \lambda_2)t} + C.$$ **Eq. 19**

By combining equations 15 and 19 it is now possible to solve the equation for N_2 as a function of time. Hence, we come to the conclusion that

$$N_2(t) = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^{-\lambda_1 t} + C e^{-\lambda_2 t}.$$ **Eq. 20**

This is the general solution to the equation 13 (which of course can be shown). In order to determine the constant of integration, C, it is necessary to know the state of N_2 at some moment in time. Let us therefore assume that the number of atoms at t=0 was zero. Hence, we get

$$N_2(t) = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) = \frac{\lambda_1 N_1(t)}{\lambda_2 - \lambda_1} \left(1 - e^{-(\lambda_2 - \lambda_1)t} \right),$$ **Eq. 21**

where the exponential decay law was used to rewrite the equation in the last step. In order to get the relationship between the activities, we can multiply both sides by λ_2 and use the definition of activity:

$$A_2(t) = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_1(t) \left(1 - e^{-(\lambda_2 - \lambda_2)t} \right).$$ **Eq. 22**

Secular equilibrium may occur if the half-life of the daughter is short in comparison with the half-life of the parent. In other words, the requirement is that $\lambda_2 \gg \lambda_1$. If this criterion is met, we may than say that $\lambda_2 - \lambda_1 \approx \lambda_2$. Equation 22 can then be simplified and rewritten as

$$A_2(t) = A_1(t) \left(1 - e^{-\lambda_2 t} \right).$$ **Eq. 23**

Equation 23 shows that the activity of the daughter will approach the activity of the parent as t approaches infinity. As the exponent in equation 23 is proportional to the half-life of the daughter, the time required to reach secular equilibrium is in the order of

half-lives of the daughter. This means that after only four half-lives the deviation from perfect equilibrium will be 6.25 %. In another two half-lives the deviation will be close to 1.5 %, which is less than the common uncertainties in most activity measurements.

It is important to realize that when secular equilibrium has been established, the daughter essentially behaves as if it had the same half-life as its parent. Therefore, it is capable of extending the secular equilibrium to its daughter if only the daughter has a short half-life in comparison not with the parent but with the grandparent. In this manner it is possible to establish secular equilibrium with a long series of radionuclides, if there is one long-lived parent and several short-lived daughters. For instance, in an isolated system all of the nuclides in the thorium chain would reach secular equilibrium with [232]Th only after a few decades.

APPENDIX B

The photographs shown below are taken from Gert Nilsson's (2004) investigation of sediments, peat lands and wetlands in the Oskarshamn area. They are reprinted with the approval of SKB and Gert Nilsson. The core on the pictures is identical to the core that was analysed in this study.

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

Source: **SKB**   Photographer: **Gert Nilsson**
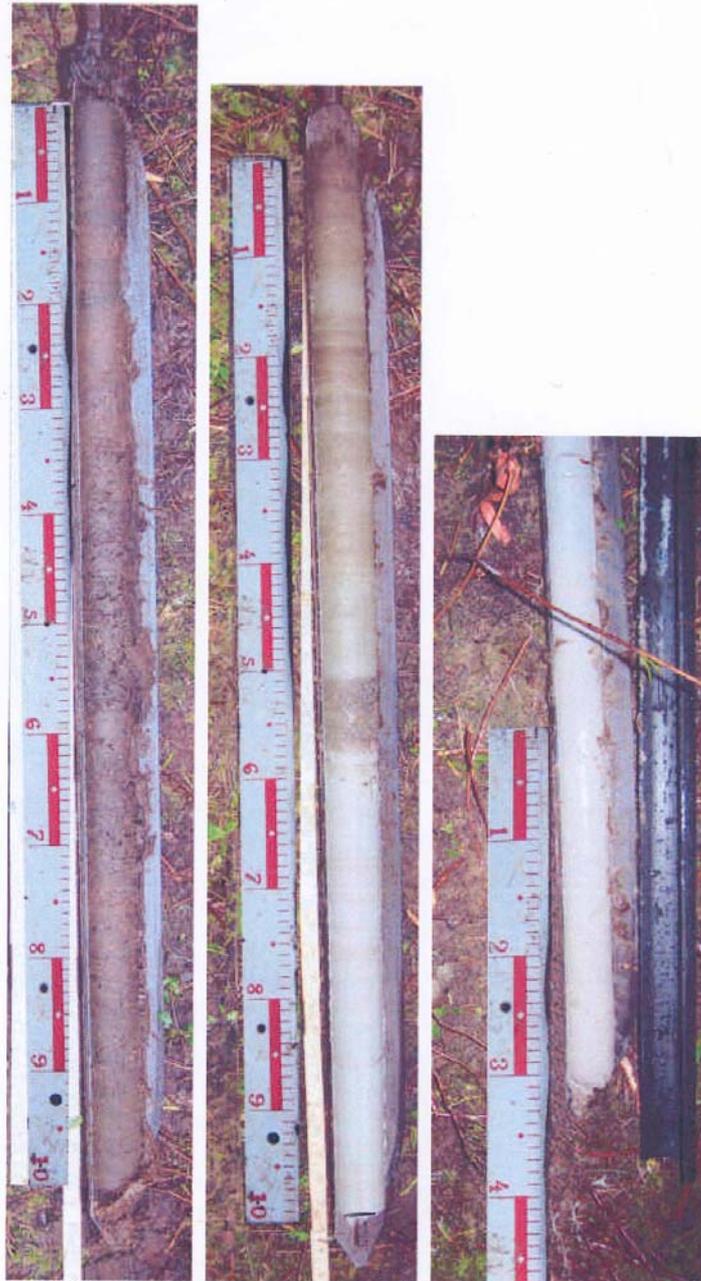
PSM006562- "*Klarebäcksossen*", peat/clay column 300 - 530 cm.
Increasing depth down - and rightwards.

Source: **SKB**   Photographer: **Gert Nilsson**